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14. ABSTRACT

Key physical characteristics including density, packing fraction, moisture uptake, and as-cured dry glass transition temperature of cyanurate networks formed from bio-based cyanate esters synthesized from the natural product anethole were examined. The results showed that both equivalently high glass transition temperatures and lower moisture uptake compared to commercial materials could be achieved, though, for the non-optimal cure schedules studied, not in the same network. The most important factor in moisture uptake appeared to be the relation between the cure schedule and the glass transition temperature of the developing network. By optimizing these parameters, it may be possible to produce networks that exhibit both a higher glass transition temperature as well as lower moisture uptake compared to commercial materials.

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HIGH-PERFORMANCE BIO-BASED CYANATE ESTER RESINS WITH LOW MOISTURE UPTAKE

22 August 2012

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Outline

- Background / Motivation
  - About Cyanate Esters
  - Why Study Non-Petroleum Feedstocks for Cyanate Esters?
- Overview of Synthesis of Cyanate Esters from Anethole
- Properties of Anethole-Based Cyanate Esters
  - Effect of Segment Rigidity
  - Comparison to Common Dicyanate Esters
- Program Integration / Future Work

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More details in: Davis et al., *Journal of Polymer Science, Part A* , 2012, in press,, doi: 10.1002/pola.26218

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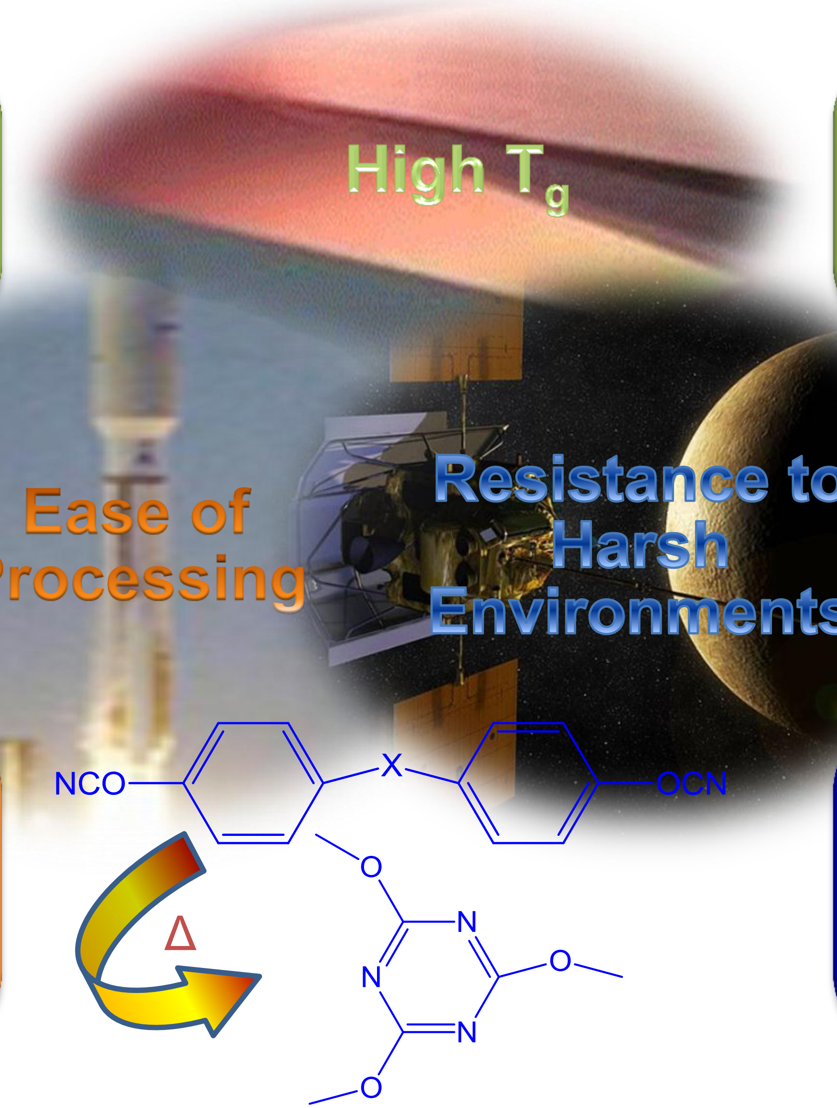
Cyanate Esters for Next-Generation Aerospace Systems

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

Resin Viscosity Suitable for Filament Winding / RTM

Compatible with Thermoplastic Tougheners and Nanoscale Reinforcements

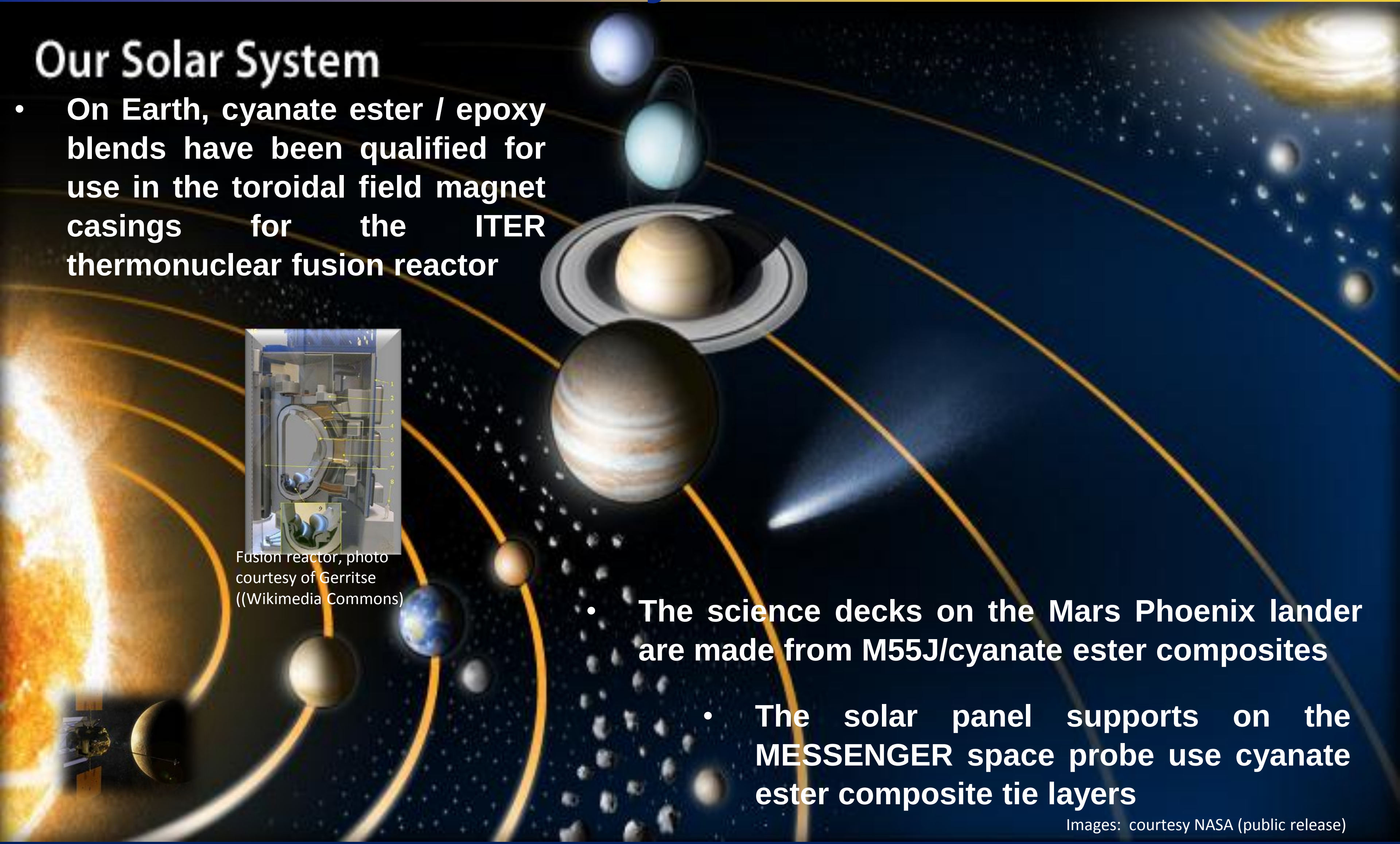


Onset of Weight Loss:
> 400 °C with High Char Yield

Good Flame, Smoke, & Toxicity Characteristics

Low Water Uptake with Near Zero Coefficient of Hygroscopic Expansion

Cyanate Esters Around the 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)

- 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

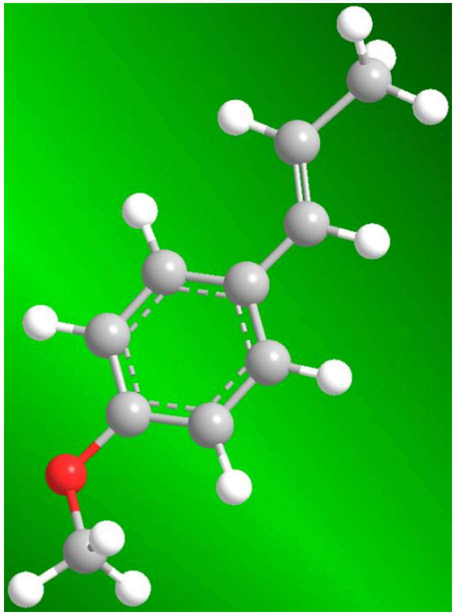
- Materials qualification efforts are costly; developing bio-based materials that deliver both improved performance and decreased dependence on petroleum enables a higher and more robust return on investment
- Cyanate esters are generally easy to process; they do not require stoichiometric balance and form co-networks readily, hence they tolerate variation in monomer chemistry relatively well


U.S. Navy photo by Photographer's Mate 3rd Class Mark J. Rebilas (RELEASED)

- 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

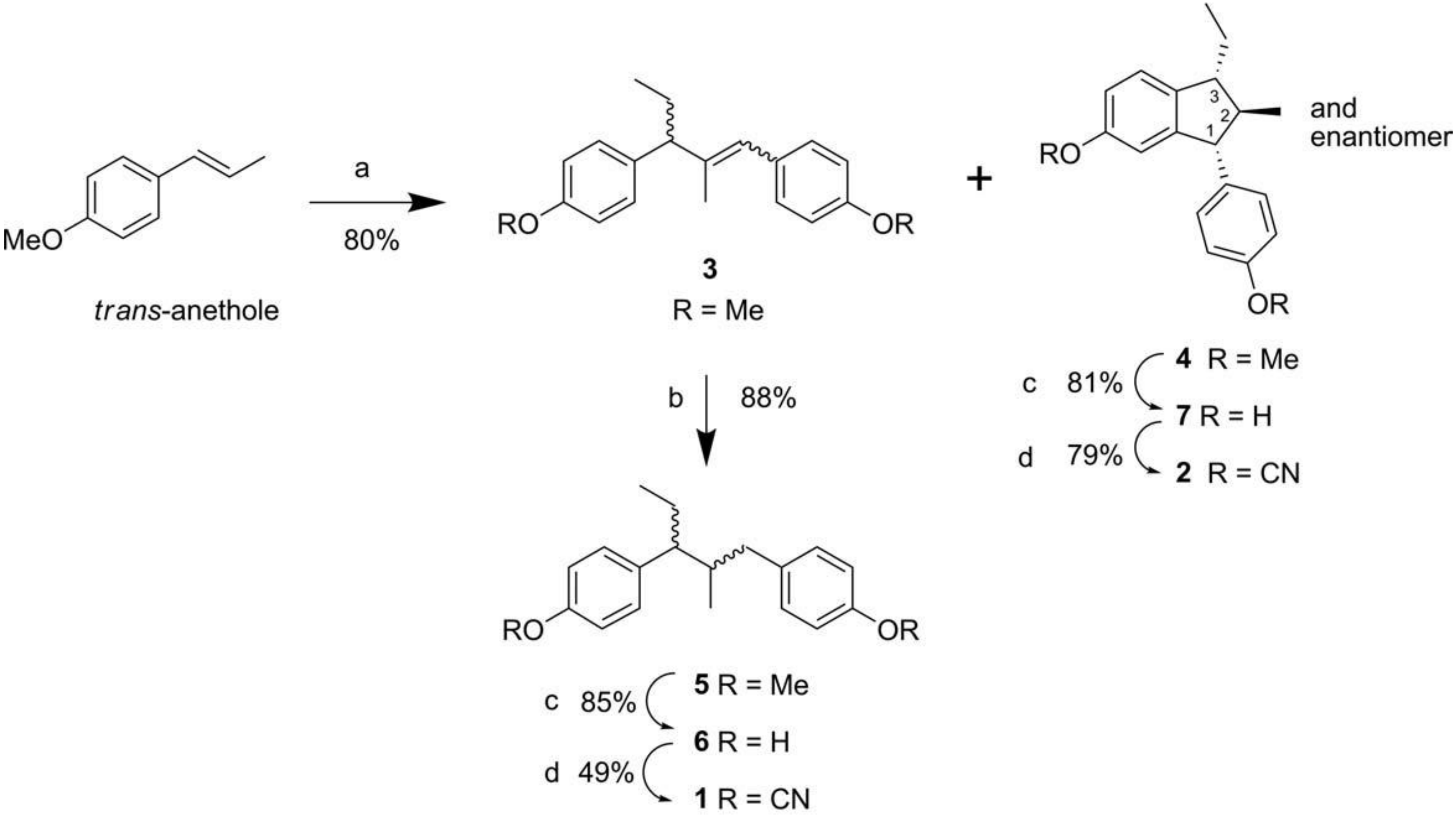
Anethole as a Monomer Source

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



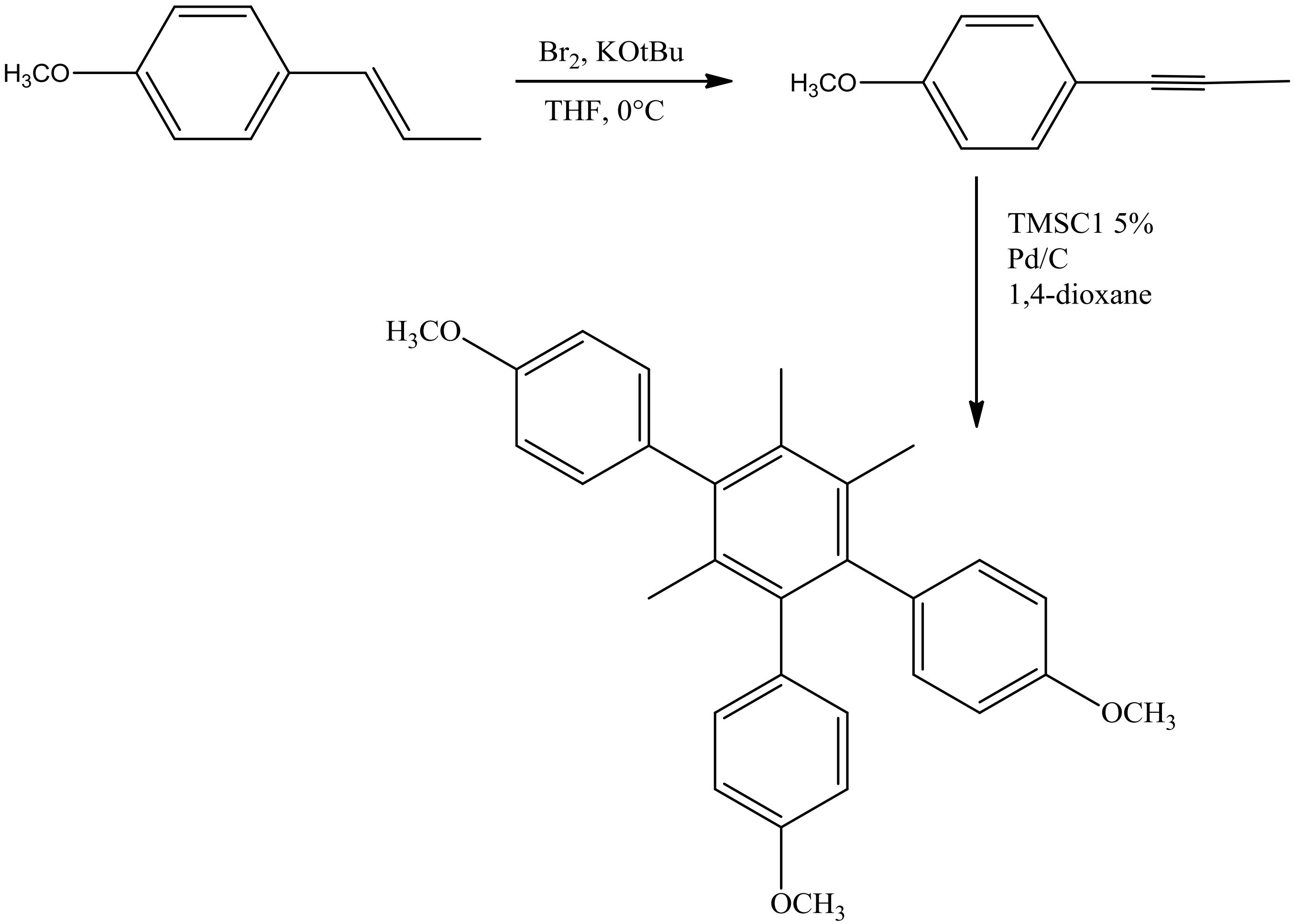
- Trans-anethole is widely available as an essential oil extracted from star anise (Illicium verum), an evergreen tree native to southwest China (Yunnan and Guangxi provinces) and northern Vietnam
- Current production is ~ 400 tons / yr, with significant use in the flavor and fragrance industry
- Simple 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) H_2SO_4, H_2O, reflux; b) H_2, Pd/C, THF; c) pyridineHCl; reflux; d) BrCN, TEA, acetone, -20 °C.

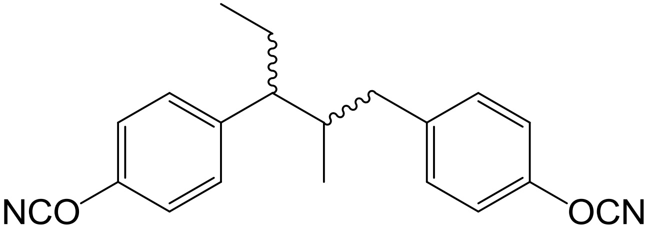
Anethole-Based Cyanate Esters: Route 2



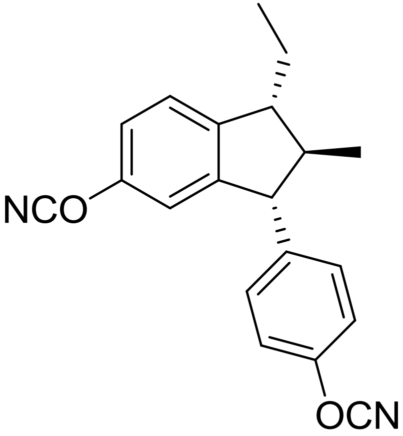
- Final product is a mixture of primarily 1,2,4 and secondarily 1,3,5 isomers. The 1,2,4 isomer was isolated and converted to cyanate ester as in route 1.

Anethole-Based Cyanate Esters: Range of Segment Flexibility

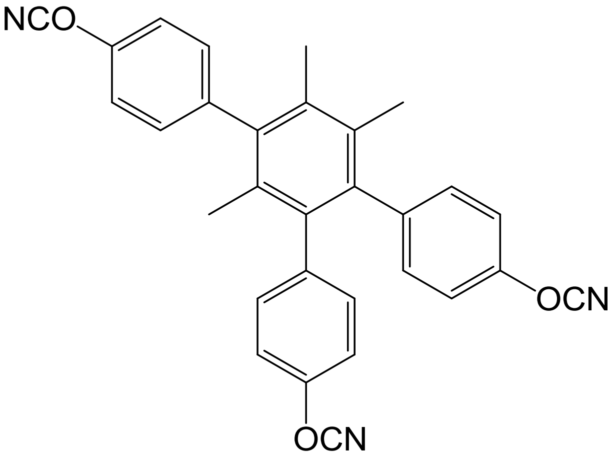
CE-1



CE-2



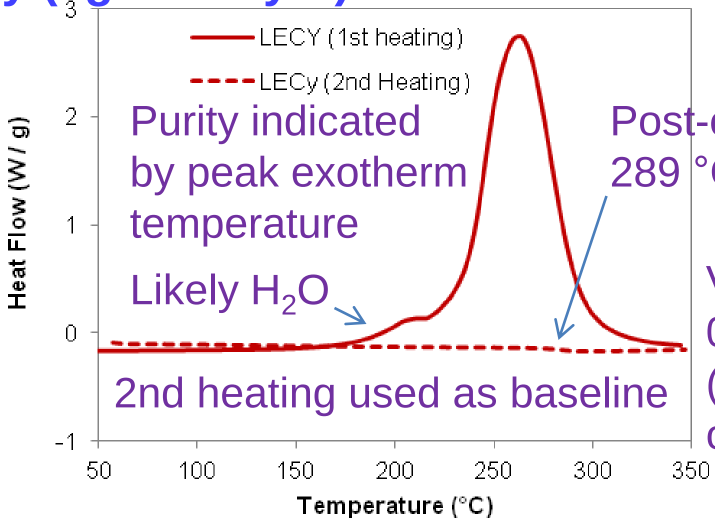
CE-3



- 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

Assessment of Processing Characteristics via DSC

LECy (aged 3.5 yrs)



Purity indicated by peak exotherm temperature

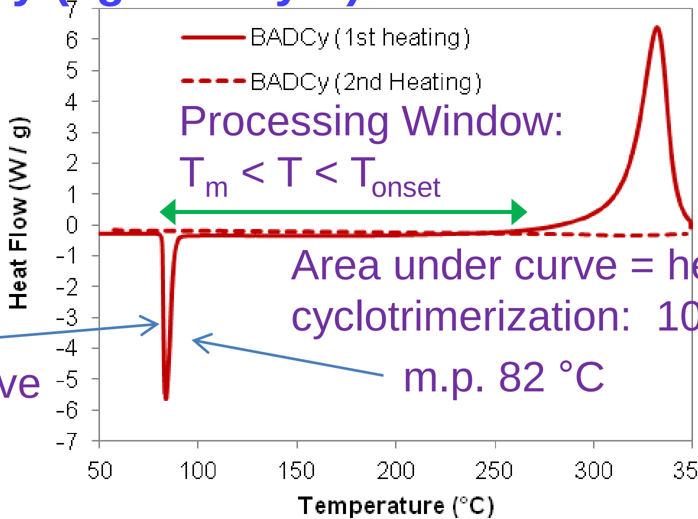
Post-cure T_g: 289 °C

Likely H_2O

2nd heating used as baseline

VH Purity: 0.986 (comparative only)

BADCy (aged 2.5 yrs)

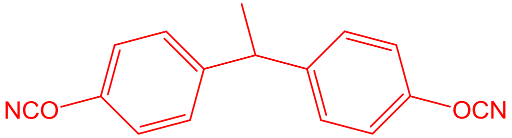


Processing Window: $T_m < T < T_{onset}$

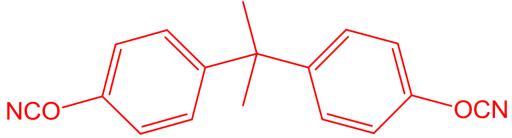
Area under curve = heat of cyclotrimerization: 108 kJ/eq.

m.p. 82 °C

LECy



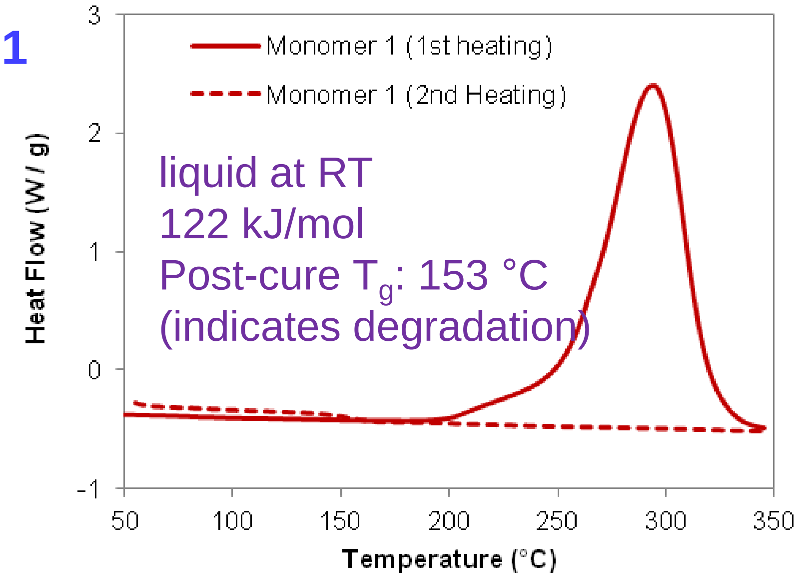
BADCy



- A non-isothermal DSC scan for cyanate esters reveals many useful processing characteristics
- Highly pure samples should show narrow meltingendotherms (if present), exotherm maxima near or above 300 °C, an exotherm of 100 – 110 kJ/eq. , relative ease of cure as indicated by a “closed”, symmetric exotherm and appropriate post-cure T_g.
- In this case, a “pot life” study of uncatalyzed BADCy and LECy (stored at ambient conditions in the low humidity at Edwards AFB) shows no changes in BADCy after 2.5 yrs and only modest contamination of LECy with no significant effects on the final network observed after 3.5 yrs
- Note: Pot life under moderate to high humidity and with catalyst will be much shorter.

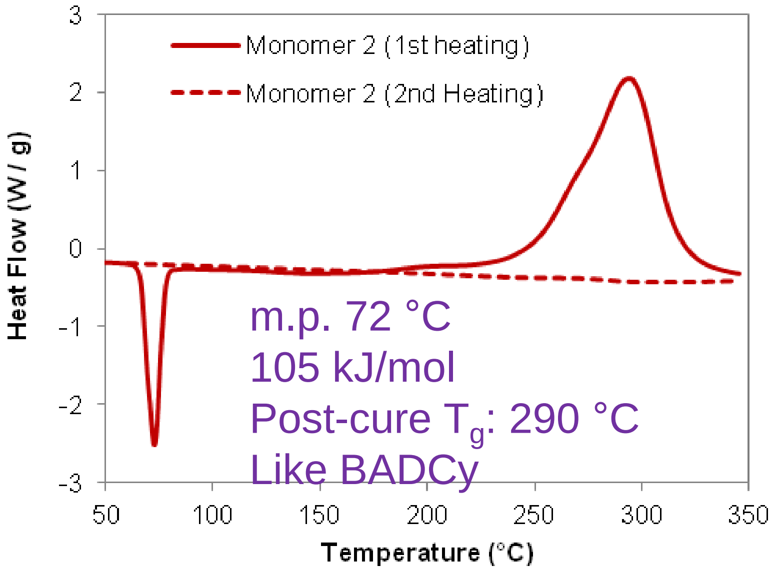
DSC of Anethole-Based Cyanate Esters

CE-1



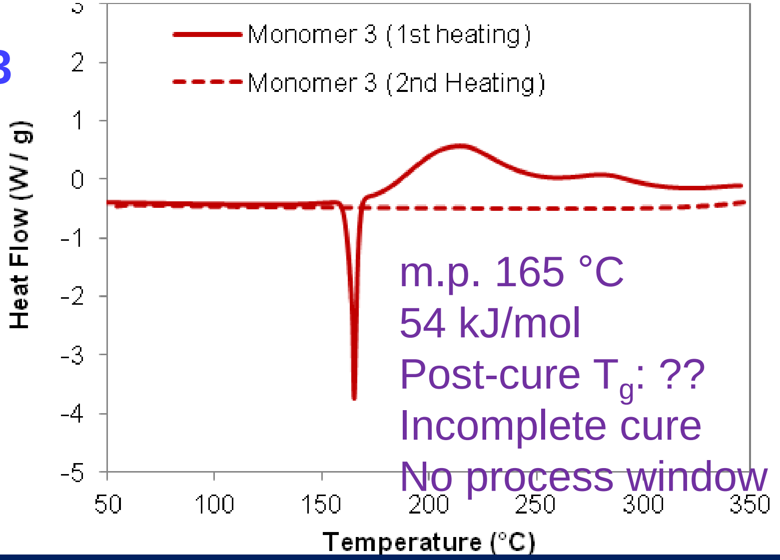
liquid at RT
122 kJ/mol
Post-cure T_g: 153 °C
(indicates degradation)

CE-2



m.p. 72 °C
105 kJ/mol
Post-cure T_g: 290 °C
Like BADCy

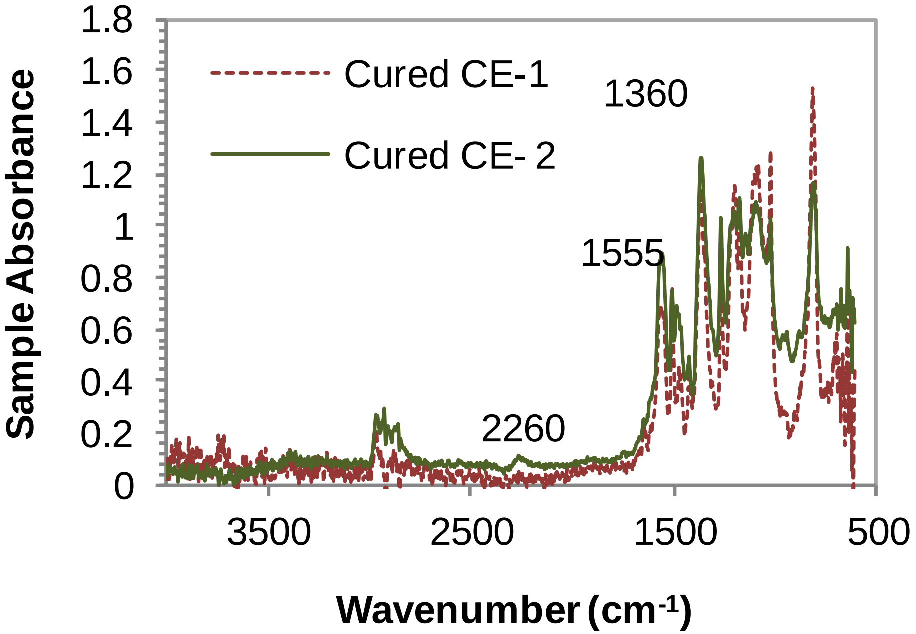
CE-3

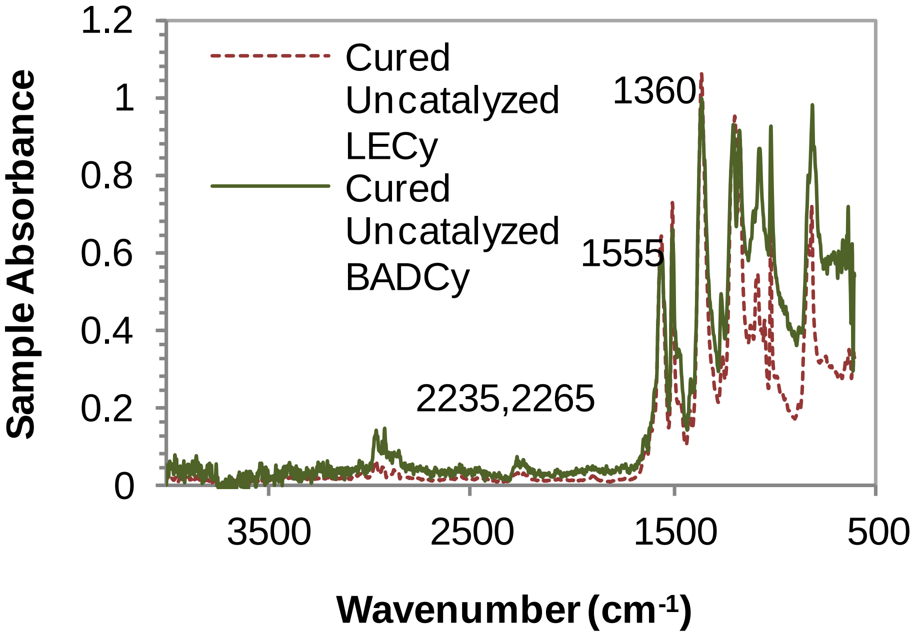


m.p. 165 °C
54 kJ/mol
Post-cure T_g: ??
Incomplete cure
No process window

- 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

Confirmation of Extent of Cure via FT-IR



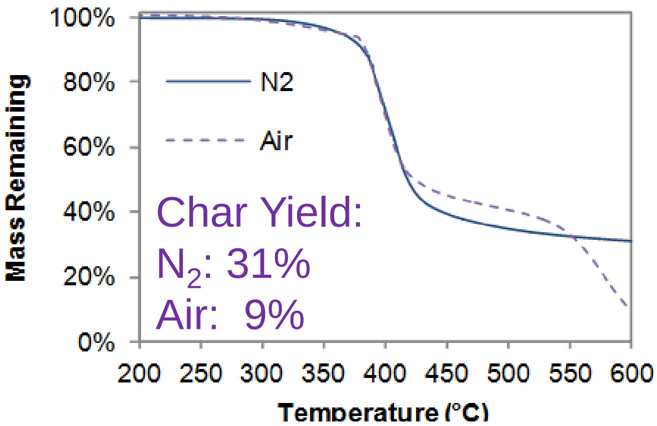


Samples cured at 150 ºC for 1hr then 210 ºC for 24 hrs under dry nitrogen

- Similar extent of cure seen in all four samples tested, with slightly lower extent of cure in BADCy and CE-2.
- As expected, the more rigid materials cure less completely. However, this effect may be due, at least in part, to differences in impurity levels.

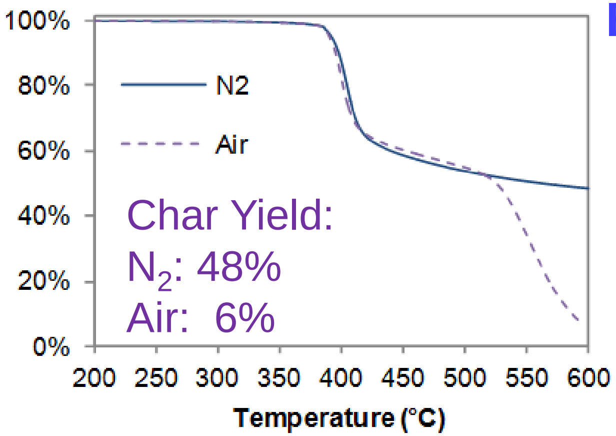
Thermochemical Stability of Anethole-Based Cyanate Esters

CE-1



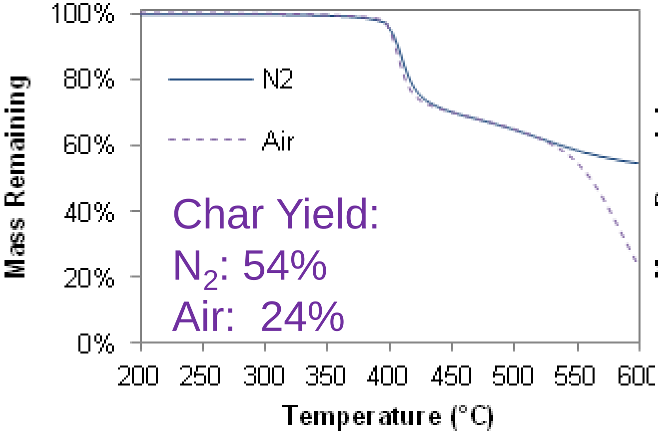
Char Yield:
N_2: 31%
Air: 9%

CE-2



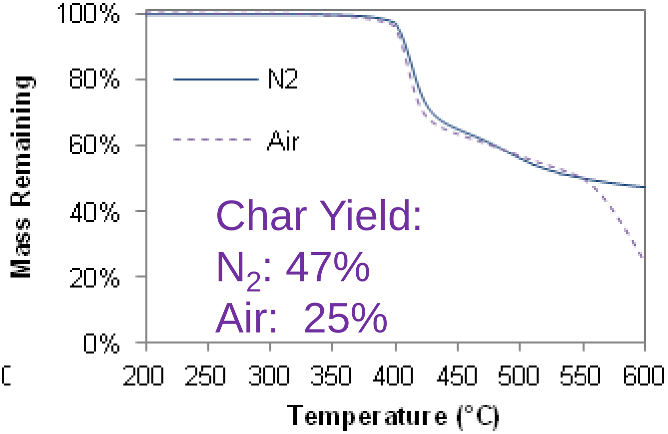
Char Yield:
N_2: 48%
Air: 6%

LECy



Char Yield:
N_2: 54%
Air: 24%

BADCy



Char Yield:
N_2: 47%
Air: 25%

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

Samples cured at 150 ºC for 1hr then 210 ºC 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_g by TMA (°C)**	**T_g After Post-Cure to 350 °C in TMA (°C)**	**“Wet” Tg After 96 h Immersion in 85 °C H_20 (°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%

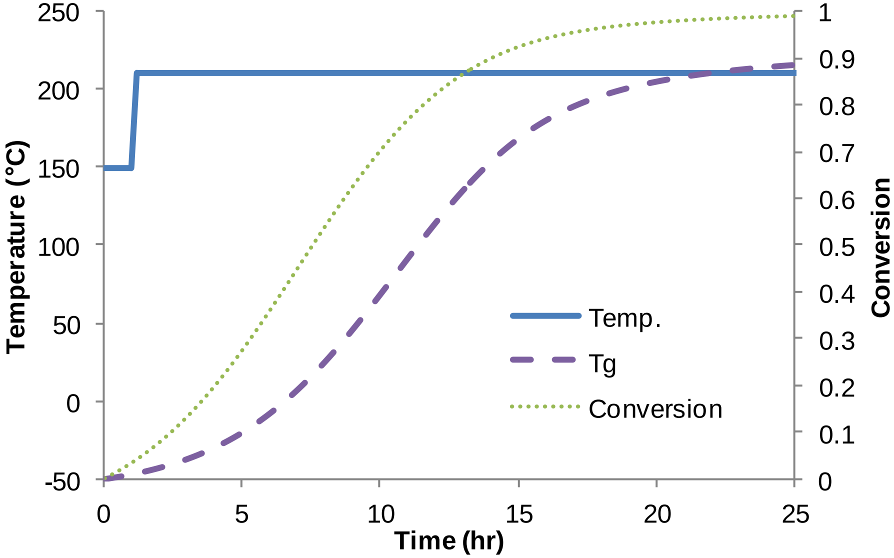
- In CE-1, water uptake is traded for glass transition temperature (as in RTX-366, which has an even lower water uptake and glass transition temperature)
- CE-2 not only processes like BADCy, but appears to give similar physical properties (though with a slight loss in wet properties)
- Note that the 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%

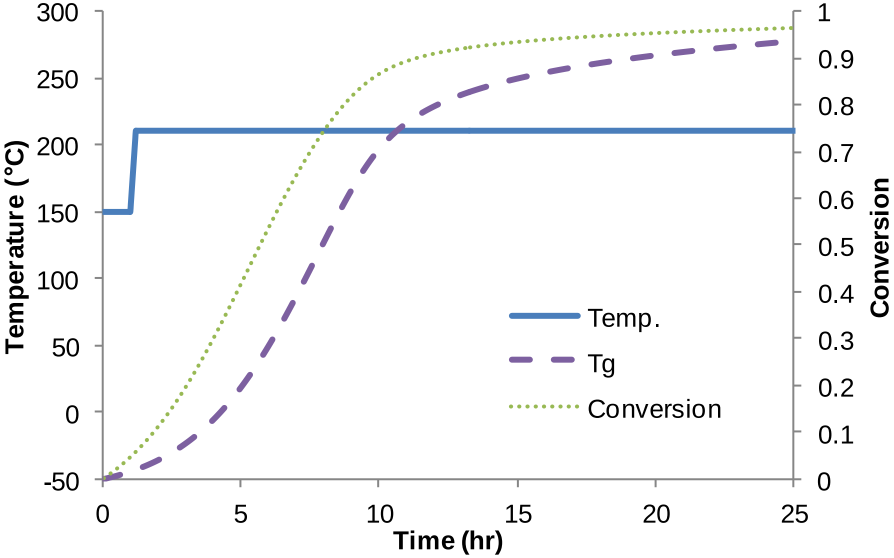
Samples cured at 150 ºC for 1hr then 210 ºC for 24 hrs under dry nitrogen

Proposed Relationship Between Water Uptake and Processing

CE-1



CE-2

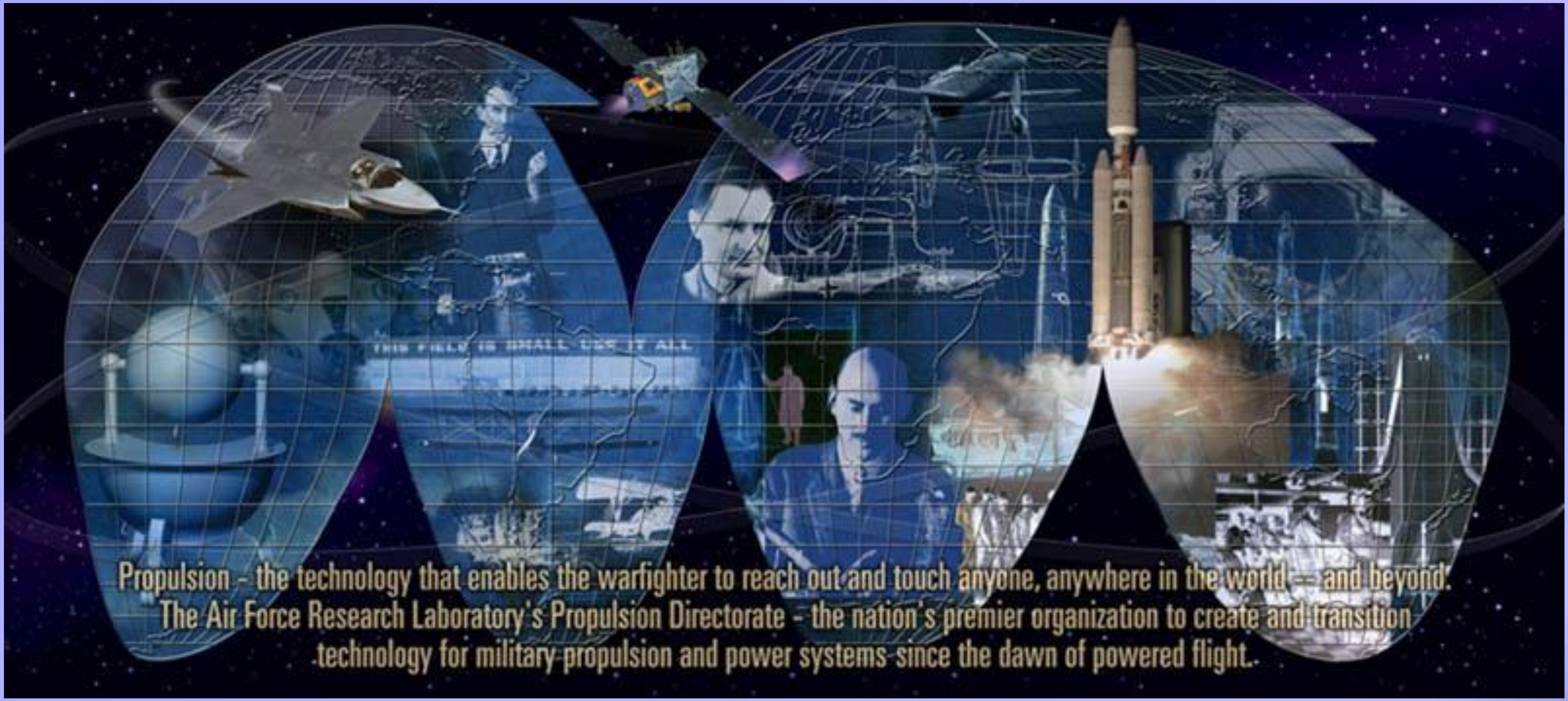


- Though water uptake correlates strongly with cyanurate density, CE-1 has a lower uptake than CE-2 despite having almost the same cyanurate density.
- When $T > T_g$, increased conversion drives down water uptake (initially due to free volume shrinkage, and after the gel point, perhaps due to increasing T_g and/or redistribution of free volume).
- When $T < T_g$, increased conversion increases water uptake due to formation of relatively large free volume regions that are “frozen in”
- The low “as cured” T_g of CE-1 indicates that $T < T_g$ for very little of the cure process, in contrast to CE-2.

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
  - Highly rigid systems exhibited poor processing characteristics and are not being pursued further
  - Moderately rigid system shows processing characteristics and physical properties similar to BADCy, now being scaled up for further investigation
  - Most flexible system is a liquid at room temperature and provides final properties that are intermediate between the commercial products RTX-366 and LECy
  - Due to the higher aliphatic content, the thermo-oxidative stability characteristics of these cyanate esters, though still significantly better than most epoxy resins, did not match those of existing commercial products.

- Areas for future work
  - Since cyanate ester blends often result in networks with synergistic improvements in properties, blending the moderately and highly flexible products from the same oxidation scheme may produce highly desirable combinations of water uptake and glass transition temperature
  - Fabrication of composite panels and, eventually, composite parts incorporating the moderately rigid cyanate ester represents the next step



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