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Predictive methods for dense polymer networks: Combating bias with bio-based structures

16 March 2016

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Outline

- Background: Polymer Networks / Cyanate Esters
- Architectural Bias
- Comparison of Petroleum-Based and Bio-Based Chemical Architectures
- Continuing Research on Structure-Property Relationships using Informatics Tools

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- Dr. Josiah Reams
- Mr. Neil Redeker
- Dr. Gregory Yandek
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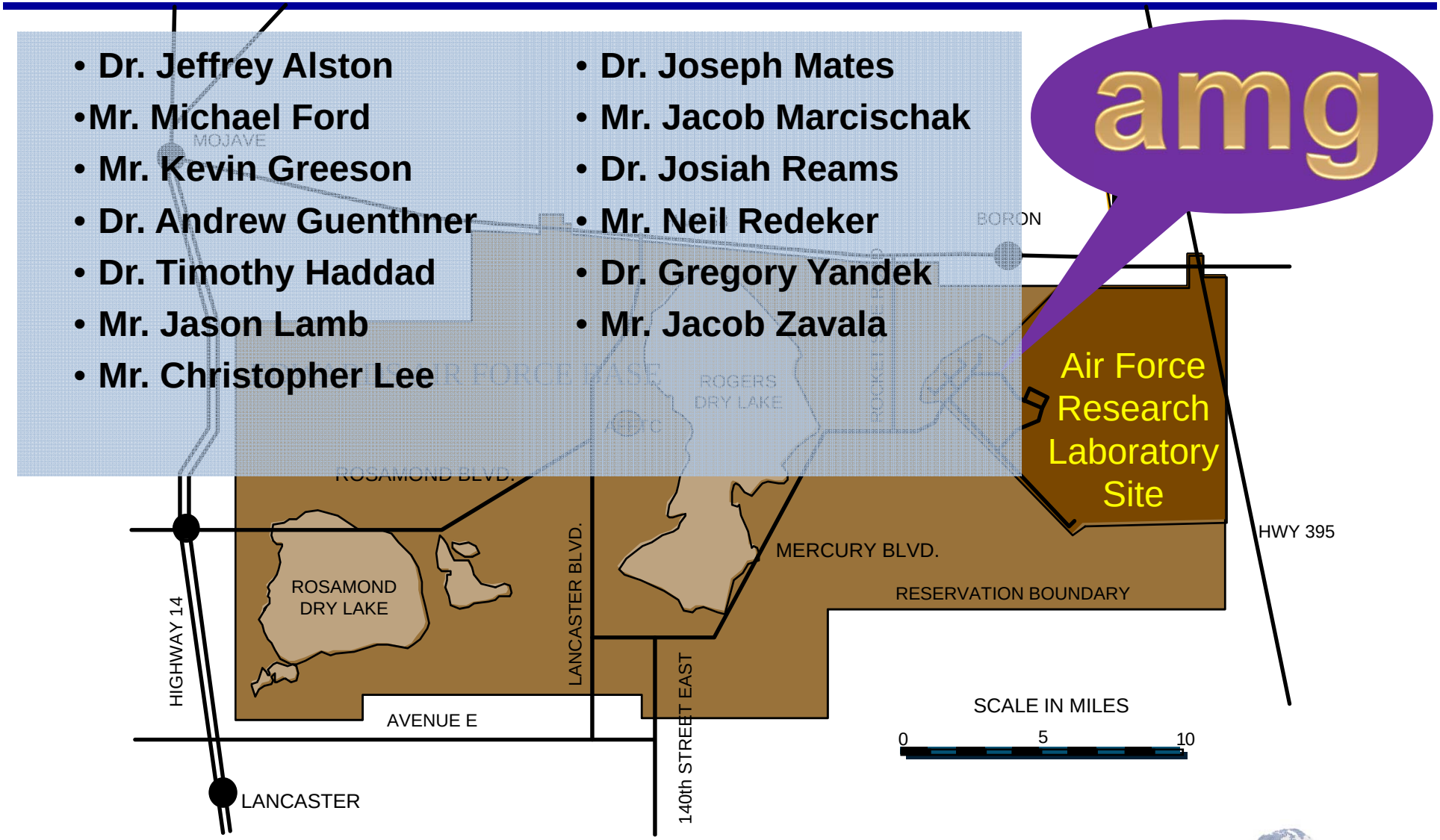
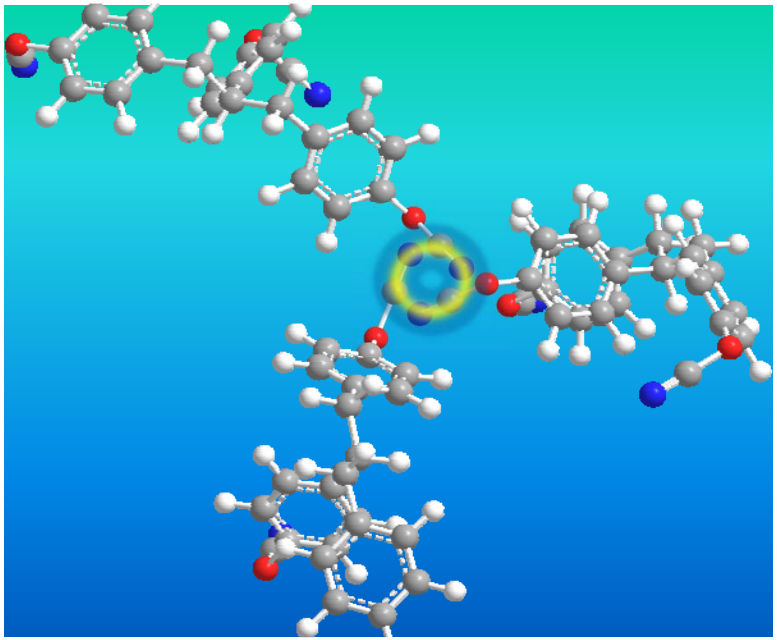


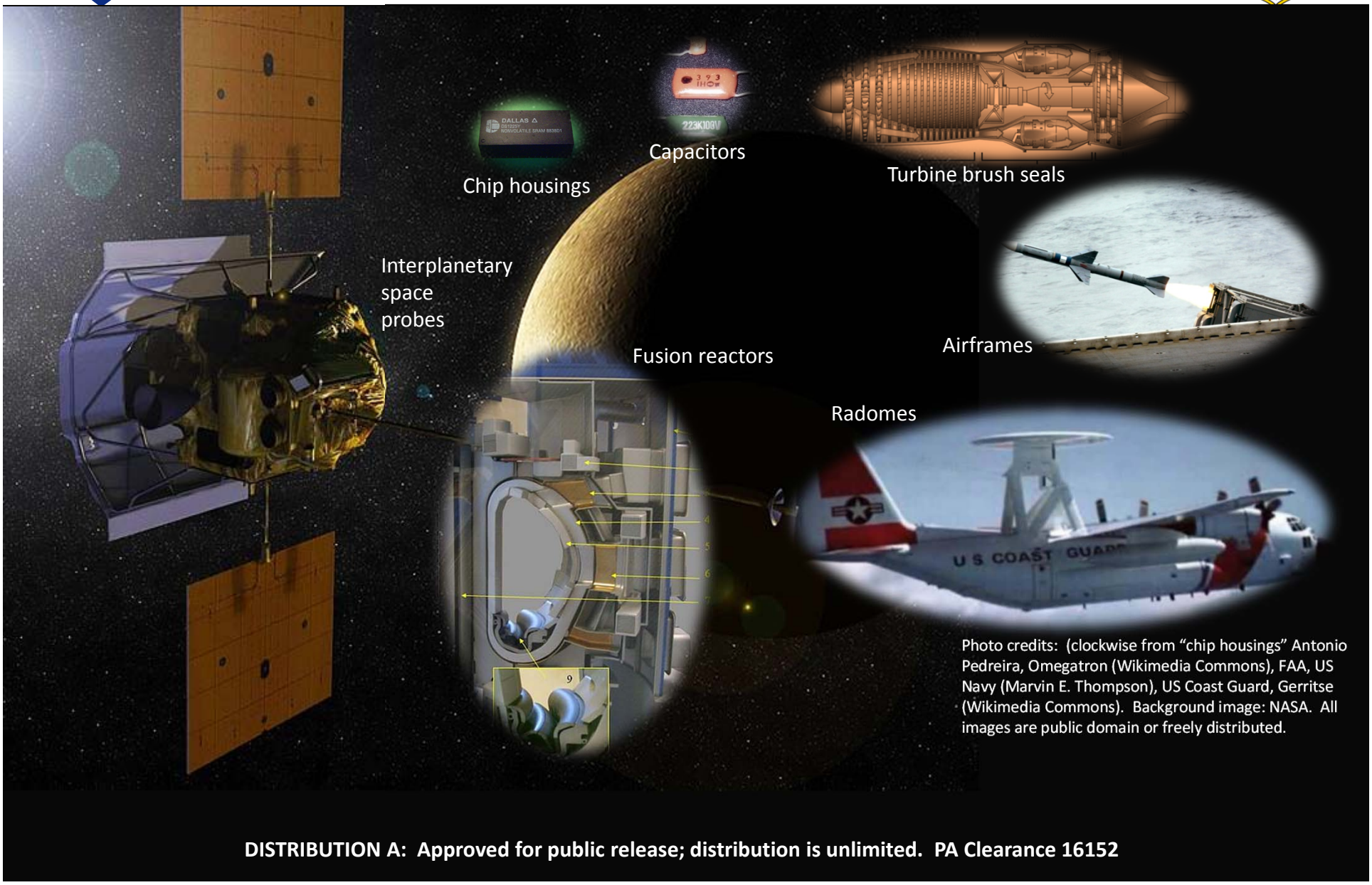
Model High-Temperature Thermosetting Polymer Networks: Cyanate Esters



Principal reaction:
3 OCN ->
Selectivity: 80% - > 98%
ΔH_f = - 110 kJ / eq.
Conversion kinetics; Auto-catalytic (may be catalyzed)
Typical conversion rate: ~50%/hr (max) at 250 °C (uncatalyzed)
Extend of conversion: Limited to T_G = T_{cure} + 30-60 °C

- A single, known reaction predominates.
- Methods for assessing the extent of side reactions, and for minimizing side reactions, are known.
- The structure of even fully cured networks is easily analyzed and described quantitatively.
- Samples are easy to prepare in the laboratory; cure conditions are readily manipulated over a very wide range of rates.

Applications of Polycyanurate Networks



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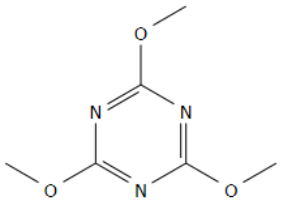
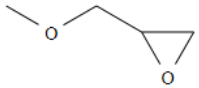
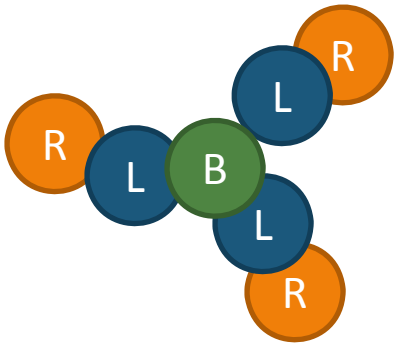
Describing Polymer Networks: Structure – Architecture – Topology

Structures

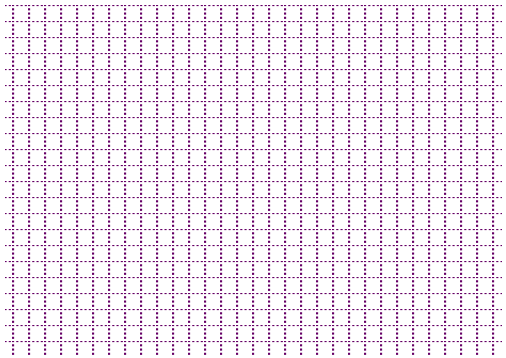


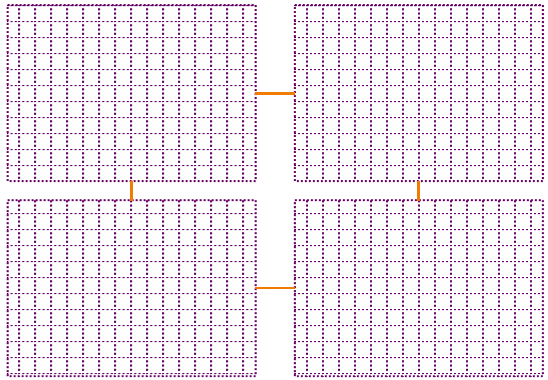


Architectures



Topologies

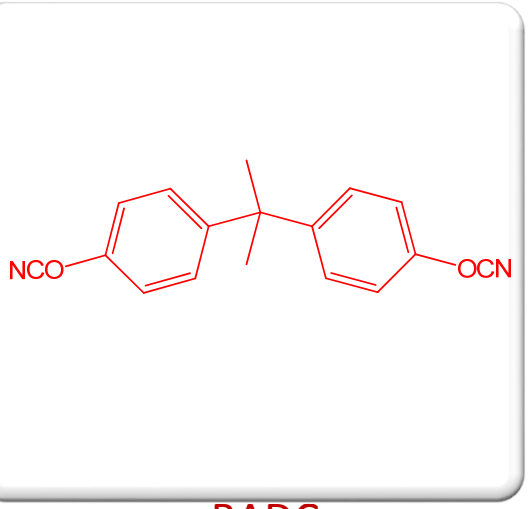




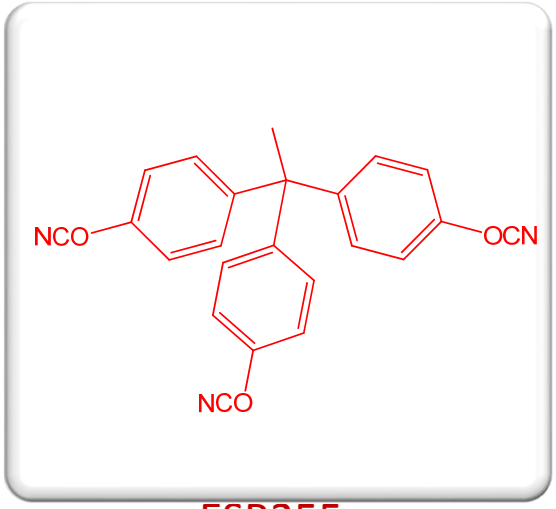
- **Networks tend to be described by three levels of hierarchy**
  - ***Chemical structure*** **usually refers to the number, type, and geometric relationship of atoms in repeated groups**
  - ***Chemical architecture*** **describes the number, type, and geometric interconnection of repeated structures**
  - ***Network topology*** **in this context describes the number, type, and geometric relationship of repeated architectural units**

Most heuristic "structure-property" methods concentrate on chemical structure only

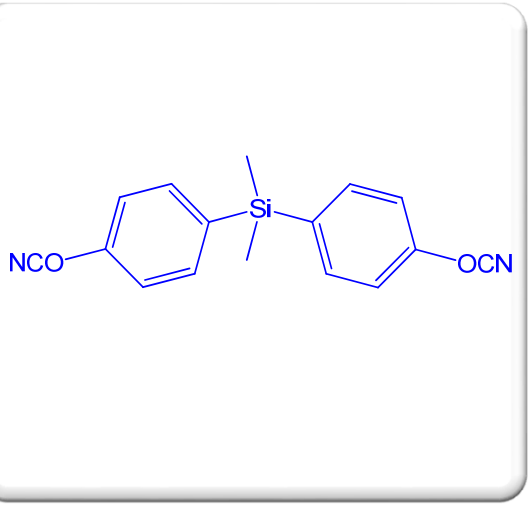
Example: Bias in Predictive Parameter Sets



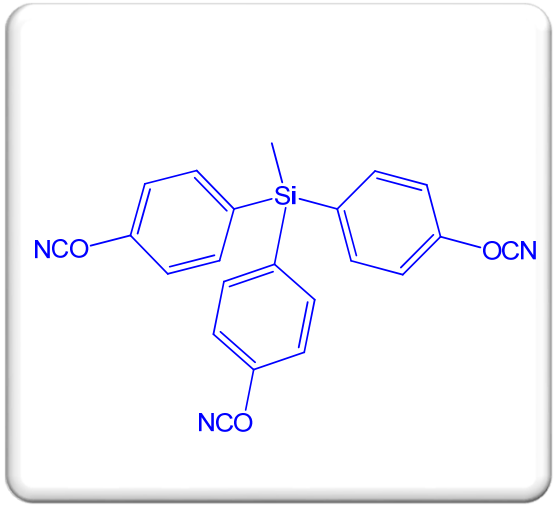
BADCy



ESR255



SiMCy



STT3

All samples were melted, blended, and de-gassed for 30 min. prior to cure in silicone molds under N_2, 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

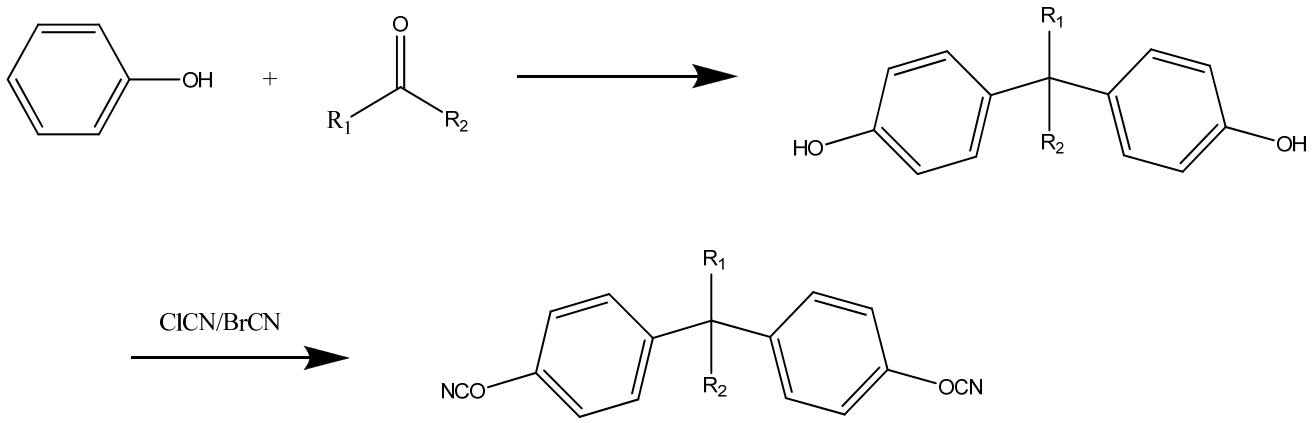
Comparison of Predicted and Experimental Melting Properties

ΔS_m (kJ/mol K, monomer)	BADCy	SiMCy	ESR255	STT3
ΔS_m (kJ/mol K, Yalkowsky)	84	84	98	98
ΔS_m (kJ/mol K, experiment)	80.0 ± 1.4	82.1 ± 0.6	75.0 ± 1.9	74.8 ± 0.8
ΔS_m^0 (kJ/mol K, Chickos)	70	78	88	95
ΔS_m^0 (kJ/mol K, experiment)	69 ± 3	81 ± 1	50 ± 14	55 ± 3
T_m (model ΔS_m & exp. ΔH_m)				
Yalkowsky (°C)	66	54	24	24
Chickos (°C)	73	50	42	29
Experiment (°C)	82.1 ± 0.2	60.4 ± 0.1	115.9 ± 0.2	117.5 ± 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 *sp³* 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 ΔS_m^0 to ΔS_m based on $\Delta_{cp,m}$ = const. = ΔS_m; $\Delta S_m = \Delta S_m^0 / [1 - \ln (T_m / 298)]$

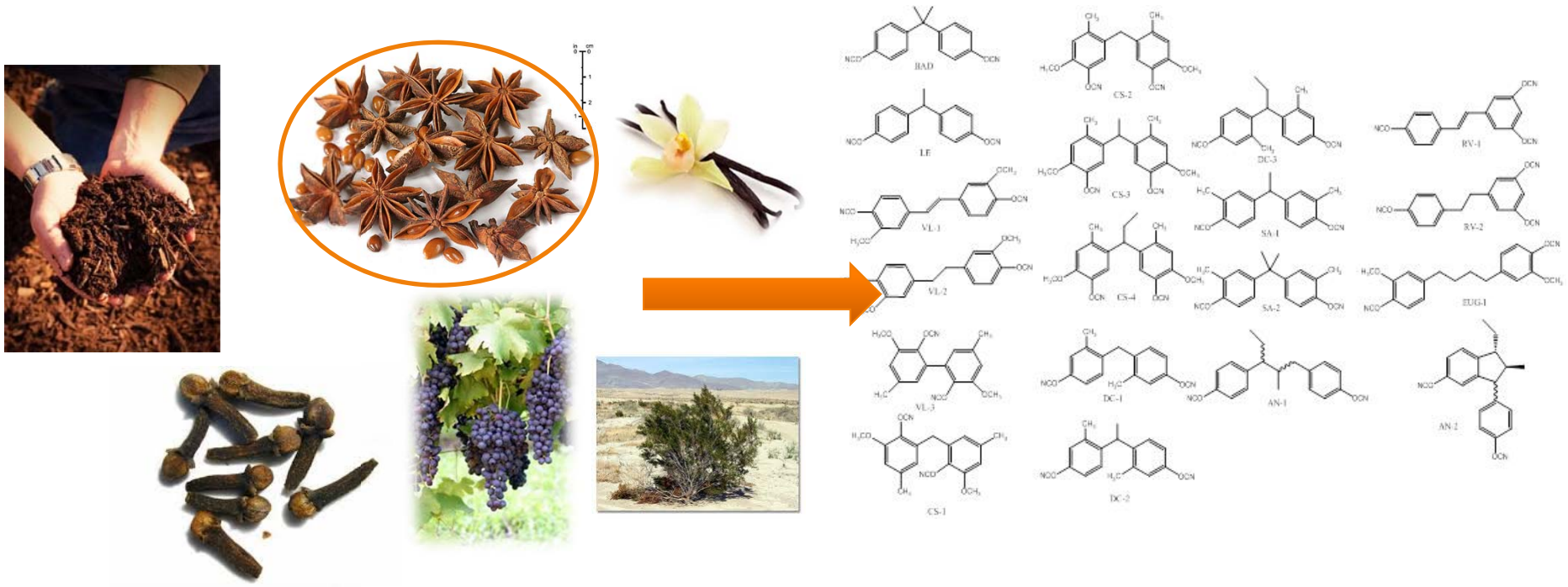
Factors that Introduce Architectural Bias in Structure-Property Relationships



- **The vast majority of monomers containing phenol groups are made by catalytic coupling of phenol, either to produce bisphenol or novolac (phenol-formaldehyde) structures, as a result of an inexpensive supply of phenol from petroleum refining.**

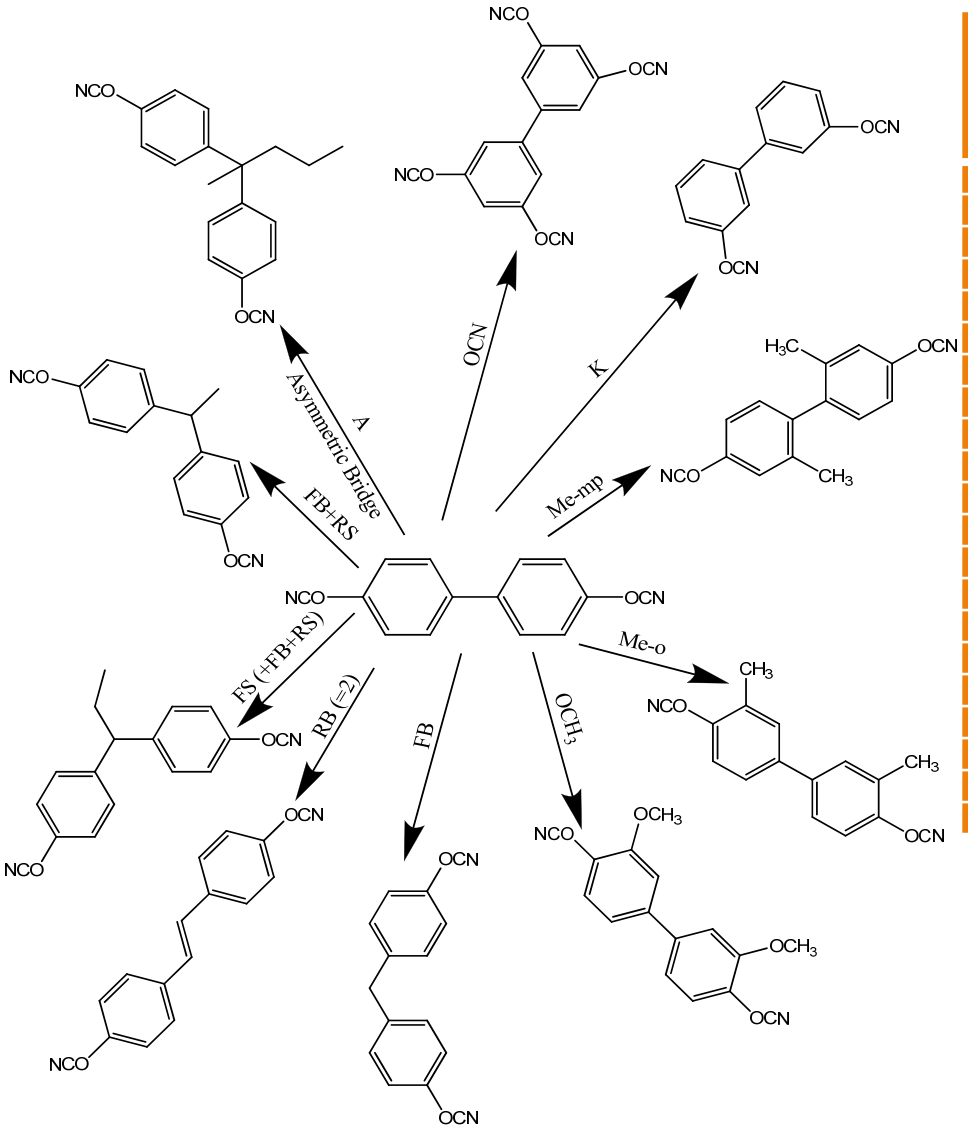
Consequently, certain architectures are over-represented in a "random" sample of network-forming phenolic monomers.

Bio-Based Phenols: Wide Range of Sources and Methods



- **Bio-based cyanate esters have been made from anethole, resveratrol, eugenol, cresol, lignin, vanillin, and even creosote oils. A much wider array of structures can be accessed from these sources than is available from refining petroleum**

Quantification of Cyanate Ester Structural Factors



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

Property Data for Cyanate Ester Monomers and Networks

Monomer/network	T_m (°C)[a]	$T_{G\text{-}fc}$ (°C)[b]	Char Yield (N_2, %)	Char Yield (Air, %)
BAD	83	323	47	25
LE	Liquid[c]	295	54	24
AN-1	Liquid[c]	223	31	9
AN-2	72	313	48	6
CS-1	151	236	33	8
CS-2	125	240	35	11
CS-3	98	206	28	11
CS-4	120	238	27	11
DC-1	88	259	53	30
DC-2	105	283	43	4
DC-3	Liquid[c]	273	43	3
EUG-1	104	167	31	1
RV-1	156	>340	74	71
RV-2	123	334	70	66
SA-1	73	236	48	11
SA-2	82	237	43	8
VL-1	237	n/a	n/a	n/a
VL-2	190	n/a	n/a	n/a
VL-3	205	n/a	n/a	n/a

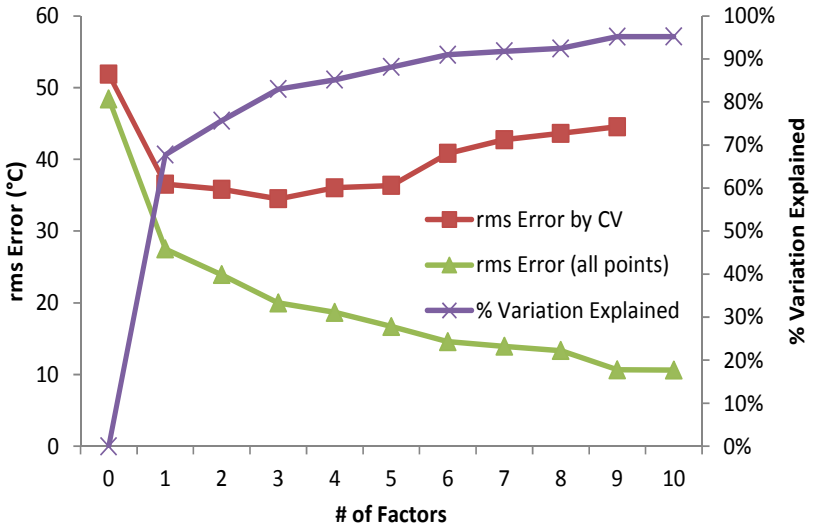
Although this data set is not large by informatics standards, it nonetheless represents a significant amount of synthetic effort.

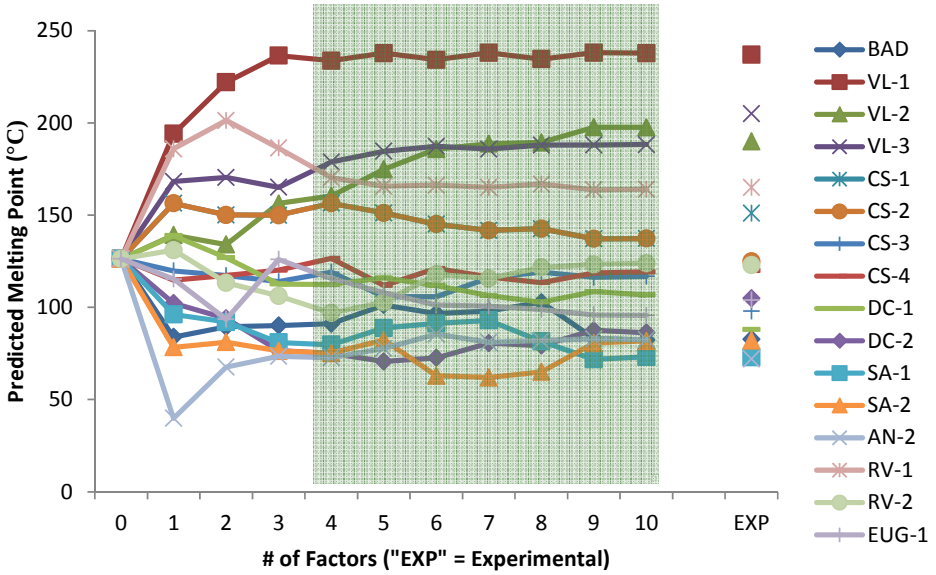
Because the data is limited, minimizing bias by investigating a wide variety of structures is important.

Four properties that have been measured and published using a well-defined, robust, and identical technique for all examples were chosen to examine predictive models.

AFRL

Predictive Models: Partial Least Squares Approach

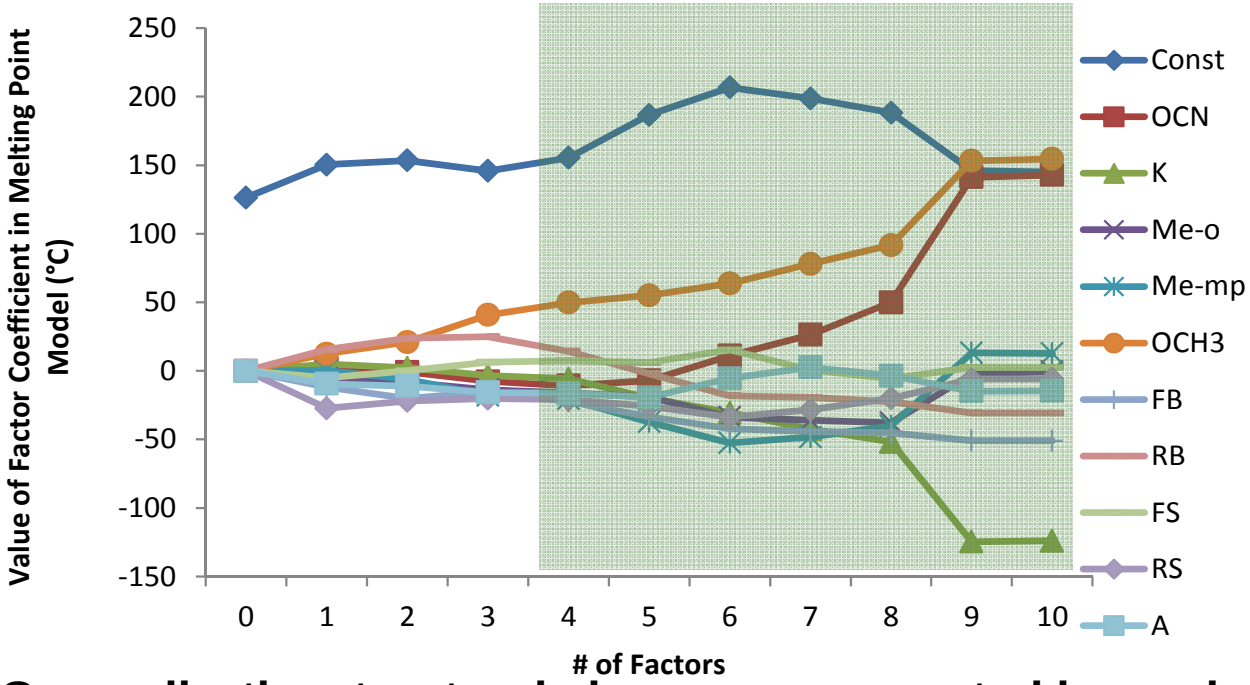




Informatics techniques like partial least squares provide methods to avoid issues associated with over-prediction when many structural variables are present

In this instance, cross-validation (leave-one-out) is utilized to establish the number of factors needed for prediction of melting points of X-L-X type cyanate ester monomers

Effect of Over-Prediction on Model Regression Coefficients



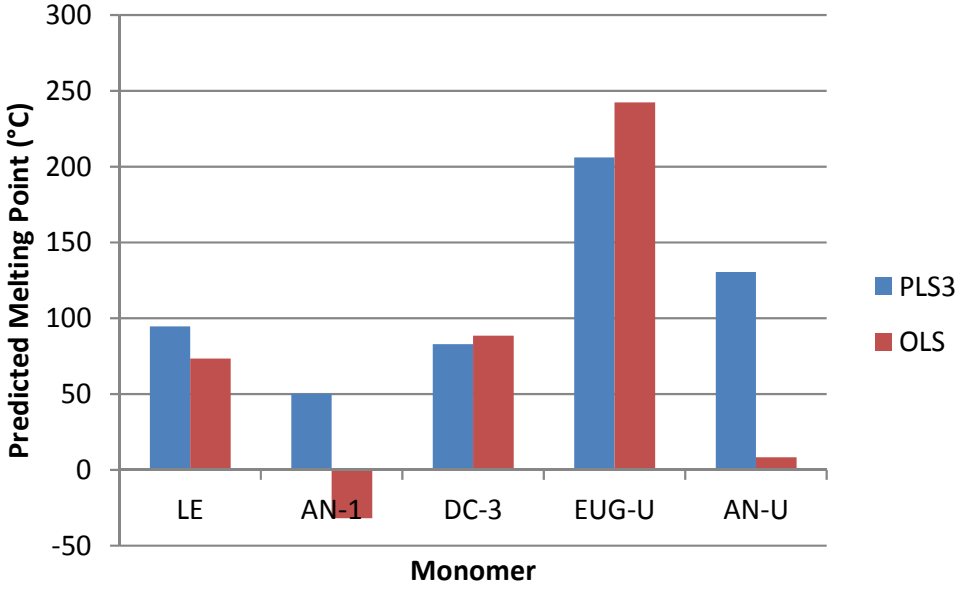
Factor	PLS	OLS
Constant	145.88	144.97
OCN	-7.64	142.86
K	-3.44	-123.97
Me-o	-13.73	-0.42
Me-mp	-18.07	12.73
OCH3	40.74	154.55
FB	-15.17	-50.97
RB	24.92	-30.87
FS	6.21	2.37
RS	-20.27	-5.86
A	-15.69	-14.60

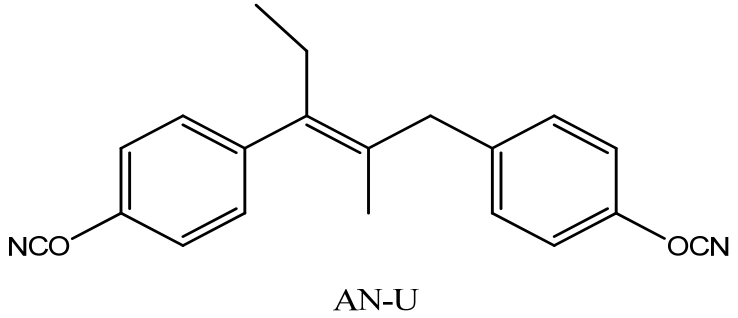
Generally, the structural changes represented by each unit change in each parameter are relatively minor. Their effect on melting point, as represented by the value of the regression coefficient, is also expected to be minor.

Analysis of the regression coefficient values therefore provides a way to detect over-prediction.

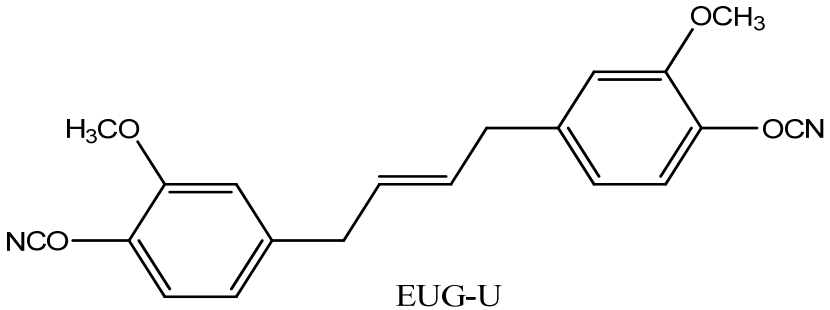
Actual Melting Point Predictions

Liquid at room temp Not yet synthesized





AN-U



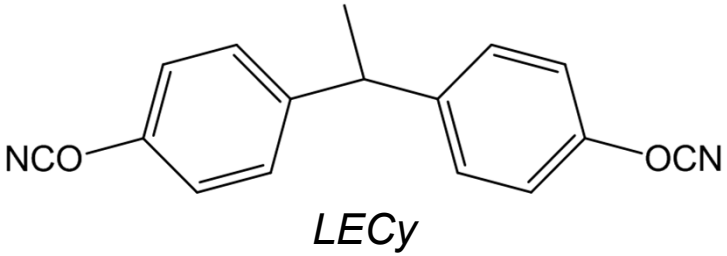
EUG-U

Useful models should indicate a low melting point for monomers that are liquids (often supercooled with a melting point of up to 70 °C) at ambient temperature.

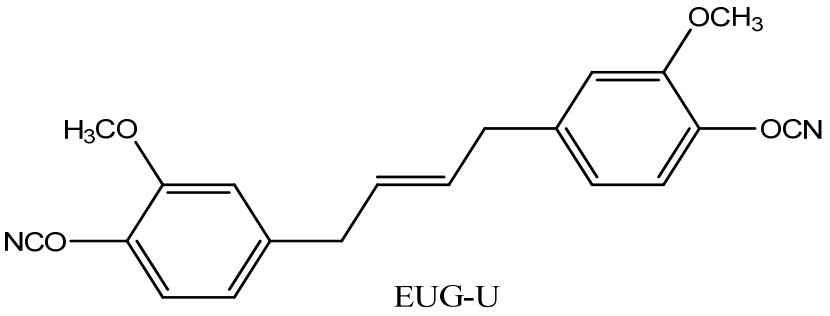
The compounds “EUG-U” and “AN-U” were not synthesized prior to model construction, and are being used as tests of genuine predictive power.

Actual Melting Point Predictions with Experimental Data

Method for Predicting Melting Point …	Prediction for LECy	Prediction for EUG-U
Partial Least Squares	95	206
Ordinary Least Squares	74	242
Measured (Lit. / DSC)	29	107



LECy



EUG-U

Summary

- Property prediction in polymer networks involves consideration of chemical structure, chemical architecture, and network topology
- The effectiveness of traditional chemical structure-property relationships for prediction of properties is often compromised by bias toward certain chemical architectures, a factor which is not adequately captured in the usual structural parameters
- The use of biologically-derived chemical structures in building structure-property relationships can often help to ensure that a wide range of structures, architectures, and even network topologies are incorporated in the correlations
- The use of informatics techniques on relatively small data sets used to build improved structure-property correlations for polymer networks is an area of continuing research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