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Thermal Decomposition and Characterization of TDI polymers using TGA coupled GC-MS

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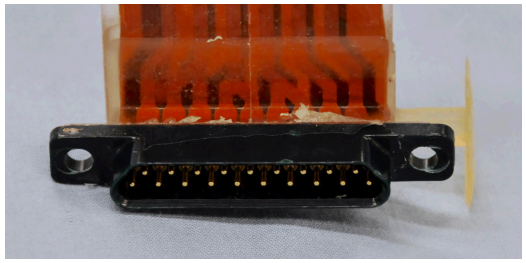
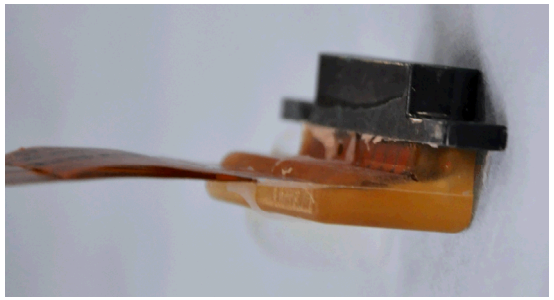
Outline

- Overview of project
  - Abnormal thermal environments
  - Modeling failure mechanisms
  - Experimental inputs and validation
- Selected Encapsulants
  - TDI and MDI foams
  - TDI elastomers
- General Decomposition Mechanisms
- Methodology
  - Thermal Gravimetric Analysis
  - Gas Chromatograph/Mass Spectroscopy
  - IST/16 coupling device
- Results and interpretation
- Lessons learned

Motivation/Background Information

- Sandia designs various electronic components to survive high shock and vibration environments.
  - Potting, encapsulants and staking materials are routinely used to dampen and secure components on printed wire assemblies.





- Understanding normal and abnormal failure mechanisms enables us to design safer, more reliable hardware
  - Normal: anticipated environments for regular use. Material properties should not change significantly but if they do change they should be reversible e.g. T_g
  - Abnormal: outside normal usage environments. Materials will fail irreversibly e.g. degradation.

Real Testing is Costly

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Modeling failure mechanisms can be used to aid in the understand of abnormal environments when testing is limited due to cost.

Require inputs (for organic materials):

- Thermal conductivity
- Specific heat
- Bulk density
- Porosity of materials
- Apparent Activation Energy (E_a) of decomposition
- Heat of reaction
- Char mass fraction
- Molecular weight of "gaseous" products
- Number of steps

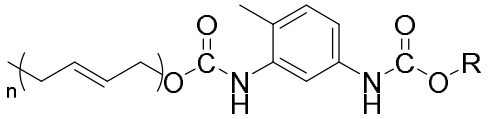
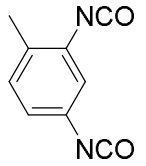
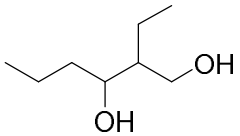
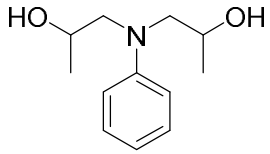
Obtainable (somewhat) using TGA and GC/MS

Complex to obtain all inputs, especially as materials change with temperature

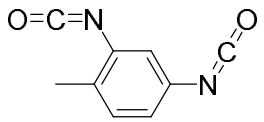
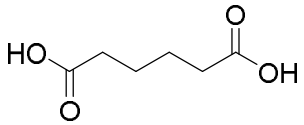
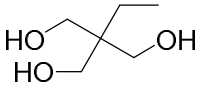
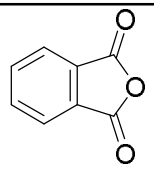
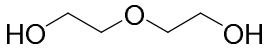
Materials of Interest

- EN-7 Elastomer: TDI based polyurethane elastomer used to encapsulate (“pot”) flexible cables on the backside of connectors
- BKC44402 Foam: TDI based polyurethane foam used as an encapsulate for rigid electronic boards
- BKC44307 Elastomer: MDI based polyurethane foam (PMDI) used as a replacement encapsulant for BKC44402 (TDI)

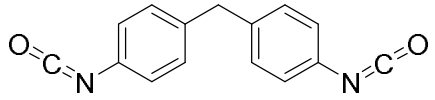
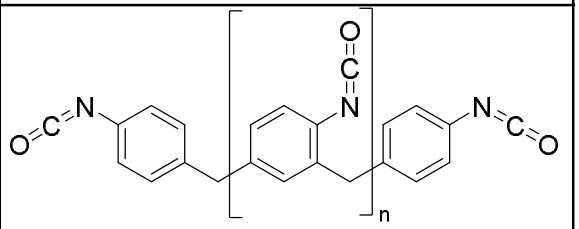
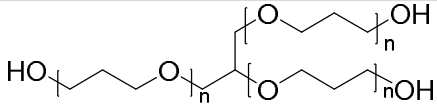
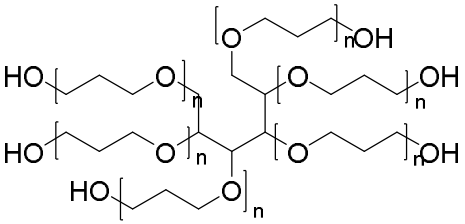
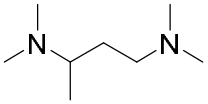
EN-7 Elastomer (TDI-based PU)

Two-part TDI-based elastomer	
Material	Structure
TDI capped polybutadiene diol (regioisomers not shown)	
Toluene diisocyanate	
2-ethylhexane-1,3-diol	
N,N'-bis(2-hydroxypropyl)aniline	
ferric acetylacetonate (catalyst)	

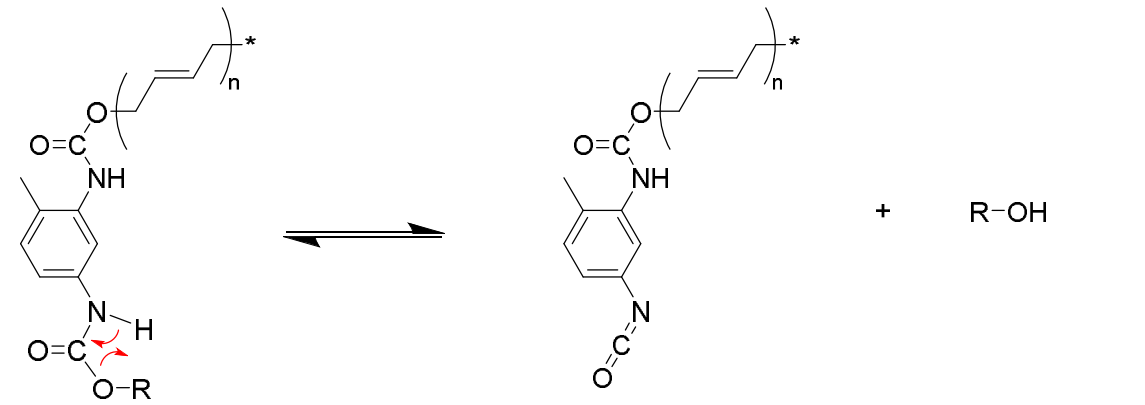
BKC44402 Polyurethane Foam

BKC44402 (TDI-based foam)	
Chemical name	Chemical Structure
toluene diisocyanate	
hexanedioic acid (adipic acid)	
2-ethyl-2-(hydroxymethyl)-1,3-propanediol	
1,3-isobenzofurandione	
diethylene glycol	
silicon oil polymer	

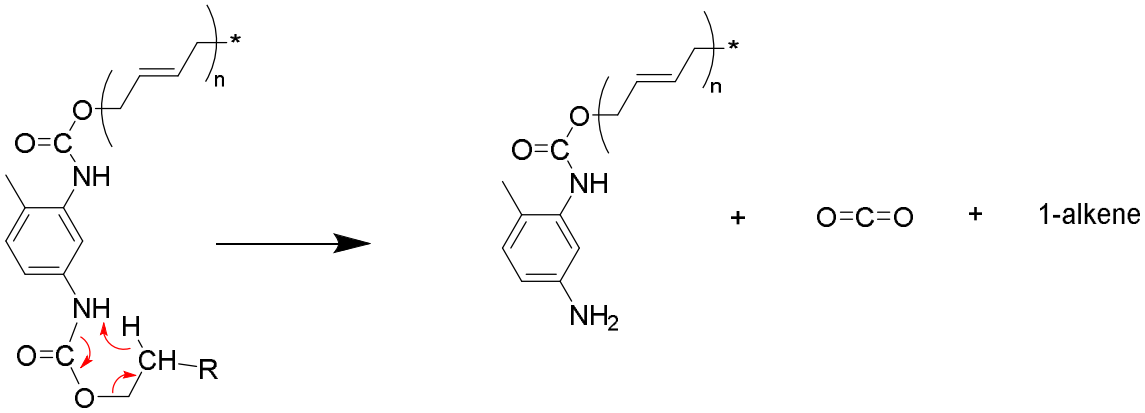
BKC44307 Polyurethane Foam

BKC44307 (MDI-based foam)	
Chemical name	Chemical Structure
4,4'-methylenediphenyl diisocyanate	
polymeric methylenediphenyl diisocyanate	
glycerol propoxylate	
sorbitol polyoxypropylene ether	
N,N,N',N'-tetramethyl-1,3-butanediamine	
silicon oil polymer	

PU Decomposition Mechanisms



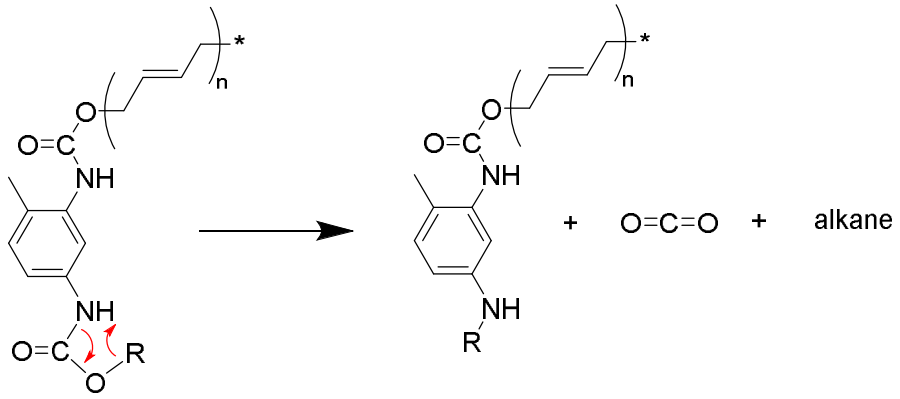
Depolymerization of urethane linkage to yield isocyantes and alcohol.



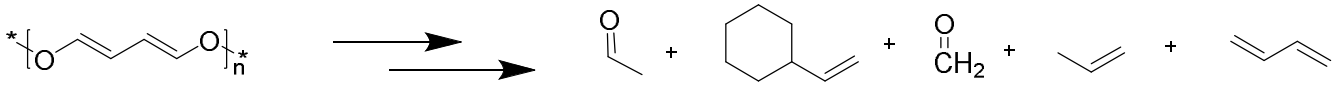
Dissociation of urethane group via six-membered ring to give alkene and CO_2

Allan, D., Daly, J., and Liggat, J. J., "Thermal volatilization analysis of TDI-based flexible polyurethane foam," Polym. Degrad. Stab. 2013, 98, 535-541.

Secondary Amine Formation and Chain Scission Mechanism



Dissociation of urethane via four-membered ring to secondary amine, CO_2 and alkane



Degradation of polyol gives via chain scission yields low MW alkenes, formaldehyde, acetaldehyde….

Can our TGA-GC/MS instrument support the proposed mechanisms?

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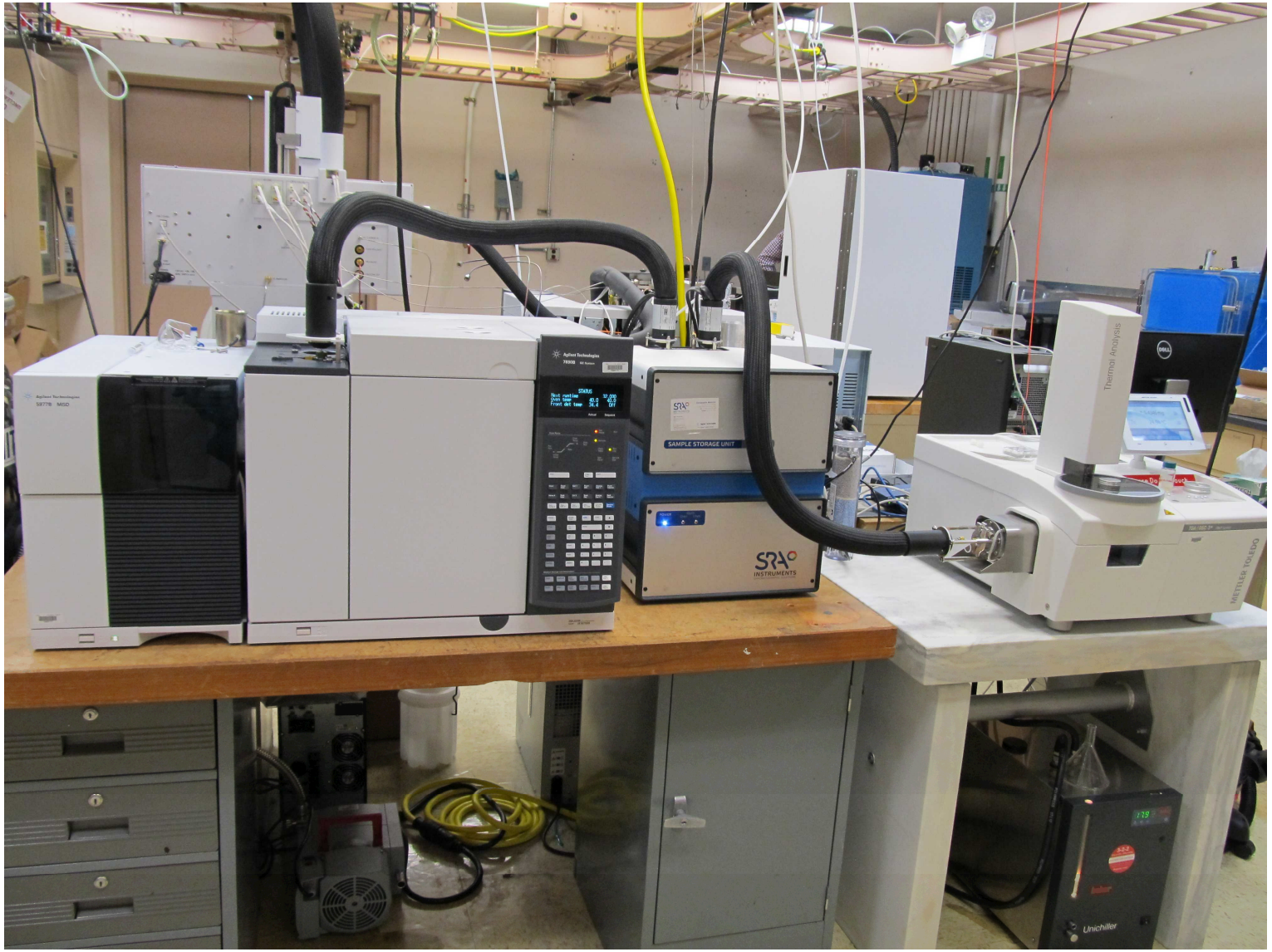
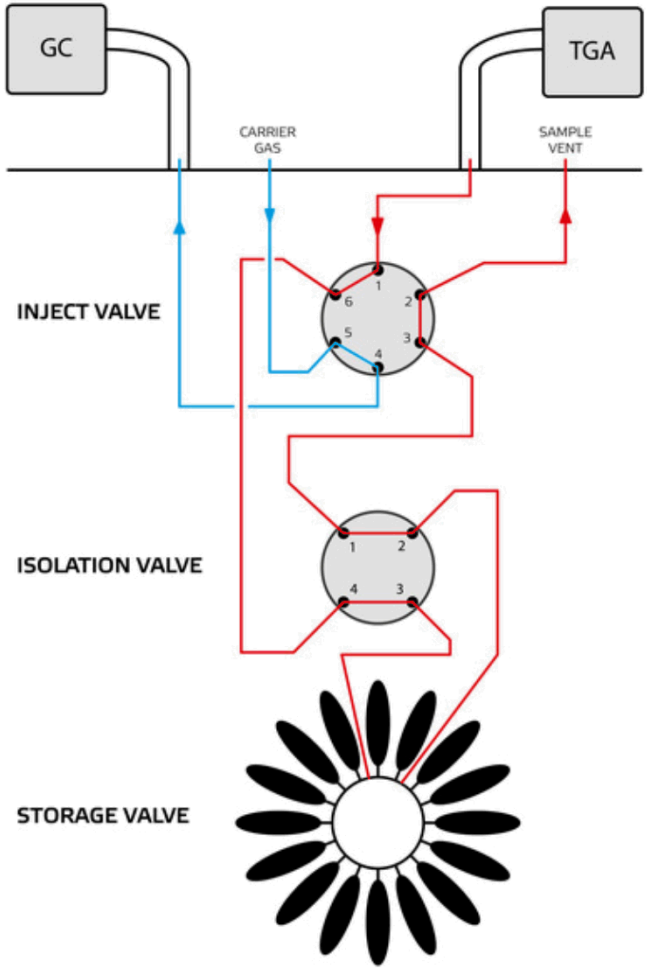
- Literature evidence for mechanism I and II are prevalent. How about mechanism III involving a four-centered rearrangement to give a secondary amine?
- How does MDI decompose and can the volatile species be detected that originate from the isocyanate?
- How does our technique compare to Thermal Volatilization Techniques (TVA)?
- Can IST-16 storage loops keep gases hot to prevent condensation?

TGA coupled GC-MS

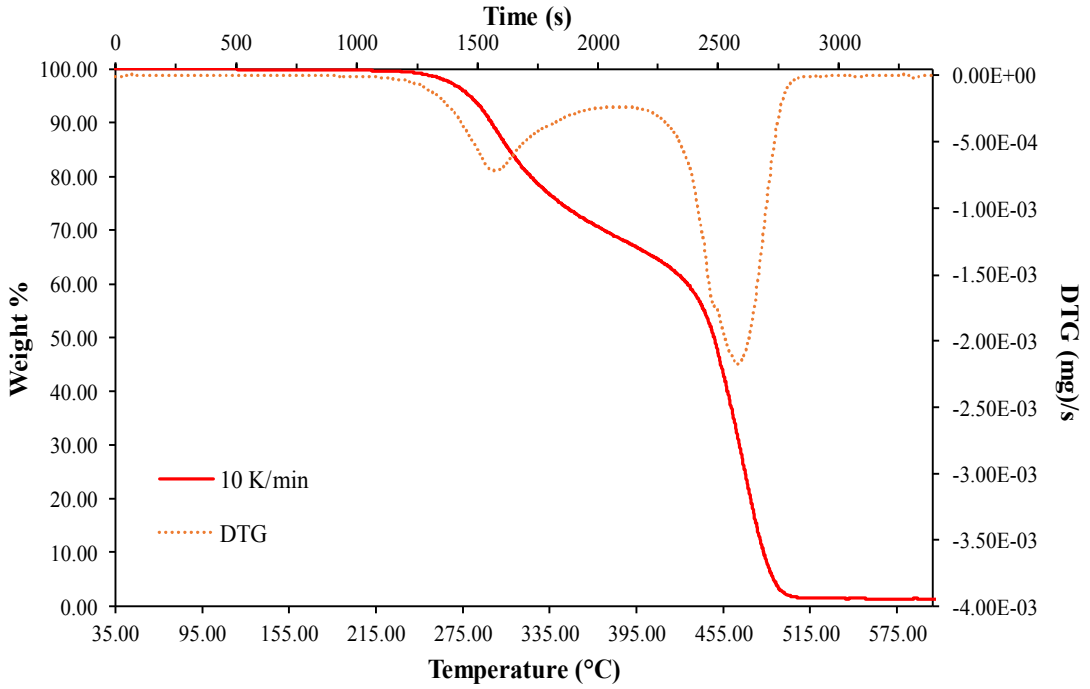


IST16 Storage Interface – SRA Instruments



- Injection of stored gas onto GC/MS made after TGA complete.
- Time between each GC-MS up to 45 minutes.
- Time between first gas sample and last can be >8 hours
- Storage loops kept at 250 °C (can be lowered)

Degradation and Capture Times for EN-7 (TDI Elastomer)



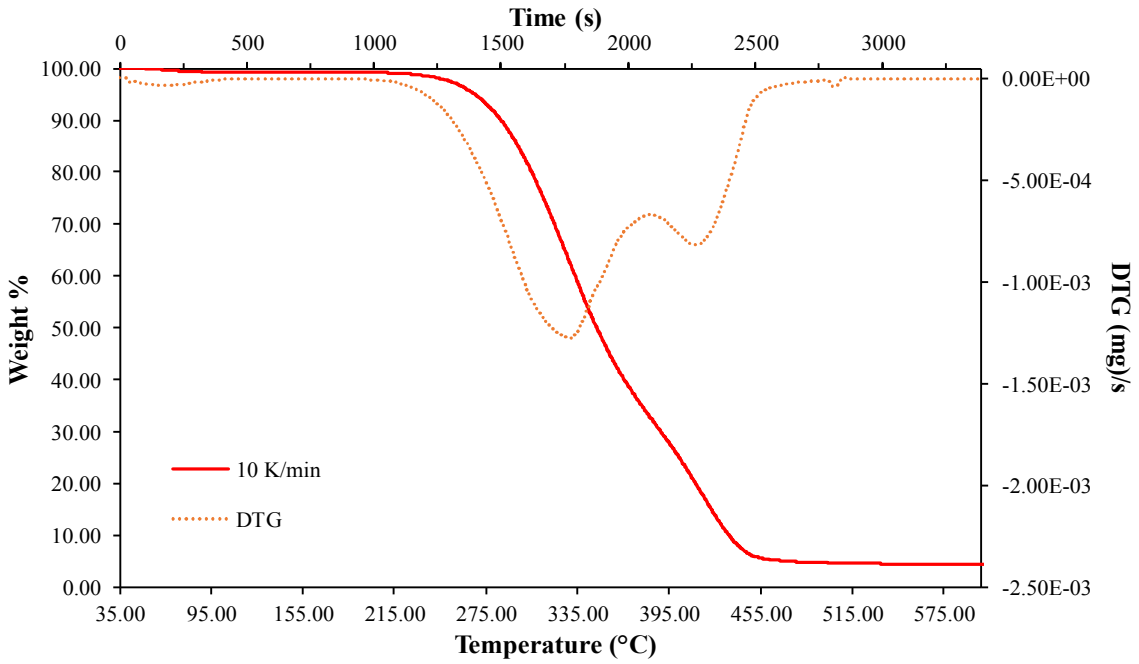
TGA of EN-7 with DTG curve

Capture Time (s)	Temperature (°C)
1200	236
1400	270
1550	296
1600	304
1700	321
1850	347
2000	372
2130	394
2250	414
2375	435
2490	454
2550	464
2610	474
2670	484
2750	498

IST16 capture time intervals for EN-7 GC/MS analysis

Two-step process beginning above 270 °C

Degradation and Capture Times for BCK4402 (TDI Foam)



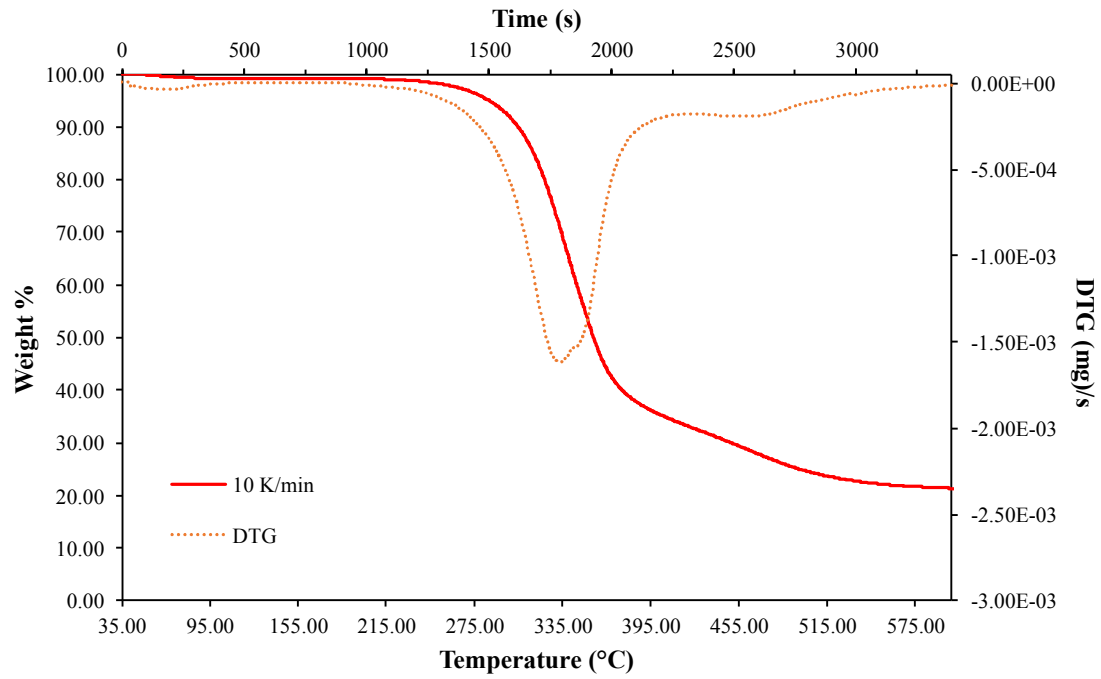
TGA of BKC44402 with DTG curve

Capture Time (s)	Temperature (°C)
800	168
1000	202
1200	237
1400	271
1600	305
1800	339
2000	373
2200	406
2400	440
2600	473
2800	506
Direct injection 1800	339

IST16 capture time intervals for BKC44402 GC/MS analysis

Two-step process >270 °C. Not well defined

Degradation and Capture Times for BKC44307 (MDI Foam)



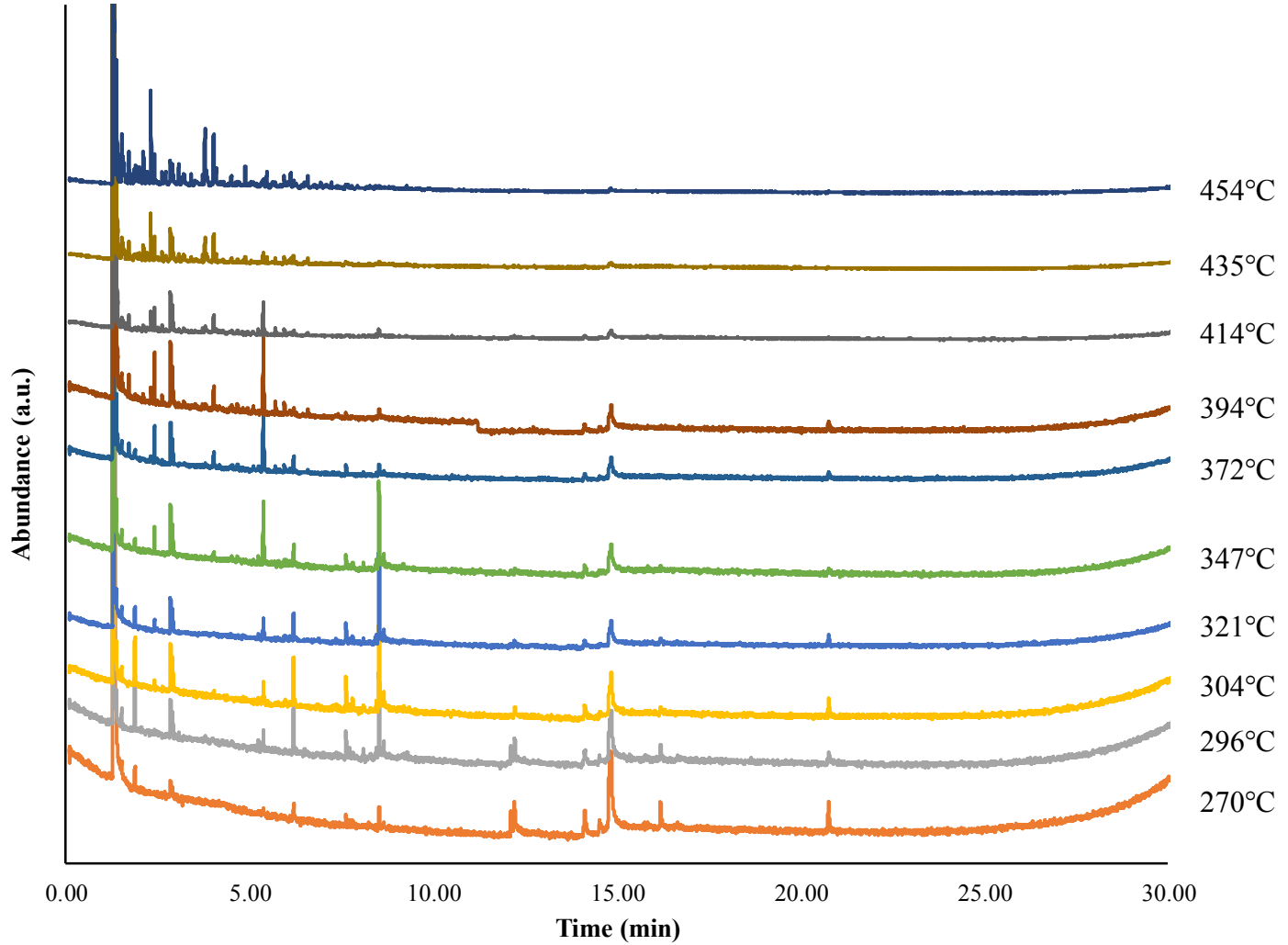
TGA of BKC44307 with DTG curve

Capture Time (s)	Temperature (°C)
1200	237
1400	271
1600	305
1700	322
1800	339
1900	356
2000	373
2200	406
2400	440
2600	473
2800	507
3000	540

IST16 capture time intervals for BKC44307 GC/MS analysis

Onset similar to other materials but undefined, multistep process

Output: Stacked Chromatograms of EN-7



10 chromatograms for each TGA run. Processed to identify species from each injection

EN-7 Decomposition Products Identified by GC/MS

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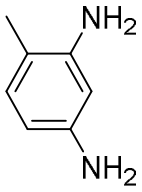
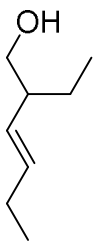
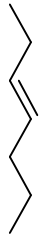
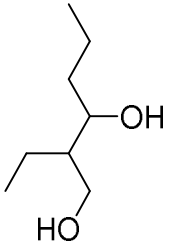
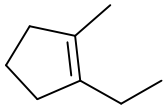
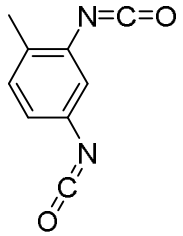
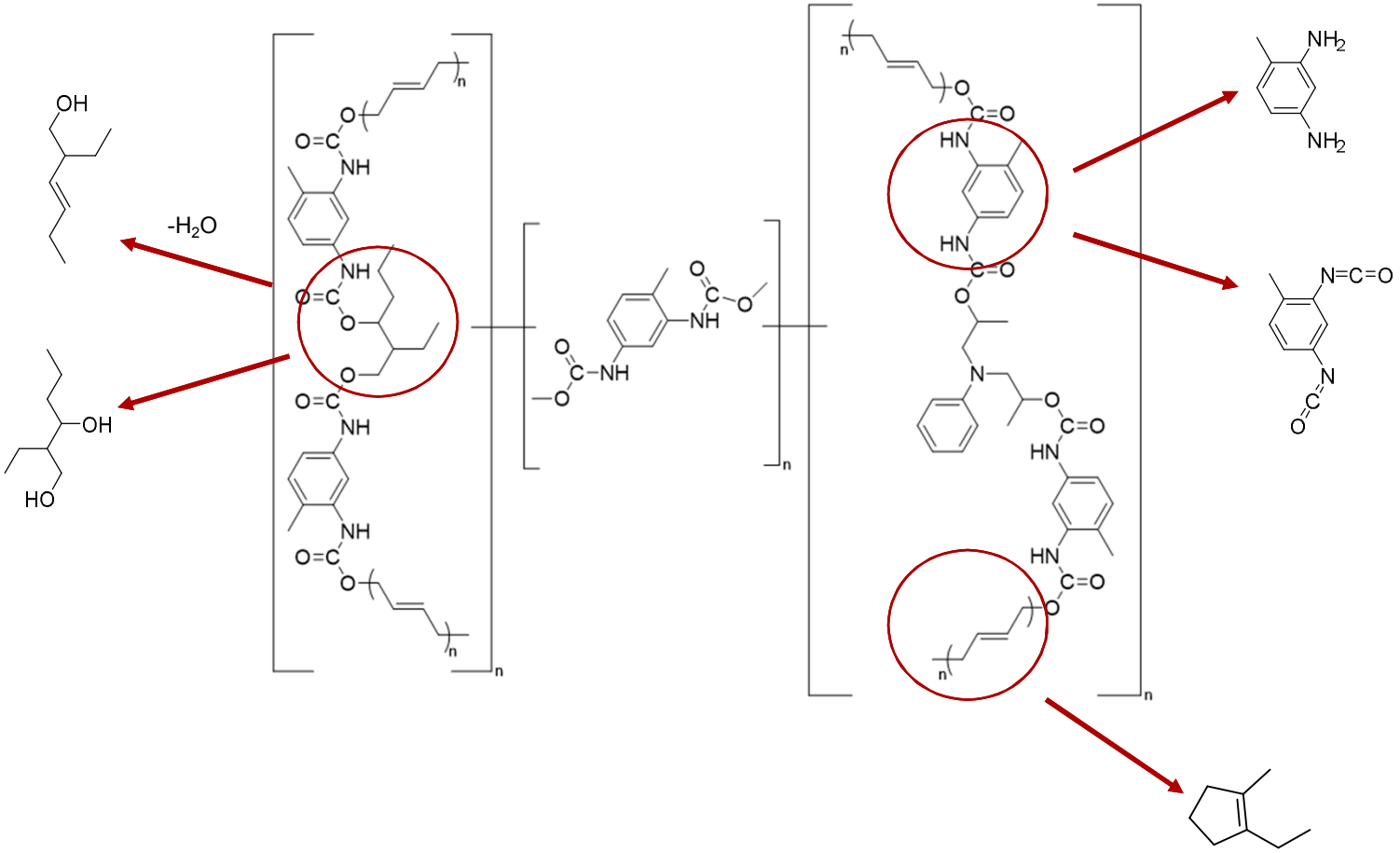
			CO_2				Cycloalkenes 	
Time Intervals (s)	1400	X	X	X	X	X	X	X
	1550	X	X	X	X	X	X	X
	1600	X	X	X	X	X	X	X
	1700	X	X	X	X	X	X	X
	1850		X	X	X	X	X	X
	2000		X	X	X		X	X
	2130		X	X	X		X	X
	2250		X	X	X		X	
	2375		X		X		X	
	2490		X				X	
Retention Time (min)		14.6	1.3	8.6	2.9	12.3	5.3 – 5.4	14.1

Structure of EN-7 and Decomposition Products



CO_2 seen at all times

BCK44402 Decomposition Products Identified by GCMS

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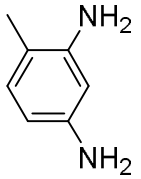
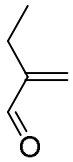
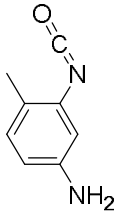
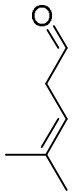
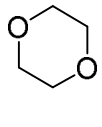
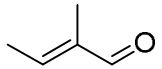
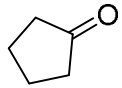
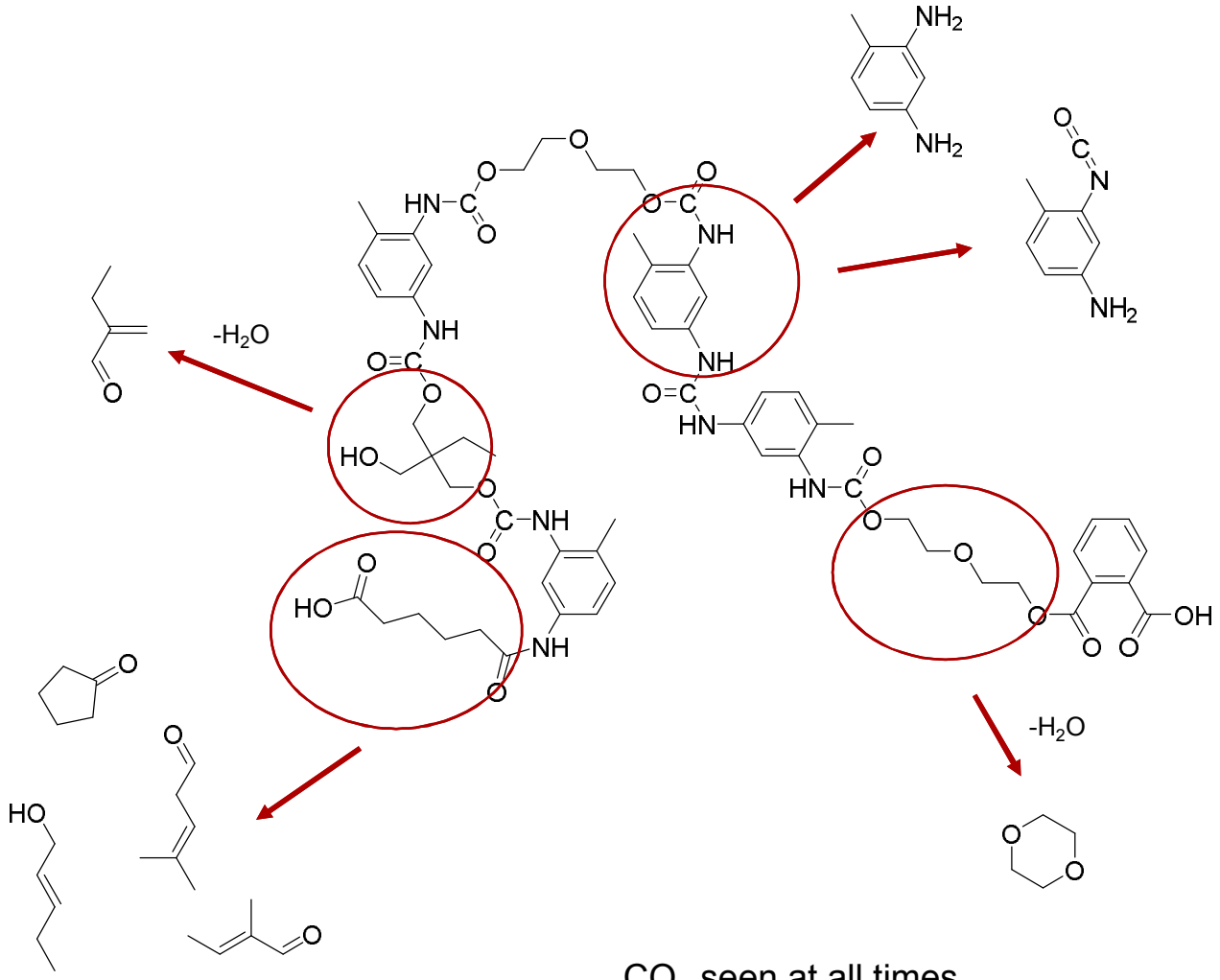
			CO_2							
Time Intervals (s)	1000	X	X							
	1200	X	X							
	1400	X	X	X						
	1600	X	X	X						
	1800	X	X		X	X	X	X	X	X
	2000	X	X		X	X	X	X	X	X
	2200		X		X	X	X	X	X	X
	2400		X			X		X	X	X
	2600		X					X	X	X
	2800		X			X		X	X	X
	Direct Injection 1800	[1]	X						X	X
Retention Time (min)		14.6	1.4	2.6	14.8	4.0	3.1	3.9	2.6	4.6

[1]TDI is identified in the direct injection at a retention time of 14.1 min

Structure of BCK44402 and Decomposition Products



CO_2 seen at all times

Decomposition Products: BCK44307

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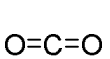
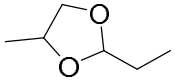
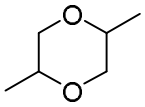
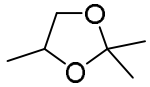
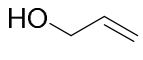
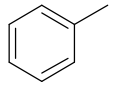
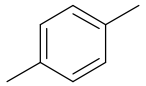
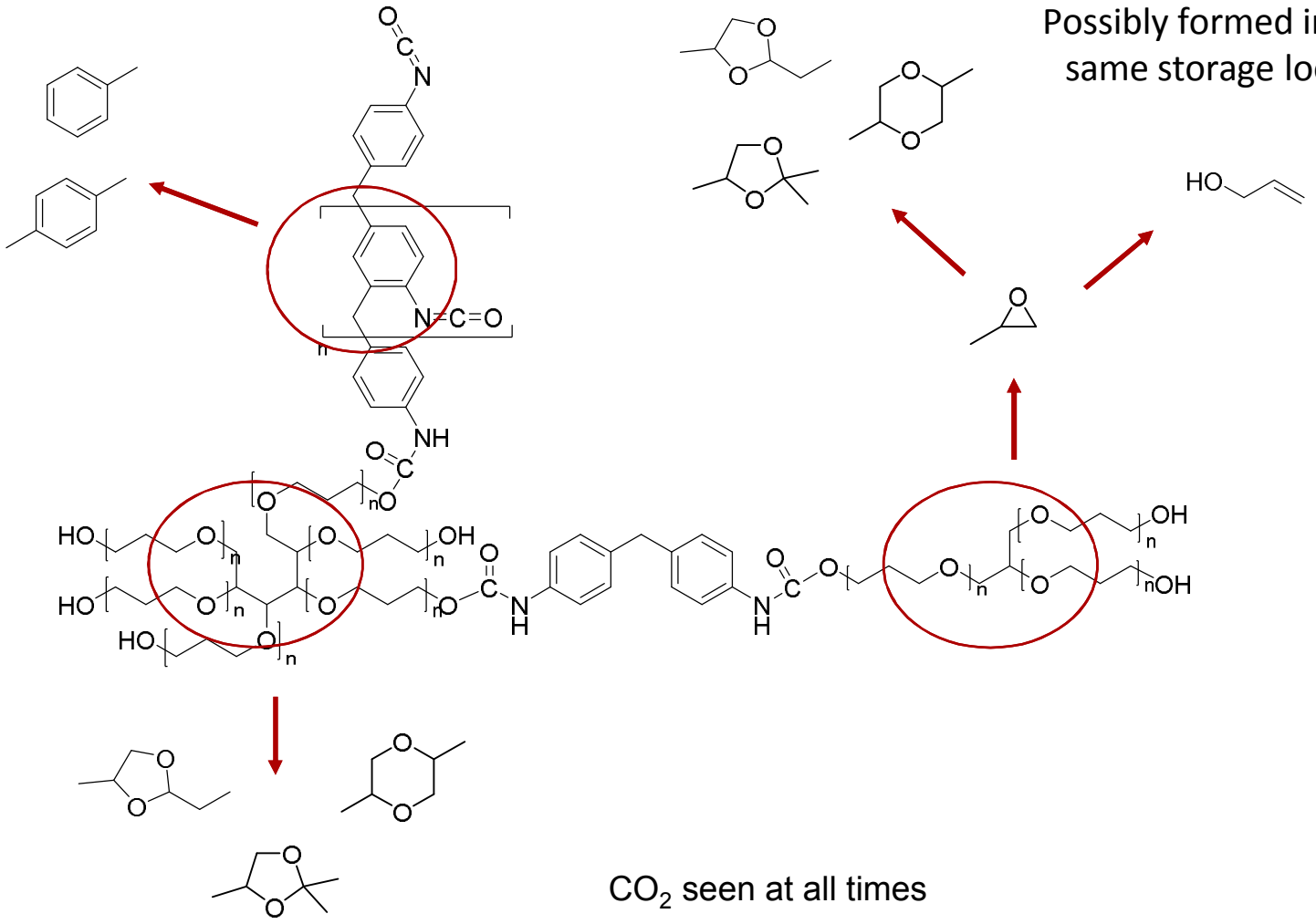
									
Time Intervals (s)	1200	X	X						
	1400	X	X						
	1600	X	X	X	X	X			
	1700	X	X	X	X	X			
	1800	X	X	X	X	X			
	1900	X	X	X		X	X		
	2000	X	X	X		X	X		
	2200	X	X	X		X			
	2400	X	X	X					
	2600	X	X	X			X	X	
	2800	X	X	X				X	X
	3000	X	X	X				X	X
Retention Time (min)		1.6	1.4	4.5	5.4	3.4	1.7	4.1	6.2

Structure of BCK44307 and Decomposition products



Mechanistic Insights

- All polyurethane materials show CO_2, alkenes and alcohols supportive of primary decomposition mechanisms.
- TDI-based materials (EN-7 and BKC44402) show diamino toluene and isocyanate formation.
- MDI-foam (BKC44307)shows no isocyanate, likely due to higher MW of monomer. At higher temperatures, aromatic species are seen, indicative of radical chain scission at methylene group of urethane linker.
- Cyclic ethers and alkenes seen throughout indicative of chain scission, rearrangement processes, possibly occurring in storage loop.
- No evidence for secondary amines.

Lessons Learned

- Hold IST16 at maximum temperature to minimize condensation inside storage loops.
- Contamination can be severe if loops are not cleaned thoroughly.
- Gases captured inside storage loops can change with time as evident between “direct” and stored injection.
- Determining procedures to operate equipment, including cleaning routine took considerable time but now more routine.
- Likely better for materials that decomposes/off-gas at lower temperature.

Acknowledgements

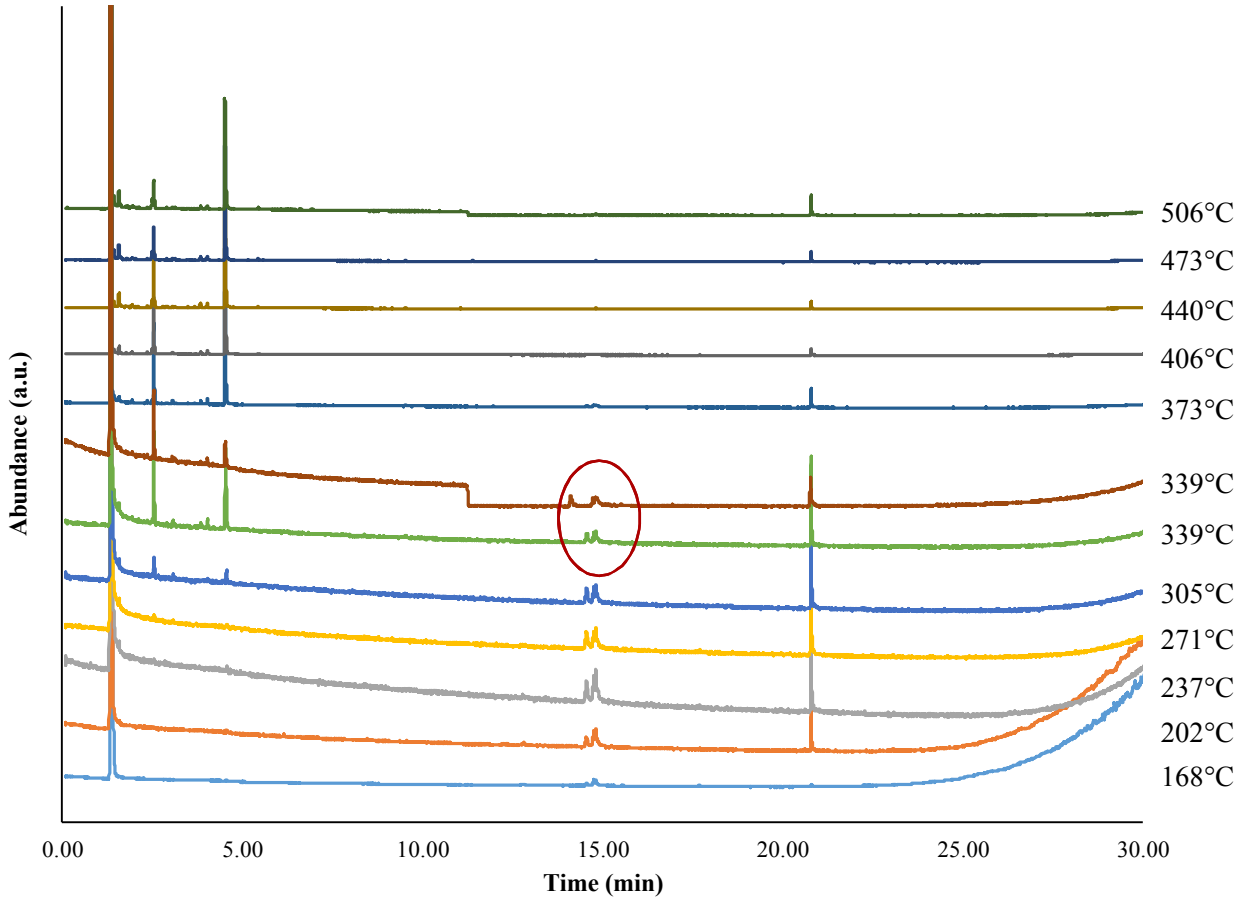
- Kale Harrison
- Dustin Murtagh
- Tito Silva

Questions

Sandia National Laboratories

Backup slides

Output: Stacked Chromatograms of BKC44402 (TDI Foam)



Comparison of direct versus collected injection shows some differences

12 chromatograms for each TGA run. Processed to identify species from each injection

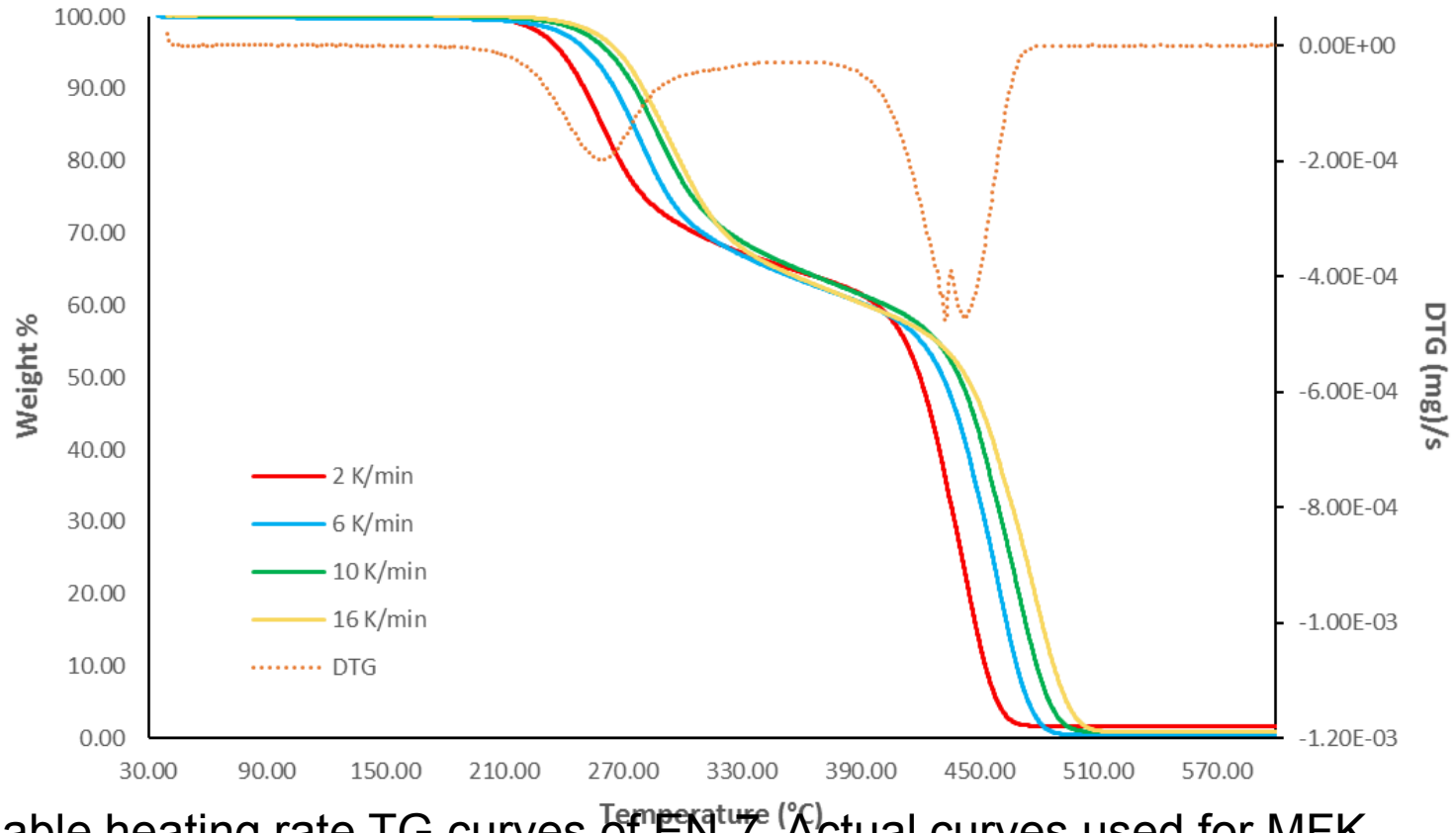
Kinetic Data Obtained Via TGA

- Model Free Kinetic Analysis compared to modeled kinetic analysis

Initial Foam $(w_1^0 B_1 + w_2^0 B_2 + w_3^0 B_3)$	Reaction i $\rightarrow$	Decomposition Products
B_1	$\frac{dB_1}{dt}$	$\xi_{11} D_{11} + \xi_{12} D_{12}$
B_2	$\frac{dB_2}{dt}$	$\xi_{21} D_{21}$
B_3	$\frac{dB_3}{dt}$	$\xi_{31} D_{31} + \xi_{32} D_{32}$

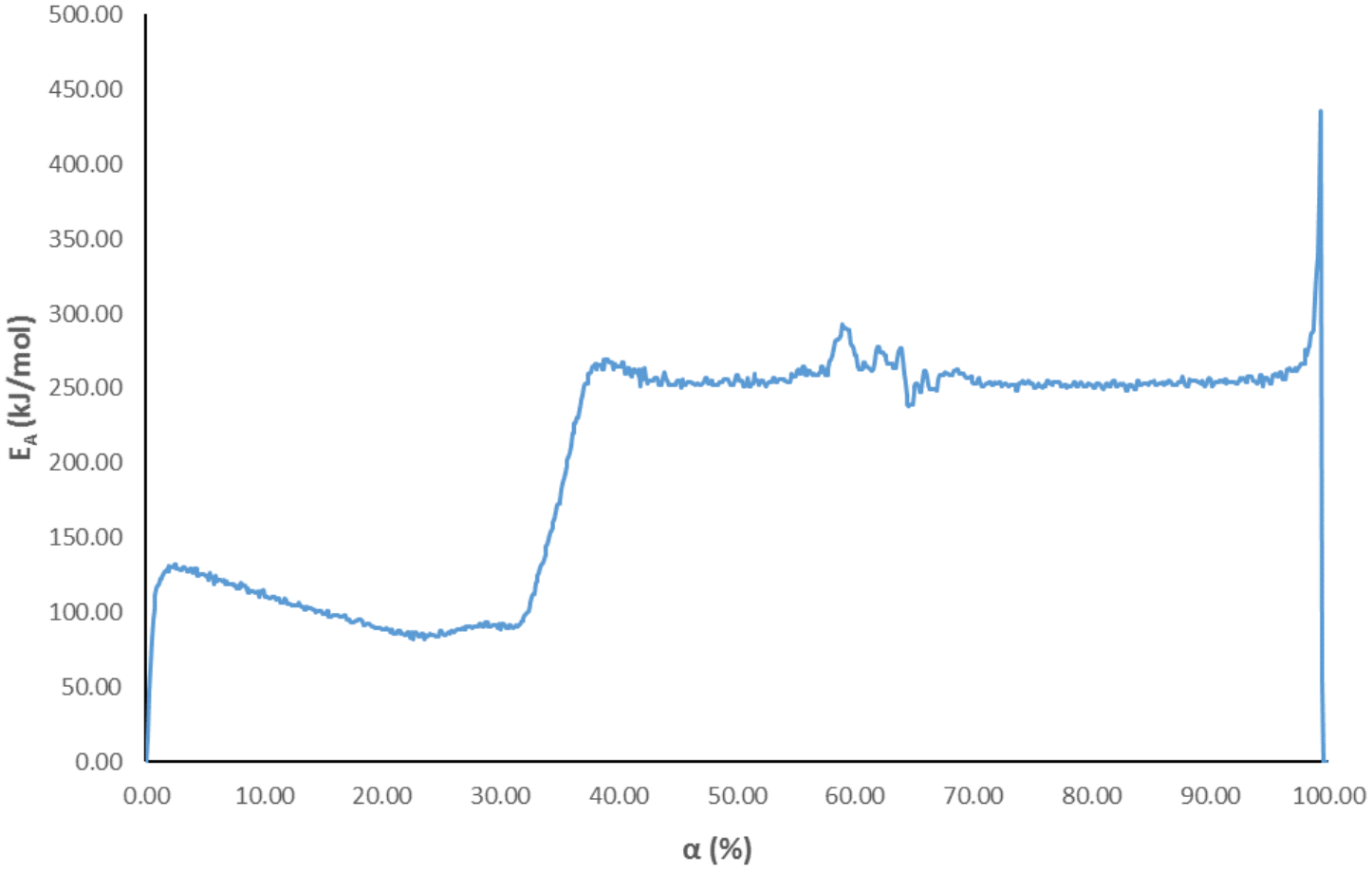
	Activation Energy, E_i (kJ/mol)	ln Pre-Exponential Factor ($1/sec^{n_i}$)	Order, n_i	Mass Fraction, w_i^0
Reaction 1	175	36.0	2.00	0.247
Reaction 2	230	41.7	2.24	0.106
Reaction 3	239	37.7	1.00	0.623 [0.647]

TGA of EN-7 with DTG curve



Variable heating rate TG curves of EN-7. Actual curves used for MFK analysis were recorded at 0.5, 1 and 2 K/min to avoid “cross-over” associated with changes in mechanism

Apparent activation energy plot as a function of conversion for EN-7



MKF gives slightly lower activation energy but heating rates used were 10x less