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

MACROMOLECULAR NETWORKS CONTAINING FLUORINATED CYCLIC MOIETIES

12 December 2015

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Outline

- Background / Motivation
  - Cyanate esters
  - Link between F and Low Water Uptake
- PFCB Dicyanate Esters
  - Monomer Properties
  - Cure Properties
  - Network Properties

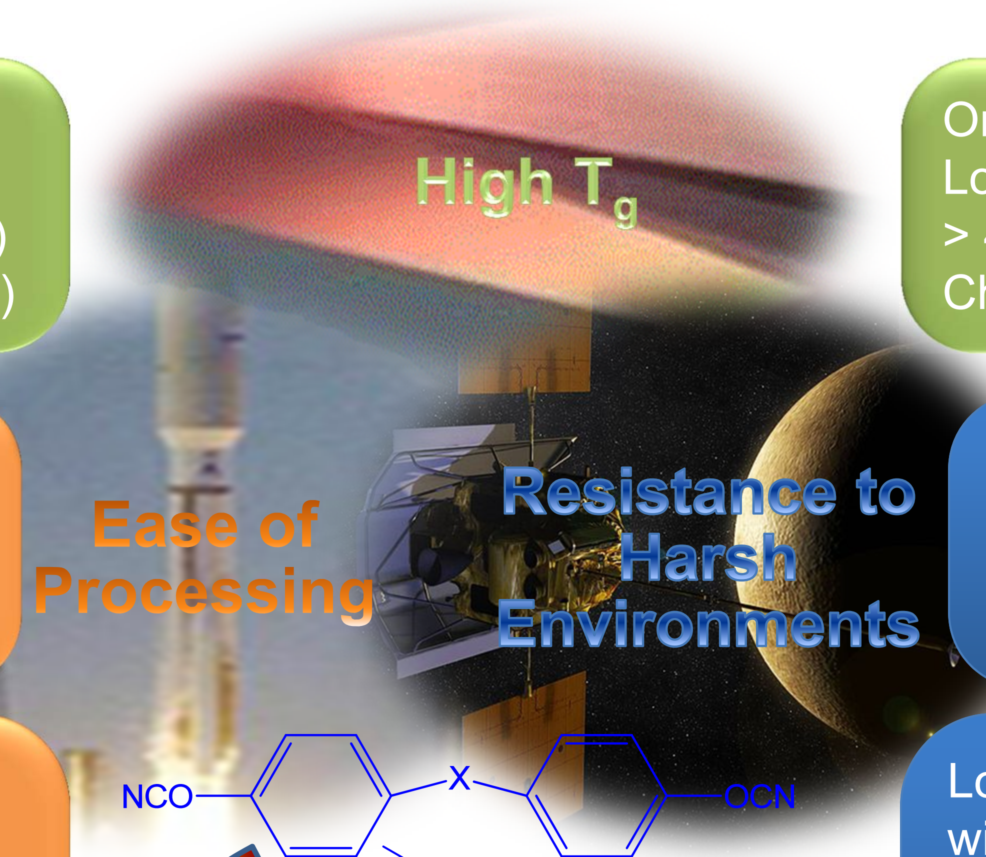
Acknowledgements: Air Force Office of Scientific Research, Air Force Research Laboratory – Program Support; AMG team members (AFRL/RQRP);

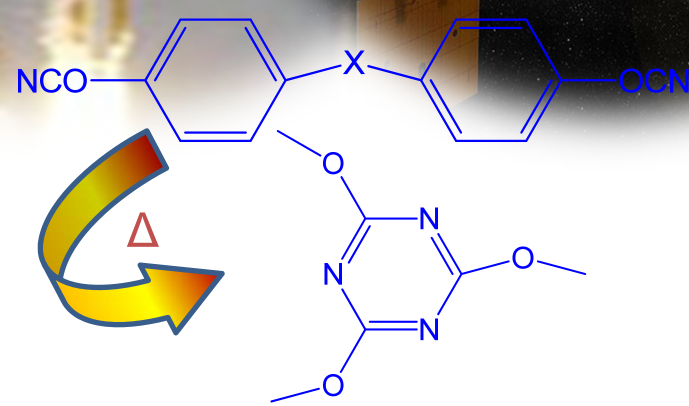
Cyanate Esters for Next-Generation Aerospace Systems

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

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

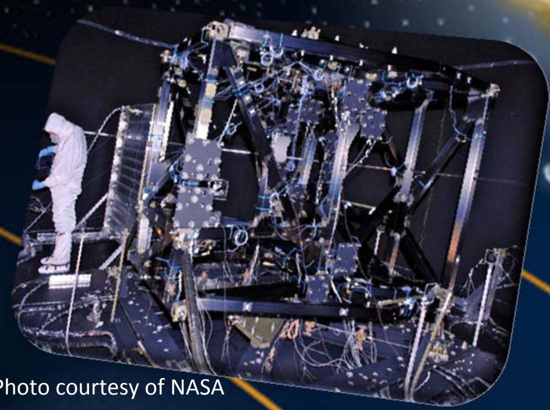
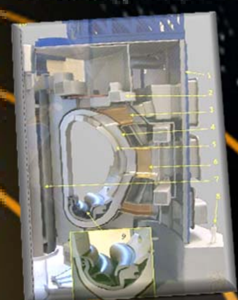


Photo courtesy of NASA

- Unique cyanate ester composites have been designed by NASA for use as instrument holding structures aboard the James Webb Space Telescope



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

- The science decks on the Mars Phoenix lander are made from M55J/cyanate ester composites

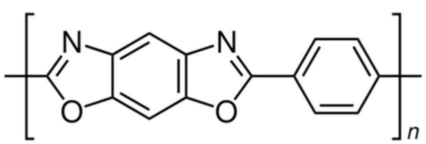
- The solar panel supports on the MESSENGER space probe use cyanate ester composite tie layers

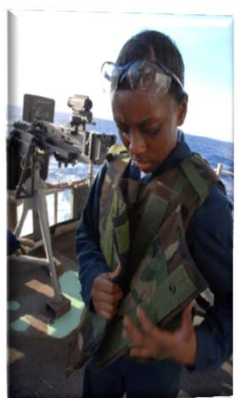
Images: courtesy NASA (public release)

Importance of Moisture Uptake in Composite Component Performance

Photo by U.S. Navy photo by Photographer's Mate 1st Class Anibal Rivera (public domain).

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

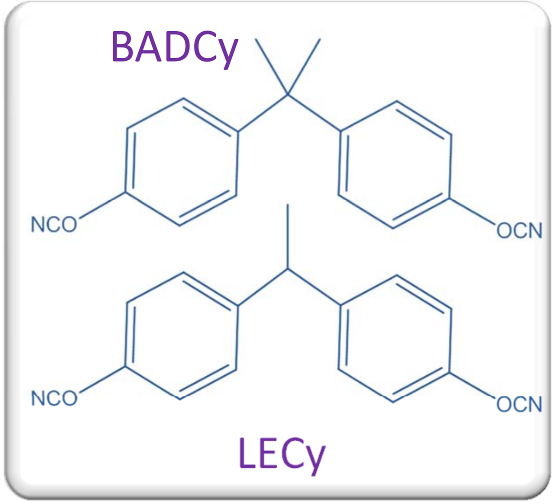


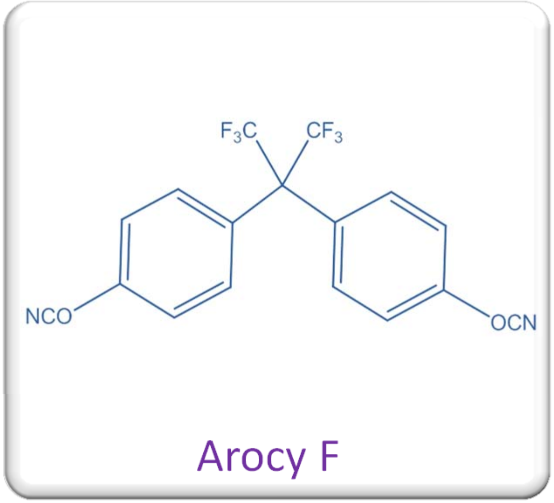


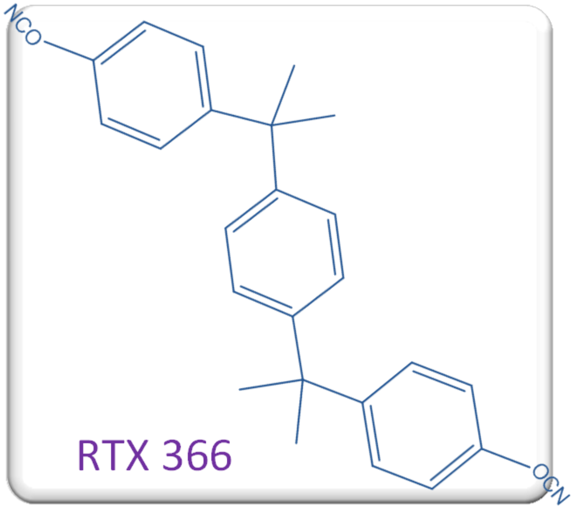
U.S. Navy photo by Mass Communication Specialist 3rd Class Torrey W. Lee (public domain)

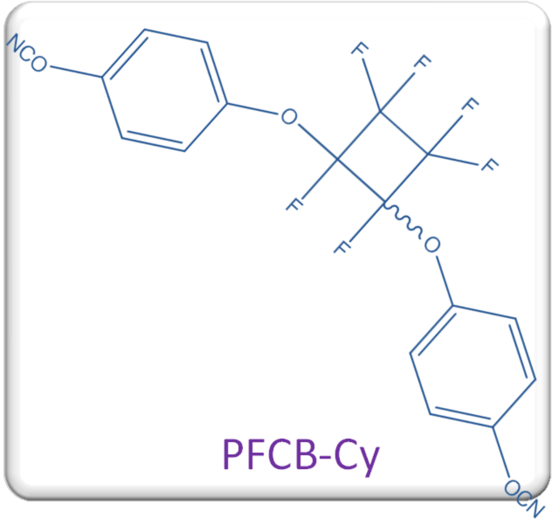
- Water can add significantly to launch or take-off weight (3% water in composite resins = about 50 lbs of extra weight on an large SRM)
- Items with high water content can fail catastrophically when suddenly heated
- Long-term exposure to water can facilitate many mechanisms of chemical degradation, necessitating substantial "knock down" factors in design allowables
- Though more stable than epoxy resins, cyanate esters can degrade on long-term exposure to hot water

Control of Moisture Uptake Through Repeat Unit Structure







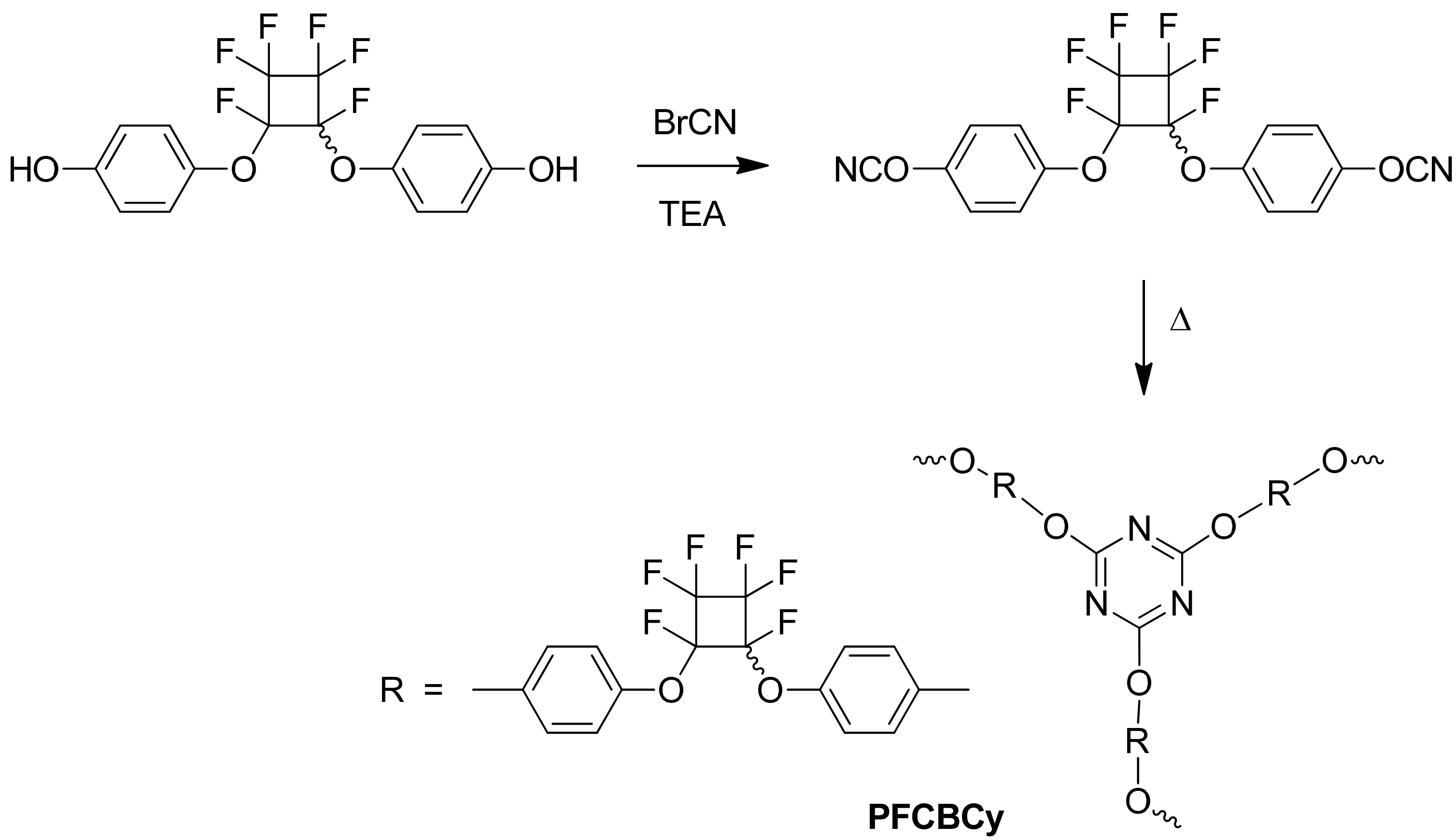


Adding fluorine reduces moisture uptake and dielectric constant but adds density.

Decreasing cyanurate density also reduced moisture uptake but reduces thermomechanical performance.

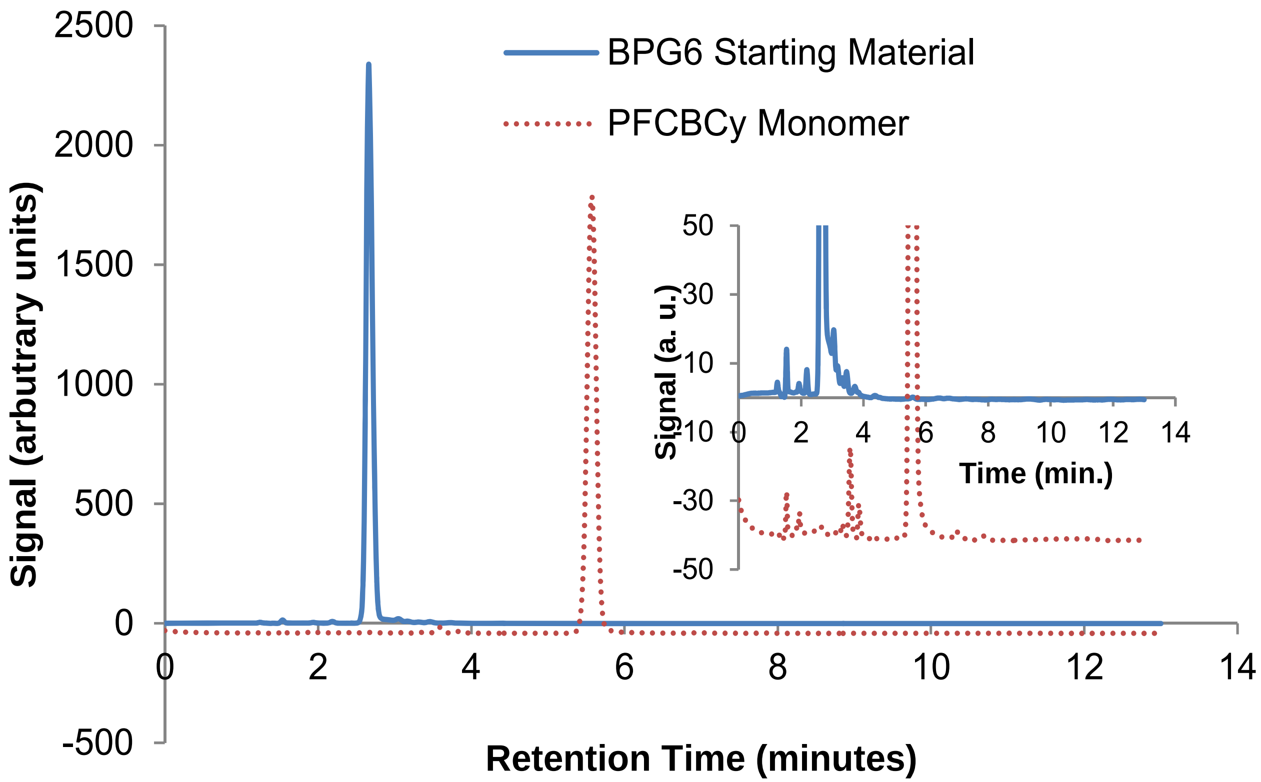
PFCB chemistry offers a new route to reduced moisture uptake through both decreased cyanurate density and fluorination.

Synthesis of PFCB Dicyanate



- 56% overall yield of monomer from Bisphenol T starting material
- Purified by washing with methanol

Purity of PFCB-Cy



- Ratio of primary peak to total: 99.1% for BPG6, 98.1% for PFCBCy
- Most likely impurity is monophenol (incomplete conversion)

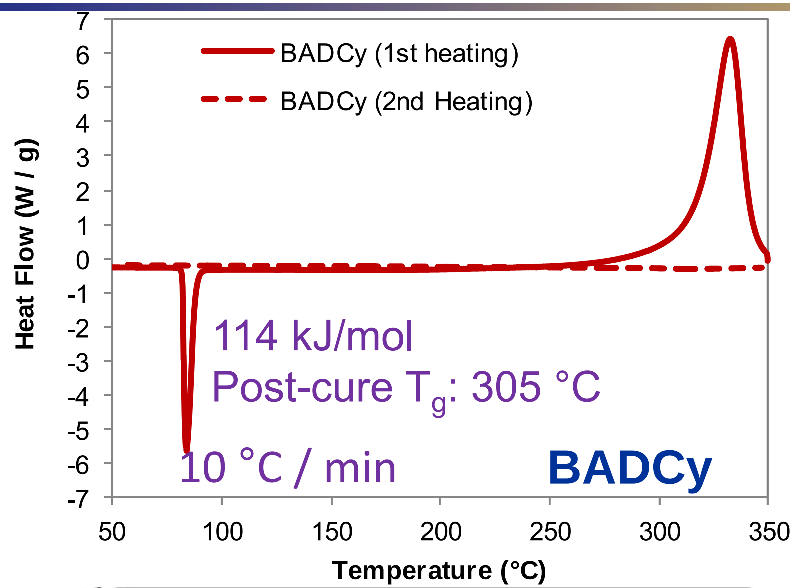
Comparative Polycyanurate Network Physical Properties

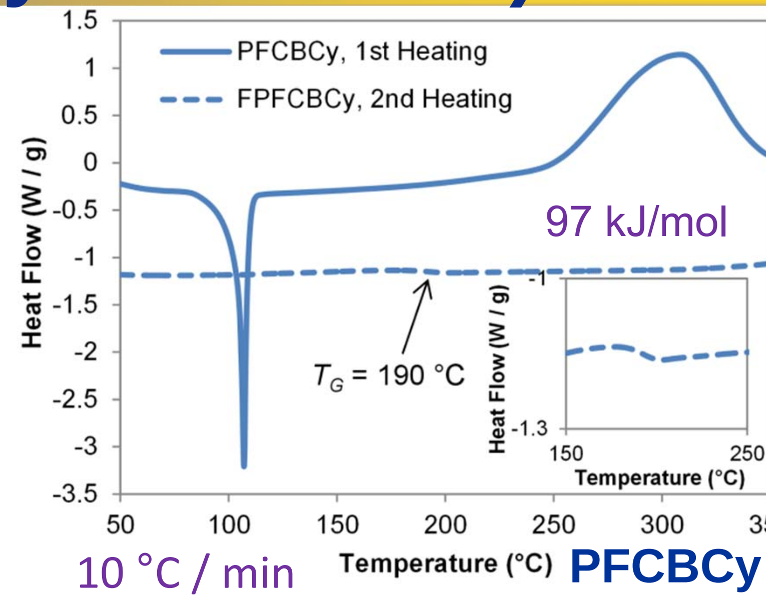
Uncatalyzed Network / Property	BADCy	LECy	RTX-366	AroCy F	PFCBCy
% F by wt.	0	0	0	29.5%	26.5%
Density (g/cc @ full cure)	1.19 (est1)	1.210 ± 0.004	1.14 (est2)	1.46 (est2)	1.59 (est3)
Cross-link density @ full cure (mmol / cc)	2.9 (est1)	3.05 ± 0.01	2.0 (est2)	2.5 (est2)	2.5 (est3)
Water Uptake (wt.% @ full cure, 96 hr @ 85 °C)	2.1 ± 0.5 (est1)	1.9 ± 0.2	0.6*	1.8*	0.56 ± 0.10
Water Uptake (mmol / cc, @ full cure 96 hr @ 85 °C)	1.4 ± 0.3 (est1)	1.3 ± 0.1	0.4*	1.5*	0.5 ± 0.1

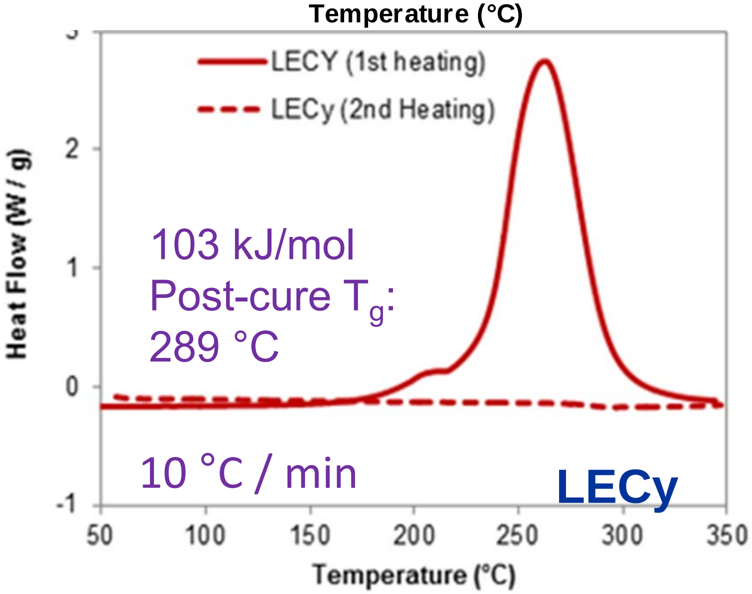
Est1: based on equivalent catalyzed system; uncertainty < 0.01 g/cc / 0.5 wt%
Est2: based on assumption of zero net shrinkage; uncertainty 0.03 g/cc
Est3: based on structure-property correlation, uncertainty 0.03 g/cc
* Conversion unknown, saturation after immersion at 100 °C

- Adding F does not necessarily reduce water concentrations in polycyanurates

DSC Comparison of PFCBCy and Other Di(cyanate Ester)s



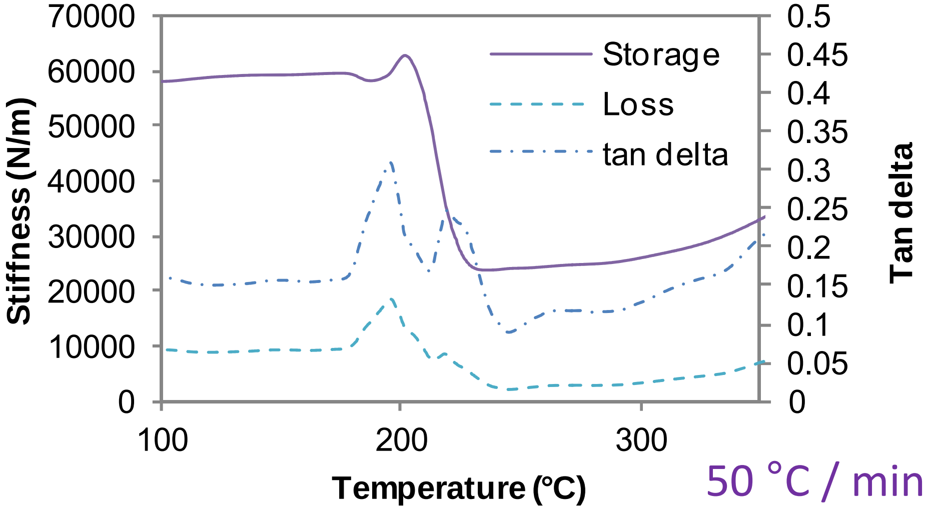




- PFCBCy monomer DSC indicates purity of 85% by van't Hoff method, likely reflection of stereoisomerism.
- Melting point is only slightly higher than BADCy, but post-cured glass transition temperatures are significantly lower than BADCy or LECy.

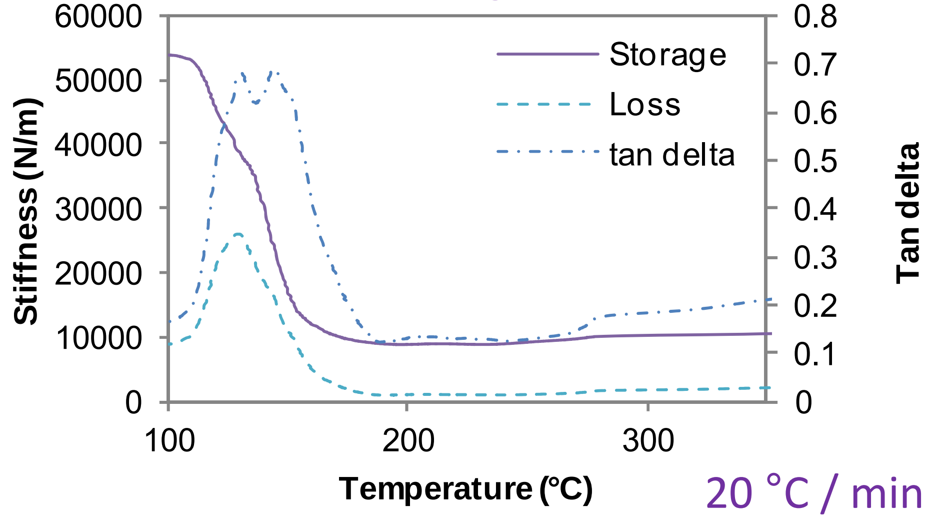
TMA Data on PFCBCy Networks

Dry, 1st Heating



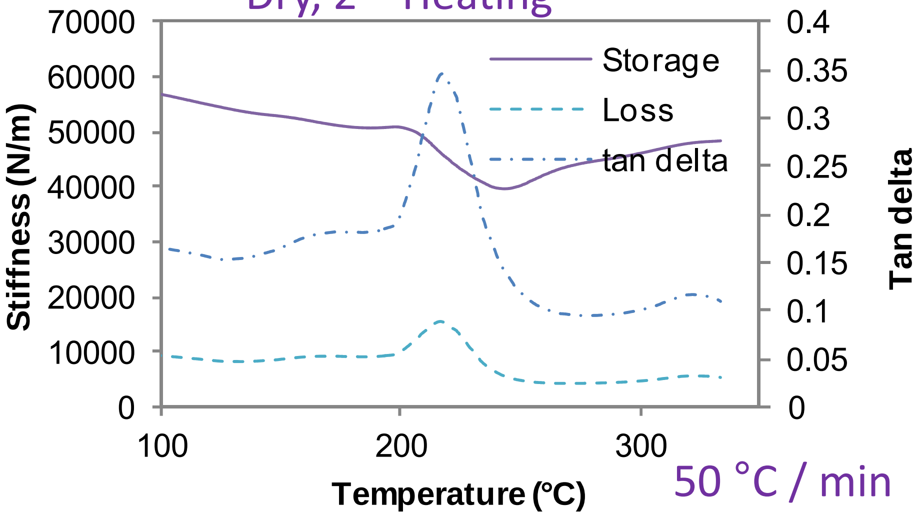
50 °C / min

Wet, 1st Heating



20 °C / min

Dry, 2nd Heating

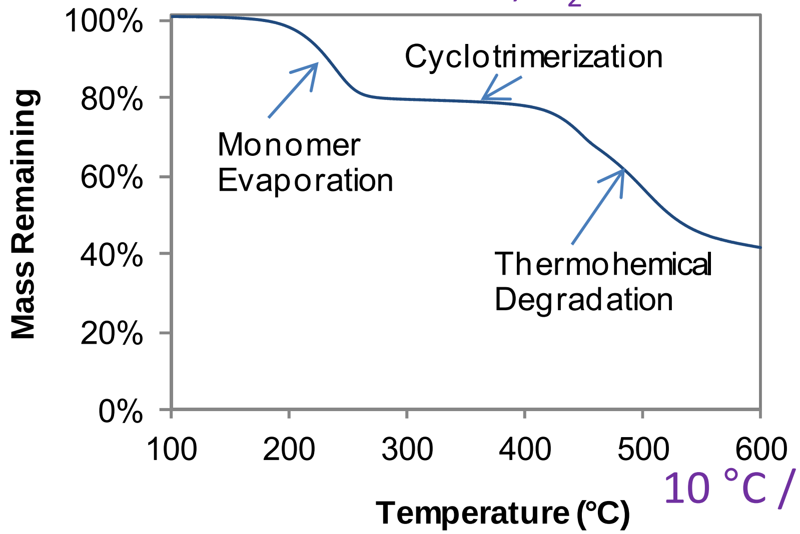


50 °C / min

- Glass transition temperature of “as cured” system is near 190 °C, in agreement with DSC.
- Residual cure in situ to a glass transition temperature of around 220 °C is seen.
- Water immersion for 96 hrs at 85 °C leads to significant network degradation

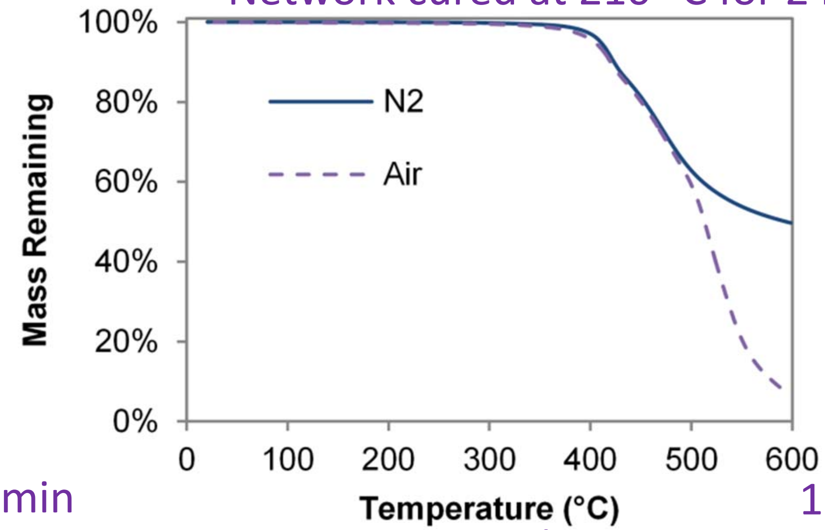
TGA Data for PFCBCy

Uncured monomer, N_2



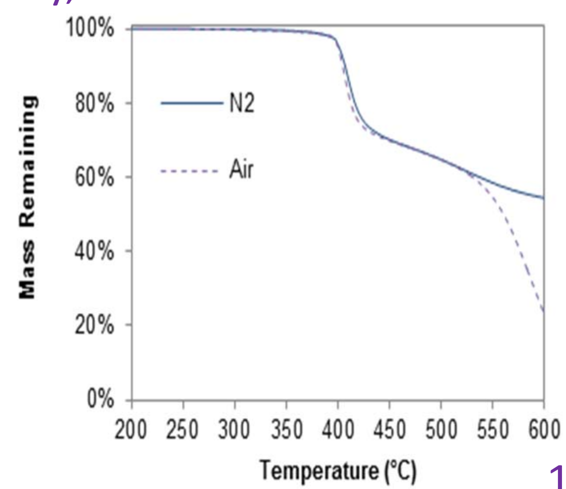
10 °C / min

Network cured at 210 °C for 24 hr



10 °C / min

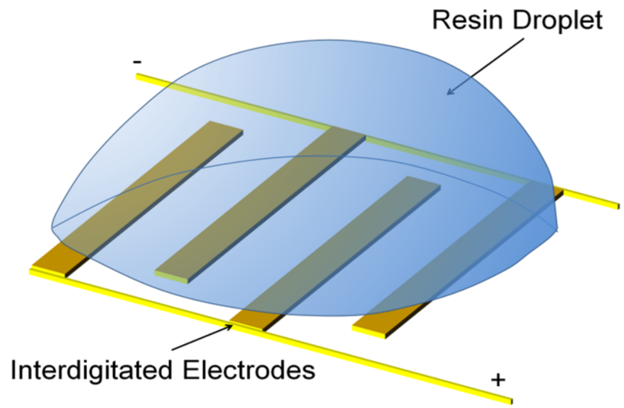
LECy, same conditions

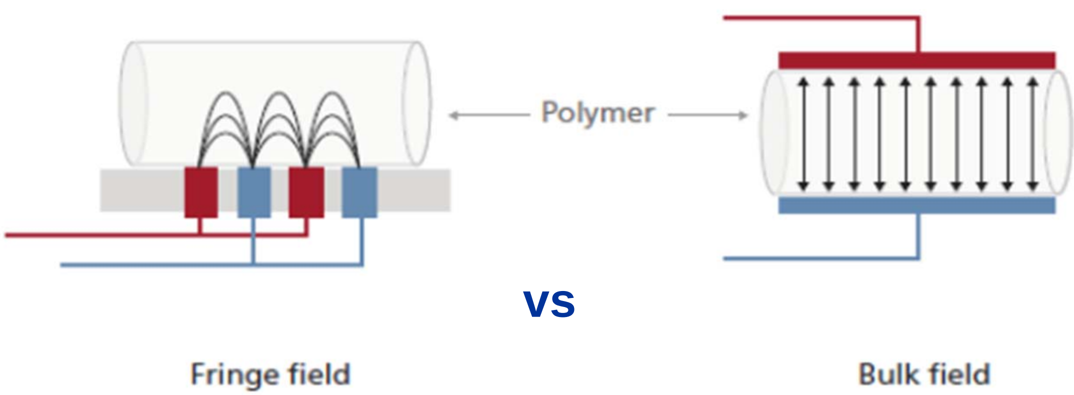


10 °C / min

- TGA of uncured monomers indicates significant monomer volatility.
- TGA of cured networks indicates modestly improved thermo-chemical stability
- The main factor influencing onset of weight loss is cyanurate decomposition, which appears to be mainly unaffected by PFCB incorporation

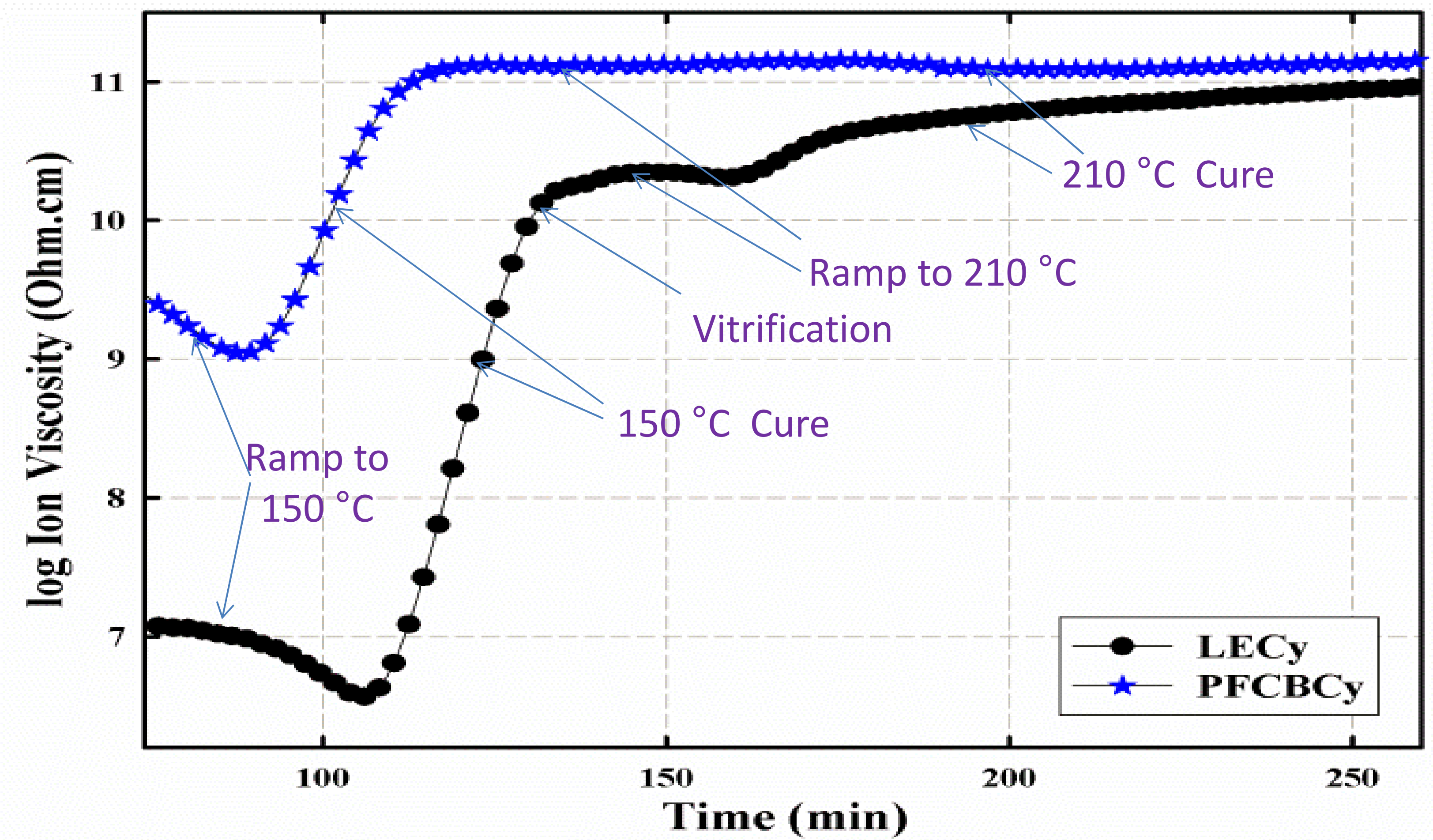
Ion Mobility Measurements





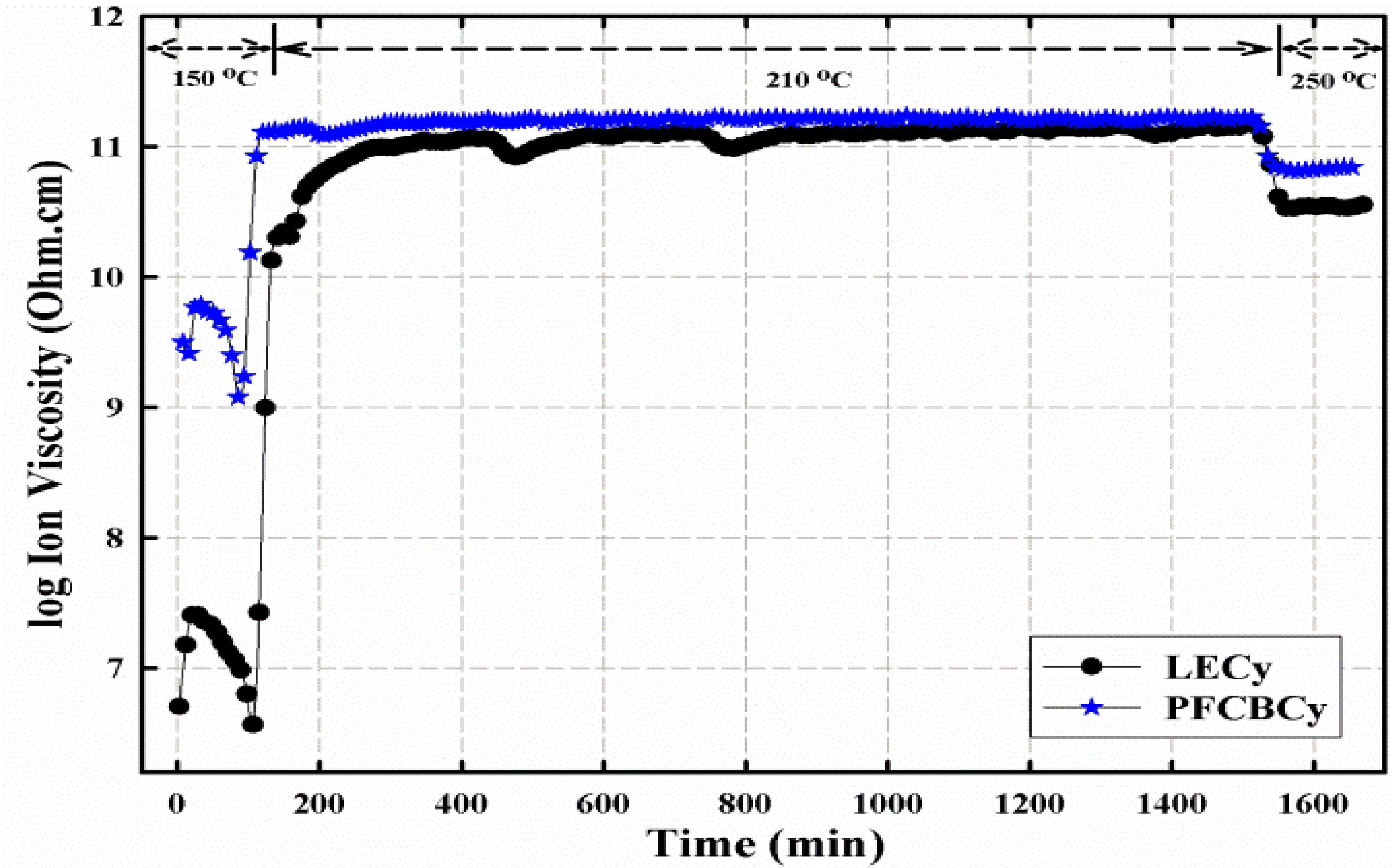
- Use of interdigitated electrodes allows for characterization of a single drop of resin
- Insensitive to physical dimensions, surface curvature, and creep

Ion Mobility Measurements (1)



- Lower ion mobility likely reflects lower water content and more rapid cure. Vitrification slows the cure of the LECy.

Ion Mobility Measurements (2)



- PFCBCy retains lower ion mobility throughout the cure process

Summary

- A combination of fluorination and lower cross-link density enables PFCBCy to achieve the lowest recorded weight-basis water uptake for a cyanate ester, 0.56% for 96 hr at 85 °C.
- On a concentration basis, the PFCBCy exhibits moisture uptake comparable to similar non-fluorinated polycyanurate networks with a relatively long contour length between cross-links.
- In general, processing conditions for PFCBCy are acceptably close to those for more widely-used monomers such as Primaset® BADCy, however, moisture sensitivity and volatilization of monomer are likely worse compared to BADCy.
- The glass transition temperature of PFCBCy networks at full cure is around 210 °C, which is slightly higher than other, low moisture polycyanurate networks.
- Ion mobility studies of the cure of polycyanurate networks reveal the generally more rapid cure kinetics of PFCBCy compared to systems such as Primaset® LECy, while also showing promise for studying molecular motion in these networks.