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AGING AND DEGRADATION STUDIES OF BUTYL RUBBER FORMULATIONS IN SUPPORT OF O-RING APPLICATIONS

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U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

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Butyl Rubbers are Used for Numerous Applications

- Butyl rubbers are used for numerous applications including rubber products, tire inner tubes, curing bladders, and protective clothing.
- Butyl rubbers are used for o-ring seals where low permeation rates are important for long-term aging of high-reliability devices
- Oxidation reduces the overall lifetime of high-reliability materials potentially altering performance
- Understanding degradation mechanisms is the gateway for sensor development to identify unique volatile degradation products for condition monitoring
  - Early warning system
  - Providing potential monitoring markers
  - Understand unique chemical signatures from gas samples

O-RINGS

O-ring Material Influences Permeability

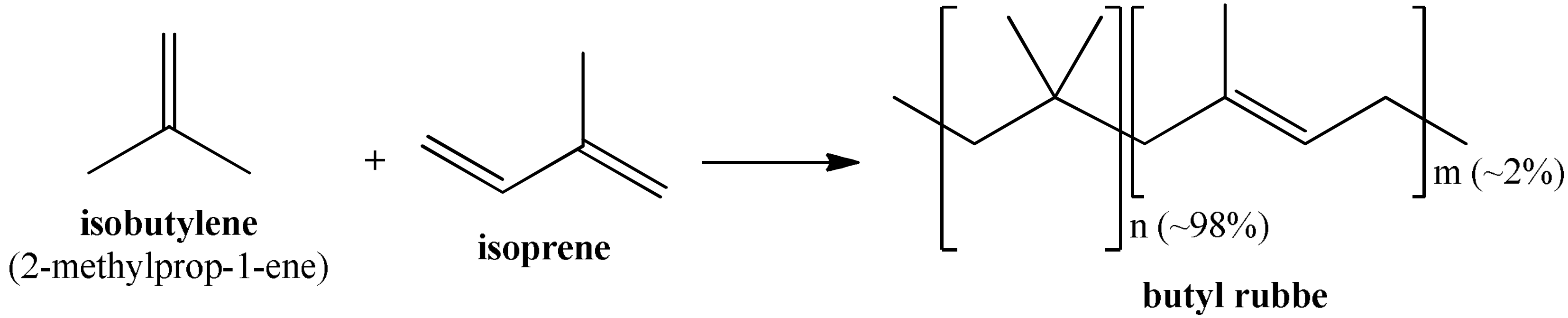
-Piston/actuators

-Environmental Seals

Material	Water permeability ccSTP/cm/s/cmHg
Butyl	~1.9×10^{-9}
EPDM	~3.5×10^{-8}
Silicone	~1.8×10^{-6}
Fluorosilicone (LS-53)	~1.5×10^{-6}

Gillen, K. T.; Green, P. F. "Moisture Permeation of Environmental Seals Used in Weapons," SAND92-2651, 1993.

Butyl Rubber Structure and Formulations



Purpose	Ingredient	Butyl # 6	Butyl # 10	Butyl # 21
		PHR[a]	PHR	PHR
Polymer	Exxon Exxpro 3433	100		
Polymer	Exxon chlorobutyl HT1066			100
Polymer	Lanxess bromobutyl 2030		100	
Antioxidant	CYANOX 2246			1.5
Reinforcing filler	N550 carbon black	65	65	33
Reinforcing filler	N330 carbon black			33
Processing aid (internal lubricant)	Polyethylene AC-617	5	5	
Accelerator	Advance 5364 ZDMC Pellets-80			1.88
Activator	Stearic acid	0.5		
Activator/Vulcanizer	Zinc oxide (French process)	2	5	5
Cure co-agent	HVA-2 or Vanax MBM		5	
Activator/Vulcanizer	SP 1045 resin	5		

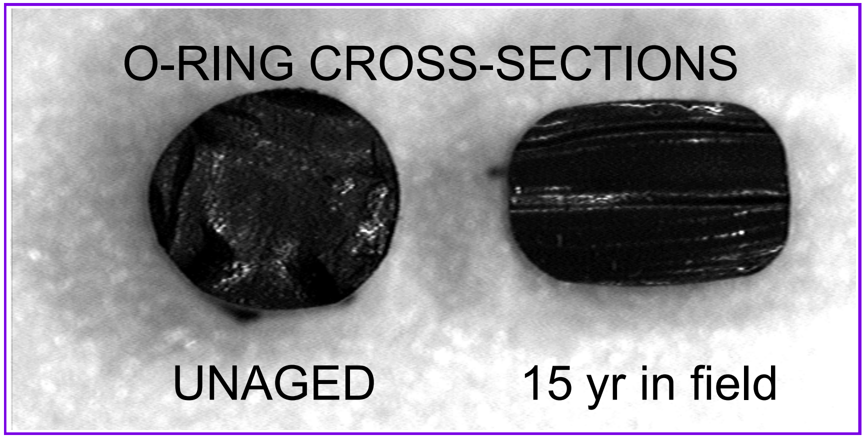
[a] PHR = parts per hundred rubber

O-rings Background

Ubiquitous in high reliability devices

Used as environmental seals or other seals

Most high reliability devices are filled with inert gases to protect interior components from oxidation, hydrolysis, contaminants (environmental or chemical)



It is of critical importance to know how o-rings age and degrade

Need to determine realistic lifetimes to ensure intended performance

O-ring Published Documentation

Bernstein, R.; Gillen, K. T. Polymer Degradation and Stability, Predicting the Lifetime of Fluorosilicone O-rings 2009, 94, 2107-2133.

Bernstein, R.; Gillen, K. T. "Fluorosilicone and Silicone O-Ring Aging Study," SAND2007-6781, Sandia National Laboratories, 2007.

Chavez, S. L.; Domeier, L. A. "Laboratory Component Test Program (LCTP), Stockpile O-Rings," BB1A3964, 2004.

Gillen, K. T.; Bernstein, R.; Wilson, M. H. *Polymer Degradation and Stability,* Predicting and Confirming the Lifetime of O-rings 2005, 87, 257-270.

Gillen, K. T.; Celina, M.; Bernstein, R. In *Polymer Degradation and Stability* Validation of Improved Methods for Predicting Long-Term Elastomeric Seal Lifetimes from Compression Stress-Relaxation and Oxygen Consumption Techniques, 2003; Vol. 82, pp 25-35.

Thermal Exposure

Thermal-Oxidation

$$\text{Polymer} + O_2 \longrightarrow \text{Oxidized Polymer}$$

Quantify amount of oxygen consumed

- Simple in theory
- Difficult in practice
- Amazingly sensitive

CSR vs Oxygen Consumption Predictions

Material	Prediction to ~50% F/Fo at 23 °C, years	
	High T E_a	Oxygen Consumption
Butyl #6	~160	~26
Butyl #10	~13,000	~1,700
Butyl #21	~170	~34

Prediction in years at 23 °C to reach ~50% force

Experimental Methods and Test Matrix

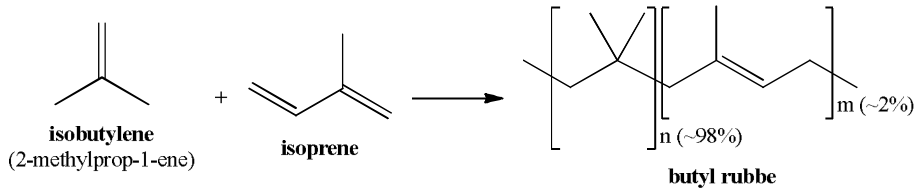
- Synthesis of Butyl Rubber using labeled starting materials (polymer or an additive)
  - Very expensive
- Aging experiment
  - Butyl Rubber were placed into 10 cc steel vessels and aged for various times (several days to 130 days) at 109°C under ambient pressures of air and Oxygen-18
- GC/MS analyses used to identify thermal-oxidative products
  - identify the specific origin of each degradation product of the base materials
  - Locate mass shifts
- Piece puzzle together to understand degradation mechanisms and rates

Material	Amounts Aged (mg)	Aging Gas	Aging Temperature (°C)	Aging Times (total days)
Butyl #6	153 & 119	Air	109	30 & 61
Butyl #10[a]	116 & 113	Air	109 & 124	30, 60, 106, & 216, & 413
	123 & 125	O-18	109	30 & 61
Butyl #21	130 & 156	Air	109	30 & 61
Laxness bromobutyl 2030	175 & 108	Air	109	30 & 61
Polyethylene AC-617	42 & 39	Air	109	31 & 63
Vanax MBM	50 & 38	Air	109	31 & 63

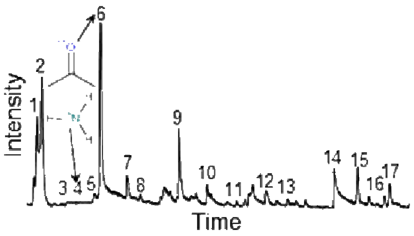
[a] Butyl #10 was aged at 109 °C for up to 216 total days then at 124 °C for 166 total days before a final aging time of 31 total days at 109 °C (i.e., 247 total days at 109 °C and 166 total days at 124 °C for a total of 413 total days of aging), as described in the text.

Sample Preparation

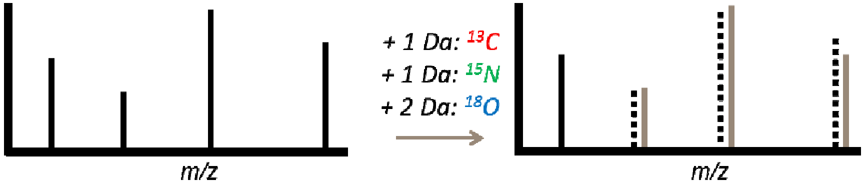
Headspace gas analysis:
- 10 cc gas injection
- cryofocusing gas chromatography MS (cryo-GC/MS)



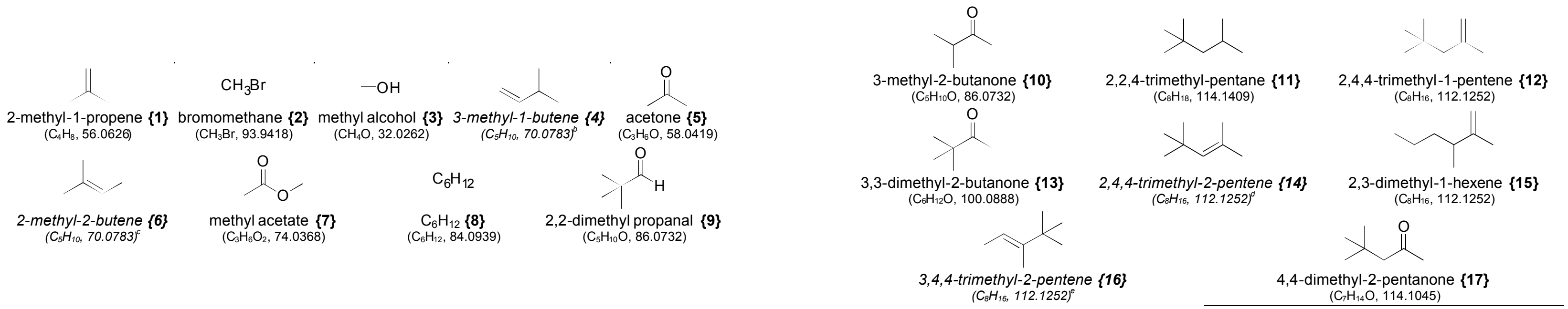
JEOL GCMate II

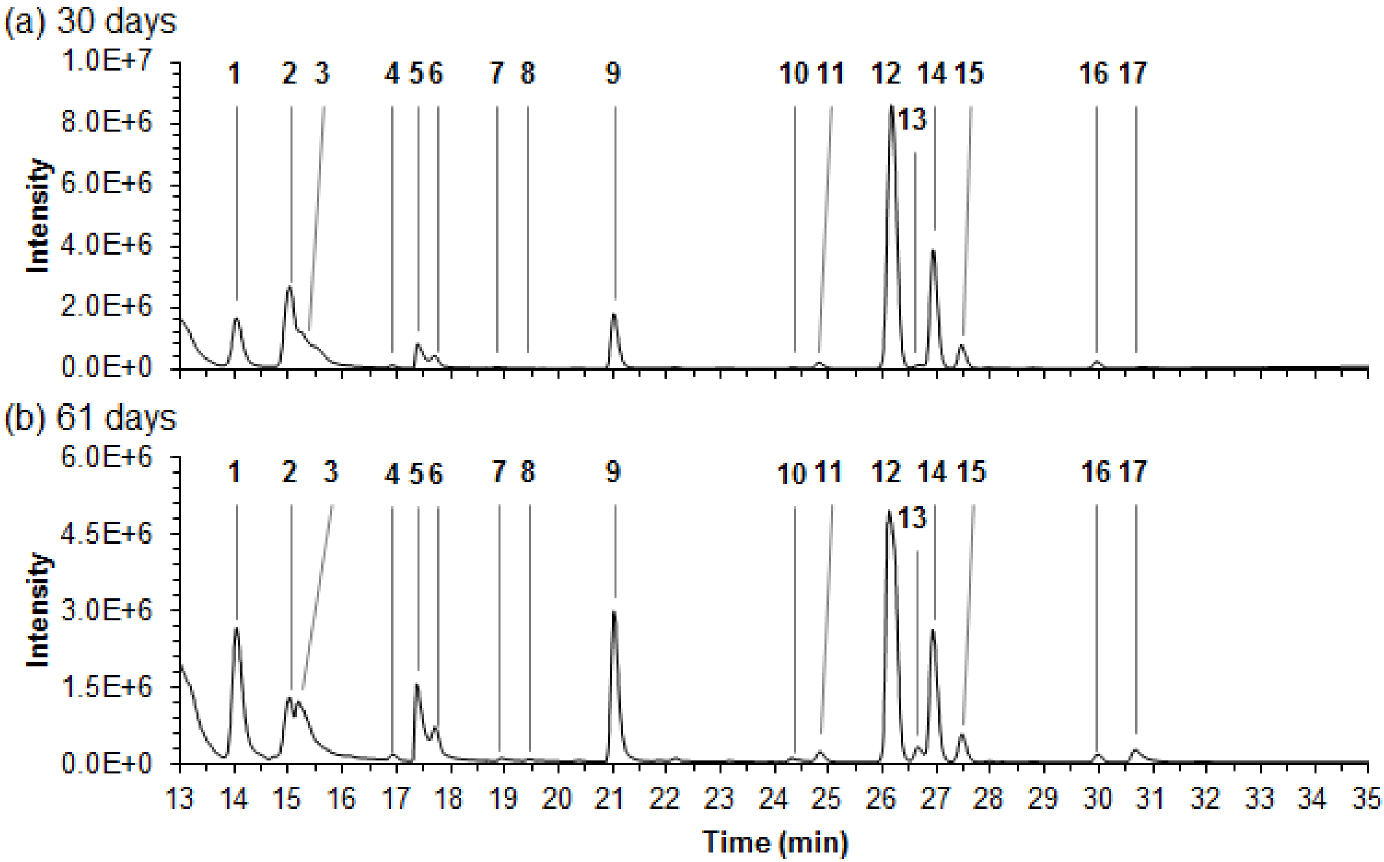


Locate isotopically labeled atoms:
- Monitor mass spectra for shifts and compare to ion fragmentation pathway

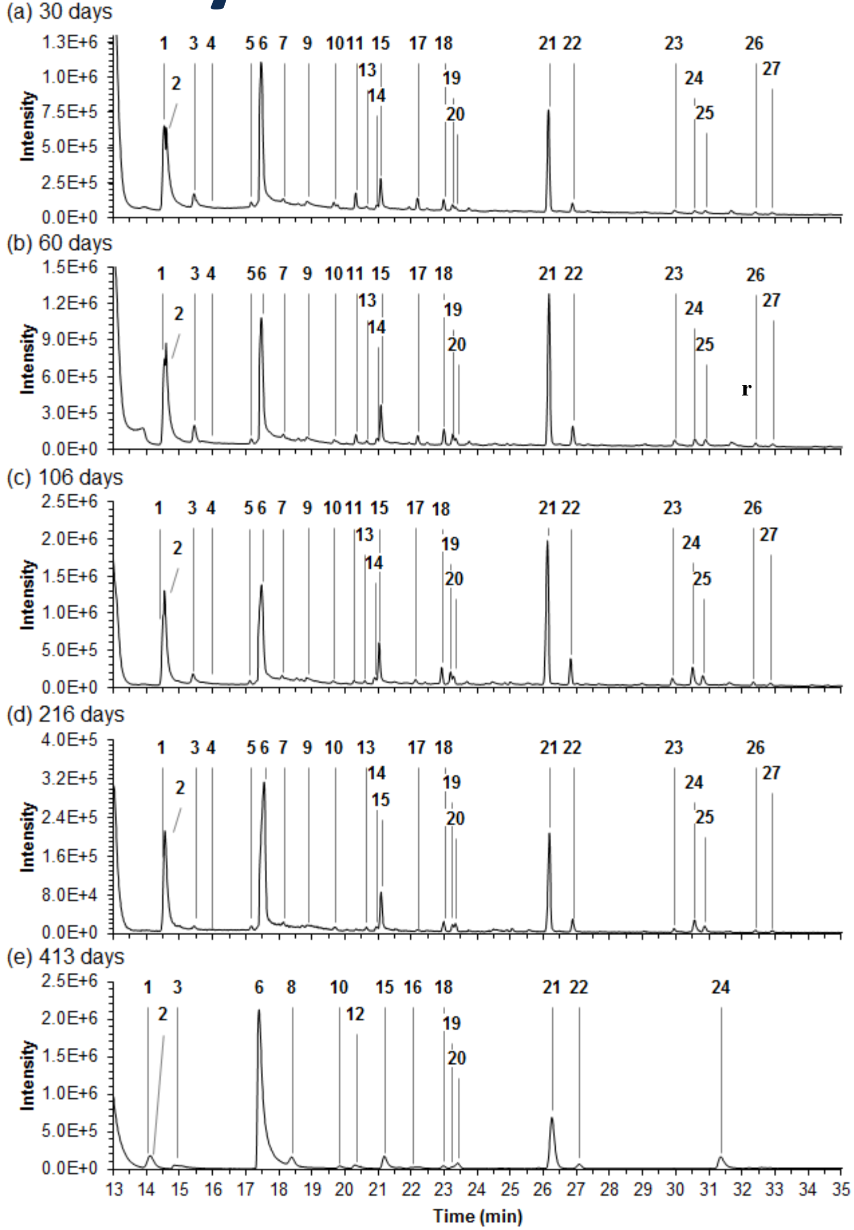


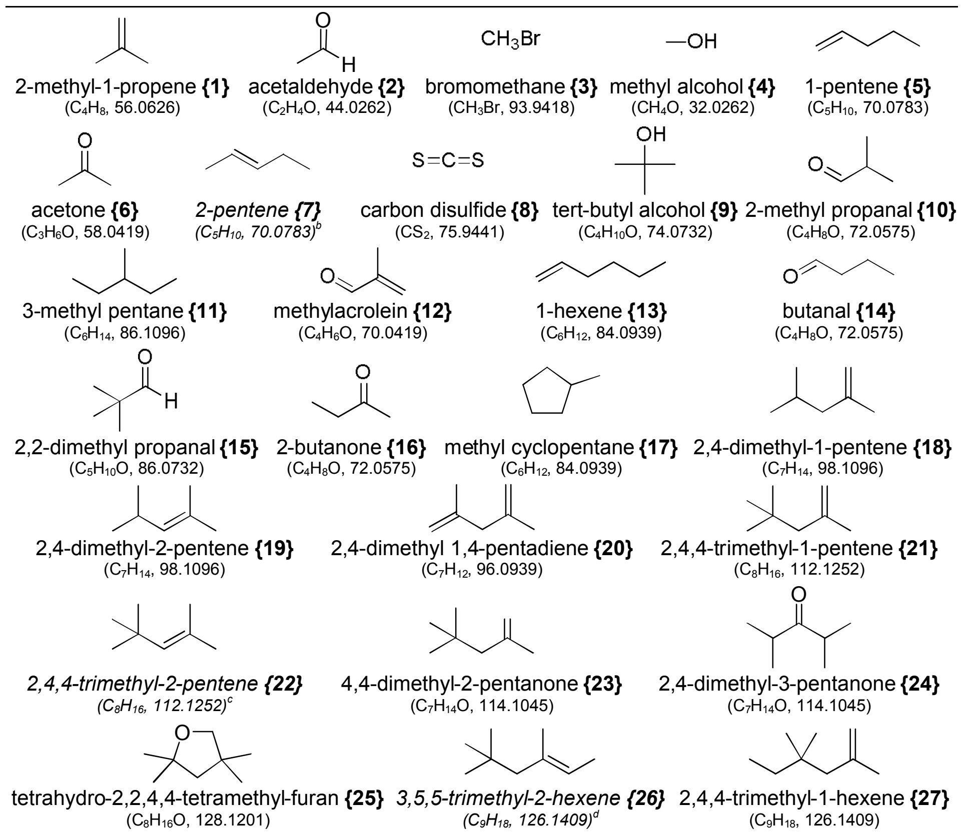
Butyl #6 Total Ion Chromatogram



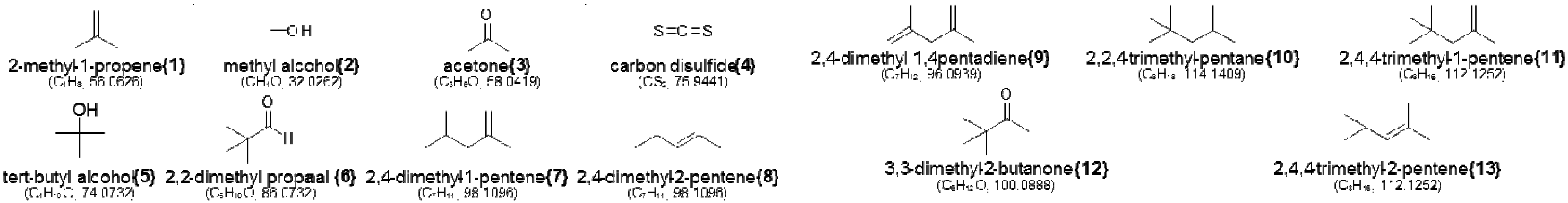


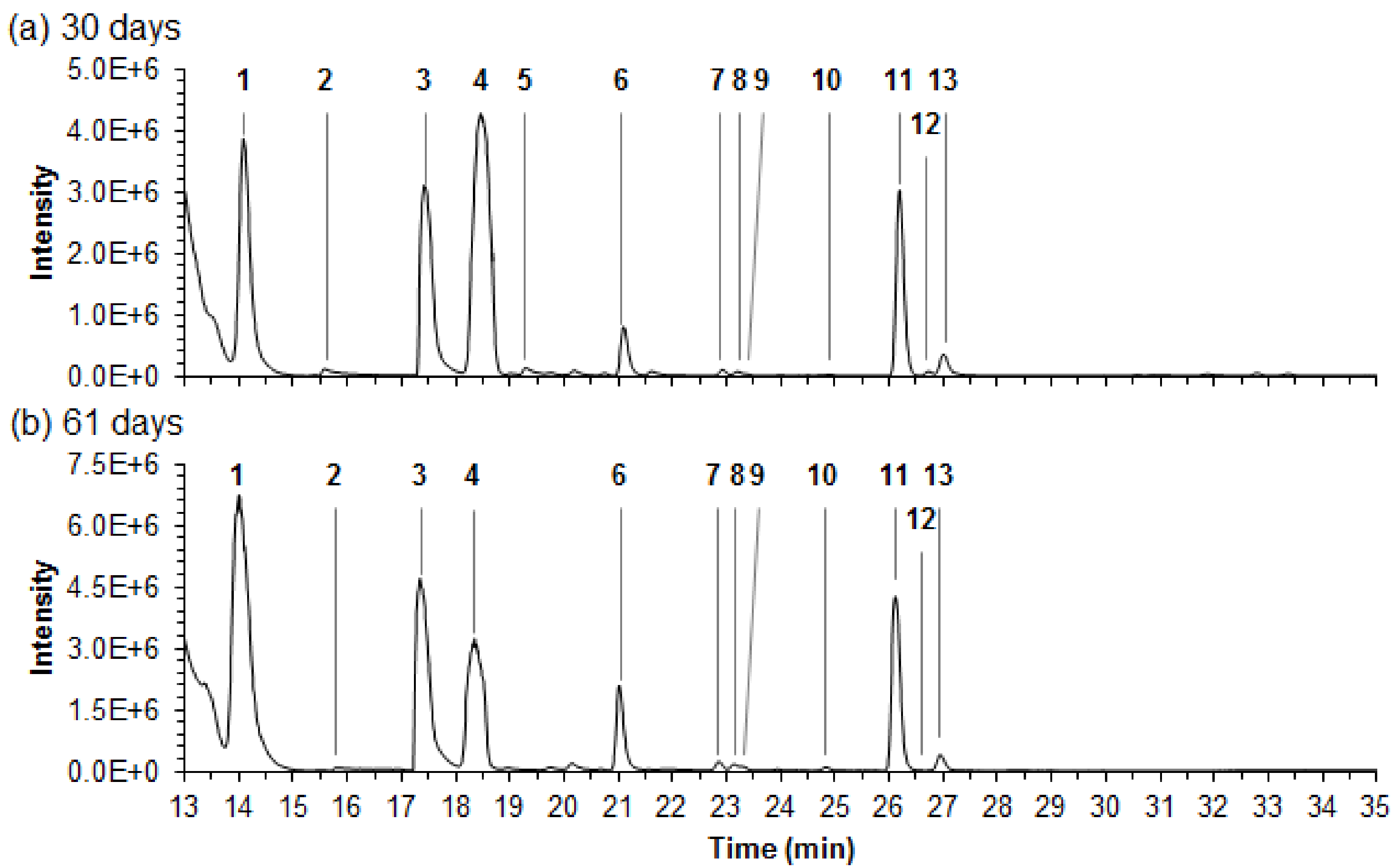
Butyl #10 Total Ion Chromatogram



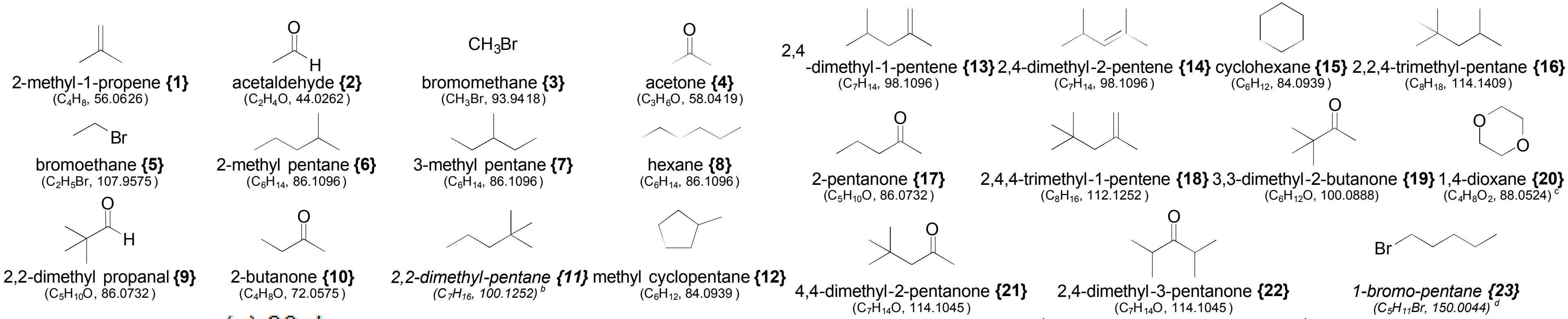


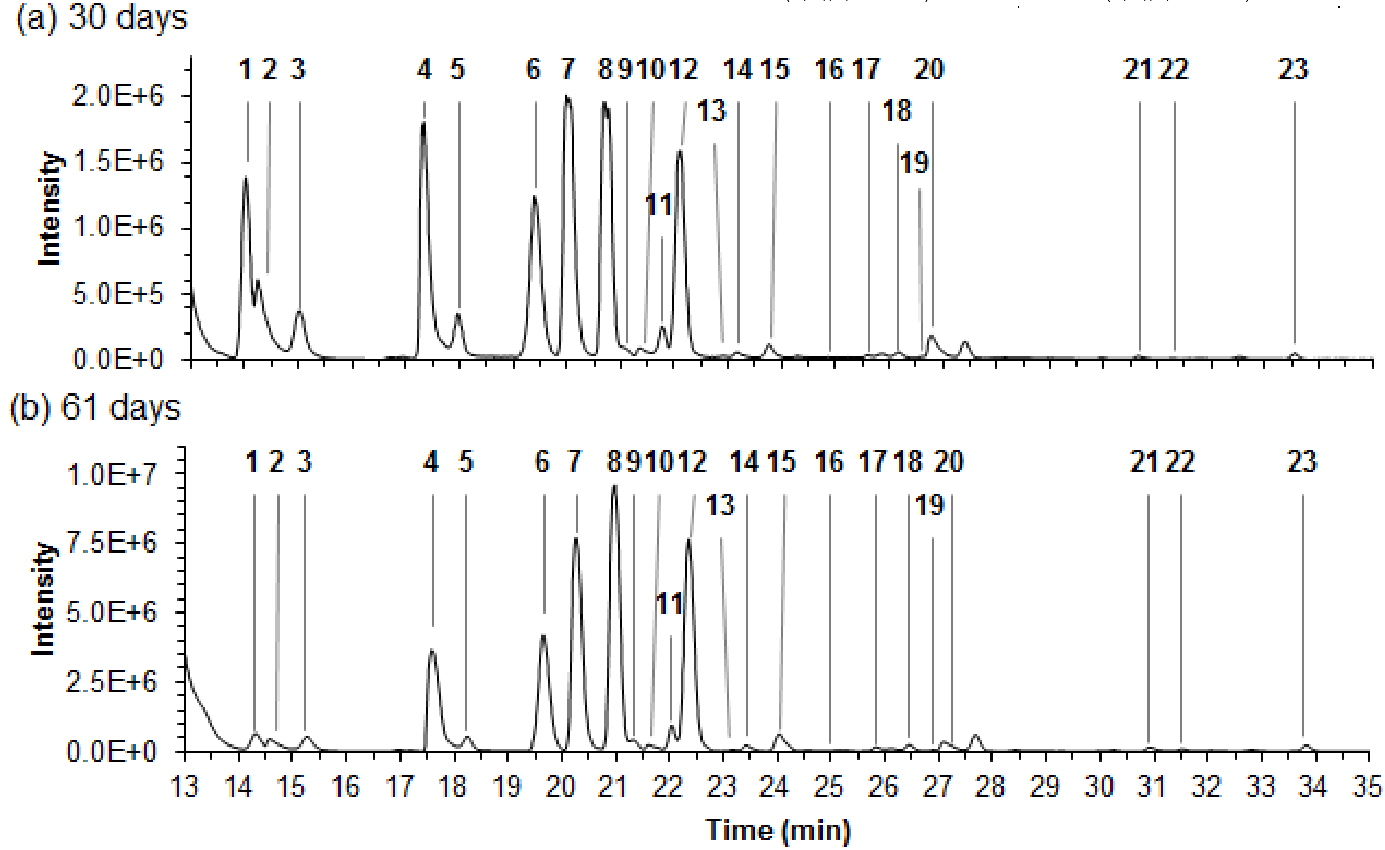
Butyl #21 Total Ion Chromatogram



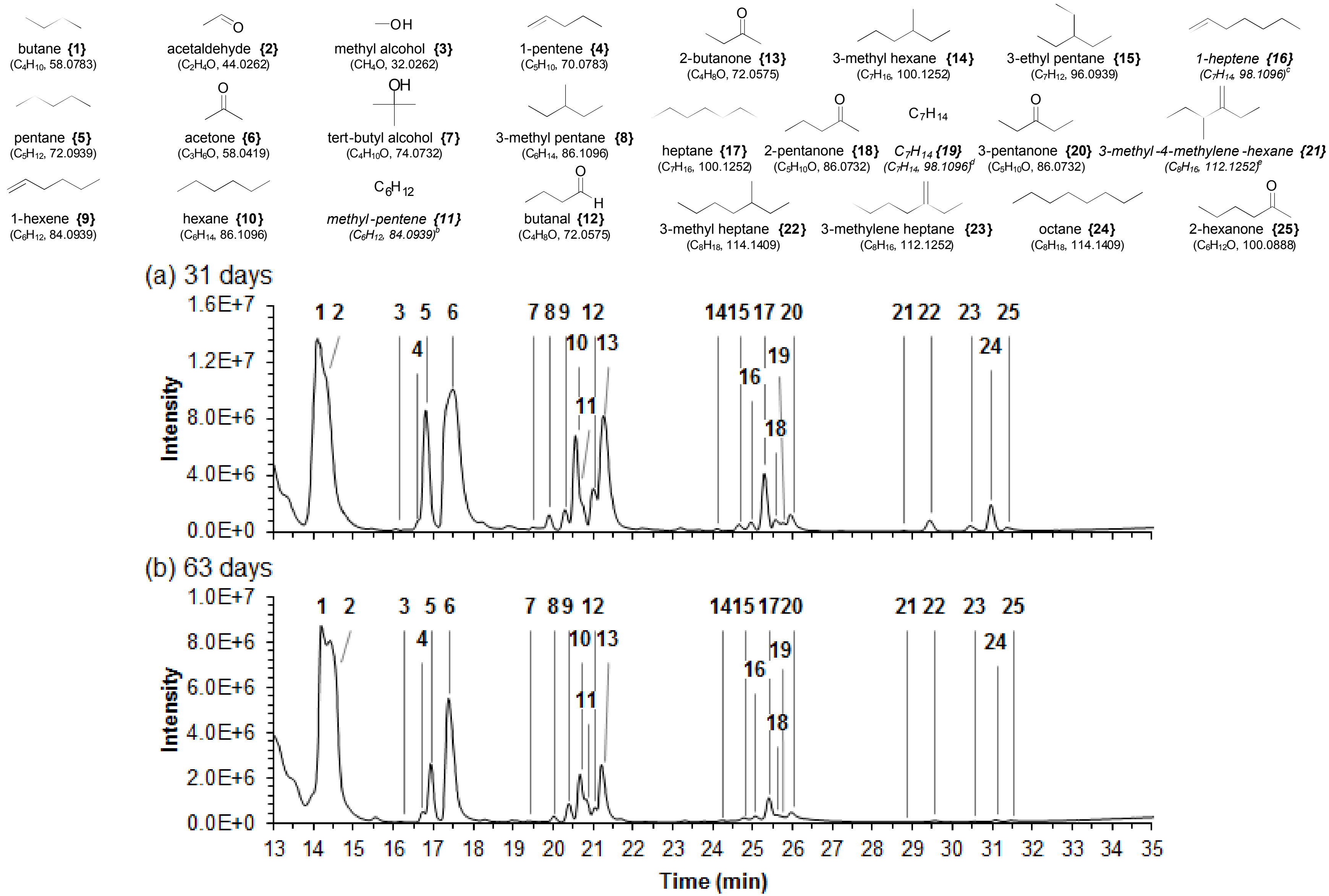


Lanxess Bromobutyl 2030 Total Ion Chromatogram

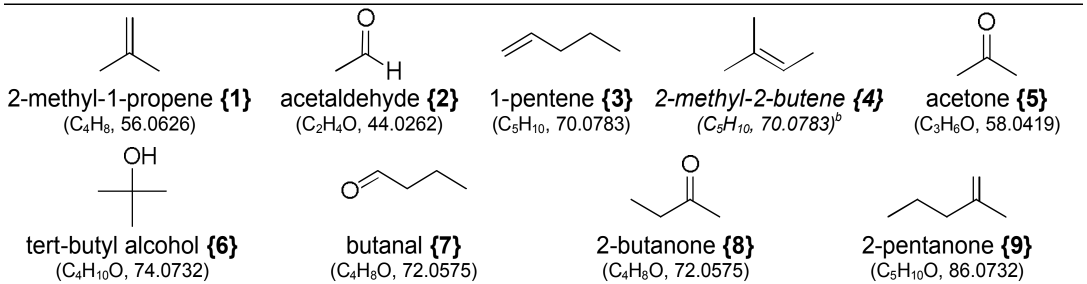


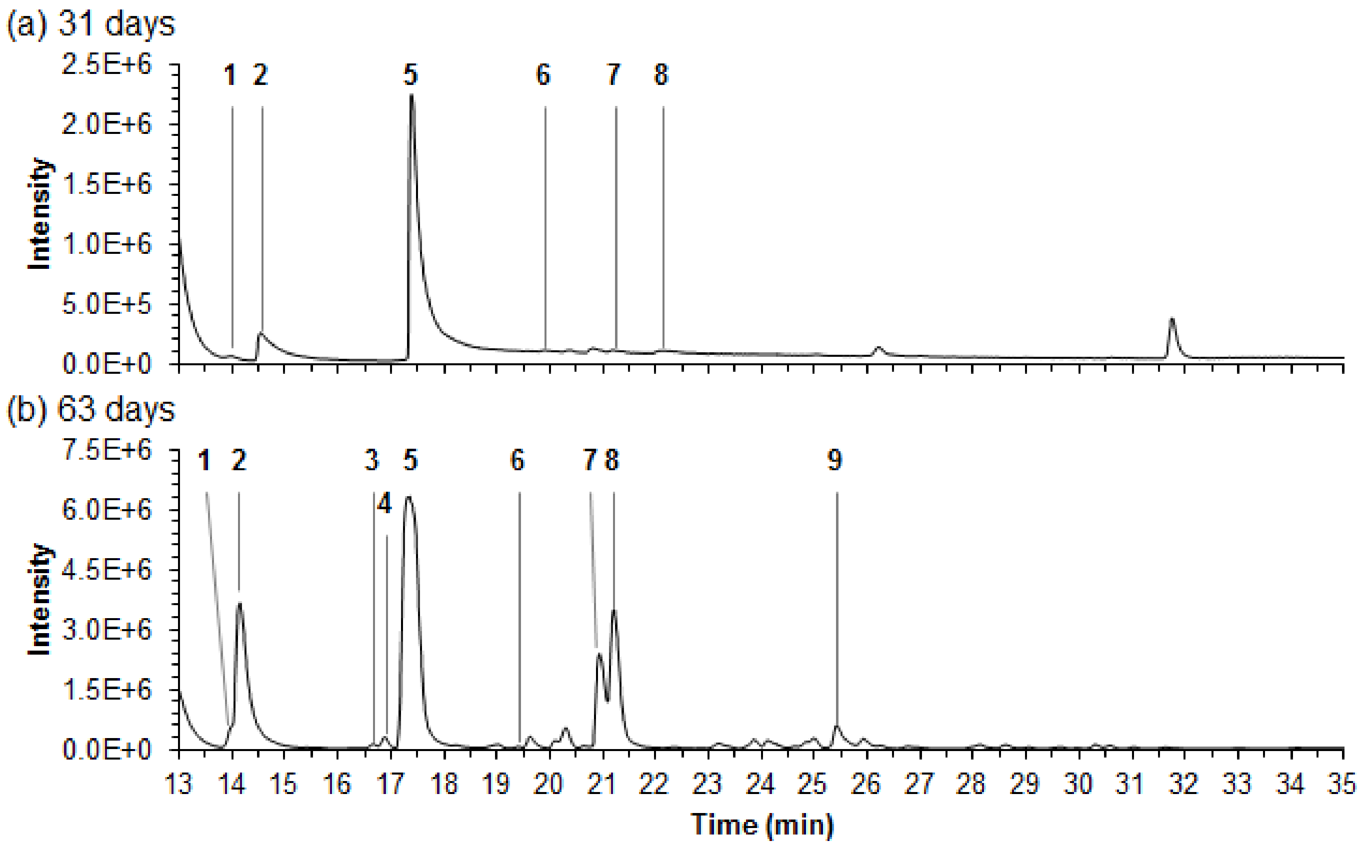


Polyethylene AC-617 Total Ion Chromatogram

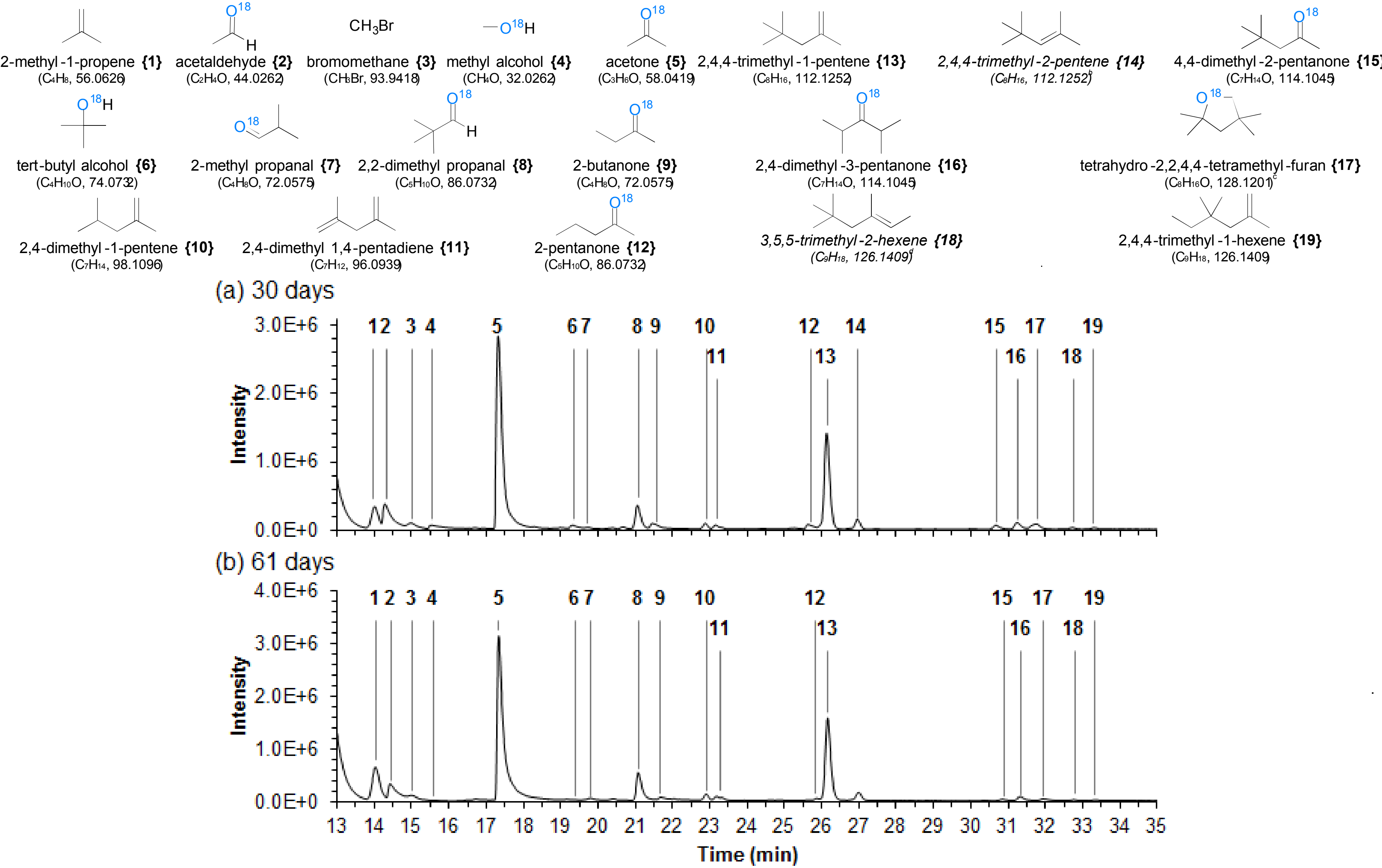


Vanax MBM Total Ion Chromatogram

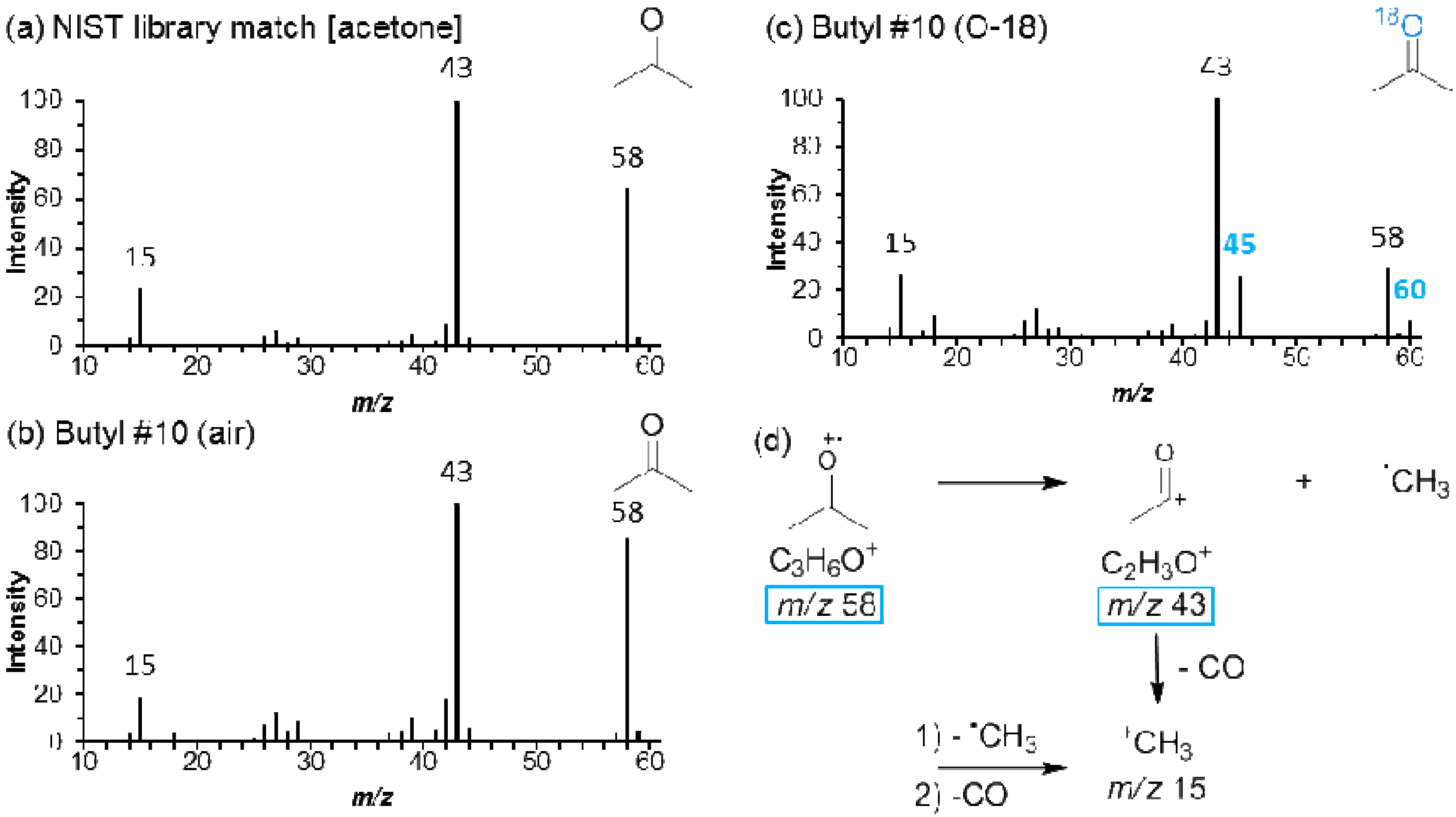




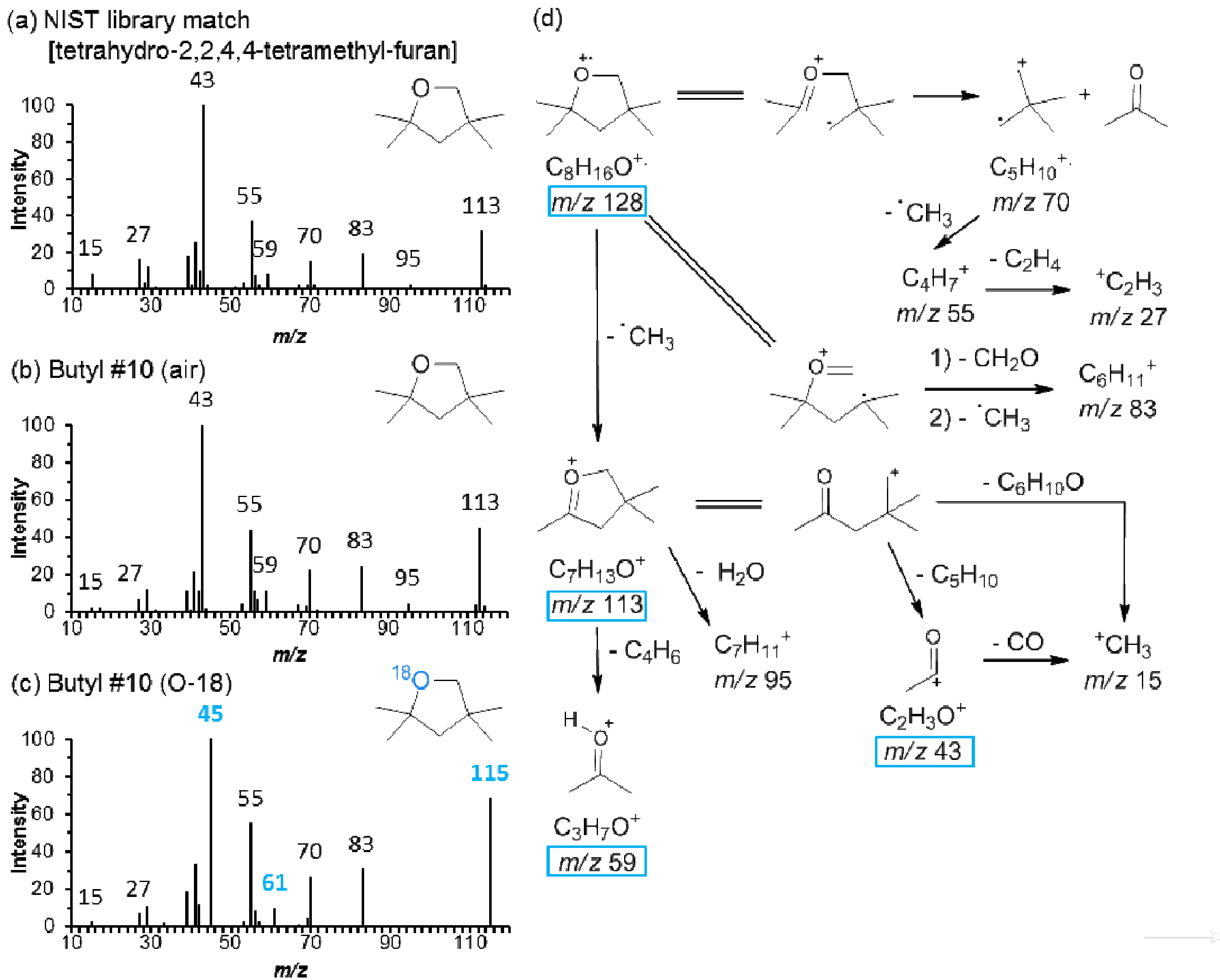
Butyl #10 O-18 Enriched Total Ion Chromatogram



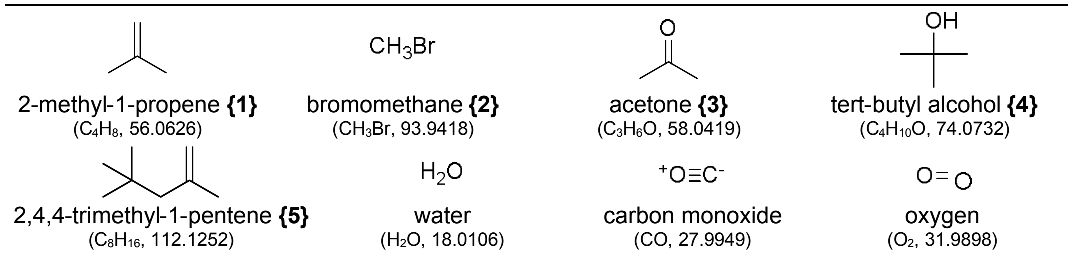
Mass Shifts Observed for Acetone

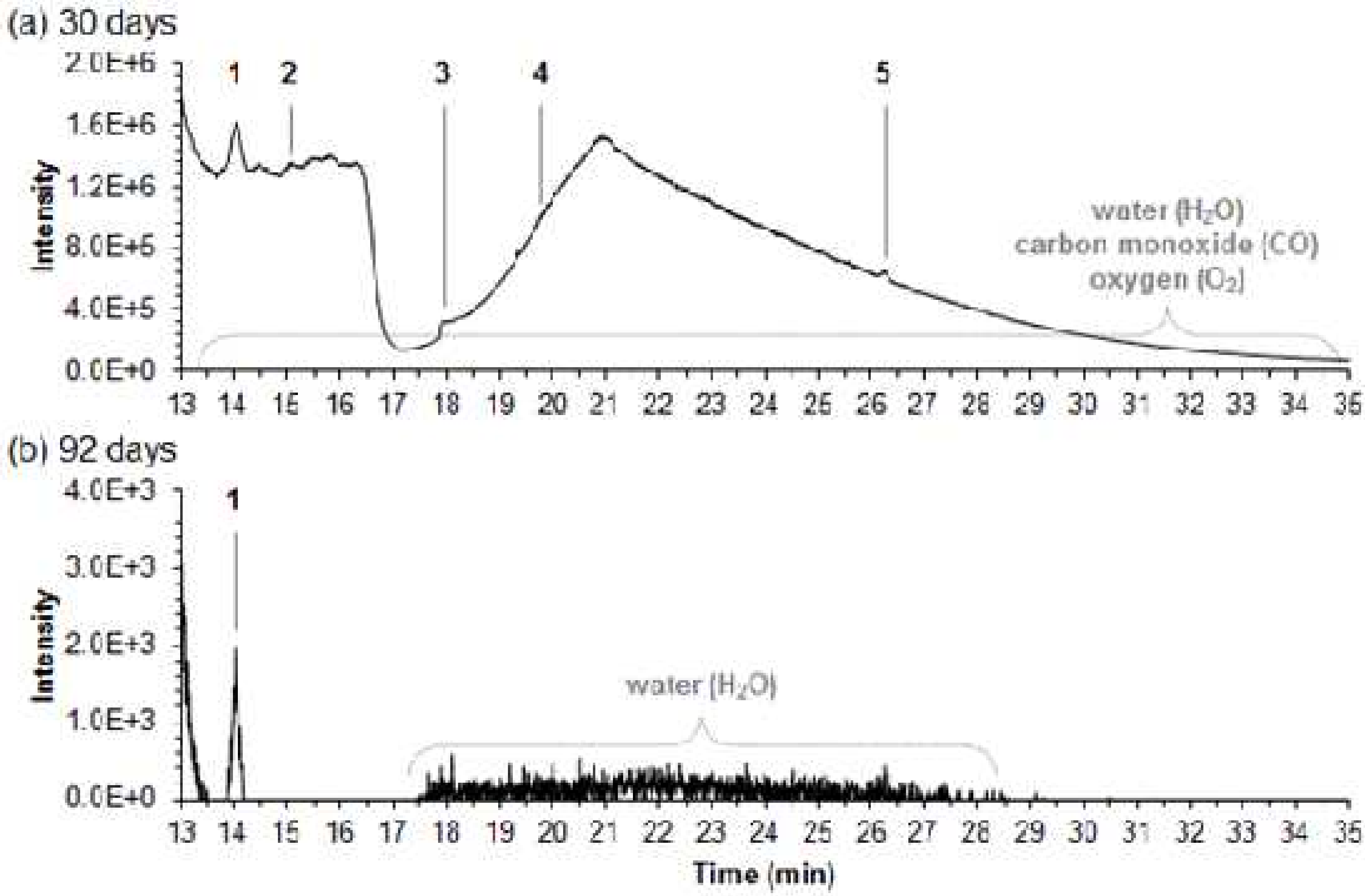


Mass Shifts for tetrahydro-2,2,4,4,-tetramethy-furan



Butyl #10 Aged in Argon Environment





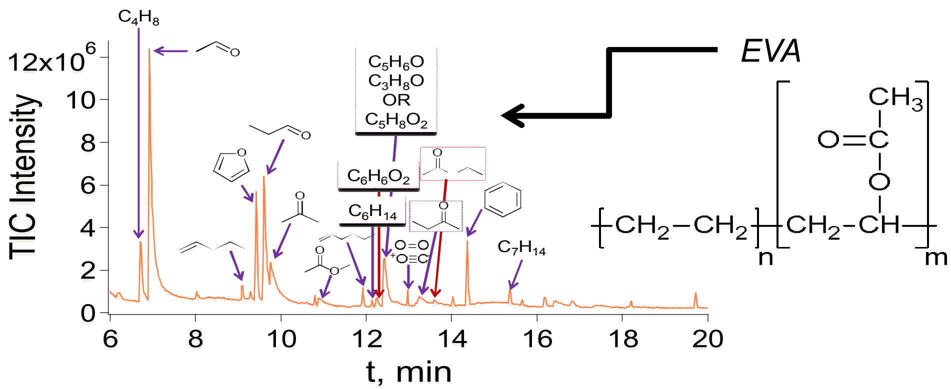
Conclusions

- Physical properties explored for various formulations of butyl rubber including tensile, compression set, thermal oxidation
  - Butyl #10 clearly out performs other formulations
  - Studies predict very long lifetime for material
- Mass spectrometry used to evaluate the evolution of decomposition products
  - Accelerated aging studies were performed
  - All materials showed significant decomposition products under thermal oxidative aging
  - Changes in compound distribution was observed but generally all compounds increased in concentration with time
  - Starting materials were investigated to understand origin of decomposition products
  - O-18 used to identify products that form from atmospheric oxygen
- Material aged in inert environment showed essentially no degradation product formation

Future Directions

- Further development of embedded chemical sensors

- New materials of interest including Poly(ethylene-co-vinyl acetate) (EVA)



Acknowledgments

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  - C8
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  Cody Washburn, Shawn Dirk, Mike White