SAND2019-12345

SANDIA REPORT
SAND2019-1025
Printed September 2019

Sandia National Laboratories

Novel Chemistry to Support the Detection of Advanced Chemical Agents

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ABSTRACT

Recent news reports coming from Asia and the UK have highlighted the emerging threats of Non-Traditional Agents (NTAs) to national security. The UK incident underscores how NTAs may linger in the environment and at trace. Building on Sandia's extensive analytical chemistry work in this field, a polysilphenylene analog of Sandia's proprietary DKAP polymer coatings was synthesized and evaluated for high temperature operation. Initial test results are inconclusive as to the improved thermal stability of the new polymer with TGA/DSC results indicating a lower glass transition (T_g) temperature for the new "Hot DKAP" material and a similar to slightly lower start to mass loss for "Hot DKAP", but slower degradation rate in clean dry air. Additional testing with a TGA-MS system to identify what the fragments lost as a function of temperature is still needed to fully characterize the materials thermal properties. In addition, the material still needs to be evaluated for thermodynamic properties for analytes of interest using either GC or SPC coated devices.

ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge the contributions and assistance of Eric Coker and Lindsey Hughes.

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EXECUTIVE SUMMARY

Recent news reports coming from Asia and the UK have highlighted the emerging threats of Non-Traditional Agents (NTAs) to national security. The UK incident underscores how NTAs may linger in the environment and at trace quantities. Building on Sandia's extensive analytical chemistry work in this field, a polysilphenylene analog of Sandia's proprietary DKAP polymer coatings was synthesized and evaluated for high temperature operation. Initial test results are inconclusive as to the improved thermal stability of the new polymer with TGA/DSC results a glass transition (T_g) temperature for the new "Hot DKAP" material of 32°C and a similar to slightly lower start to mass loss for "Hot DKAP", but slower degradation rate in clean dry air. Mass spectroscopy data indicates that the slower degradation seen in the TGA correlates to a 65°C shift in mass apexes to warmer temperatures for the HotDKAP indicating a significant increase in thermal stability over DKAP. Further thermodynamic and air lifetime stability testing needs to be completed to confirm these results.

ACRONYMS AND DEFINITIONS

Abbreviation	Definition
DKAP	A phosphonate selective bis(3,5 trifluoromethyl)phenol functionalized siloxane
HotDKAP	A polysilphenylene backbone analog of DKAP
GC	Gas Chromatography
PC	Preconcentrator
NMR	Nuclear Magnetic Resonance
T_g	Glass Transition Temperature
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetric Analysis
MS	Mass Spectrometer
TIC	Total Ion Count
m/z	Mass to charge ratio

1. INTRODUCTION

The extremely low thermal mobility and vapor pressure of NTAs forces detection instrumentation to operate at elevated temperatures. These high temperatures degrade many current-generation polymer formulations and thus means there is a lack of highly-selective chemical films suited for NTA and chemical warfare agent (CWA) detection. Due to this technical shortfall, the ability to engineer NTA detectors in highly-portable form factors for wearable and unmanned systems sensors has been limited.

DKAP, a polymer developed nearly 20 years ago, by Dave Wheeler to provide a sensor coating for highly sensitive and specific detection of phosphonate based CWAs, has formed one of the core technologies of the MicroChem Lab effort. The polymer is used extensively on sensors for selective detection, but past research has demonstrated the value of the polymer for applications such as gas chromatography (GC) coatings and selective preconcentrator materials. Unfortunately, the thermal stability (required for NTA targets) of highly polar polymers is a known challenge, and experimental evidence suggests DKAP is no exception. A solution to the thermal stability challenge exists for highly polar COTS polymers used in GC columns- introducing a polyphenylene copolymer into the backbone of the silicone material increases the thermal stability of the material by 40-60 °C. Figure 1-1 shows an example of the effect on a COTS polymer and one concept of the polyphenylene siloxane backbone analog of DKAP to be synthesized. The hypothesis is that by replacing the existing polysiloxane backbone with the polysilphenylene polysiloxane backbone a similar increase in thermal stability may be achieved. This would allow the DKAP material to be used in all stages- sample collection, GC separation, and detection- of a notional system targeted for NTAs.

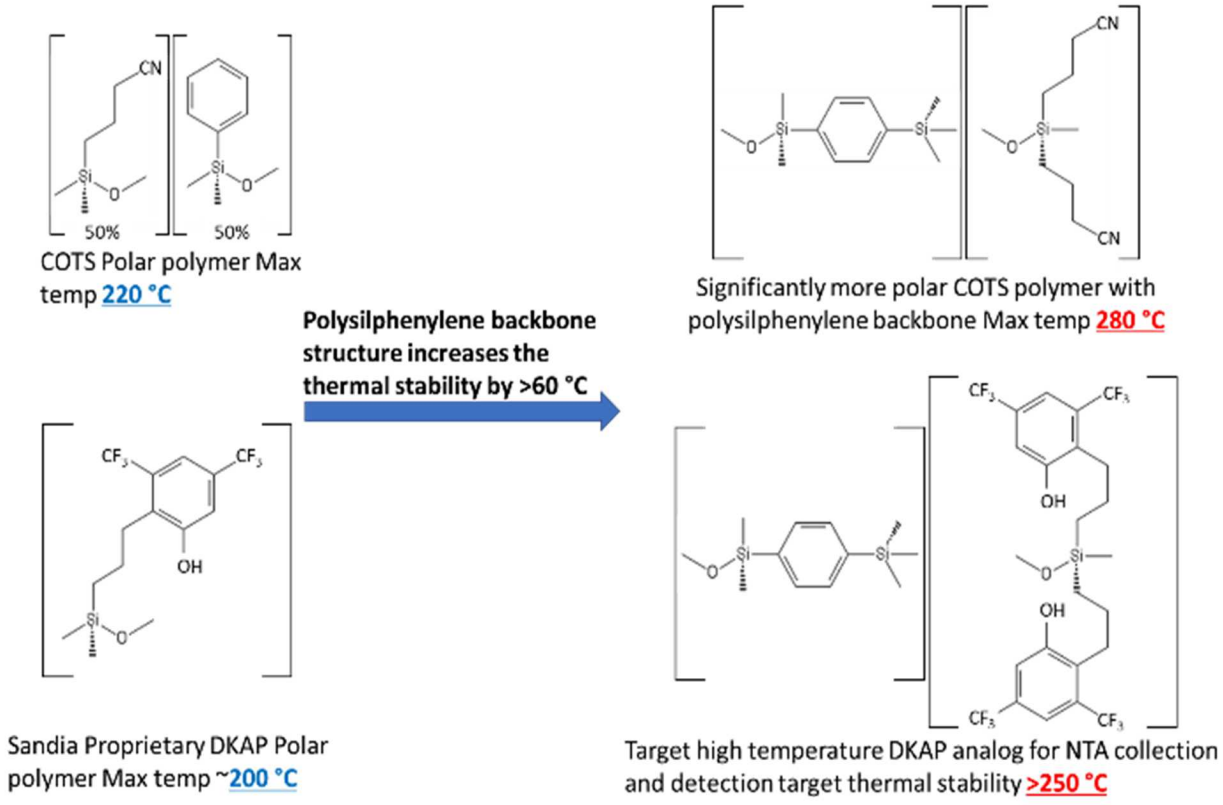

Figure 1-1. Comparison of thermal stability of COTS polymer with and without polysilphenylene polysiloxane backbone and the concept of a DKAP analog.

2. EXPERIMENTAL

HotDKAP is a poly(silphenylenesiloxane) polymer backbone (Figure 2-4) functionalized with the same bis(trifluoromethyl)phenol moiety found in DKAP (Figure 2-2). The backbone was synthesized as reported by Liu et al.. [1]

Briefly the bis(aminosilane) monomer was synthesized (Figure 2-3) and reacted with a commercial disilanol. NMR showed that the reaction proceeded cleanly, although with some homopolymerization of the disilanol, resulting in a 1:1.2 ratio of the monomethylsilphenylene to dimethylsilphenylene moieties in the polymer.

After purification of the polymer by repeated precipitation from toluene/methanol the polymer was functionalized with 2-allyl-3,5-bis(trifluoromethyl)phenol (4) via a Pt-catalyzed hydrosilylation reaction. This reaction is highly exothermic and when the Pt catalyst is added at elevated temperature, as is done in the synthesis of the DKAP polymer, the exotherm causes crosslinking, likely between the reactive Si-H groups, and yields an insoluble gel. However, dropwise addition of the catalyst at room temperature followed by heating to 80°C yields a soluble polymer.
NMR analysis of the final polymer (**5**) clearly shows incorporation of the bis(trifluoromethyl)phenol moiety (**Error! Reference source not found.**). The almost complete disappearance of the Si-H peak (Figure 2-1b) and integration of the aromatic and methylene protons in the product (**5**) shows that the hydrosilylation reaction proceeded to high conversion with one bis(trifluoromethyl)phenol group incorporated per Si-H in the starting material (**3**). Note that in the spectra for DKAP and HotDKAP (**5**) one of the H_{Ar} peaks of the 3,5-bis(trifluoromethyl)phenol moiety is obscured under the residual solvent peak of the benzene.

The final polymer (**5**) was light brown and glassy at room temperature. The T_g was measured by DSC and found to be ~32°C.

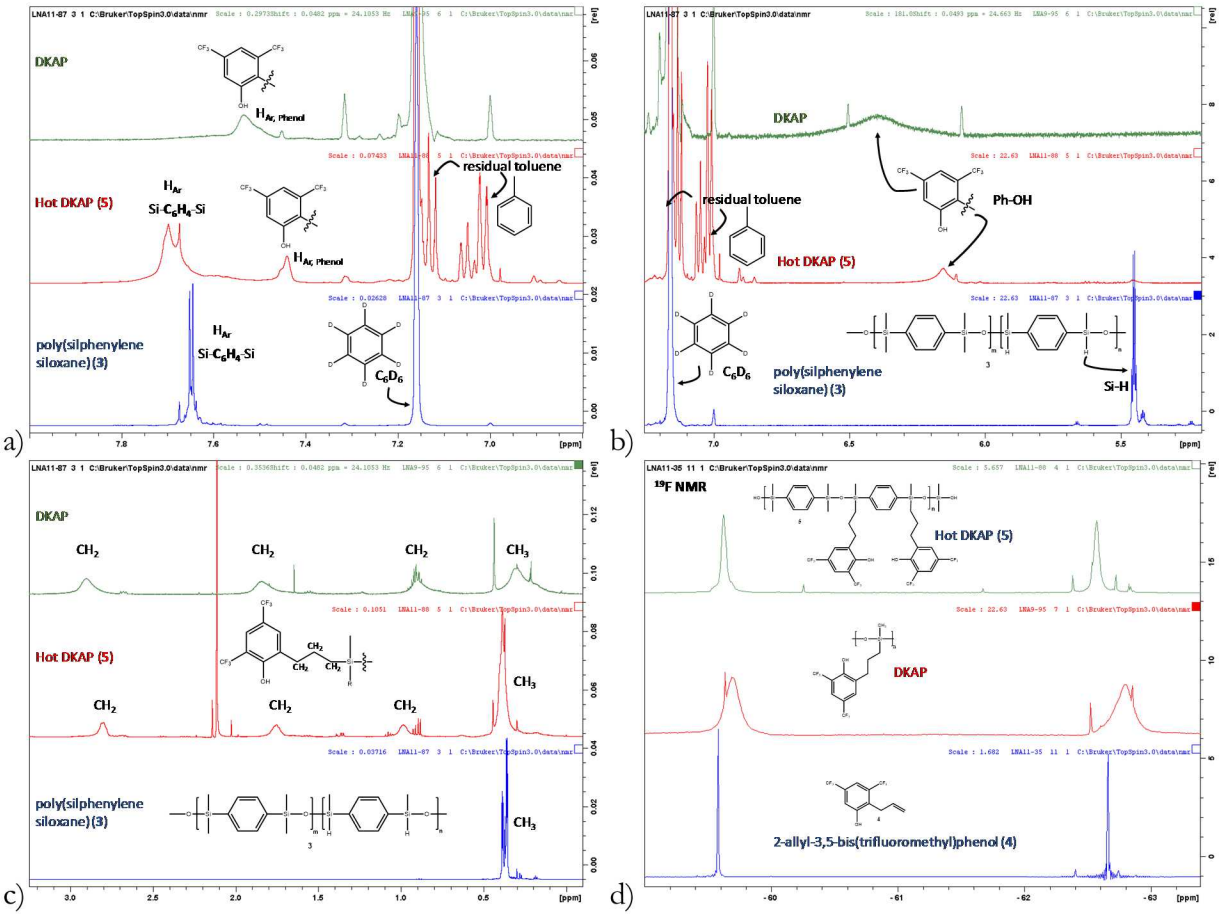

Figure 2-1. Expanded 1H spectra and 19F NMR for DKAP, HotDKAP (5), and precursors.

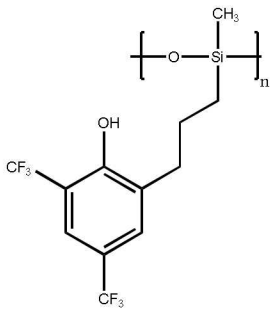

Figure 2-2. Structure of DKAP polymer.

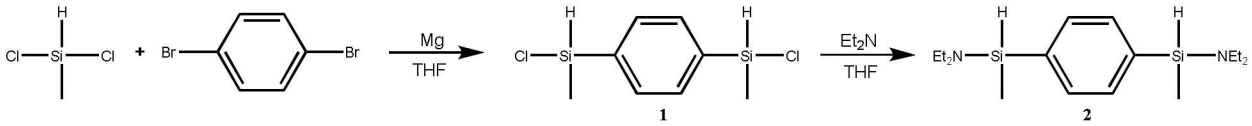

Figure 2-3. Synthesis of bis(aminosilane) monomer from commercial starting materials.

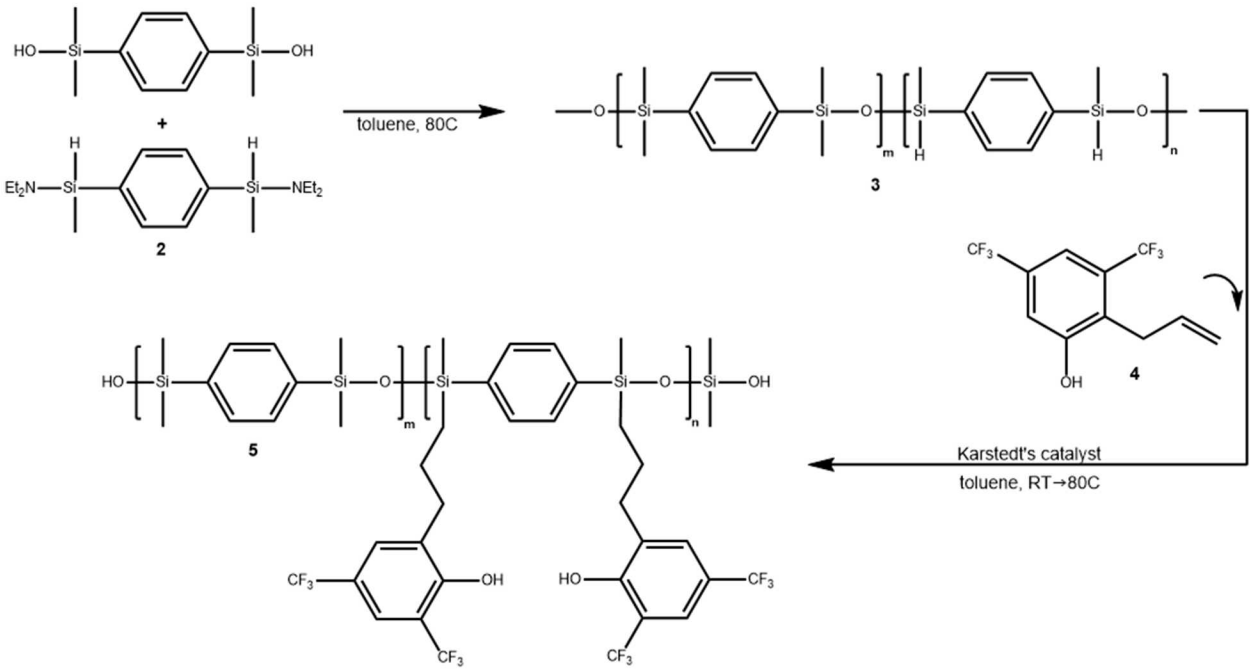

Figure 2-4. Synthesis of HotDKAP backbone from bis(aminosilane) and disilanol monomers followed by functionalization with the bis(trifluoromethyl)phenol active groups via a Pt-catalyzed hydrosilylation.

3. RESULTS AND DISCUSSION

Initial thermal stability testing via thermogravimetric analysis (TGA) in air is shown in Figure 3-1. The plot the TGA of DKAP is shown by the red dashed line, and the TGA for the HotDKAP sample is shown by the blue dashed line. The correlating solid lines are the DSC data, however because the samples were exceptionally viscous the data is suspect. The dotted line is the temperature of the system in Celsius. Initial evaluations indicated that the thermal decomposition started at the same temperature, or slightly earlier for the HotDKAP, however the decomposition appeared to take longer for the Hot DKAP relative to DKAP. This led to repeating the analysis with a TGA-MS system to monitor fragments formed during decomposition. Figure 3-2 shows plots of the total ion count (TIC) and common ion fragments [m/z: 69 and 91 (left plots) and m/z: 229, 243, 304, 313, and 332 (right plots)] formed by both HotDKAP (top row) and DKAP (bottom row). Figure 3-3 shows possible structures for each of the mass fragments.

The TGA-MS plots show that the key mass fragments for the thermal decomposition of DKAP appear in the hot-DKAP plots as well and at nearly the same starting point. The data analysis is still preliminary, but it appears the HotDKAP structure increases the stability as indicated by the ~65 °C shift in the apex of the common mass fragments. This needs to be confirmed with thermodynamic testing and GC coating lifetime testing.

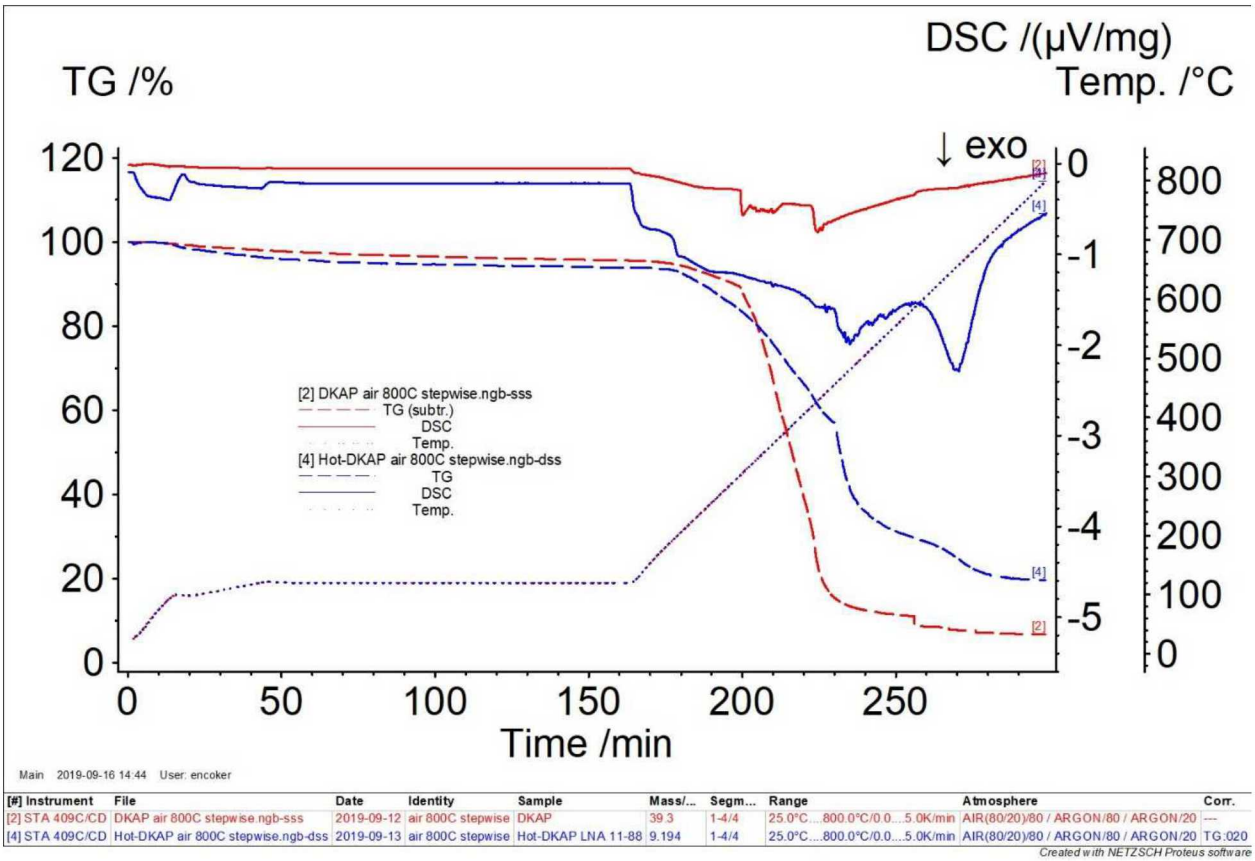

Figure 3-1. Thermogravimetric analysis of DKAP (red dashed line) and HotDKAP (blue dashed line)

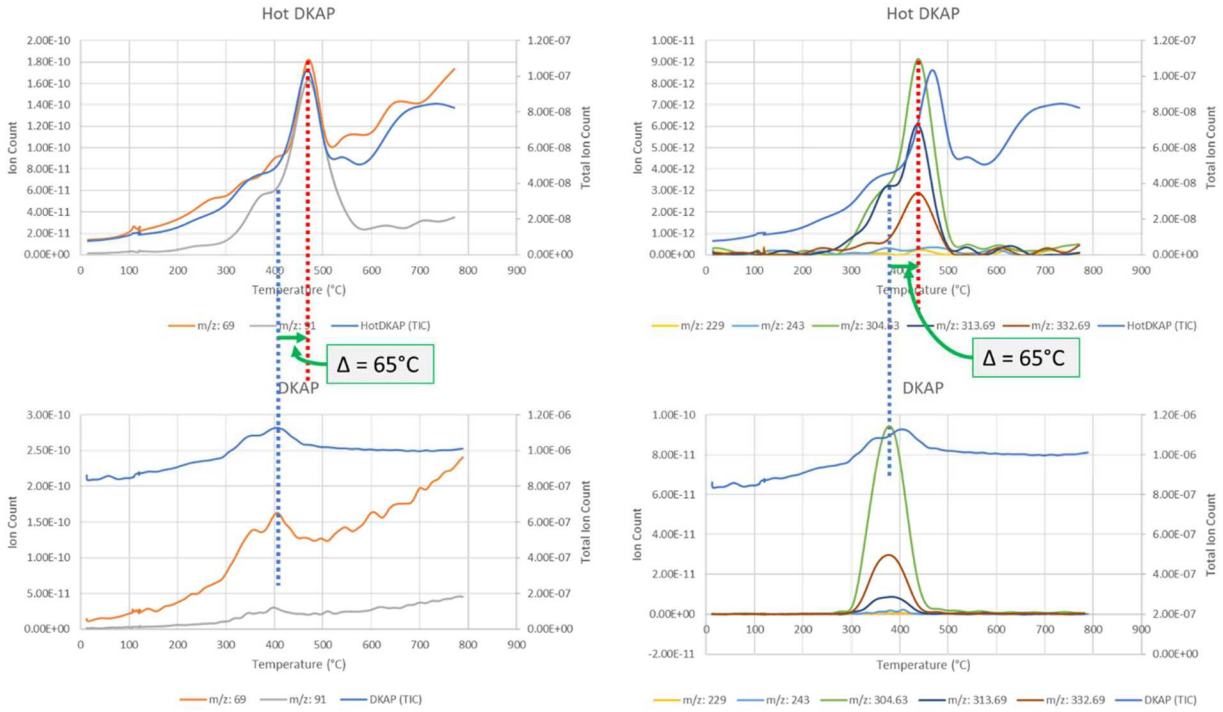

Figure 3-2. Plots of ion counts for common fragments: 69 and 91 (left) 229, 243, 304, 313, and 332(right) and the TIC both for both hotDKAP (top) and DKAP (bottom)

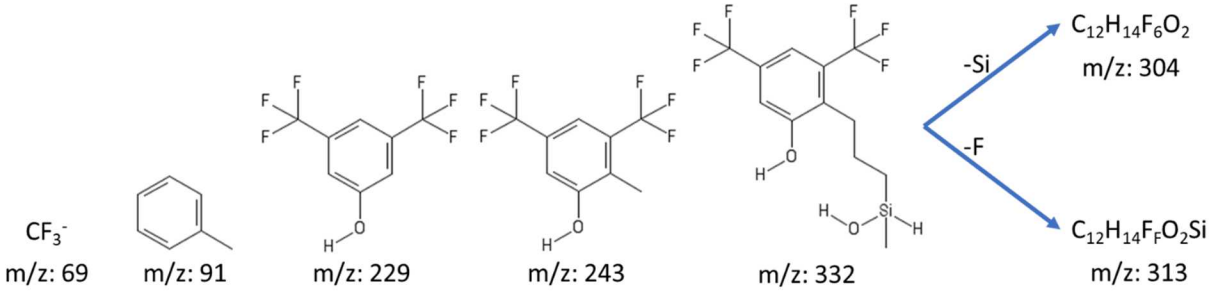

Figure 3-3. Possible structures for m/z fragments: 69, 91, 229, 243, 304, 313, and 332.

4. CONCLUSIONS AND FUTURE WORK

The next steps are to use the material produced in this work to coat a pair of capillary columns and a pair of smart preconcentrators. The columns will be used to evaluate the thermodynamics of the film relative to DKAP and to do longterm aging in air studies at slowly elevated temperatures. If the HotDKAP shows similar thermodynamic properties to DKAP the coated SPCs will be evaluated with the DKAP for lifetime with repeated firings looking at mass capture from a constant flow of constant low concentration DMMP. The results from these two studies will be combined with the data contained in here to write a final journal publication.

REFERENCES

[1] Liu, Y., Imae, I., Makishima, A. and Kawakami, Y., "Synthesis and characterization of poly (silphenylenesiloxane) s containing functional side groups, a study to high-temperature elastomer," Science and Technology of Advanced Materials. 27-34 (2003).

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