

LOW VOLATILITY HALON FIRE EXTINGUISHING AGENTS WITH REDUCED GLOBAL ENVIRONMENTAL IMPACTS

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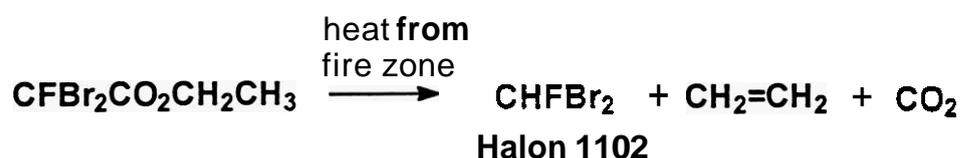
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Abstract

The continuation of work on non-volatile precursors (NVPs), including some new candidate agents which pyrolyze in the heat of a fire to generate Halon-like fire extinguishing agents, will be discussed. This paper will provide a brief review of previous accomplishments and a wrap-up of work in progress to date.

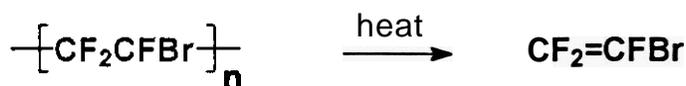
NVP agents have greatly reduced ODP, GWP and toxic vapor properties, and pose greatly reduced atmospheric emissions due to fire extinguishing operations or from accidental releases. Agent requirements for fire fighting operations would be greatly reduced, in comparison to conventional agents, most of which evaporate en route to a fire when delivered as streaming agents. Greatly extended throw ranges would result in increased safety for firefighters, since NVP agents can be projected from much greater distances.

In recent years, the search for replacements for Halon fire extinguishing agents has intensified and a number of alternative materials, particularly solids and powders are under consideration. In this communication we would like to report on our continuing work on non-volatile precursors (NVPs), which thermally decompose to produce Halon-like agents capable of fire extinguishment. NVPs offer several advantages for fire fighting applications. Such materials would be expected to show significant reductions in ODP, GWP and toxic vapor properties, atmospheric emissions due to accidental releases, and agent requirements for fire fighting operations. They would also expect to give substantial enhancement to the physical and chemical mechanisms of fire suppression. One early example of such NVPs was **ethyl dibromofluoroacetate** (EBDFA) which decomposes to Halon 1102.



Although EBDFA is not an NVP, but rather a liquid of **low** volatility, It did exhibit superior performance in cup burner tests. Almost all of the compounds in these early studies were compounds of simple molecular structure to establish the feasibility of the premise that decomposition products were capable of improved fire extinguishment.

The investigation then shifted to consideration of solid polymeric materials since these substances offered several advantageous properties. They would have no volatility in storage, long shelf life stability, and high molecular weights were not necessary for use in fire suppression applications. As there has been considerable recent interest in powders as halon alternatives these materials should be excellent candidates for such applications. While particle size in currently used solid fire suppression materials is a concern, the particle size in the polymeric materials may be effectively adjusted for maximum efficiency and minimum toxicity. These materials also have simple repeat units that could effectively imitate the thermal behavior of the simple molecular compounds of the early studies. In particular, interest focused on polymers that would decompose thermally by an "unzipping" mechanism and produce small molecules capable of fire extinguishment. These materials would decompose cleanly and produce no significant char or other residues. We therefore looked at the thermal properties of several materials to develop reasonable screening criteria for choosing candidates for further investigation. It appears that the determination of the thermal gravimetric analysis (TGA) curve is an excellent method of determining the feasibility of candidates for further testing. A candidate material for large scale fire testing, polybromotrifluoroethylene (PBTFE), was selected in this fashion as it appeared to decompose cleanly to bromotrifluoroethylene.



The TGA curve for PBTFE, shown in Figure 1, indicates complete decomposition occurs by 300' C and the thermal transition is relatively sharp. A small amount of decomposition is observed at 150' C, due to small amounts of water present in the sample.

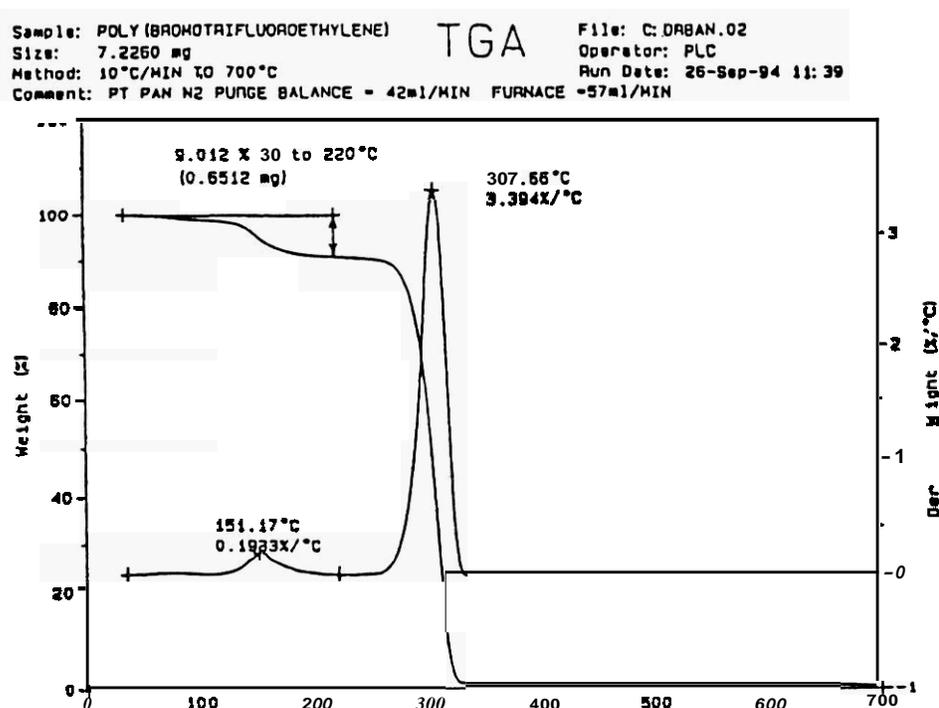
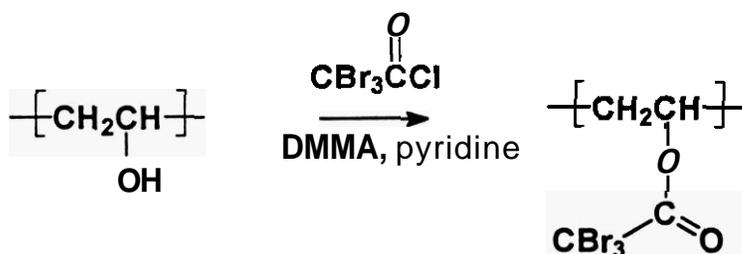


Figure 1. TGA of Polybromotrifluoroethylene (PBTFE)

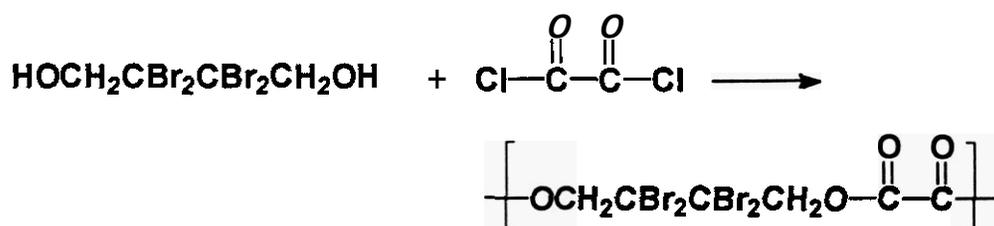
The bromotrifluoroethylene and water vapor were identified as the decomposition products by their infrared spectra. This TGA profile clearly shows that the material would have high shelf stability at ambient temperature, but would readily decompose at low fire temperatures. Further testing of this material showed promise for fire extinguishment and has been selected for large scale fire testing. We are investigating synthetic methods to accomplish the large scale preparation of 5 kilos of the material for field testing at Tyndall AFB.

Two other candidates were selected for further testing after determining that their TGA profiles were similar to that of PBTFE. Polyvinyl alcohol was acetylated with

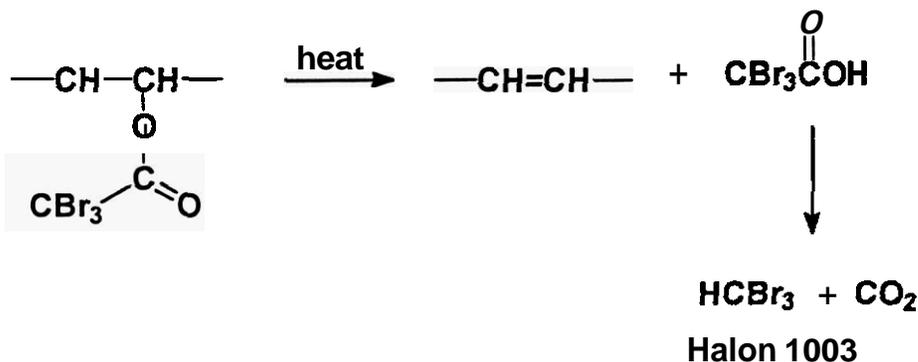
tribromoacetyl chloride to 50 percent substitution and a condensation polymerization was carried out with



oxalyl chloride and 2,2,3,3-tetrabromo-1,4-butanediol.



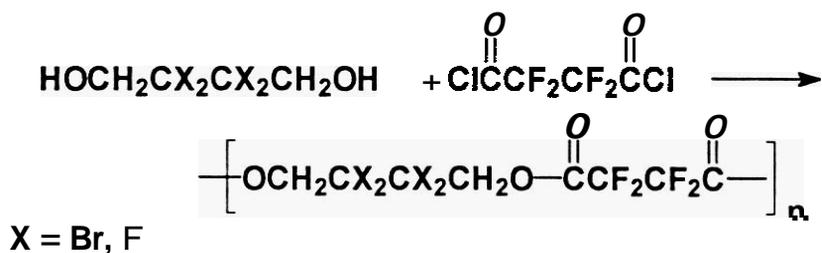
For both of these materials, excellent pyrolytic profiles were obtained in the **TGA** curves with little or no charring observed. The expected mode of decomposition of the polyvinyltribromoacetate would give Halon 1003, while



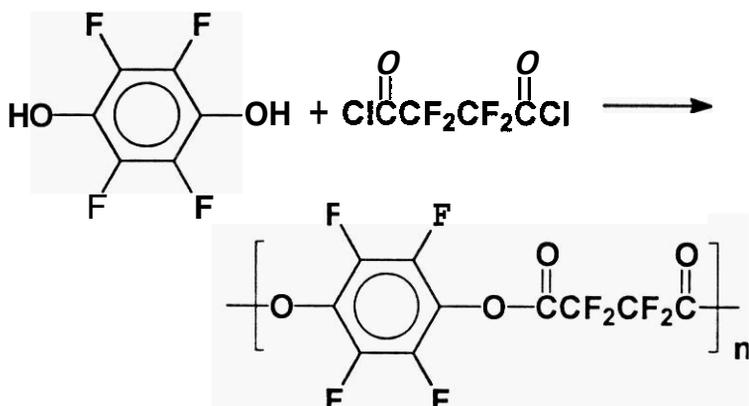
decomposition of poly(1,4-(2,2,3,3-tetrabromobutane)oxalate) would be expected to produce brominated olefins and carbon dioxide, although we have not fully investigated the products of this reaction. We are currently investigating methods of large scale preparation of these polymers as well.

The potential success of these linear polymeric materials with high halogen content has led to the current synthetic efforts which center around systems with fluorine

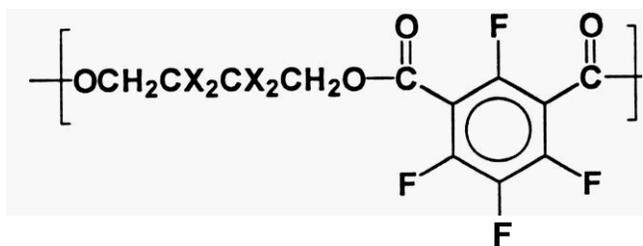
substitution. Fluoro polymers were possible candidates as they have been used for a number of applications such as linings for valves, pipes, cable insulation as they do not support combustion. In addition a number of volatile fluorocarbons, potential products of thermal decomposition, are currently used in fire suppression applications. The commercially available 2,2,3,3-tetrafluorosuccinic acid was converted to the acid chloride for condensation polymerizations with both linear flexible monomer units



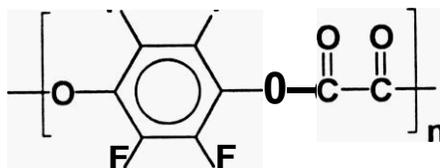
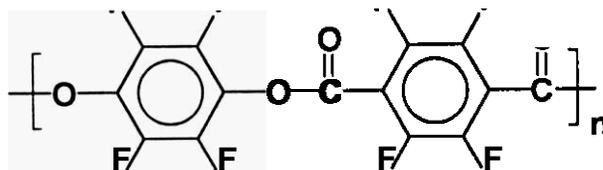
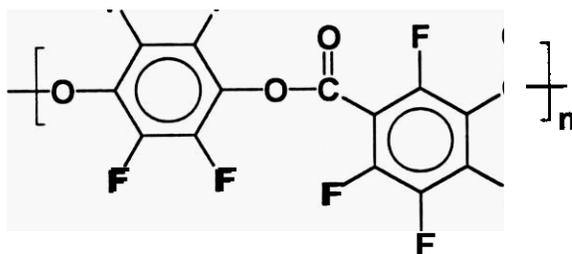
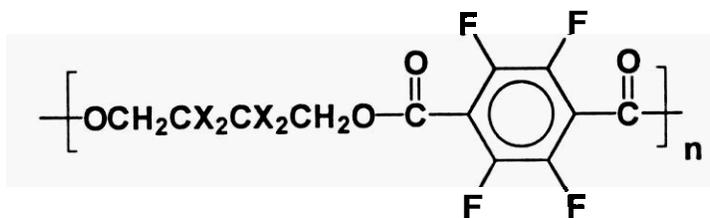
or with the more rigid aromatic fluoro compounds.



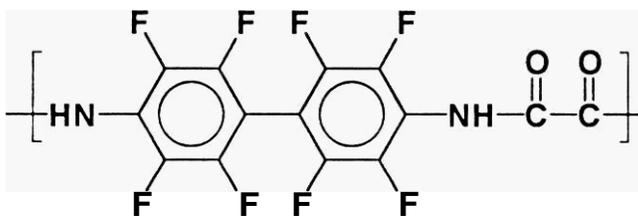
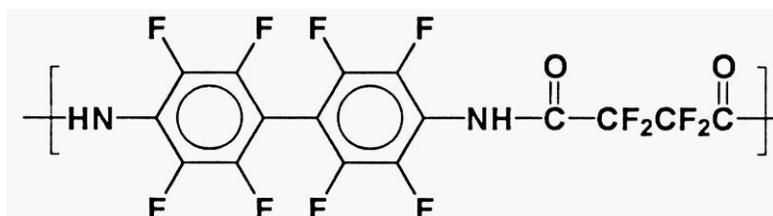
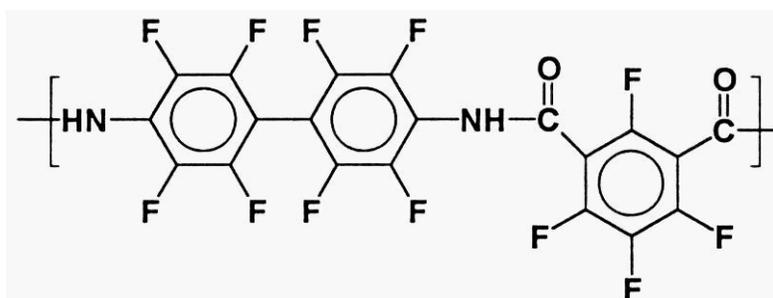
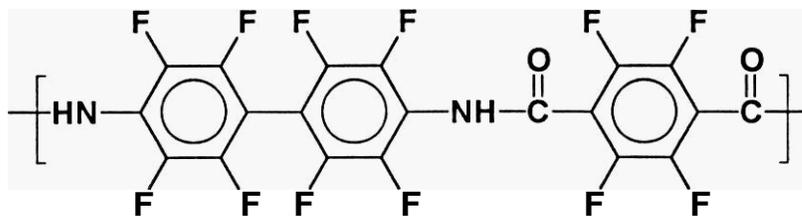
Using these same reaction sequences, we are now investigating preparation and characterization of the following series of polyester structures.



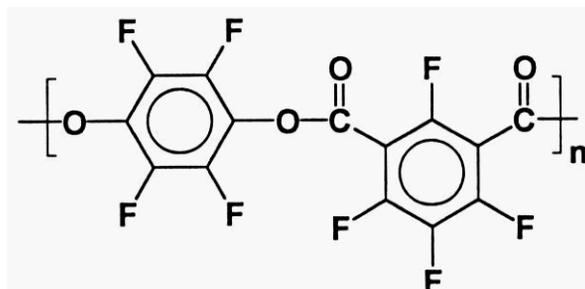
X = Br, F



In addition to the polyesters, polyamides are also being prepared as perfluorinated amines are readily available.



The TGA profile of one of these materials, shown below



indicates a more complex two stage decomposition and but again shows no charring or residue.

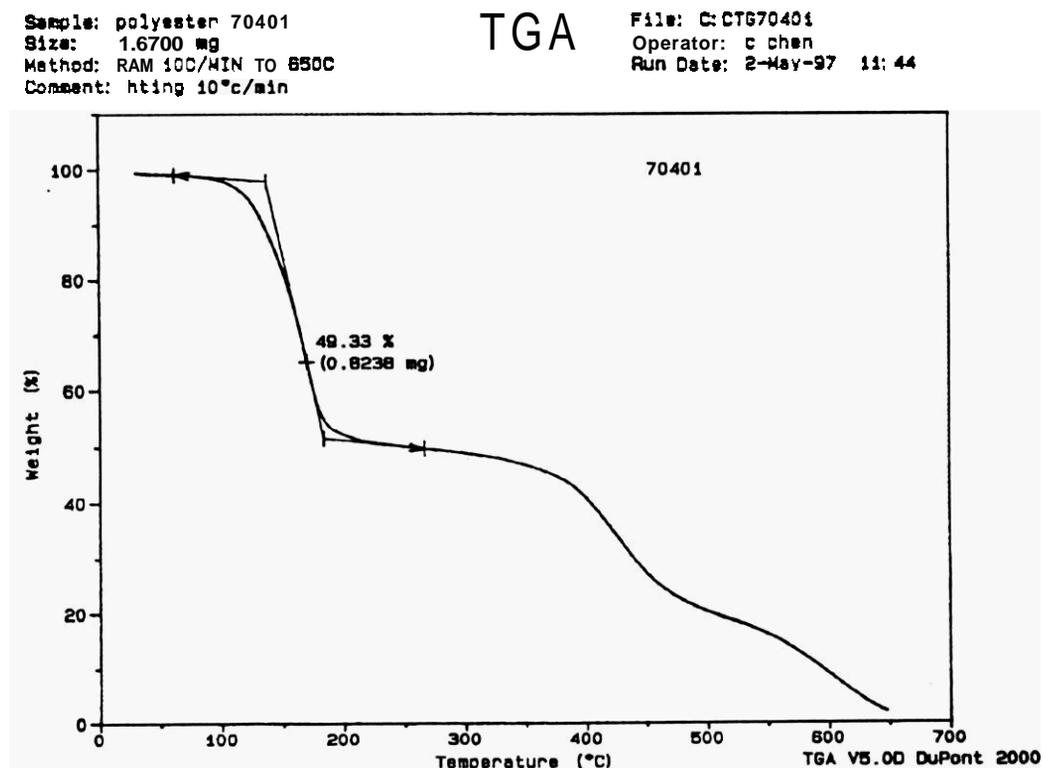


Figure 2. TGA profile of perfluoro polyester

We are in the process of investigating this perfluoro polyester as well as the other perfluorinated materials for potential NVP applications at the present time.

The objective of this project was to investigate new and novel solid materials as NVPs for potential fire suppression or extinguishment applications. In this study we have identified several candidates for further testing on a large scale and have developed reasonable screening criteria for future NVPs by the use of TGA profiles. Although quantitative structure-property relationships are not yet available for the decomposition mechanisms of the NVPs prepared, our results allow us to better identify and select candidates for further testing based on analysis of the thermal properties of these and future materials.

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