

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

<b>1. REPORT DATE (DD-MM-YYYY)</b> Jan 2014		<b>2. REPORT TYPE</b> Briefing Charts		<b>3. DATES COVERED (From - To)</b> Jan 2014- Mar 2014	
<b>4. TITLE AND SUBTITLE</b>  BIO-BASED CYANATE ESTER RESINS: IMPROVED PERFORMANCE THROUGH NETWORK STRUCTURE ENHANCEMENT				<b>5a. CONTRACT NUMBER</b> In-House	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b>  Andrew J. Guenthner, Josiah T. Reams, Gregory R. Yandek, Christopher M. Sahagun, Kevin R. Lamison, Benjamin G. Harvey, Matthew C. Davis, William Lai, Lee R. Cambrea, Thomas J. Groshens, and Joseph M. Mabrys				<b>5d. PROJECT NUMBER</b>	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b> Q0BG	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b>  Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				<b>8. PERFORMING ORGANIZATION REPORT NO.</b>	
<b>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>  Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Drive Edwards AFB CA 93524-7048				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b> <b>AFRL-RQ-ED-VG-2014-047</b>	
<b>12. DISTRIBUTION / AVAILABILITY STATEMENT</b> Distribution A: Approved for Public Release; Distribution Unlimited					
<b>13. SUPPLEMENTARY NOTES</b> Briefing Charts presented at ACS National Meeting and Expo, Dallas, TX., March 16, 2014. PA#14119					
<b>14. ABSTRACT</b> Briefing Charts					
<b>15. SUBJECT TERMS</b>					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>  SAR	<b>18. NUMBER OF PAGES</b>  24	<b>19a. NAME OF RESPONSIBLE PERSON</b> Joseph Mabry
<b>a. REPORT</b>  Unclassified	<b>b. ABSTRACT</b>  Unclassified	<b>c. THIS PAGE</b>  Unclassified			<b>19b. TELEPHONE NO</b> (include area code) 661-275-5857



## **BIO-BASED CYANATE ESTER RESINS: IMPROVED PERFORMANCE THROUGH NETWORK STRUCTURE ENHANCEMENT**

17 March 2014

*Andrew J. Guenthner,<sup>1</sup> Josiah T. Reams,<sup>2</sup> Gregory R. Yandek,<sup>1</sup> Christopher M. Sahagun,<sup>3</sup>  
Kevin R. Lamison,<sup>2</sup> Benjamin G. Harvey,<sup>4</sup> Matthew C. Davis,<sup>4</sup> William Lai,<sup>4</sup> Lee R. Cambrea,<sup>4</sup>  
Thomas J. Groshens,<sup>4</sup> and Joseph M. Mabry<sup>1</sup>*

<sup>1</sup>Aerospace Systems Directorate, Air Force Research Laboratory  
Edwards AFB, CA 93524

<sup>2</sup>ERC Incorporated, Air Force Research Laboratory  
Edwards AFB, CA 93524

<sup>3</sup>National Research Council / Air Force Research Laboratory  
Edwards AFB, CA 93524

<sup>4</sup>Naval Air Warfare Center, Weapons Division  
China Lake, CA 93555



# AFRL Mission



*Leading the discovery, development, and integration of affordable warfighting technologies for our air, space, and cyberspace force.*



# Cyanate Esters for Next-Generation Aerospace Systems



Glass Transition Temperature  
200 – 400 °C (dry)  
150 – 300 °C (wet)

High  $T_g$

Onset of Weight Loss:  
> 400 °C with High Char Yield

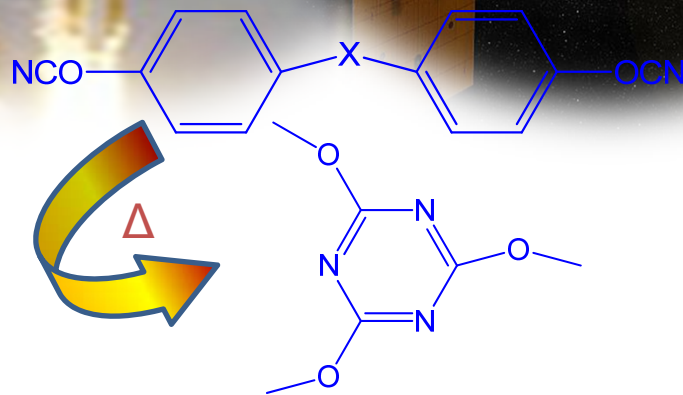
Resin Viscosity Suitable for Filament Winding / RTM

Ease of Processing

Resistance to Harsh Environments

Good Flame, Smoke, & Toxicity Characteristics

Compatible with Thermoplastic Tougheners and Nanoscale Reinforcements



Low Water Uptake with Near Zero Coefficient of Hygroscopic Expansion

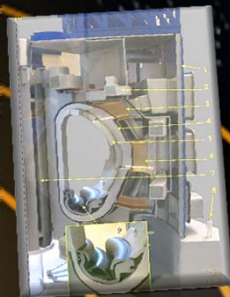


# Cyanate Esters Around the Solar System



## Our Solar System

- On Earth, cyanate ester / epoxy blends have been qualified for use in the toroidal field magnet casings for the ITER thermonuclear fusion reactor



Fusion reactor, photo courtesy of Gerritse ((Wikimedia Commons)

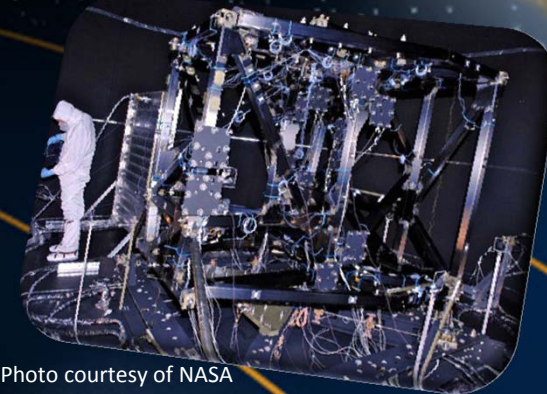


Photo courtesy of NASA

- Unique cyanate ester composites have been designed by NASA for use as instrument holding structures aboard the James Webb Space Telescope
- The science decks on the Mars Phoenix lander are made from M55J/cyanate ester composites
  - The solar panel supports on the MESSENGER space probe use cyanate ester composite tie layers

Images: courtesy NASA (public release)



# Why Bio-Based Cyanate Esters



- Materials qualification efforts are costly; developing bio-based materials that deliver both improved performance and decreased dependence on petroleum enables a higher and more robust return on investment
- Cyanate esters are generally easy to process; they do not require stoichiometric balance and form co-networks readily, hence they tolerate variation in monomer chemistry relatively well
- The superior flame, smoke, and toxicity characteristics of cyanate esters, the excellent adhesion and durability characteristics of the networks, and the very high selectivity of the reaction (which makes de-polymerization easier), all confer benefits from a sustainability perspective
- Bio-based feedstocks for cyanate esters are interesting because of the combinations of physical properties provided by structure of the molecules themselves, not just because of the cost or environmental impacts





# Anethole as a Monomer Source



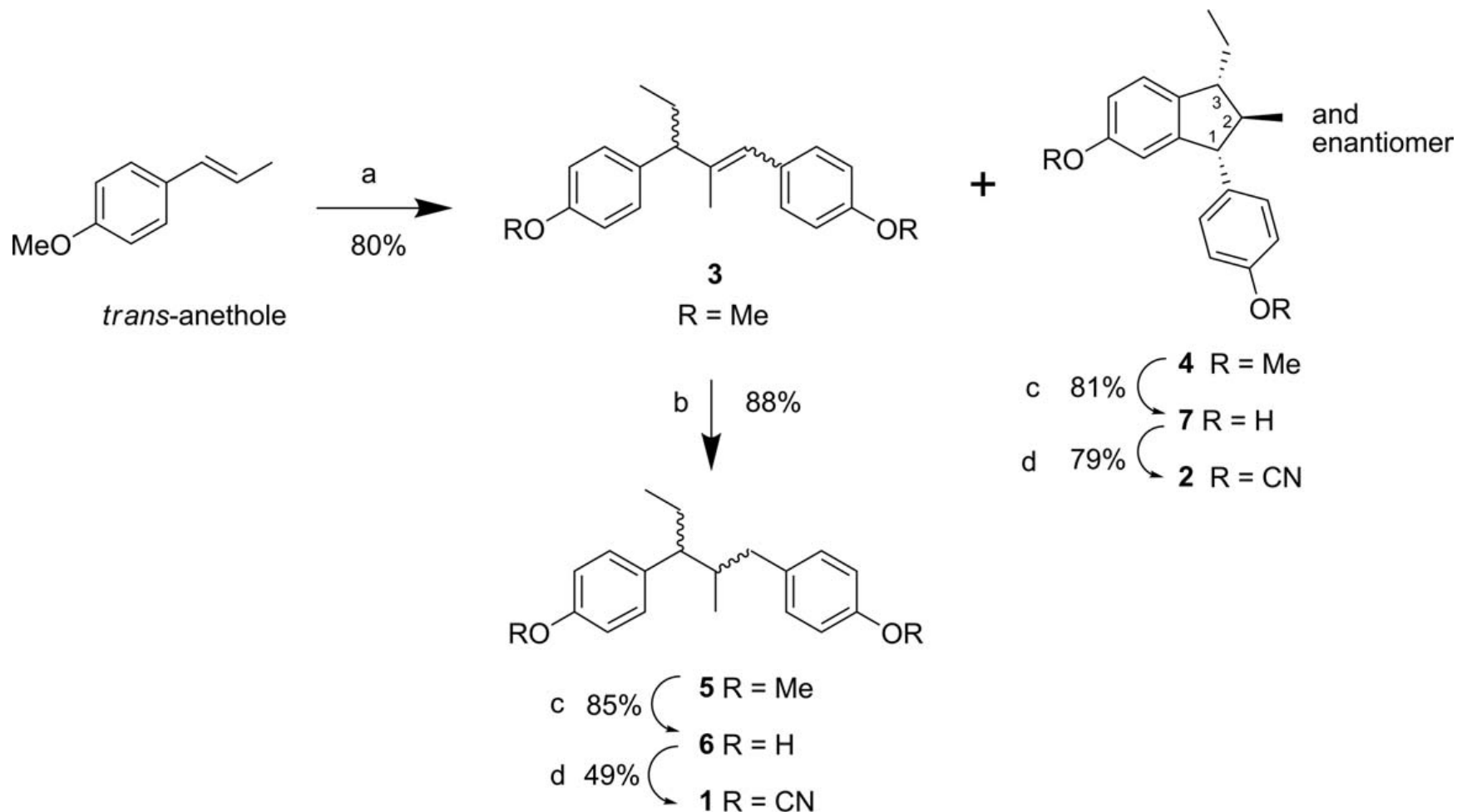
Photograph of fruits of star anise ("Illicium verum"), taken 17th October 2006 by Brian Arthur and released under the GNU Free Documentation License. All remaining rights reserved



- Trans-anethole is widely available as an essential oil extracted from star anise (*Illicium verum*), an evergreen tree native to southwest China (Yunnan and Guangxi provinces) and northern Vietnam
- Current production is ~ 400 tons / yr, with significant use in the flavor and fragrance industry
- Simple steam distillation of the star anise fruit yields ~90% trans-anethole
- The sizes of the global markets for trans-anethole and cyanate esters are similar



# Anethole-Based Cyanate Esters: Route 1



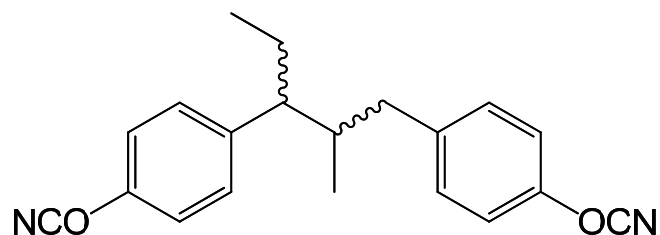
Reagents & conditions: a)  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , reflux; b)  $\text{H}_2$ , Pd/C, THF; c) pyridineHCl; reflux; d) BrCN, TEA, acetone,  $-20^\circ\text{C}$ .



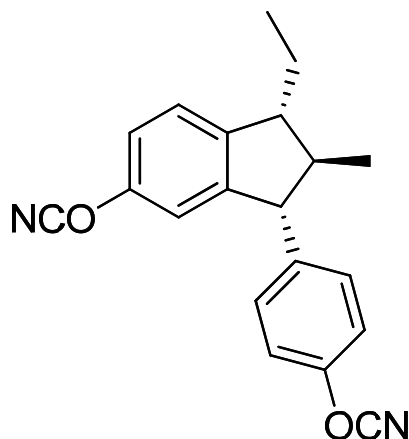
# Anethole-Based Cyanate Esters: Range of Segment Flexibility



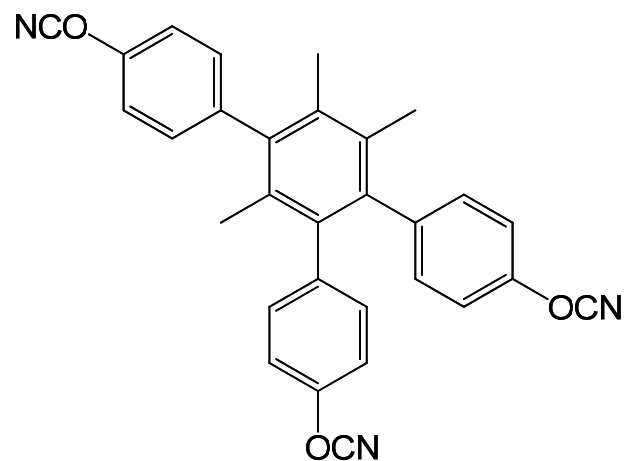
CE-1



CE-2



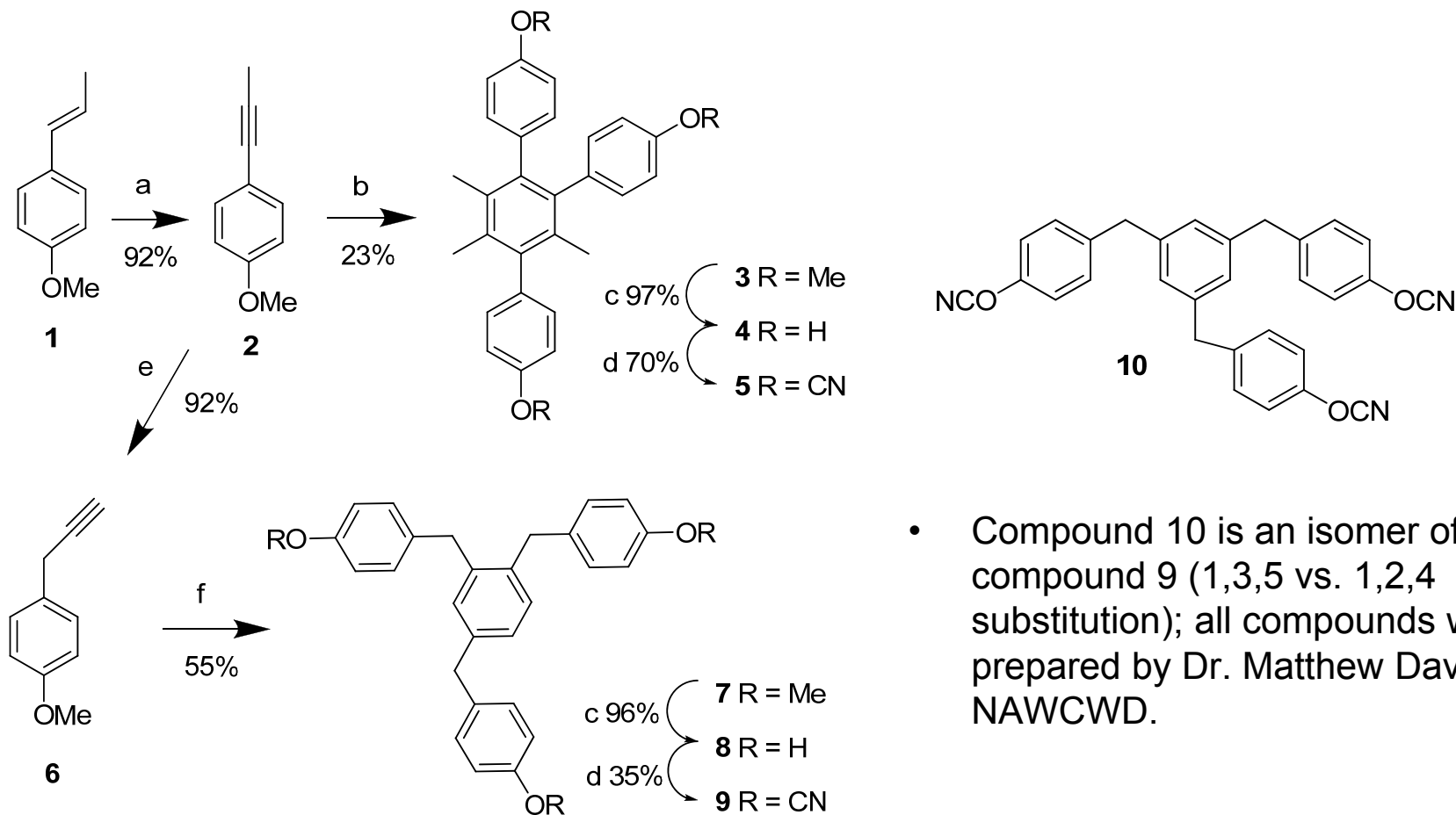
CE-3



- CE-1 will form networks with a high level of segment flexibility; multiple stereoisomers should inhibit the formation of crystals
- CE-2 will form networks with a moderate amount of segment rigidity
- CE-3 will form highly rigid networks



# Trianethole-Based Cyanate Esters and Related Compounds

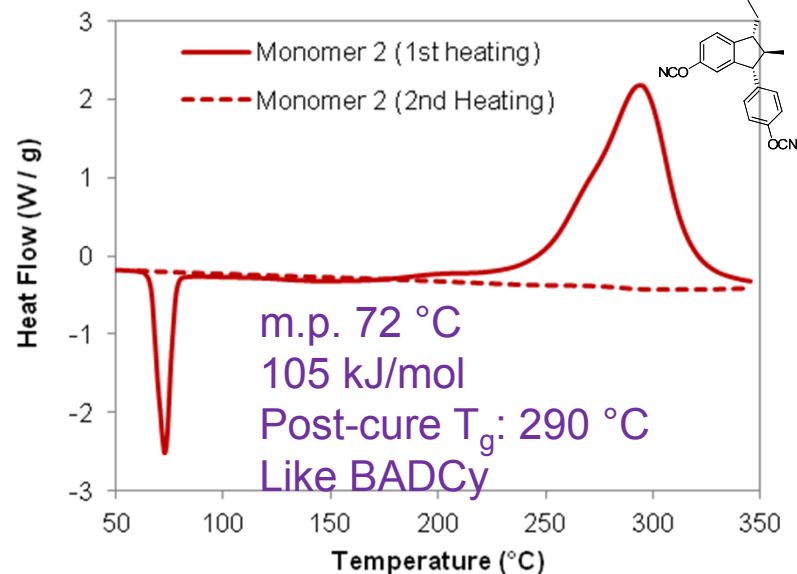
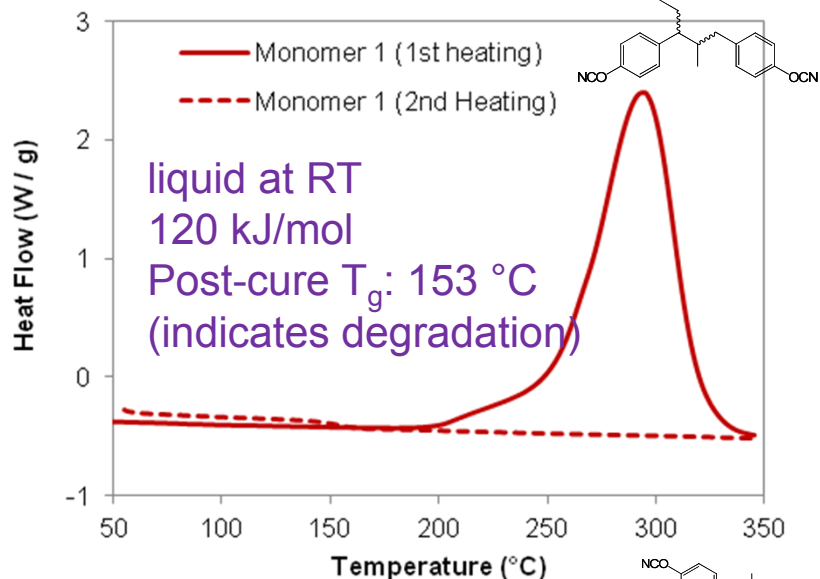


Reagents & conditions: a) 1. Br<sub>2</sub>, THF, 0 °C; 2. KO<sup>t</sup>Bu, THF, 0 °C to reflux; b) TMSCl, 5% Pd/C, dioxane, reflux; c) pyridine, POCl<sub>3</sub>, H<sub>2</sub>O, reflux; d) BrCN, TEA, acetone, -20 °C; e) BuLi, Et<sub>2</sub>O, hexanes, rt; f) CoI<sub>2</sub>, ZnBr<sub>2</sub>, Zn, MeCN; g) pyridineHCl, reflux.

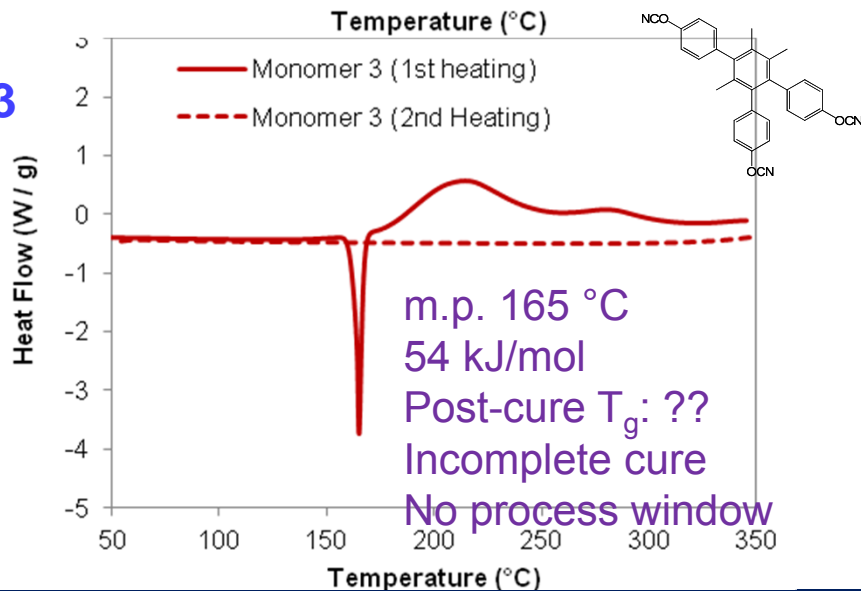
- Compound 10 is an isomer of compound 9 (1,3,5 vs. 1,2,4 substitution); all compounds were prepared by Dr. Matthew Davis at NAWCWD.



# DSC of Anethole-Based Cyanate Esters



CE-3



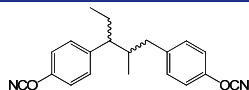
- The various coupling routes produce cyanate esters with a wide range of network segment rigidities
- CE-3 (high rigidity) is very difficult to process
- CE-2 has moderate rigidity and is similar in processability to BADCy
- CE-1 is of low (relative) rigidity, making it the easiest to process



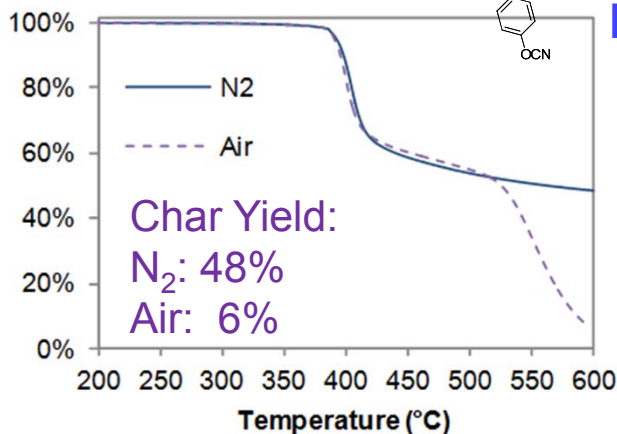
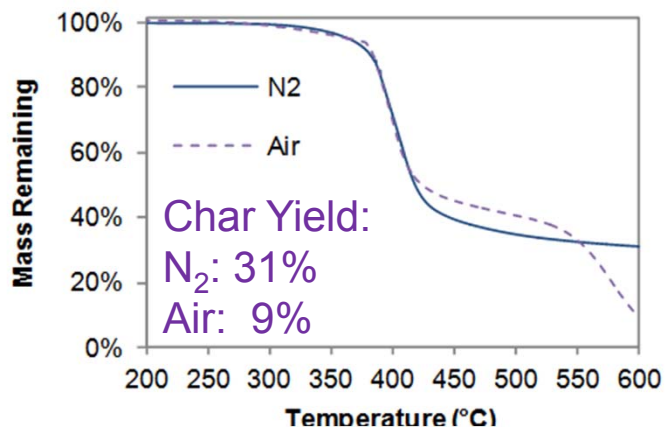
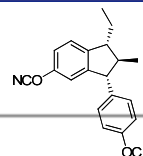
# Thermochemical Stability of Anethole-Based Cyanate Esters



### CE-1



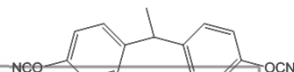
### CE-2



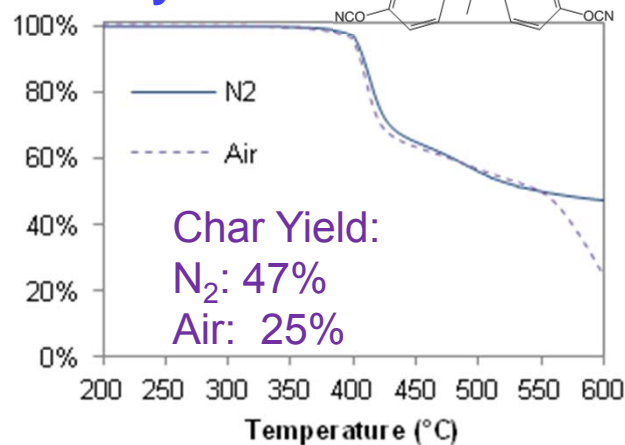
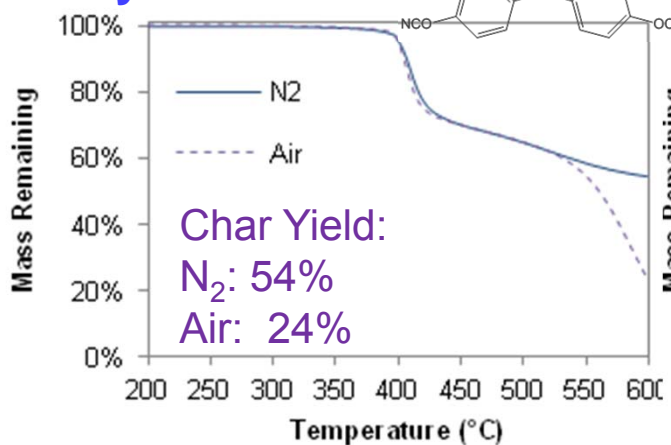
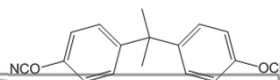
## Network Composition: Excludes Hydrogen Atoms

	Wt % Aro- matic	Wt % Aliph- atic	Wt % OCN
CE-1	50	25	25
CE-2	50	25	25
LECy	60	10	30
BAD Cy	57	14	29

### LECy



### BADCy



Samples cured at 150 °C for 1hr then 210 °C for 24 hrs under dry nitrogen



# Physical Properties of Anethole-Based Cyanate Esters



Com-pound	Density (g/cc)	Cyanurate Density at Full Cure (mmol/cc)	As-Cured Dry T <sub>g</sub> by TMA (°C)	T <sub>g</sub> After Post-Cure to 350 °C in TMA (°C)	“Wet” Tg After 96 h Immersion in 85 °C H <sub>2</sub> O (°C)	Water Uptake
CE-1	1.154	2.42	213	223	190	1.14%
CE-2	1.176	2.45	279	313	223	1.66%
LECy	1.231	3.11	291	295	239	1.75%
BADCy	1.208	2.89	275	323	240	1.34%

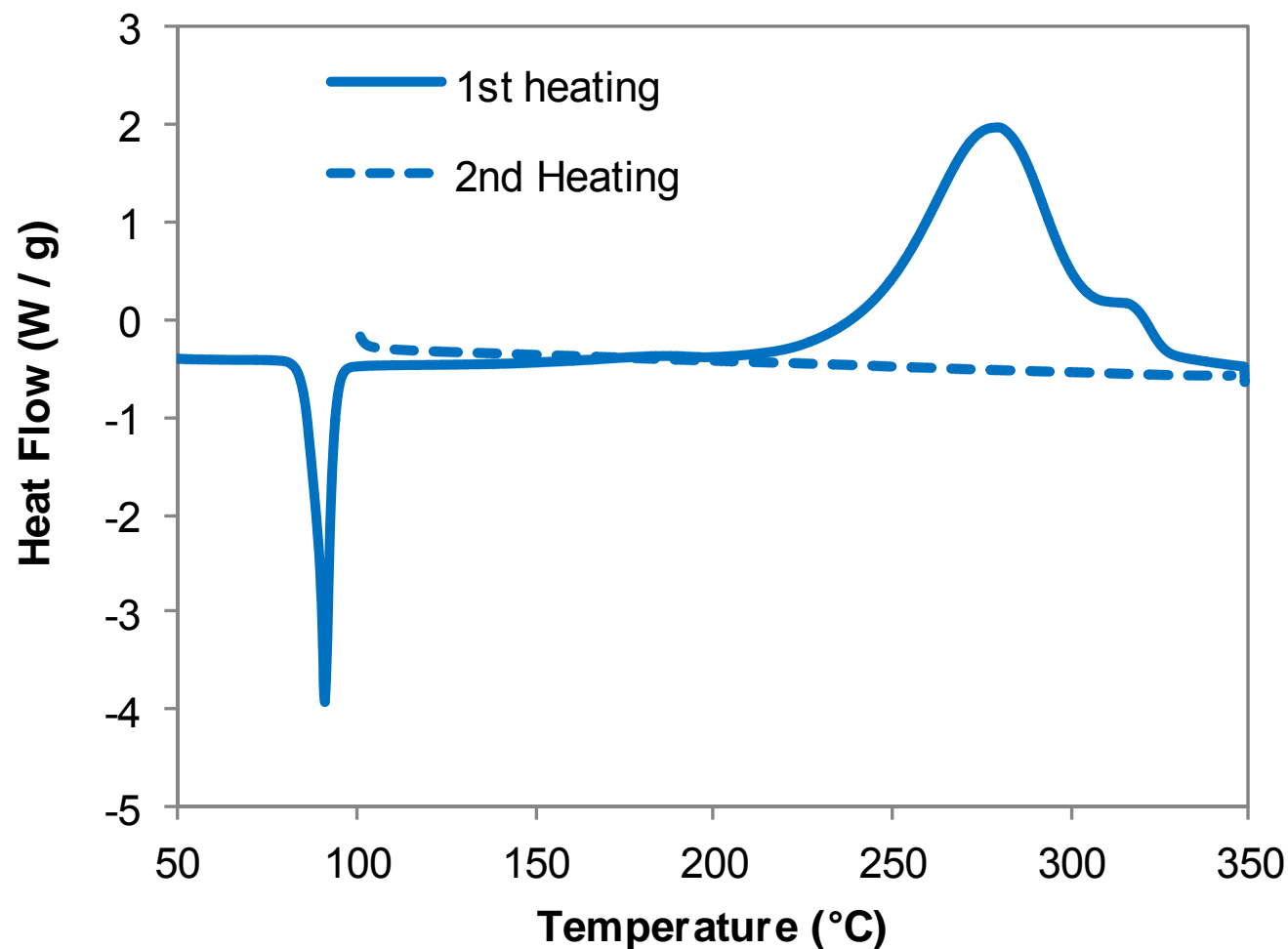
- In CE-1, water uptake is traded for glass transition temperature (as in RTX-366, which has an even lower water uptake and glass transition temperature)
- CE-2 not only processes like BADCy, but appears to give similar physical properties (though with a slight loss in wet properties)
- Note that the water uptake of LECy and BADCy without catalyst was significantly lower than expected

LECy (cat)	1.220	3.08	275	290	193	2.34%
BADCy (cat)	1.201	2.86	267	304	186	2.10%

Samples cured at 150 °C for 1hr then 210 °C for 24 hrs under dry nitrogen



# DSC of Trianethole Tricyanate (9)

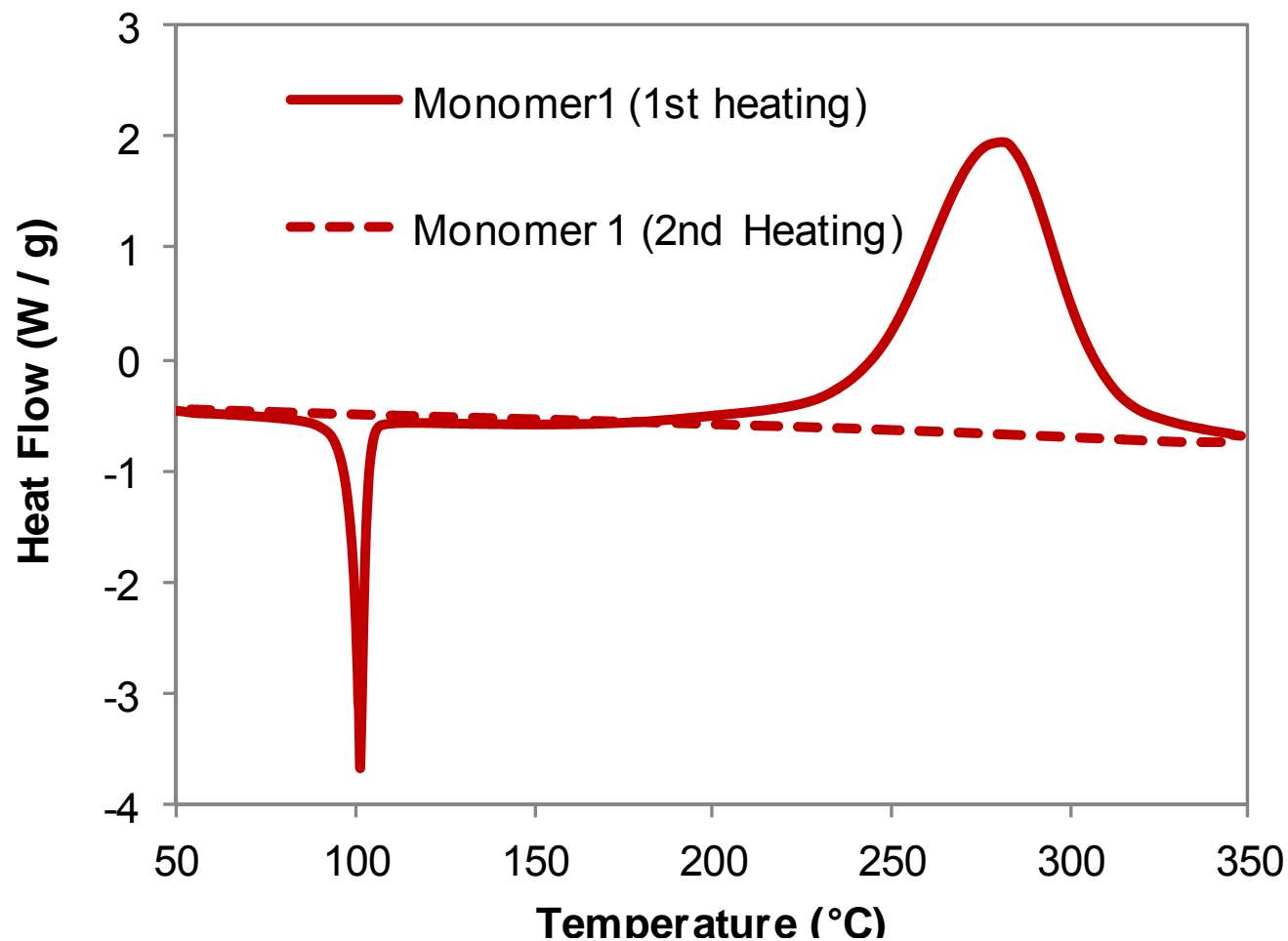


10 °C / min.

- 1,2,4 Isomer



# DSC of 1,3,5 Isomer (10)



10 °C / min.

- 1,3,5 Isomer



# Comparative DSC Data



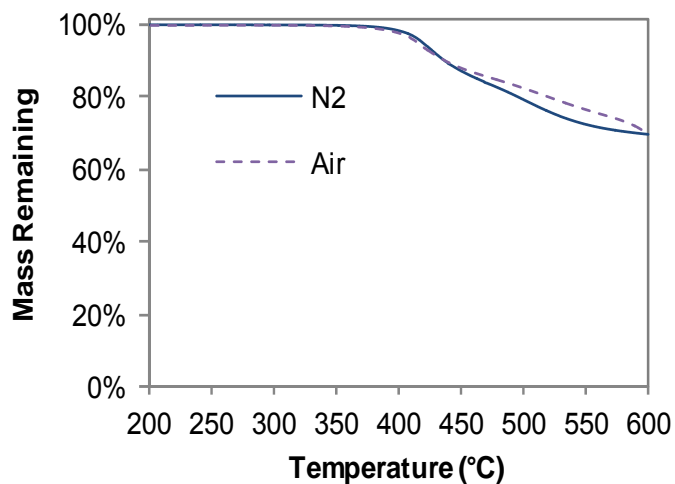
Comparison of DSC data for monomers **5**, **9**, **10** and BADCy

Compound	$T_m$ (°C)	Cure Onset (°C)	Exotherm Max (°C)	$\Delta H_{cure}$ (J/g)	$\Delta H_{cure}$ (kJ/cyanate ester)
<b>5</b>	165	170	215	600	54
<b>9</b>	85	225	280	620	97
<b>10</b>	101	230	280	780	123
<b>BADCy</b>	82	270	330	810	108

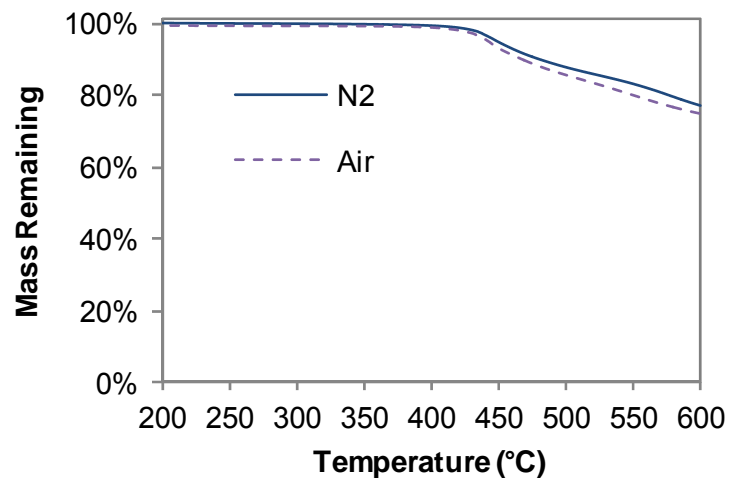
Post-cure  $T_G$  values were not observed for 5 and 9, and were 324 °C for 10 and 305 °C for BADCy



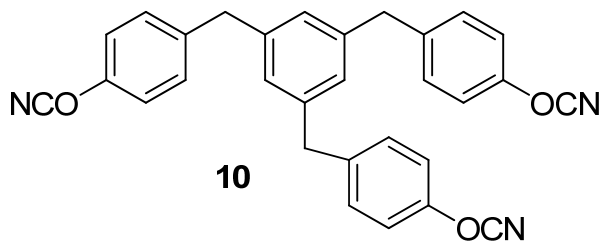
# Comparative TGA of Tricyanate Esters



- 1,2,4 Isomer (9)



- 1,3,5 Isomer (10)





# Comparative TGA Table for Tricyanate Esters



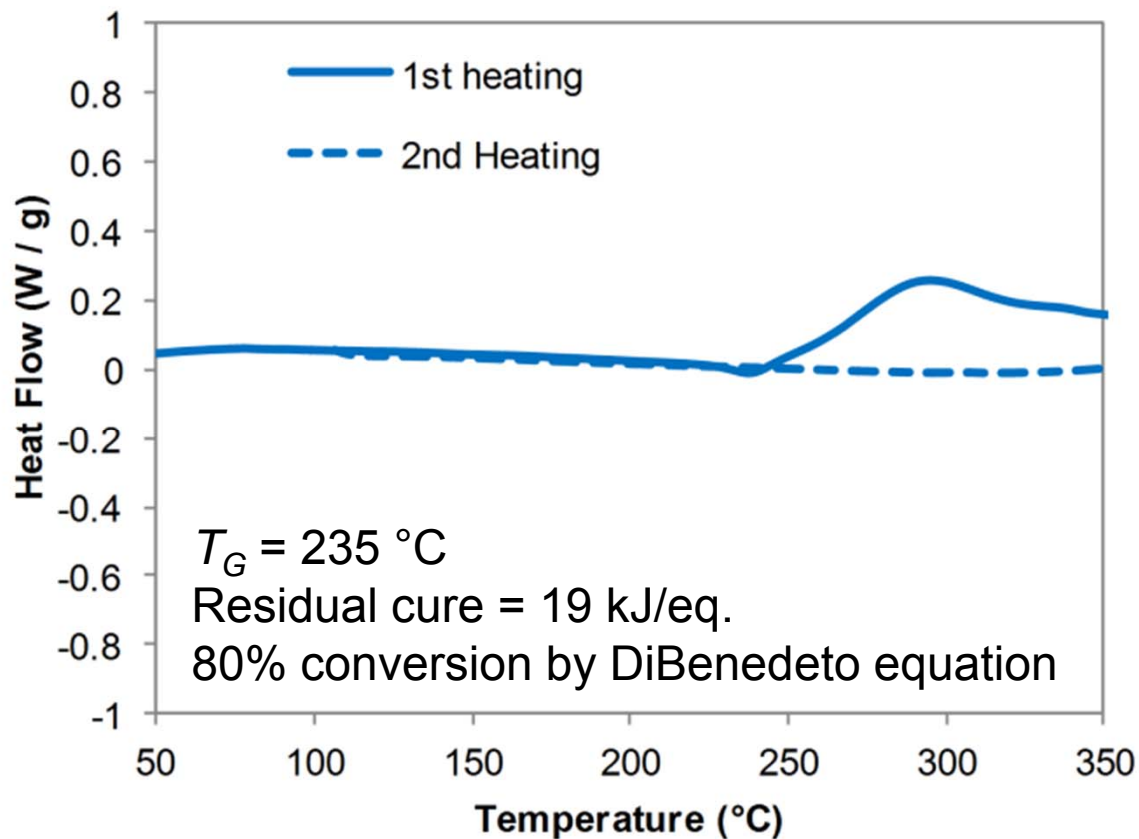
Comparison of TGA data for cured **9**, **10** and BADCy

Compound	T @ 5% weight loss (°C)		Char Yield 600 °C (%)		% incremental weight loss @ T (°C)					
	N <sub>2</sub>	Air	N <sub>2</sub>	Air	N <sub>2</sub>			Air		
					450	550	600	450	550	600
<b>9</b>	419	415	69	70	13	15	3	12	11	7
<b>10</b>	449	443	77	75	5	12	6	7	13	5
<b>BADCy</b>	402	400	47	25	35	15	3	37	13	25

- Higher initial weight loss in both nitrogen and air for compound 9 (the 1,2,4 isomer) probably due to less complete cure; larger losses in BADCy are known to be the result of the instability of the quaternary carbon from studies of analogous polymers (e.g. polycarbonate)



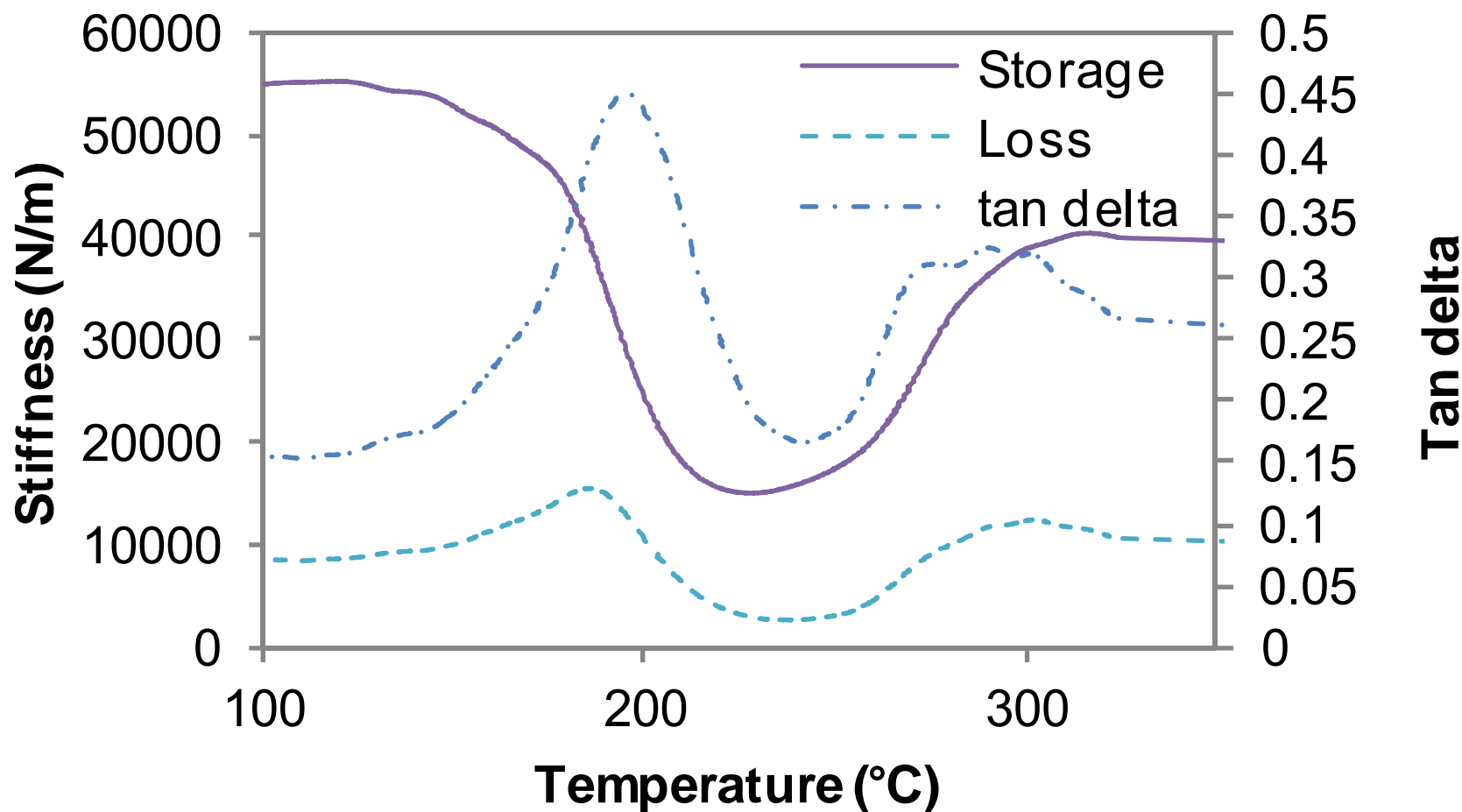
# DSC Scan of “As Cured” 1,2,4 Isomer



10  $^\circ\text{C}$  / min.



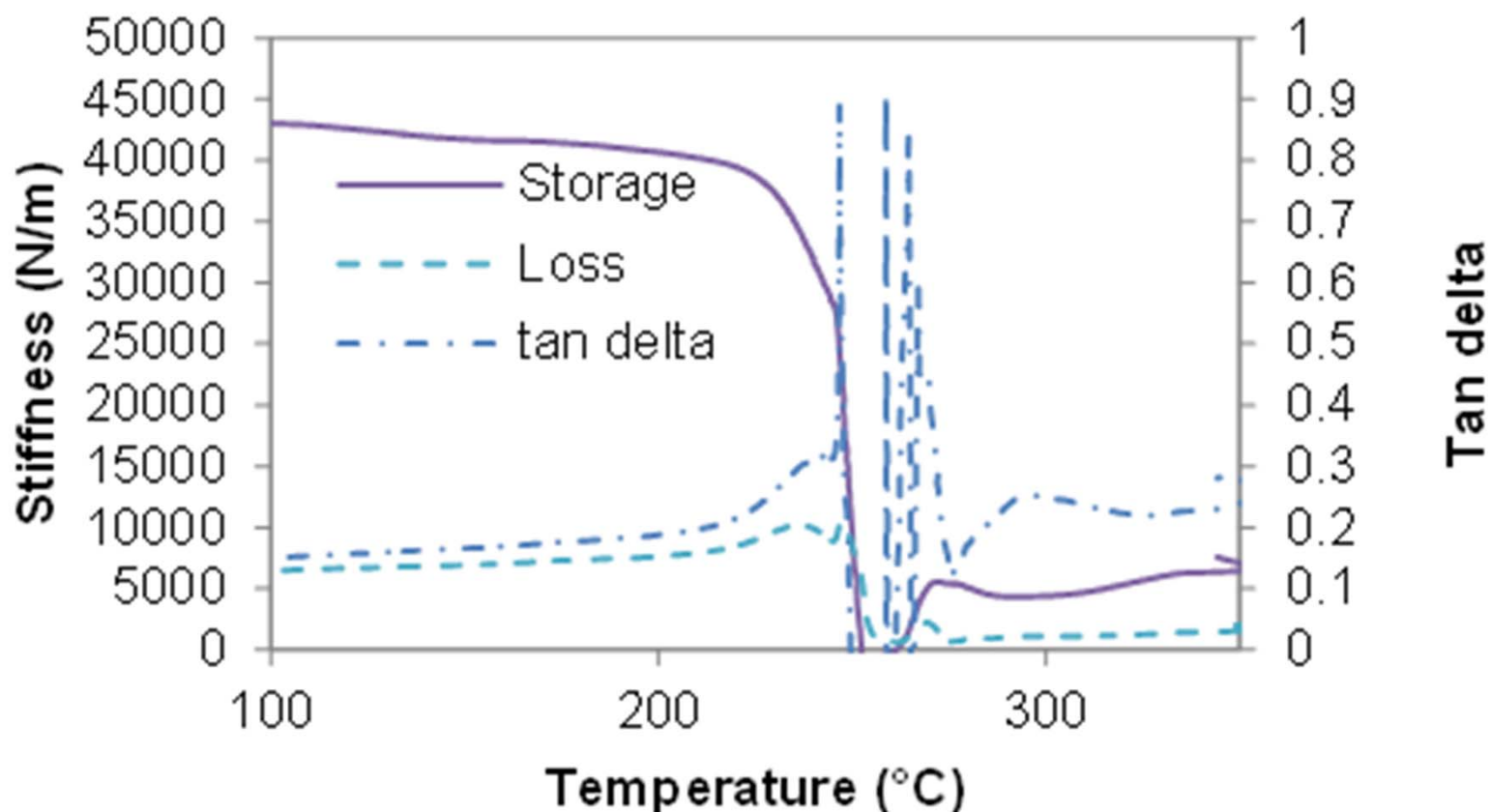
# “Wet” TMA of 1,2,4 Isomer (80% Conversion Prior to Immersion)



20 °C / min.



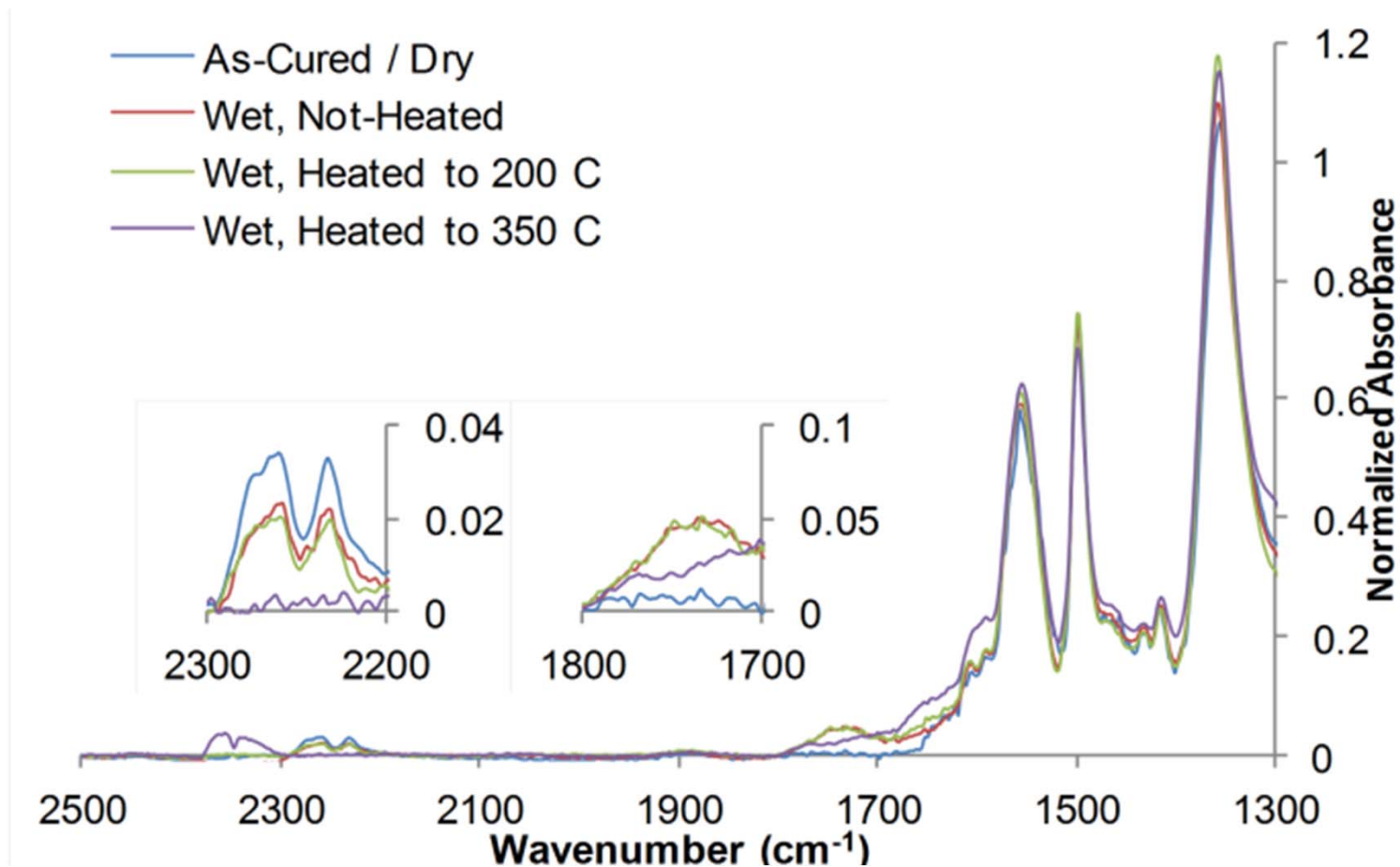
# “Wet” TMA of 1,3,5 Isomer (95% Conversion Prior to Immersion)



20 °C / min.



# FT-IR Data on Wet 1,2,4 Isomer (87% Conversion Prior to Immersion)



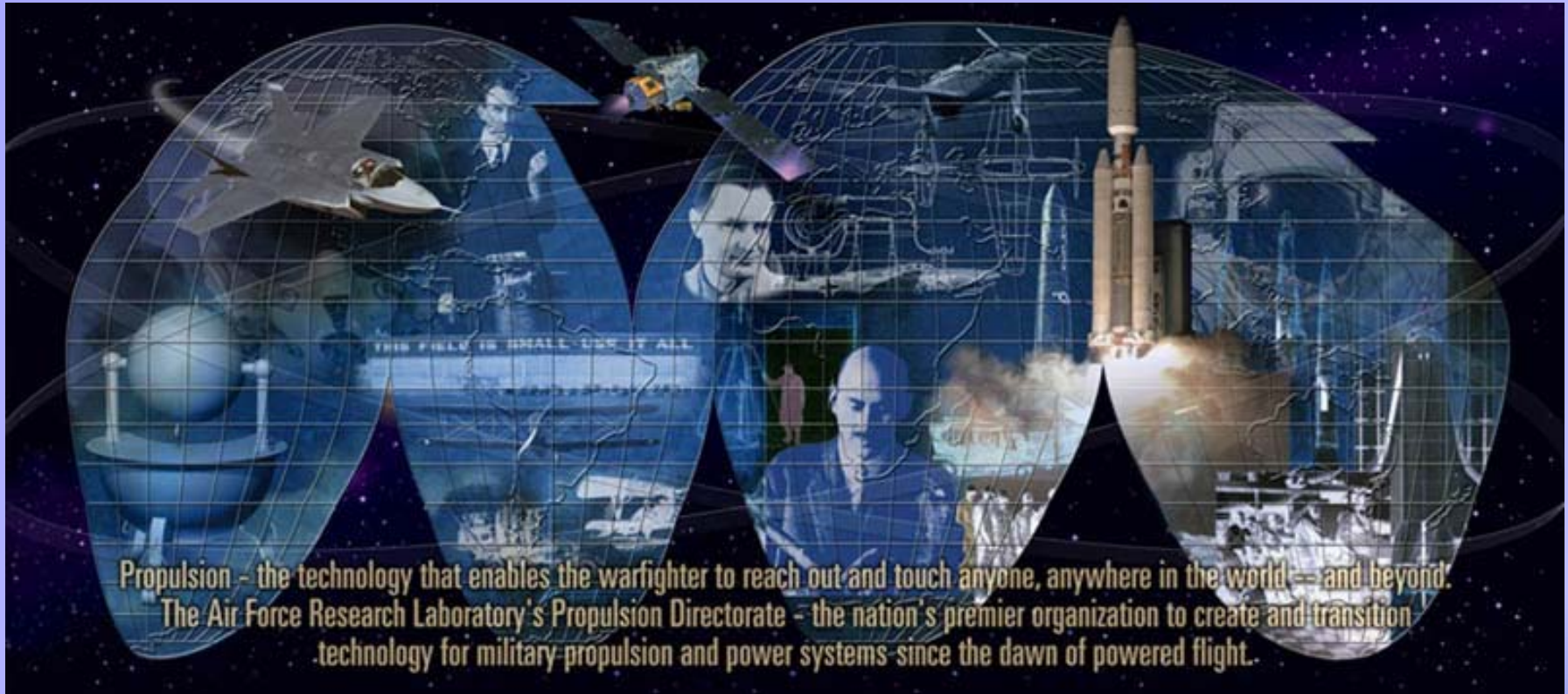
- Careful sample prep + high # of scans = quantifiable results!
- Residual -OCN to carbamate conversion, and destruction of carbamate clearly seen



# Summary / Future Work



- Oxidative coupling of anethole can be used to form cyanate ester monomers that impart a broad range of segment flexibility to cured networks
  - Tricyanates, when not overly rigid, offer a very high glass transition temperature along with thermo-oxidative stability similar to PT-30, but require higher temperatures for full cure
  - Moderately rigid system shows processing characteristics and physical properties similar to BADCy
  - Most flexible system is a liquid at room temperature and provides final properties that are intermediate between the commercial products RTX-366 and LECy, with very low water uptake (~1% after 96 hours at 85 °C)
- Areas for future work
  - Since cyanate ester blends often result in networks with synergistic improvements in properties, blending the products may produce highly desirable combinations of water uptake, thermo-oxidative stability, processing characteristics, and glass transition temperature
  - Fabrication of composite panels and structures incorporating these resins is underway



# AFRL

THE AIR FORCE RESEARCH LABORATORY  
LEAD | DISCOVER | DEVELOP | DELIVER



Distribution A. Approved for public release; distribution is unlimited.  
AFRL Public Affairs #