Thermal Stability of Highly Fluorinated Phosphonium Salts

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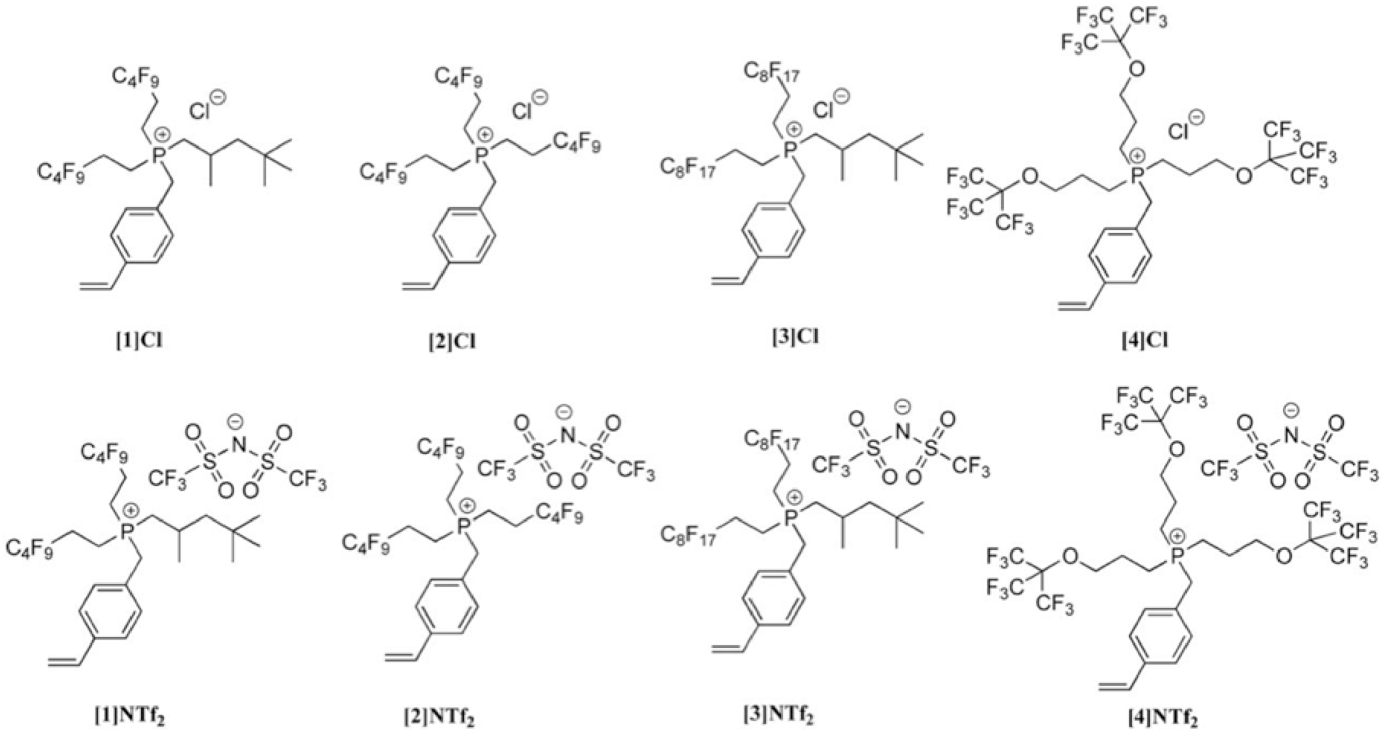
ABSTRACT

An array of highly fluorinated polymerizable phosphonium salts (HFPPS) were synthesized from PH_3 gas via the radical addition to the corresponding olefin. The thermal properties of these new monomers were characterized and correlated to their chemical structure. The molecular design of the monomers had a pronounced effect on their thermal degradation profiles. Monomers utilizing the bis(trifluoromethylsulfonyl)imide ion displayed significantly higher thermal stability in comparison to their chloride analogues. Depending on rate of heating, the onset for degradation was altered dramatically. This has significant implications for the general analysis and discussion of quaternary phosphonium salts.

INTRODUCTION

The incorporation of quaternary salts in to polymeric systems has recently been of interest. Applications in gas separation and as antimicrobial agents are prospective frontiers for such materials.[1-2] These polymers manifest their properties from the high ion-content along the backbone chain. Most of this research has centred on nitrogen-based monomers because of their ease of use and synthesis. Phosphonium salts have received less attention despite their greater chemical and thermal stability.[3] We are interested in exploring the chemistry and applications of the phosphonium cation in polymeric systems. Our motivation for this approach stems from the excellent control over molecular structure, taking advantage of PH_3 gas as our starting material.[4] Previous work in our group has shown the hydrophobic effects of a fluorinated phosphonium cation when used as a coating.[5] We are interested in applying this approach to polymeric systems by comparing monomer structure to performance (Figure 1). An important parameter for the application of such a material is its thermal stability, as this determines the working temperature limit. Like other quaternary salts, very slight modifications to the ion-pair will result in dramatic changes in their degradation.[3] Thermal characterization of such compounds is crucial to understanding their chemical behaviour, and ascertaining structure-property relationships for future application. Thermal gravimetric analysis (TGA) can be performed to obtain thermal stability and provide insight in to decomposition mechanisms of these salts. This technique is ubiquitous within the field of -onium salt (and ionic liquid) chemistry and remains a staple for in-depth analysis. A detailed discussion of the thermal degradation of ionic liquids and related salts can be found elsewhere.[6] A very large number of factors influence the thermal degradation of such salts. These range from molecular properties such



[1]Cl [2]Cl [3]Cl [4]Cl

[1]NTf$_2$ [2]NTf$_2$ [3]NTf$_2$ [4]NTf$_2$

Figure 1: Array of highly fluorinated polymerizable phosphonium salts.

as alkyl chain lengths, cation structure/composition, and choice of anion, to experimental parameters such as rate of heating, atmosphere, and impurities (wet vs dry). The vast majority of salts analyzed by TGA are nitrogen based. Phosphonium salts have been investigated to a much lesser degree, both in terms of depth and scope. We are interested in the thermal properties obtained by fluorinating such salts, and whether molecular architecture, and anion choice have a pronounced effect on their thermal properties.

Experimental

All relevant synthetic information and hydrophobic performance in UV-curable systems can be found elsewhere.4 TGA studies were conducted on a Q600 SDT TA instrument. A sample (10 mg) was placed in an alumina cup and heated (2-20 °C/min) from room temperature to 600 °C under a nitrogen atmosphere. Thermal stability was obtained by calculating the onset temperature (T_{onset}) using TA Universal Analysis.

Results and Discussion

The observed decomposition temperature of all compounds followed a general trend characteristic of phosphonium. The onset temperature (T_{onset}) for compounds [1]Cl, [2]Cl, and [3]Cl were approximately 295°C, while compounds [1]NTf_2, [2]NTf_2, and [3]NTf_2 were stable until approximately 370°C at 10 °C/min (Figure 2 and 3; Table 1)

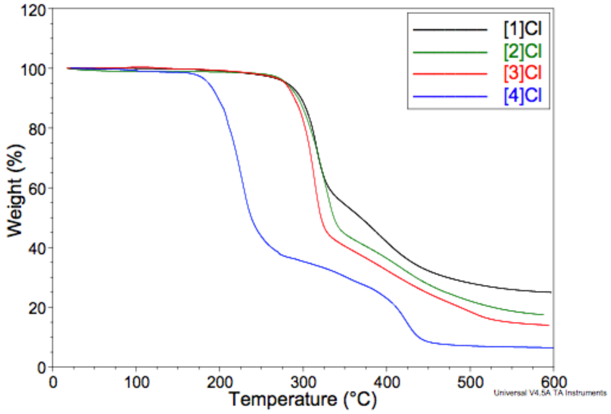


Figure 2: TGA traces of [1-4]Cl

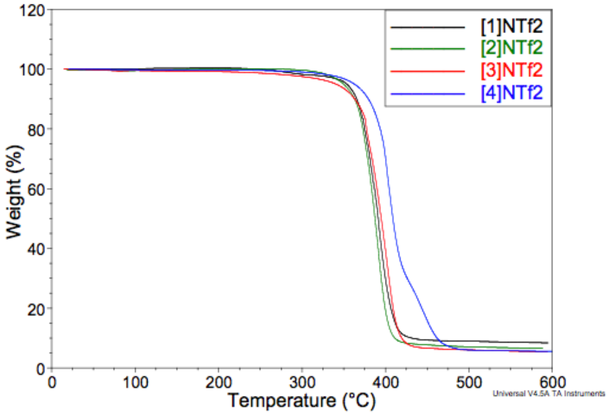
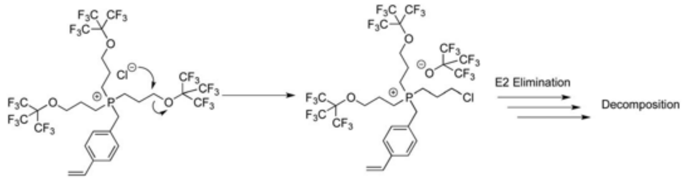


Figure 3: TGA traces of [1-4]NTf_2

Phosphonium Salt	**T_{onset} (°C)**
[1]Cl	296
[2]Cl	291
[3]Cl	293
[4]Cl	197
[1]NTf_2	367
[2]NTf_2	371
[3]NTf_2	374
[4]NTf_2	389

Table 1: T_{onset} of synthesized phosphonium salts

The decreased basicity of bis(trifluoromethylsulfonyl)imide relative to chloride likely inhibited the decomposition pathway by nucleophilic attack of the β-hydrogen. The decomposition point of [4]Cl was found to be exceptionally low in comparison to its analogues. This led us to believe that an alternative decomposition pathway was present. We postulated that the electronegativity of the perfluoro-tert-butoxy group might allow for its displacement in the presence of a chloride anion at high temperatures. Deprotonation of a β-hydrogen to form perfluoro-t-butanol would result in decomposition (Scheme 1).



Scheme 1: Proposed thermal decomposition mechanism of [4]Cl.

The plausibility of this mechanism is supported by the relative basicity between chloride and perfluoro-tert-butoxide, with their conjugate acids having pKa values of -7 and 5.2, respectively. The increase in thermal stability from 198 to 389°C upon ion exchange with the bulky, non-nucleophilic NTf2 anion also supports this mechanism. We decided to further investigate this phenomenon. Compound [4]Cl was heated slowly within a mass spectrometer and the fragments consistent with perfluoro-tert-butanol elimination were monitored. After 532 s, a positively charged fragment at m/z = 197 was observed and attributed to $[(CF_3)_3COH - (HF_2)]$. Upon further heating, the signal at m/z = 197 was observed at a maximum after 889 s. The experiment was repeated under identical conditions using [4]NTf_2 and no signal at m/z = 197 was observed until 925 s, indicating greater thermal stability. Additionally, there was no evidence for the displacement or cleavage of the styrenic moiety from the phosphonium salt. The slight increase in thermal stability of [4]NTf_2 relative to the other NTf_2 salts may be due to the reduced acidity of the β-hydrogen.

Currently there are thousands of reported T_{onset} temperatures reported for quaternary nitrogen and phosphonium salts. This information is meant to relay quantitative information on the thermal stability of such molecules to derive suitable comparisons, and for computer modeling. Experimental parameters for the TGA experiment however can greatly influence the results, potentially complicating interpretation. To demonstrate this effect, [2]NTf_2 was heated at 2, 5, 10, and 20°C/min and T_{onset} was determined (Figure 4).

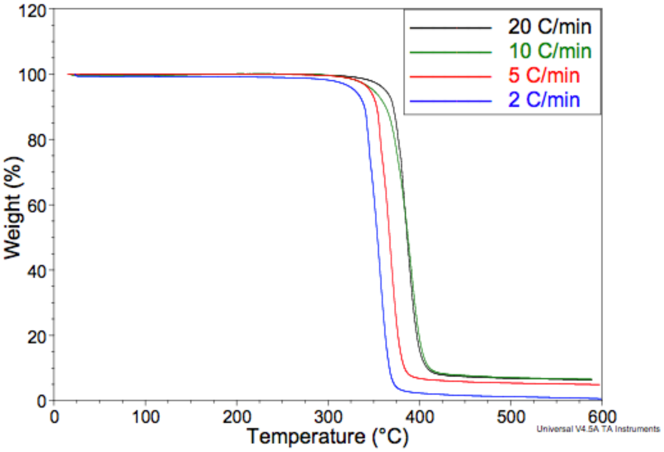


Figure 4: TGA plots of [2]NTf_2 at different heating rates

At 2 and 5°C/min, the T_{onset} was observed at 340 and 355°C respectively. For heating rates at both 10 and 20°C/min, T_{onset} was observed at approximately 365-370°C. Given that thermal decomposition is a function of both temperature and time, the faster heating rates gave information on the short-term stability of the compound, while the slower rates provided information towards long-term stability. Isothermal experiments provide complimentary data for understanding the effects of heating at temperatures below T_{onset}. [2]NTf_2 was heated at 240°C for 16 hours to determine its stability at a temperature much lower than any of the T_{onset} values obtained (Figure 5).

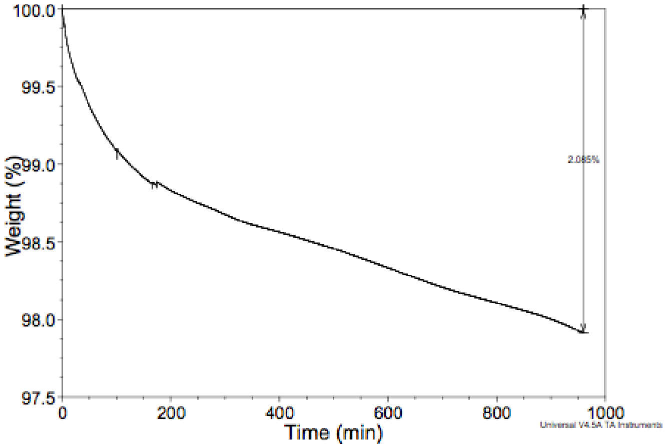


Figure 5: Isothermal plot of [2]NTf_2 heated at 240°C

Even at this low temperature, there was a 2% mass loss and significant browning of the sample. The decomposition rate was initially high, but after 200 minutes, reaches a steady state for the remainder of the experiment. While the faster scan rates suggest high stability, it's important to account for the time dimension within the experiment. This phenomenon has been previously observed for imidazolium based salts and provides a better description of long-term stability[7]. Care must be taken in describing the thermal stability of similar phosphonium salts as this parameter changes depending on experimental setup.

CONCLUSION

Thermal gravimentric analysis was used to determine the thermal stability of various fluorous phosphonium salts. Replacing the chloride with NTf_2 significantly increased the short-term stability of these compounds by ~100°C. T_{onset} for [4]Cl was found to be much lower than the other analogues. This was due to the nucleophilic character of the chloride anion, which replaced the perfluoro-t-butanol group through an Sn2 type process, ultimately resulting in decomposition. Replacement of chloride with NTf_2 inhibited this degradation pathway, increasing T_{onset} by over 200°C for [4]NTf_2. Finally, we examined the effects of heating rate on [2]NTf_2 to demonstrate the inherent variability in thermal analysis of such salts. T_{onset} was dropped to lower temperatures as the heating rate was lowered, while an isothermal experiment at a temperature lower than T_{onset} still resulted in slight decomposition.

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