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# Syntactic Polysulfide Degradation Observed by SPME GC/MS

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## Abstract

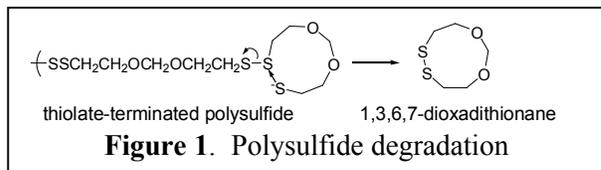
We have utilized SPME GC/MS to monitor the degradation of syntactic polysulfide in the presence of Viton A at elevated temperature. This approach allowed the identification of products from two distinct degradation mechanisms. Small-scale laboratory experiments of this type are directly applicable to gas sampling for enhanced surveillance.

## Introduction

Our group utilizes Solid Phase Microextraction (SPME) Gas Chromatography-Mass Spectrometry (GC/MS) to monitor weapon headspace species, characterize non-nuclear material outgassing signatures and measure outgassing products of material aging and compatibility experiments. The use of SPME GC/MS to measure degradation products of polymers is a fairly recent development.<sup>1</sup> As polymers degrade, volatile and semi-volatile products can be given off and extracted by the SPME fiber. Analysis of these products by GC/MS reveals information on the nature of the degradation. Recently, we have examined the degradation of syntactic polysulfide in the presence of Viton A. In the process of evaluating possible effects of syntactic polysulfide on Viton A, we discovered that our Viton A actually had an unexpected effect on the polysulfide, causing it to degrade after several weeks at 70°C. Results from those experiments will be presented here along with a brief discussion of the applicability of these laboratory results to enhanced surveillance.

## Results and Discussion

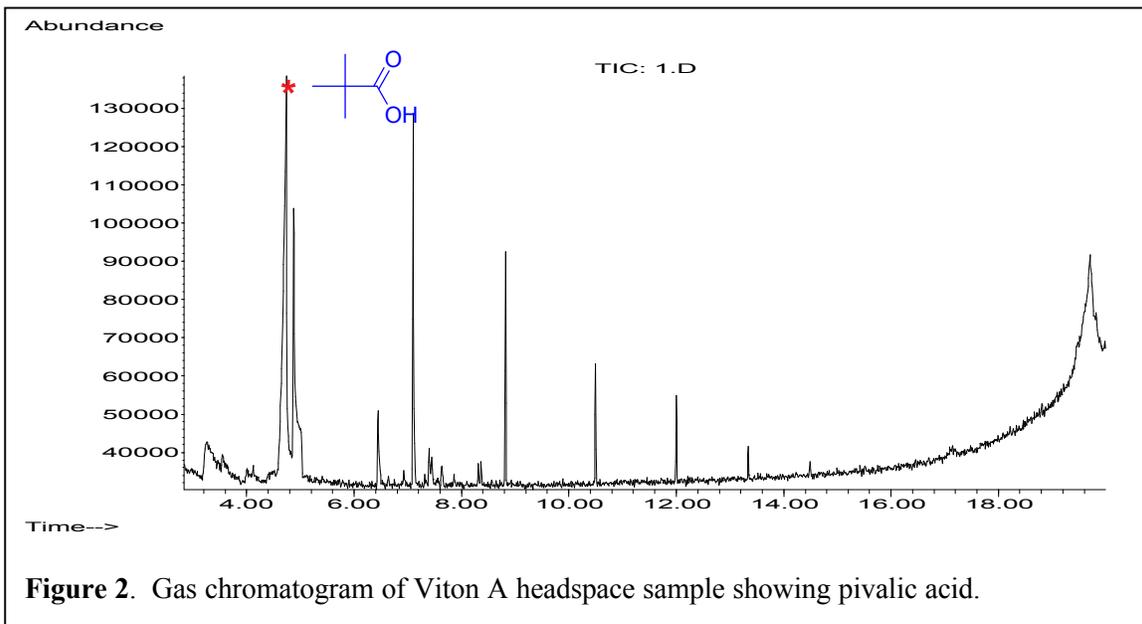
When prepared with a lead oxide curing agent, syntactic polysulfide can undergo a degradation mechanism in which a terminal thiolate group reacts with the nearest disulfide linkage to generate a volatile disulfide-containing cyclic molecule (1,3,6,7-dioxadithionane) as seen in **Figure 1**.<sup>2</sup> This compound is readily detected by GC/MS. In



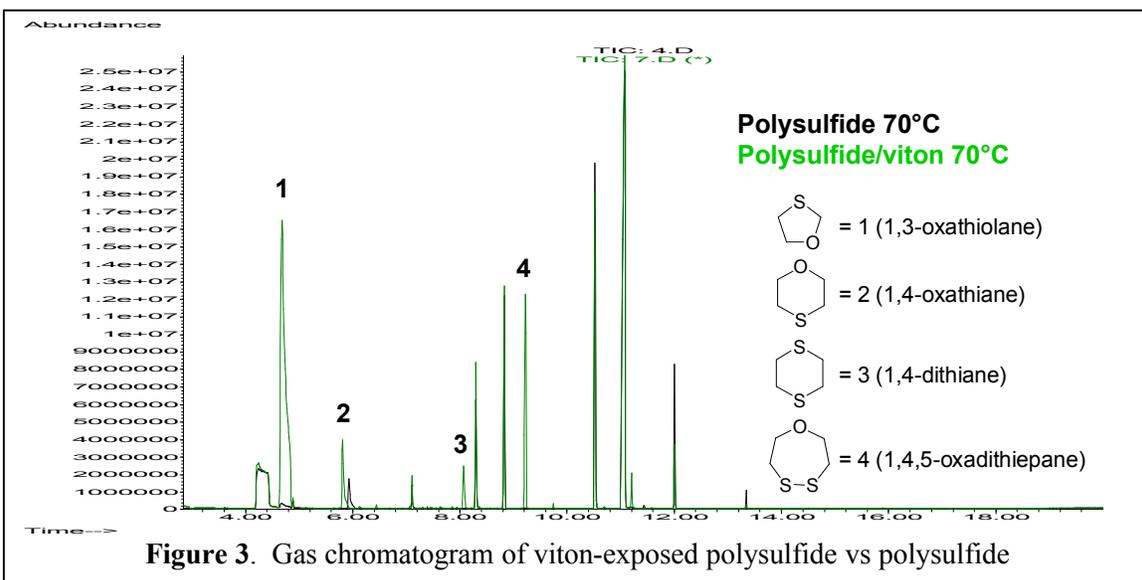
our experiments to date, this degradation route has not resulted in a visible impact on the physical state of the polymer. In our microcompatibility experiments in which approximately 100 mg each of syntactic polysulfide and Viton A were

aged at room temperature and 70°C for several weeks, we observed significant changes in the state of the polysulfide. It darkened slightly and changed from a firm, spongy

material to a soft, almost liquid, material. These changes only occurred at the higher temperature in the presence of Viton A. SPME GC/MS (**Figure 2**) of the Viton revealed most of the outgassing species are fluorocarbons, which would not be expected to degrade polysulfide. One compound that could affect the polysulfide was found. Pivalic acid, or 2,2-dimethylpropanoic acid, may catalyze the degradation of polysulfide, resulting in the generation of additional volatile cyclic compounds.<sup>2</sup>



Analysis of the outgassing species present in the viton-exposed polysulfide vs polysulfide alone shows the appearance of several new sulfur-containing cyclic compounds (**Figure 3**). Monitoring of the viton-exposed polysulfide over several months has shown that the relative abundances of compounds 1-4 in the chromatogram continue to increase.



## Conclusions

We have utilized SPME GC/MS to monitor the degradation of syntactic polysulfide in the presence of Viton A at elevated temperature. This approach allowed the identification of products from two distinct degradation mechanisms. Small-scale laboratory experiments of this type are directly applicable to gas sampling for enhanced surveillance. Monitoring weapon systems for volatile organics in the headspace may reveal the state of non-nuclear components. Laboratory experiments help differentiate “normal” degradation signatures from detrimental degradation and provide insight into the source of unusual or unexpected headspace species. It should be noted that syntactic polysulfide has a long history of reliability in the stockpile, and we believe our observations most likely represent a curious, but nonetheless intriguing, laboratory anomaly.

## Experimental

General sample preparation for SPME-GC/MS analysis: Materials are prepared for SPME headspace sampling by placing either the individual material or two materials (usually 10-100 mg) in a headspace vial that is sealed under nitrogen. Samples are aged at room temperature or 70°C for at least two weeks prior to analysis.

Automated analysis conditions: Samples are analyzed by SPME GC/MS using an automated system under the following conditions: 75 µm Carboxen-PDMS SPME fiber, conditioned for 20 min at 260°C; headspace sampled at 50°C for 5 min and injected into the GC for 1 min at 250°C. The Agilent 6890 GC is set for splitless injection, purge @ 0.5 min, using a Restek RTX5-MS column (30 m, 0.25 mm ID, 0.25 µm film) with a 1.0 mL/min constant flow of helium. The 20 min run has the following temperature profile: 40°C/2 min, 15°C/min to 300°C, hold 0.67 min. An Agilent 5973 mass spectrometer scans the mass range from 20-450 at a rate of 1.75 scans/sec with a filament delay of 2.75 min.

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