

# 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> 30 September 2015		<b>2. REPORT TYPE</b> Briefing Charts		<b>3. DATES COVERED (From - To)</b> 16 Sept 2015 – 30 Sept 2015	
<b>4. TITLE AND SUBTITLE</b> Designing Composite Resins in the 21st Century: Ending the “End Group” Fallacy				<b>5a. CONTRACT NUMBER</b>	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> Andrew J. Guenther				<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> AFRL-RQ-ED-VG-2015-369	
<b>12. DISTRIBUTION / AVAILABILITY STATEMENT</b> Approved for public release; distribution unlimited					
<b>13. SUPPLEMENTARY NOTES</b> For presentation at SAMPE High Desert Symposium; Lancaster, CA; September 30, 2015 PA Case Number: # 15589; Clearance Date: 9/24/2015					
<b>14. ABSTRACT</b> Briefing Charts/Viewgraphs					
<b>15. SUBJECT TERMS</b> N/A					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b>
<b>a. REPORT</b>	<b>b. ABSTRACT</b>	<b>c. THIS PAGE</b>			<b>19b. TELEPHONE NO</b> (include area code)
Unclassified	Unclassified	Unclassified	SAR	20	N/A



**Integrity ★ Service ★ Excellence**

# Designing Composite Resins in the 21<sup>st</sup> Century: Ending the “End Group” Fallacy

**30 Sept 2015**

**Andrew J. Guenther, Ph. D.**

*Air Force Research Laboratory,  
Rocket Propulsion Division  
Edwards AFB, CA 93524*

*Tel: 760 382 3366; [andrew.guenther@us.af.mil](mailto:andrew.guenther@us.af.mil)*



# Outline



- **Inspiration from Rising Sciences**
- **The “End Group” Fallacy**
- **New Approaches to Composite Resin Design**
- **Examples: Payoffs and Cautions**



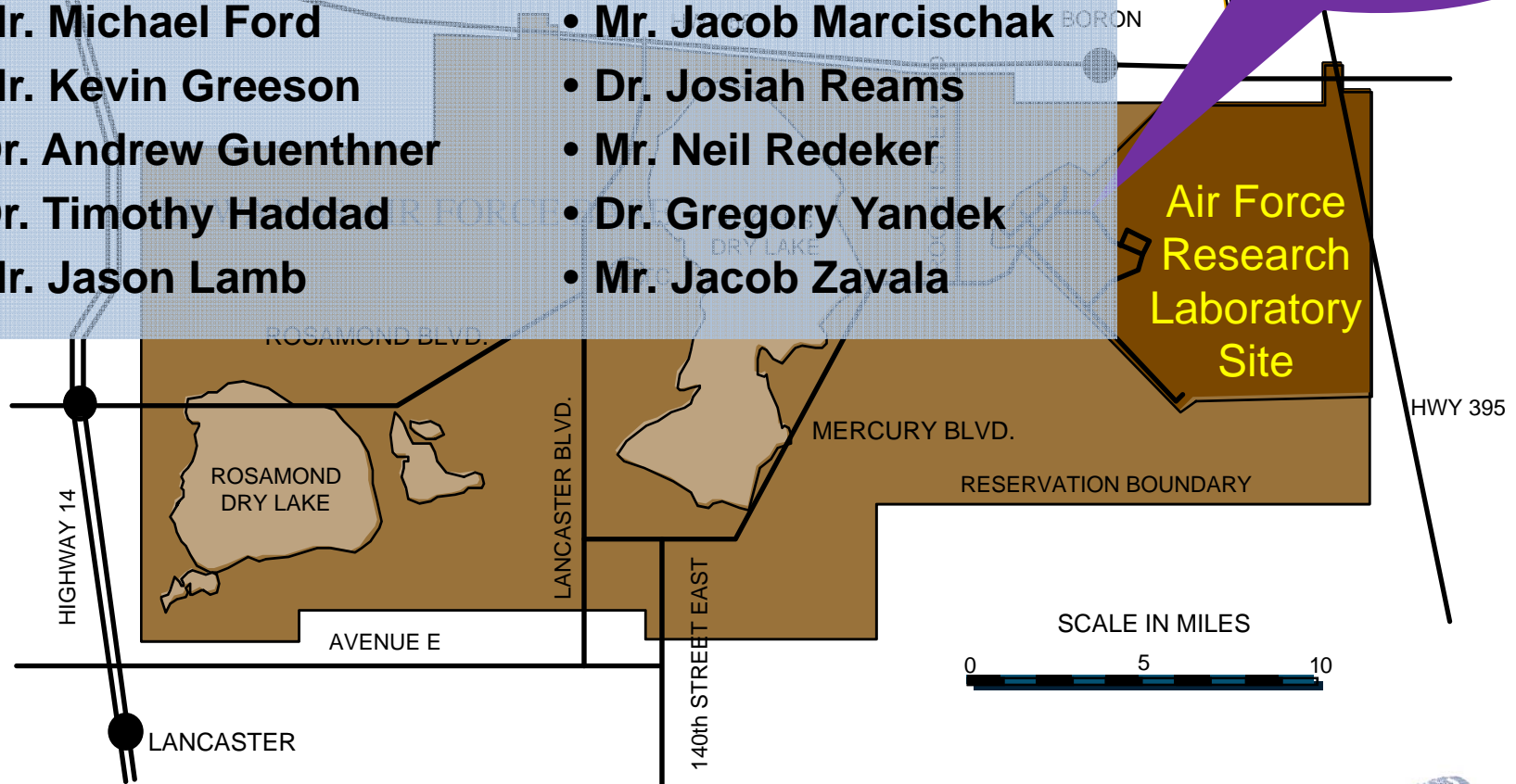
**Acknowledgements: Air Force Research Laboratory, Air Force Office of Scientific Research, AMG Group Members**



# Applied Materials Group



- Dr. Jeffrey Alston
- Dr. Raymond Campos
- Ms. Yvonne Diaz
- Mr. Michael Ford
- Mr. Kevin Greeson
- Dr. Andrew Guenther
- Dr. Timothy Haddad
- Mr. Jason Lamb
- Mr. Christopher Lee
- Dr. Joseph Mabry
- Dr. Joseph Mates
- Mr. Jacob Marcischak
- Dr. Josiah Reams
- Mr. Neil Redeker
- Dr. Gregory Yandek
- Mr. Jacob Zavala

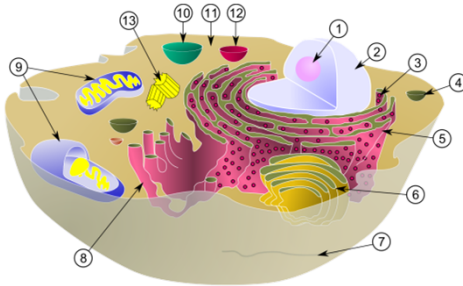




# “Rising” Sciences in the 21<sup>st</sup> Century



## • Biology



Author: MesserWoland and  
Szczepan1990

## • Digital Matter



Makerbot Industries



## • Medicine



US Air Force

## • Autonomy



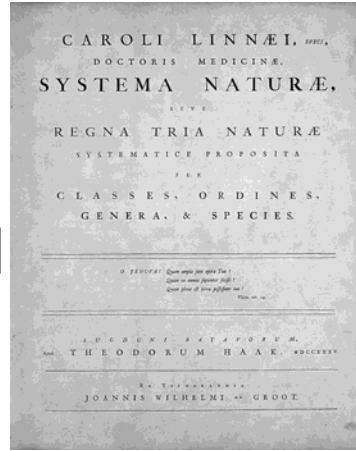
Author: Steve Jurvetson



# An Example from Biology

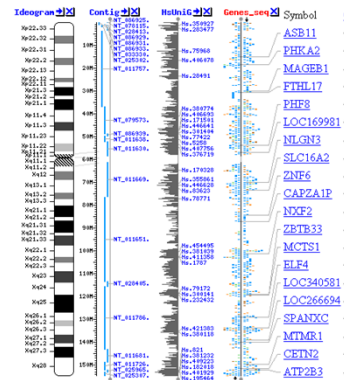


- 100 Years Ago
  - System: Linguistic Taxonomy / Inferred Heuristics



- Today
  - System: Hierarchical Informatics

- Tools: Microscope, Cell Culture, Notebooks



- Tools: Sequencers, Simulators, Editors, “Big Data” Analytics

Which one does composite resin chemistry resemble?





# The “End Group Fallacy”



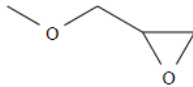
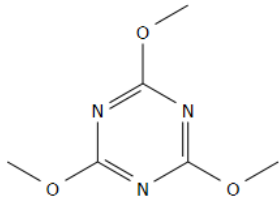
- The “End Group Fallacy” is the bias that results from the current dominant classification and inferred heuristics system for composite resins.
- Resins are described according to a reactive group class, “epoxy”, “BMI”, “polyimide”, with the inference that key properties are shared among members of each group. From the standpoint of how to classify resin systems, such a system is sensible.
- In reality, a very large number of properties, including Tg and TOS, do not fall into separate classes determined by end group chemistry. Rather, many of these properties are sensitive to the topology and architecture of the networks.



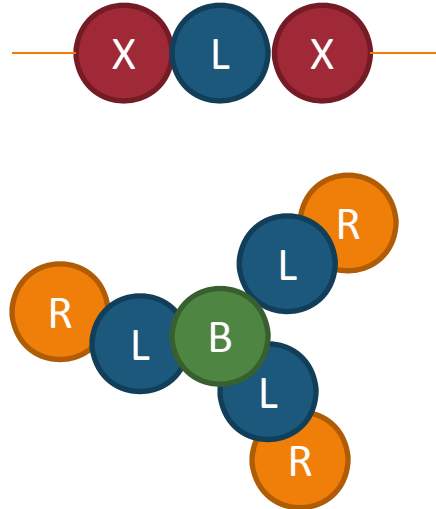
# Structure – Architecture - Topology



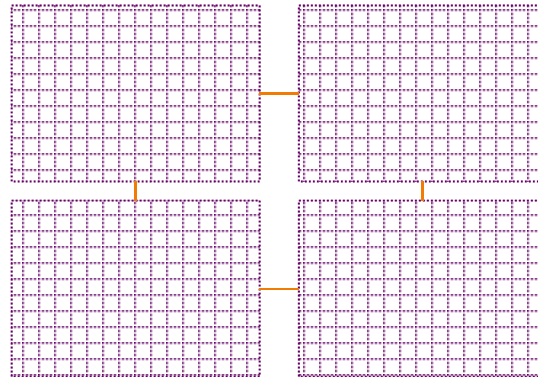
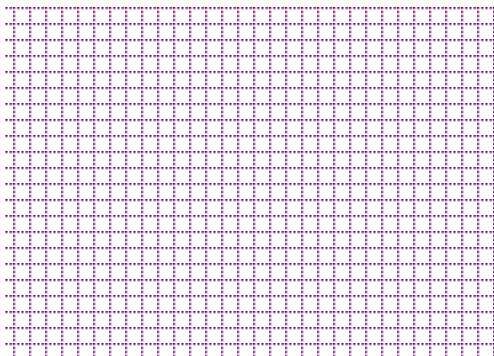
## Structures



## Architectures



## Topologies

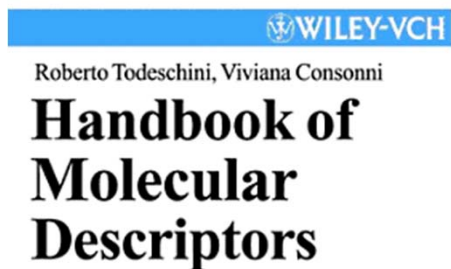


- There are three levels of hierarchy in networks:

- *Structure* is the number, type, and geometric relationship of atoms in repeated groups
- *Architecture* describes the number, type, and geometric interconnection of repeated structures
- *Topology* describes the number, type, and geometric relationship of repeated architectural units



# Digitizing Chemical Structures



Methods  
and Principles  
in Medicinal  
Chemistry  
Volume 11  
Edited by  
R. Mannhold,  
H. Kubinyi,  
H. Timmerman

- **Methods for converting small molecule chemical structures to strings of information are well-established and in wide use**
- **Extensions for polymers have been published but are not as extensive**
- **Further extensions for networks are straightforward, but not much used**



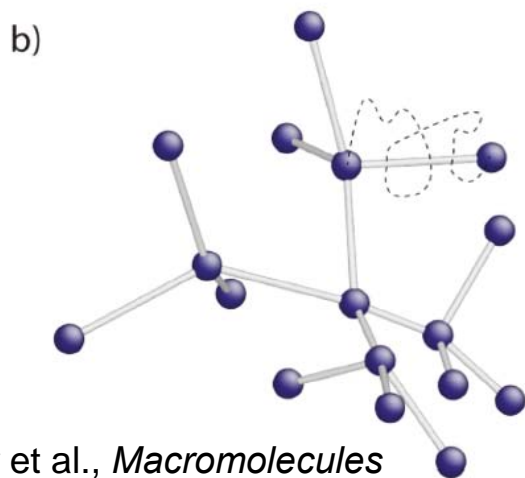
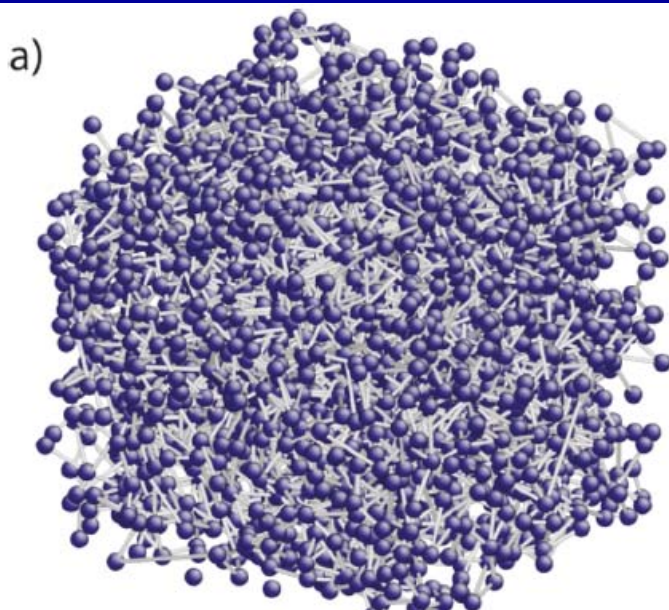
# How Complex Are Networks?



- Even the most complex cure reactions might have ~100 repeated chemical structures.
- Architectural features can be described in terms of just seven groups
- Topology can be described in terms of a very few parameters (typically 2 or 3)
- A “cheminome” for a composite resin is likely not more than 10,000 units x 10,000 unit scale per each  $\ll 10^6$  bits
- In reality, most properties are controlled by  $\ll 10$  units. Modern informatic methods can determine how to construct the units with the most valuable information content.
- Therefore, no reason that chemometrics / informatics cannot be used with composite resins



# Network Automata



- In correspondence with cellular automata, a system of differential equations describes the evolution of structures, architectures, and topologies in polymer networks
- Identical to reaction kinetics at the structural level
- Can include mechanical effects
- Demonstrated for lightly cross-linked, low  $T_g$  networks using several hundred thousand units with sparse topology

Figure 3. (a) Representation of typical bead–spring cell employed in the mesoscopic model approach. Cross-link junctions are represented schematically as beads connected through springs (straight bars) which serve as the polymer chains. For simplicity of the image, the bead radius has been chosen arbitrarily. (b) Breakout consisting of one central bead connected to nearest and next-nearest neighbors. The dashed line represents schematically the real chain that has been replaced by a single, effective entropic spring with  $k = (3k_B T) / \langle R^2 \rangle$ .

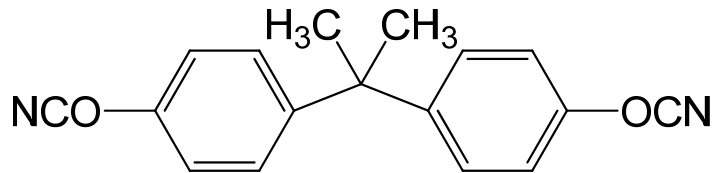
Mayor et al., *Macromolecules*  
2011, 44, 8106 (LLNL).



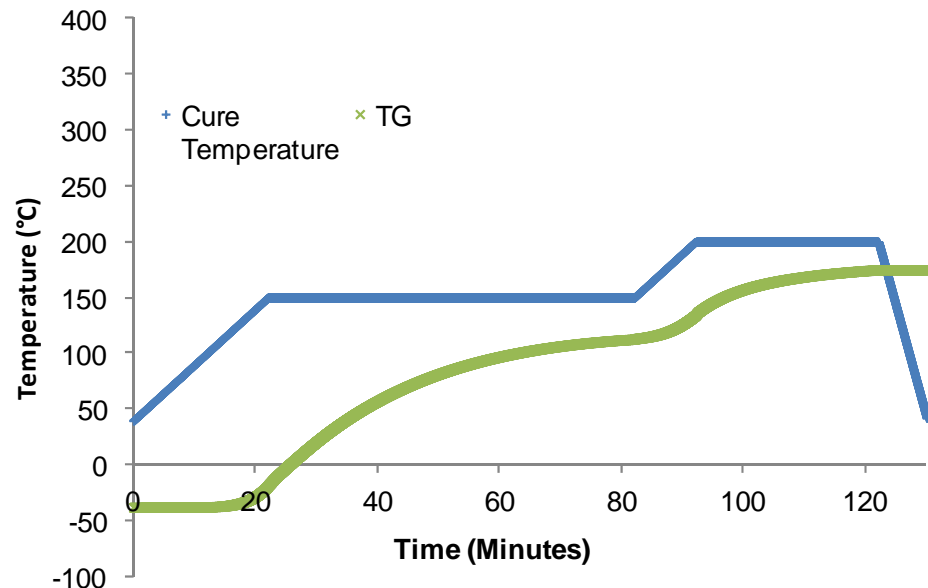
# “State of the Art” Network Automata Example



- Cure kinetics + diBenedetto equation = Tg development kinetics -- 8 parameters predict Tg of network through any process – 6 DSC experiments provide all needed parameters

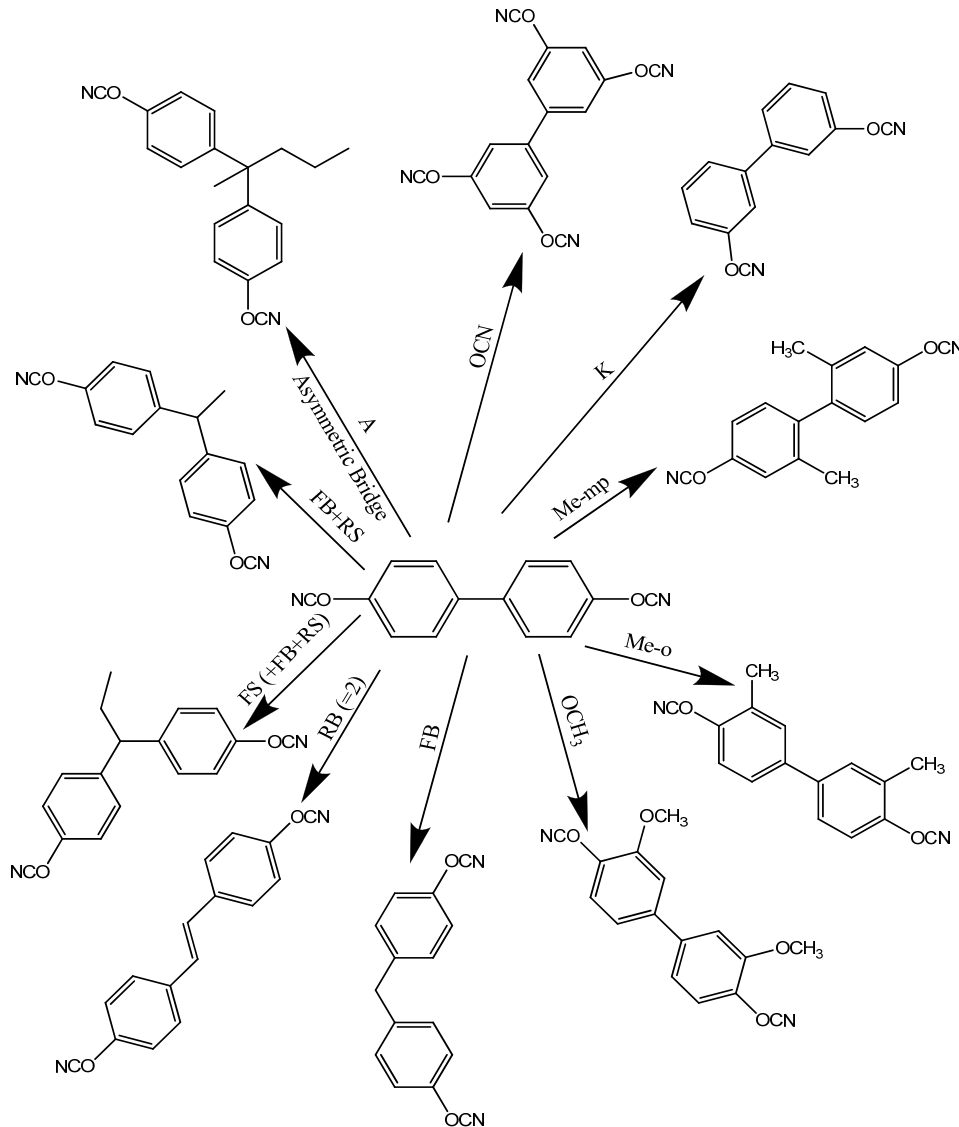


Catalyst: 30 : 1 nonylphenol :  
Cu(acac)<sub>2</sub> @ 2 phr (160 ppm  
Cu)





# Example: Bio-Based Monomers

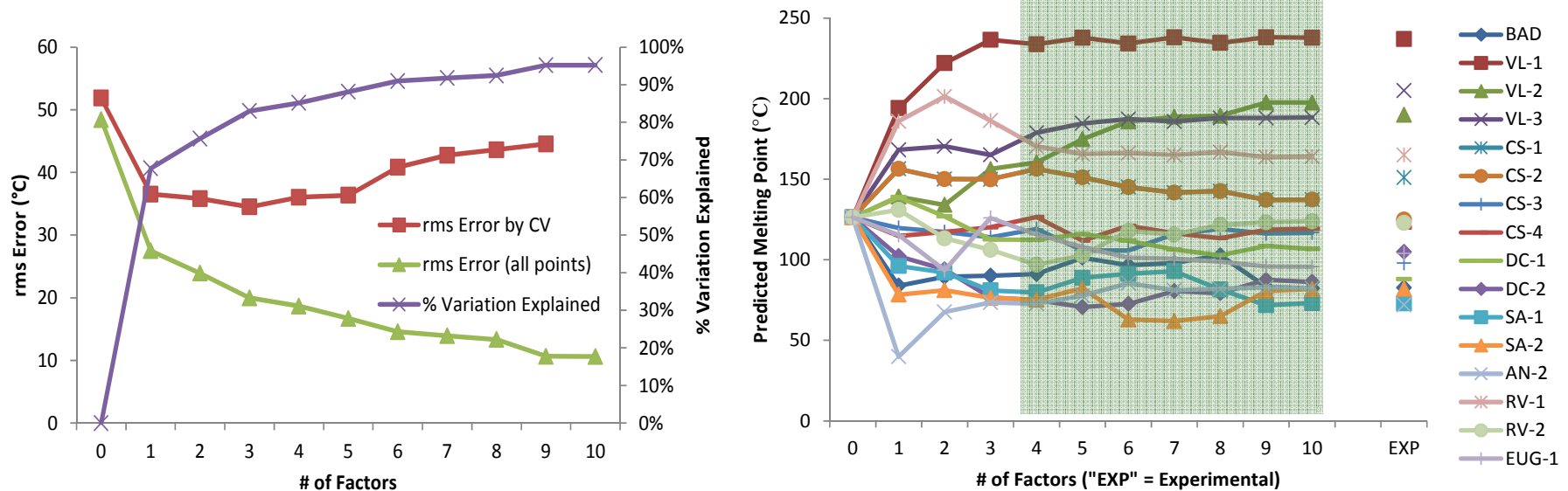


Monomer	OCN	K	Me-mp	Me-o	OCH3	FB	RB	FS	RS	A
BAD	0	0	0	0	0	1	0	0	2	0
LE	0	0	0	0	0	1	0	0	1	1
AN-1	0	0	0	0	0	3	0	1	2	1
AN-2	0	0	0	0	0	0.5	0.5	1.5	3.5	1
CS-1	0	1	1	0	1	1	0	0	0	0
CS-2	0	1	1	0	1	1	0	0	0	0
CS-3	0	1	1	0	1	1	0	0	1	1
CS-4	0	1	1	0	1	1	0	1	1	1
DC-1	0	0	1	0	0	1	0	0	0	0
DC-2	0	0	1	0	0	1	0	0	1	1
DC-3	0	0	1	0	0	1	0	1	1	1
EUG-1	0	0	0	0	1	4	0	0	0	0
RV-1	1	0.5	0	0	0	0	2	0	0	0
RV-2	1	0.5	0	0	0	2	0	0	0	0
SA-1	0	0	0	1	0	1	0	0	1	1
SA-2	0	0	0	1	0	1	0	0	2	0
VL-1	0	0	0	0	1	0	2	0	0	0
VL-2	0	0	0	0	1	2	0	0	0	0
VL-3	0	1	1	0	1	0	0	0	0	0
AN-U	0	0	0	0	0	1	2	1	2	1
EUG-U	0	0	0	0	1	2	0	0	0	0

The structure of bio-based monomers and networks with an X-L-X architecture (X = phenyl cyanate ester / phenyl cyanurate) is quantified using 10 parameters



# Predictive Models: Partial Least Squares Approach

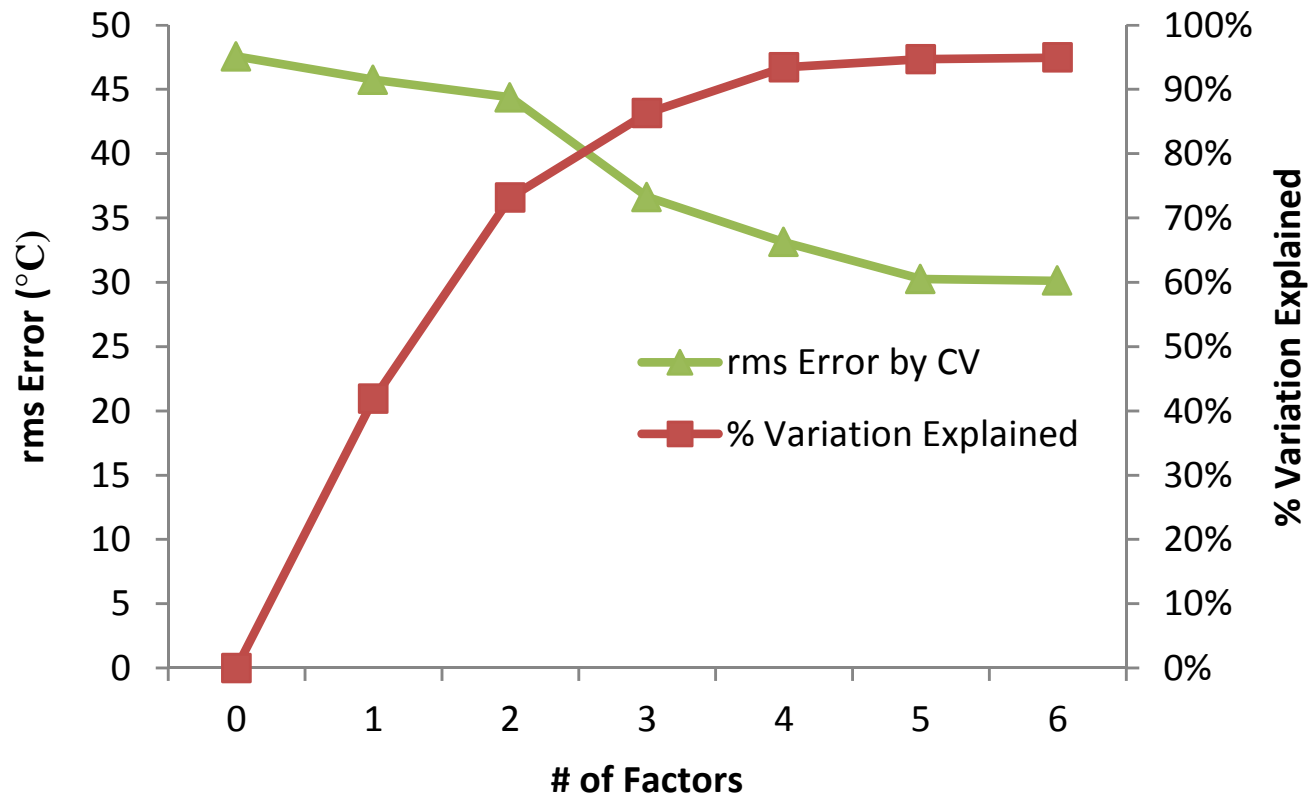


Partial least squares is a typical informatics technique; it looks for correlated parameters that simultaneously describe the most variation in both input and output data sets

The method is iterative; to generate subsequent regression components, the method is repeated for the residuals from the previous set of predicted and experimental values



# Predictive Power for Tg at Full Cure

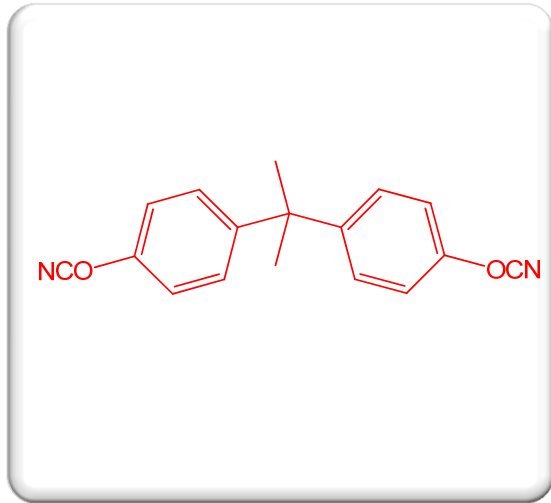


**Error characteristics of partial least squares model for glass transition temperature at full cure.**

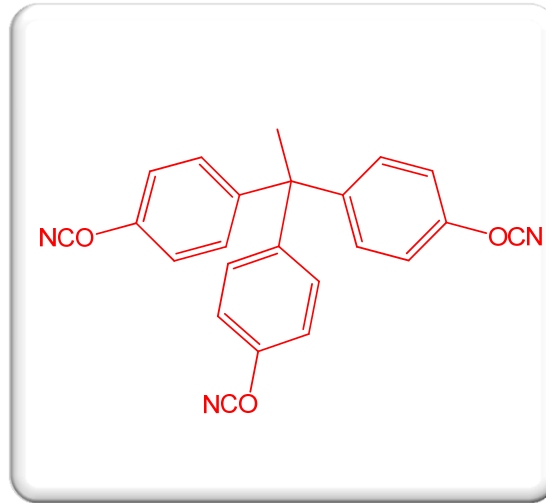
**These results indicate there are only about 4 important structural parameters  
Effects of topology are not considered**



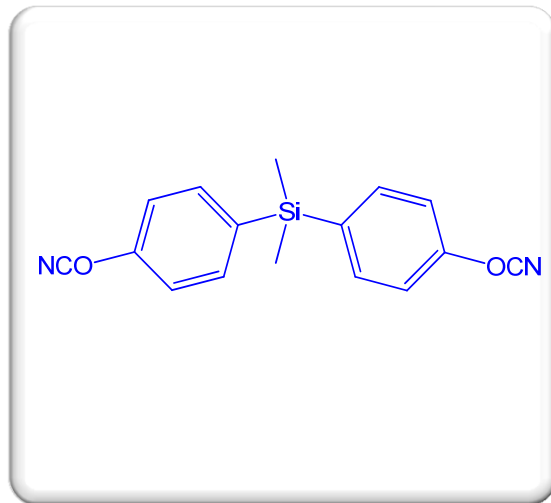
# Example: Bias in Predictive Parameter Sets



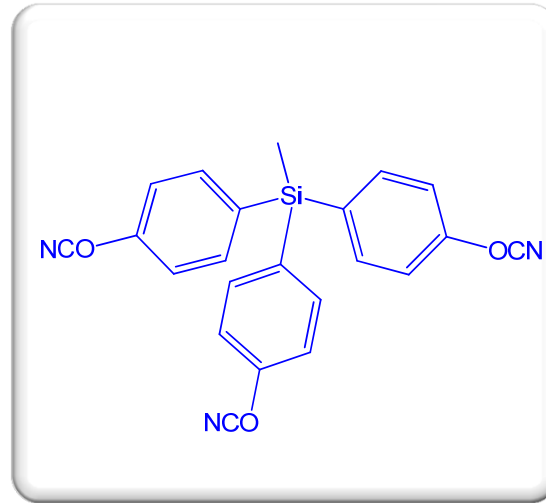
BADCy



ESR255



SiMCy



STT3

All samples were melted, blended, and de-gassed for 30 min. prior to cure in silicone molds under N<sub>2</sub>, cure schedule for 1 hr at 150 °C followed by 24 hrs at 210 °C, with ramp rates at 5 °C / min.

**In this case, we are interested in comparing models for two different architectures, one very common, the other somewhat rare**



# Comparison of Predicted and Experimental Melting Properties



$\Delta S_m$ (kJ/mol K, monomer)	BADCy	SiMCy	ESR255	STT3
$\Delta S_m$ (kJ/mol K, Yalkowsky)	84	84	98	98
$\Delta S_m$ (kJ/mol K, experiment)	$80.0 \pm 1.4$	$82.1 \pm 0.6$	$75.0 \pm 1.9$	$74.8 \pm 0.8$
$\Delta S_m^0$ (kJ/mol K, Chickos)	70	78	88	95
$\Delta S_m^0$ (kJ/mol K, experiment)	$69 \pm 3$	$81 \pm 1$	$50 \pm 14$	$55 \pm 3$
$T_m$ (model $\Delta S_m$ & exp. $\Delta H_m$ )				
Yalkowsky (°C)	66	54	24	24
Chickos (°C)	73	50	42	29
Experiment (°C)	$82.1 \pm 0.2$	$60.4 \pm 0.1$	$115.9 \pm 0.2$	$117.5 \pm 0.1$

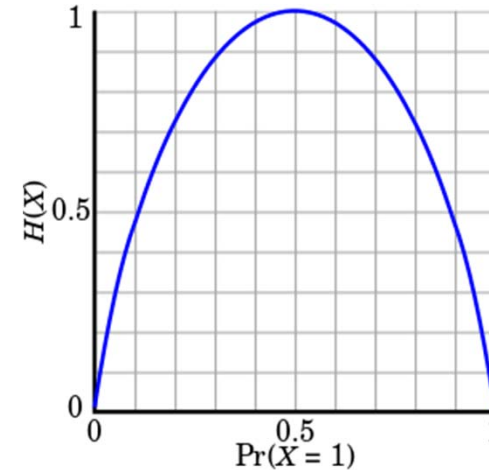
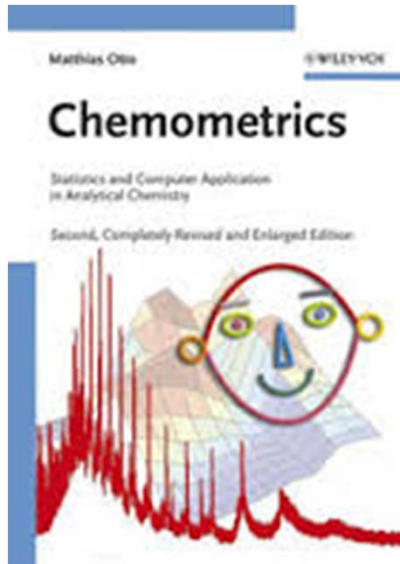
• Yalkowsky model over-predicts entropy of melting for tricyanates, in part because the rules for counting anisotropy do not consider star-like arrangements, and a triphenyl substituted  $sp^3$  is still counted as flexible. These factors explain about 70% of the error.

• Chickos model has a similar pattern of predictive success, perhaps because “bis-like” prolate organic compounds are more studied than “tris-like” “pitchfork” structures

Conversion from  $\Delta S_m^0$  to  $\Delta S_m$  based on  $\Delta_{cp,m} = \text{const.} = \Delta S_m$ ;  $\Delta S_m = \Delta S_m^0 / [1 - \ln(T_m / 298)]$



# Predictive Parameter Sets, M&S, Databases, and Heuristics



Author: Broma and Alessio Damato

- A new bit of data for a database is most valuable when it describes the least known aspect of the data
- Good M&S can derive rules (such as elastic modulus as a function of topology) for reliably estimating the lesser known parameters from accessible experiments
- Databases and heuristics can be used to train and validate predictive systems, but are poor substitutes for QSARs

Distribution A: Approved for public release; distribution is unlimited.





# Summary



- **Significant advances in materials science for composites can be achieved by moving from a “heuristic classification” approach to an “informatics” approach to describe chemistry**
- **Although end-group chemistries play an important role as a predictive factor in composite resin processing and performance, they exist within a framework of structure-architecture-topology; often, other parts of the framework are more important predictors of performance**
- **Even complex polymer network structures can be described in terms of a comparatively small number of predictive parameter sets; fundamental scientific insight and access to a variety of chemical structures is required in order to understand what the most valuable predictive parameters are**

