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PACIFIC NORTHWEST 50 1965-2015 Years NATIONAL LABORATORY

Hyperbranched Alkanes for Lubes

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Pacific Northwest National Laboratory

2016 Annual Merit Review

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Project ID: FT035

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Overview

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Timeline

- FOA research project supporting DOE/industry lubricant-technologies projects
- October 15, 2013-September 30, 2015
- No cost time extension granted thru September 30, 2016

Budget

Project funded by DOE/VT:

FY14 - 15: $1,099,166

$ 999,966 – VTO

$ 99,200 – Cost share (Evonik)

Objectives (from FOA000793)

- Develop novel lubricant formulations that are expected to improve the fuel efficiency of light-, medium-, heavy-duty, and/or military vehicles by at least 2%
- Drop-in lubricant for the legacy fleet
- GF-5 testing platform

Partners

- Oak Ridge National Laboratory
- Evonik Industries

Relevance and Project Objectives

- Project Objectives:
  - Develop novel viscosity index improvers (VIIs) for lubricant formulations that will improve the fuel efficiency of light- and medium-duty vehicles by at least 2%
  - Develop VIIs with a dual function, such as friction reduction
  - Verify performance in test engines
- Scope of work for this project is divided into two components
  - Component-1: Design, synthesis and screening of molecular structures with unique hyperbranched architectures for proof-of-concept experiments
  - Component-2: Perform specialized testing (viscosity and friction) as well as engine testing on the developed additives that pass the screening criteria
- Impact: increase fuel efficiency, increase fuel economy, reduce CO_2 emissions.

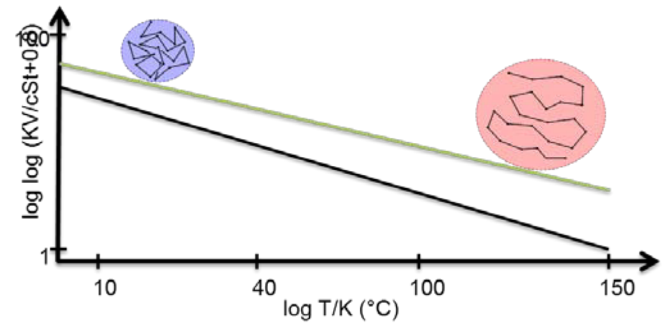
- *Project addresses fuel economy improvements from a molecular level, through a novel design of viscosity index improvers*

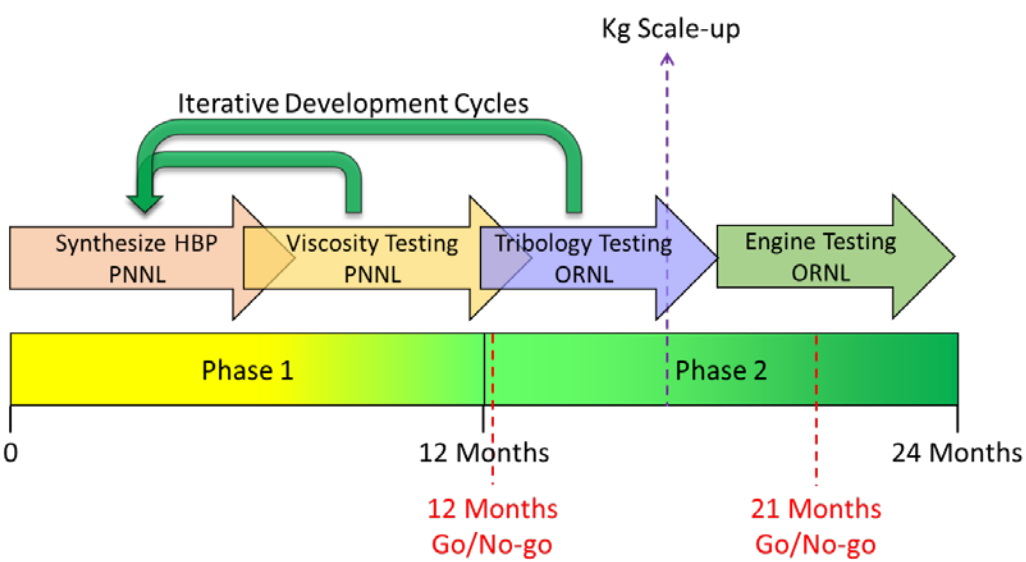
Milestones

Milestones	Proposed date of Accomplishment	Status
Milestone 1. *Kick-off meeting held at PNNL, Updated PMP*	October 15 2014	Completed February 5, 2014
Milestone 2. *Establish viscosity testing baselines using commercial base oils and commercial hyperbranched polymers*	December 30 2013	Completed April 1, 2014
Milestone 3. *Select 3 candidates for viscosity studies based on molecular weight and polarity of end groups considerations, of synthesized materials from commercial precursors via end-capping.*	March 30 2014	Completed May 30, 2014
Milestone 4. *Correlate viscosity dependence with the nature of the functional groups for a given set of hyperbranched polymers.*	May15 2014	Completed May 30, 2014
Milestone 5. *Select 3 candidates for ORNL rheology/tribology studies, from compounds prepared in house via polymerization.*	July 15 2014	Completed October 30, 2014
Milestone 6. *Identify at least one compound with promising viscosity index (at least 150) between 20-100 °C.*	September 30 2014	Completed October 15, 2014
Milestone 7. *Demonstrate suitable tribology performance for 1 analog.*	March 15, 2015	Completed August 1, 2015
Milestone 8. *Identify 1 candidate suitable for engine testing*	June 15, 2015	Completed August 15, 2015
Milestone 9. *Attain 2% fuel efficiency improvement target (engine testing)*	September 15 2015	Completed March 30, 2016

Approach/Strategy

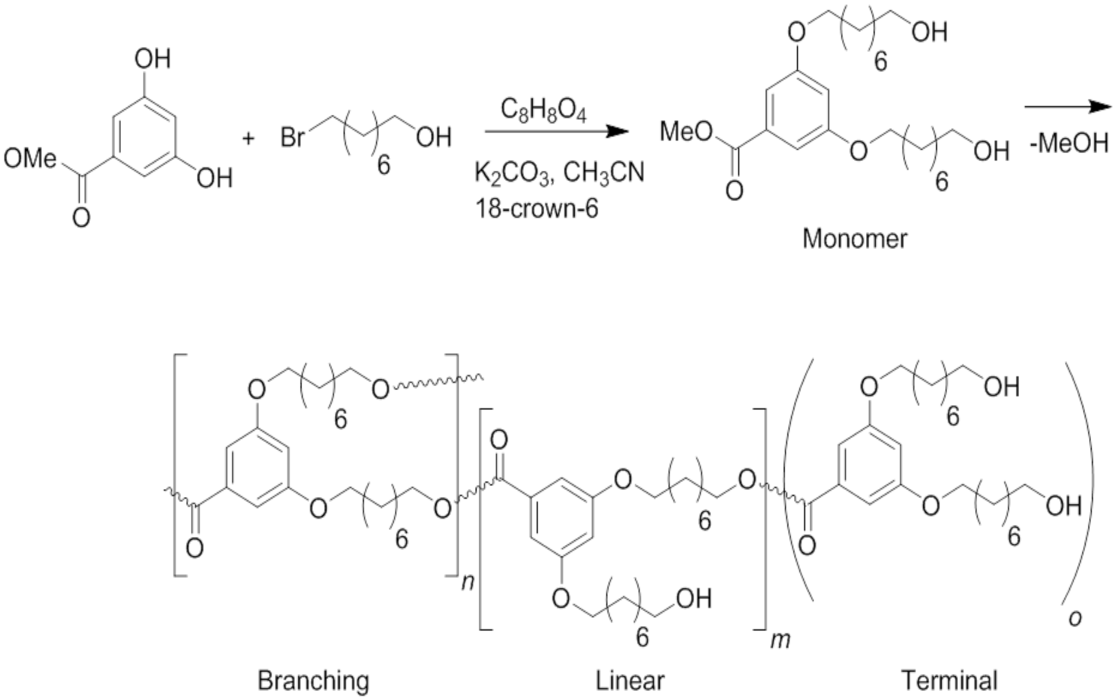
- Develop VMs or VIIs exploring a hyperbranched architecture
- The hyperbranched nature imparts shear stability (literature)
- Introduce polar functionality for friction control





- Go/No-Go 9/2014
  - Evaluate if hyperbranched polymers are feasible as VII (VI>150)
- Go/No-Go 6/2015
  - Enough progress for engine testing (viscometrics in full formulation)

Technical Accomplishments
Hyperbranched Architectures



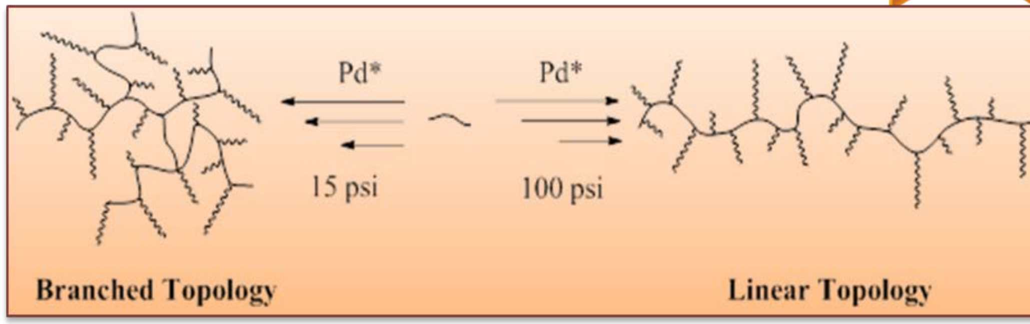
- Simple and short synthesis once you “know how”
- Post modification of the polymer intermediate with long-chain, aliphatic acyl chloride
- Polymerization difficult to control
- Final product too polar, most analogs difficult to dissolve in oil
- Low molecular weight (Mw) results in modest VI (~120)
- 10-20% friction reduction versus commercial benchmark near boundary and mixed regimes

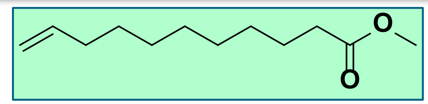
Conclusion: The original design strategy needed re-evaluation

Robinson et.al. “Probing the molecular design of hyper-branched aryl polyesters towards lubricant applications.” Sci. Rep. 2016, 6, 18624.

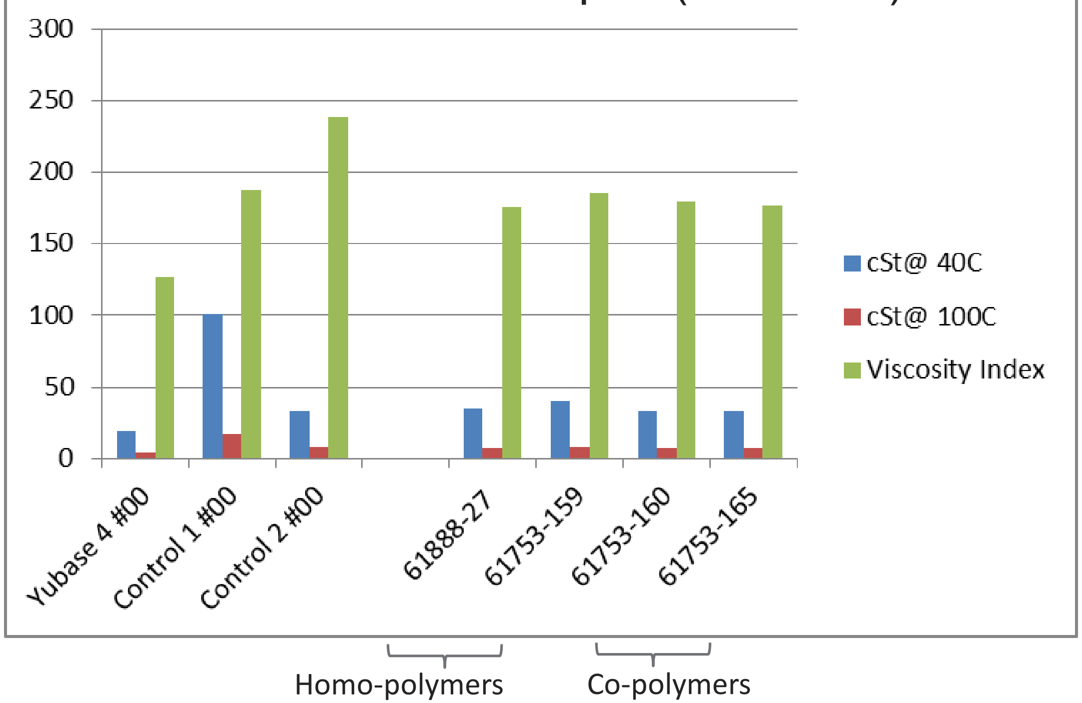
Technical Accomplishments
More Branched Architectures

- Polyethylenes
  - Re-designed to increase lipophilicity
  - Amenable to include polar co-monomers
  - Dramatic increase in oil solubility
  - Branching is controlled by reaction conditions





Measurements in Group III (Yubase 4)

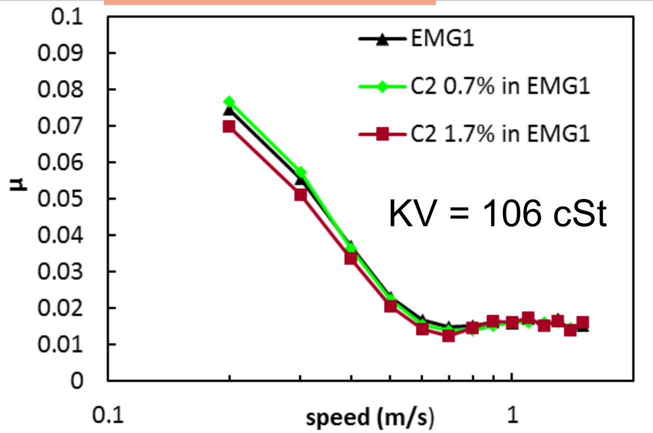


- All analogs outperform Control 1
- Polar group has little to no influence on VI
- Polar group has a significant influence on KV 25

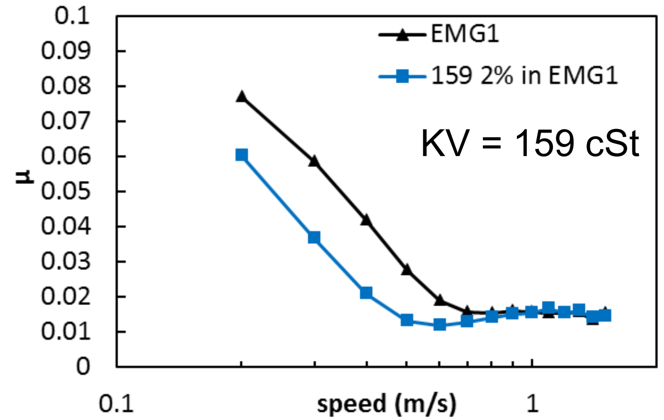
Conclusion:
Achieved competitive VIs

Technical Accomplishments
Hyperbranched Structures- Friction data

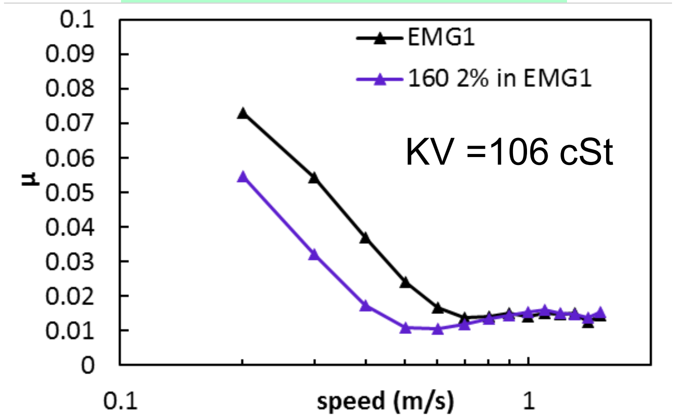
No friction benefit



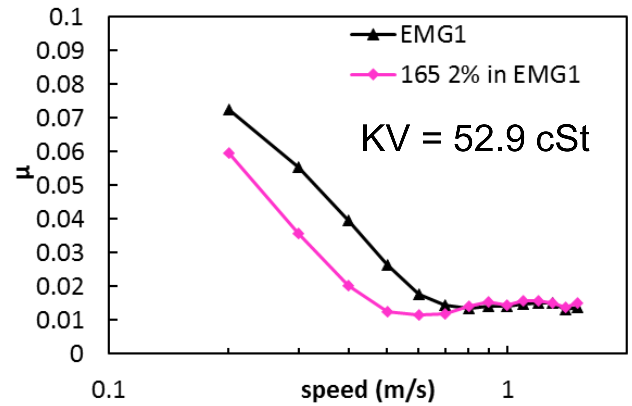
Substantial friction benefit



Substantial friction benefit



Substantial friction benefit

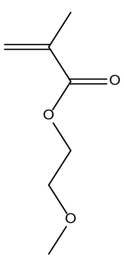


- KVs are RT values
- Control 2 has marginal friction benefit
- Polar analogs (160 and 165) provide substantial benefit

Conclusion: Dual function VII achieved

Technical Accomplishments
Multibranched Polymers

- Great design flexibility
- Well-controlled architecture via ATRP
- Amenable to introduction of polar groups/segments
- Focus on 3-arm architecture
- Manuscript in preparation
- Co-monomers introduced:



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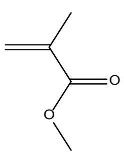

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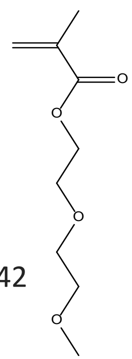

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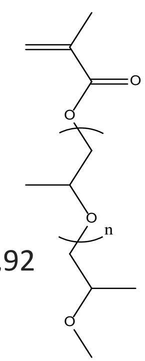

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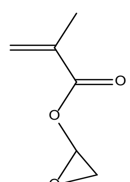

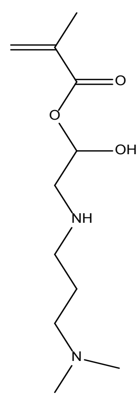

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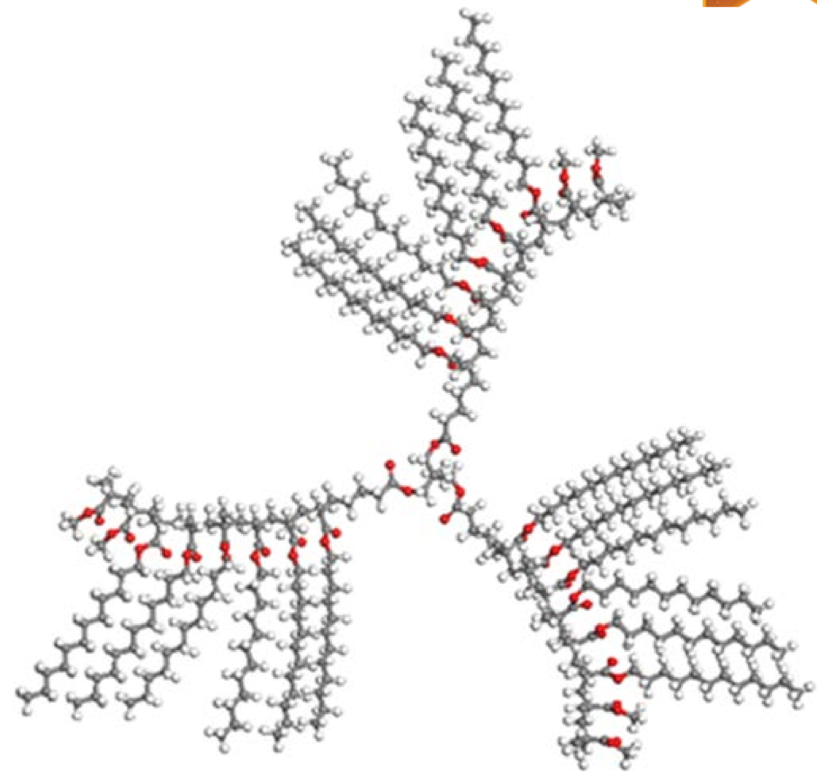
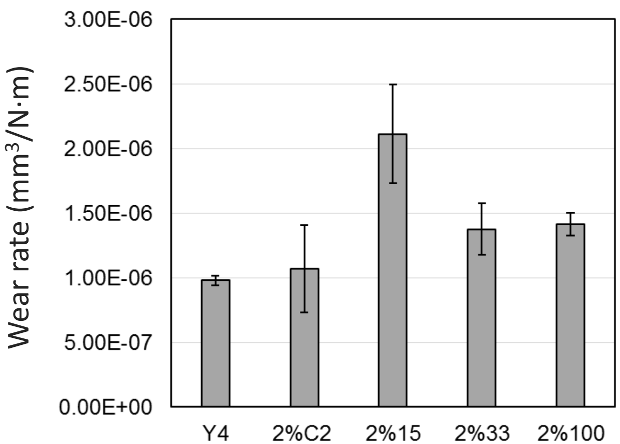
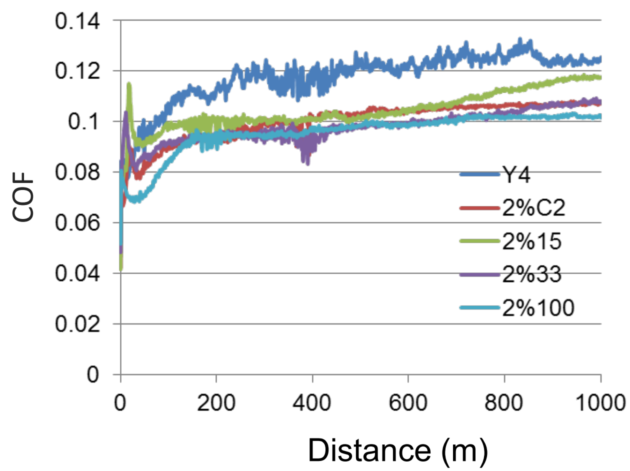


Conclusion: *Designed and synthesized macromolecules that comprise friction modifier moieties (O, N)*

Technical Accomplishments
Multibranched Polymers

- Studied effect of polarity on viscosity and friction
- Studied the effect of # of arms on viscosity and friction (Robinson et. al. "Effects of star-shaped poly(alkyl methacrylate) arm uniformity on lubricant properties." *J. Appl. Polym. Sci.* **2016**, *ASAP*, doi: 10.1002/app.43611)
- Patent application filed around branched and hyperbranched structures: Cosimbescu et. al. "Branched Polymers as Viscosity and/or Friction Modifiers for Lubricants." US Patent Application No. 30636-E filed August 11, 2015. U.S. Provisional Application No. 62/035,802 filed August 11, 2014
- After screening over 20 analogs, 3 candidates were selected as top performers (viscosity and friction) and were further tested at ORNL





Conclusion:** After careful consideration (performance, ease of synthesis, scalability), **compound 33 was chosen for scale-up and engine testing

Testing conditions: 100 °C, 1000 m, 100 N, steel ball against cast iron flat

Technical Accomplishments
Bridging the Gap to Engine Testing

- Going from a 10g scale to 1.5 kg scale = challenging
- We generated 1.2 kg of polymer in 3 batches
- Formulation development:
  - 10.1% HiTec 11100
  - 2% neat polymer
  - 87.9% Yubase 4
- Blend Studies to determine best concentration and viscosity grade

Conc. (wt %)	40 C (cSt)	100 C (cSt)	VI
1.0 (117E)	44.1	9.6	210.4
1.5 (117D)	55.5	12	219.8
2.0 (117A)	70.1	15.4	233.8
4.0 (117B)	142.1	31.4	263.4
6.0 (117C)	247	55.1	284.6

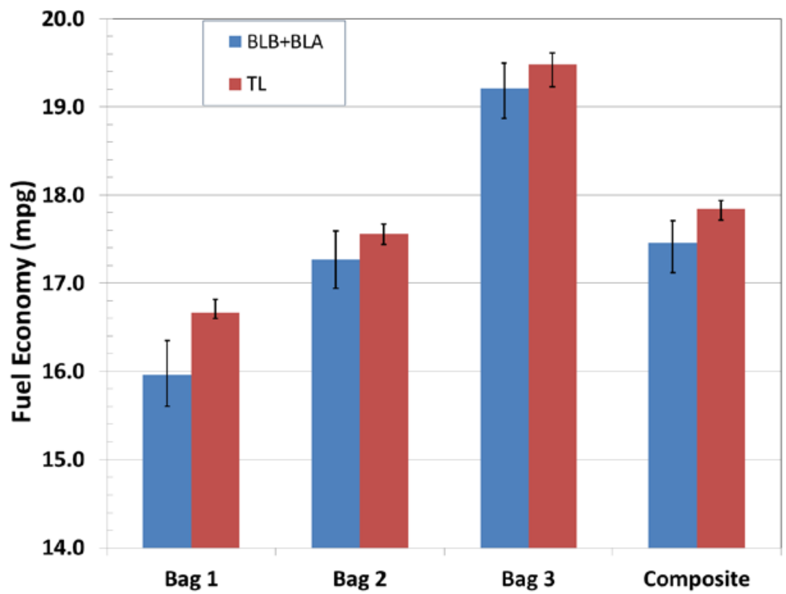
Sample	117A (2%)	117D (1.5%)	117E (1%)
HTHS (150C)	2.8	2.54	2.29
CCS (-35C)	5962	5184	4962

Technical Accomplishments
Engine Testing

- Chosen formulation:1.538% PNNL polymer, 10.1% HiTec 11100, Yubase4
- 11 gallons of final lubricant were prepared

3-Phase Federal Test Procedure (ORNL)
Reference Oil 20W30

- City Fuel Economy improves 2.3% (composite 3-bag result)
  - 4% on the cold Bag 1
  - Less than 2% on Bags 2 and 3
- HFET fuel economy improves 1.7%
- SSFE improvement ranges from 1 to 2%. Higher improvement measured at lower speeds



FTP Test Results for PNNL Lube versus average of BLB and BLA runs. Range bars show maximum and minimum of 5 tests

Sequence VI-E (SwRI)
Reference oil 20W30

FEI1 80/20 Eng Hr Adjusted	1.11%
FEI2 10/90 Eng Hr Adjusted	0.90%
FEI Sum	2.01%

BLB: baseline lube before test: BLA: baseline lube after test

Responses to Previous Year Reviewers' Comments

- This project was not reviewed last year.

Collaboration and Coordination

Conducted friction screening/studies (J. Qu, Y. Zhou) and engine testing (B. West and S. Sluder)

Provided guidance on finished formulation, provided one of the benchmark polymers, HTHS measurements and blend studies measurements of the final lubricant (D. Gray, J. Ellington)

Provided general advice and direction for the project (E. Bardasz). Through this connection, we acquired a second benchmark material

Ran simulations of various architectures to predict molecular size changes with temperature and thus VI trends (A. Martini, U.S. Ramasamy)

Kindly provided additive-free, Group III oil as a testing matrix, as well as DI package to prepare finished lubricant (J. Guevremont, J. Styer)

Insightful discussions on tribology and shear studies (R. Erck, G. Fenske)

Remaining Challenges and Barriers

- **Shear stability** is a major concern for polymers, and it has not been addressed during this project, except indirectly
  - Shear stability typically increases with the degree of branching
  - Our top performers are only moderately branched
- **Slightly adverse wear**
  - Understand the source of accentuated wear in the chemistries we pursued
- **Commercialization**
  - Very slow
  - Industry barriers not well understood

Proposed Future Work

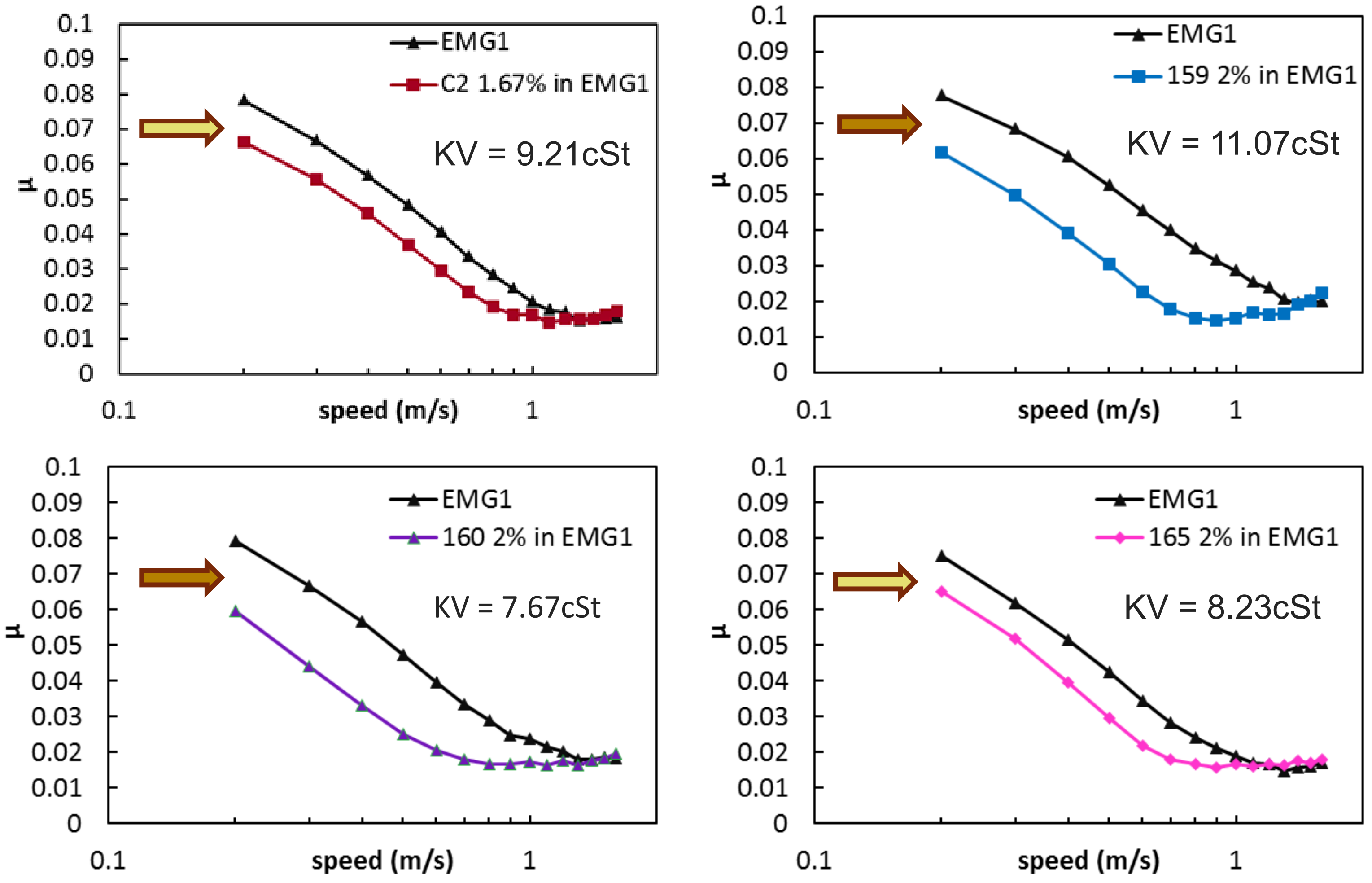
- **Continue to develop hyperbranched structures**
  - 16 arms or more
  - Evaluate shear stability/degradation
  - Refine correlation approaches to extend structure-property correlations beyond lubricity, maximizing the use of available fuel sets.
- **Continue to explore new chemistries**
  - Reduce wear via anti-wear moieties delivered by polymers
  - Test polymeric additive in VM and FM packages (industry collaboration)
- **Develop and Strengthen Industrial Relationships**
  - Persistence
  - Patience

Summary

- All of our top candidates outperformed the benchmarks:
  - Control 1 was outperformed in VI
  - Control 2 was outperformed in Friction
- We have shown that polymers can be designed to have dual properties, VM and FM
- One candidate selected for engine testing was scaled up (1.2kg) and 11 gal of lubricant were generated for two engine tests
- Engine testing demonstrated feasibility of the PNNL polymer with commercial packages (potential adoption) and superior performance
  - 3 Phase test
    - City Fuel Economy improves 2.3% (composite 3-bag result, as high as 4%)
    - HFET fuel economy improves 1.7%
    - SSFE improvement ranges from 1 to 2%. Correlating lubricity to specific fuel substructures.
  - Sequence VI-E test
    - FEI Sum 2.01%

Backup Slides

BPEs Friction at 100 C



- 160 has the lowest viscosity, yet the highest reduction in friction

Viscosities and VIs of branched/star polymers

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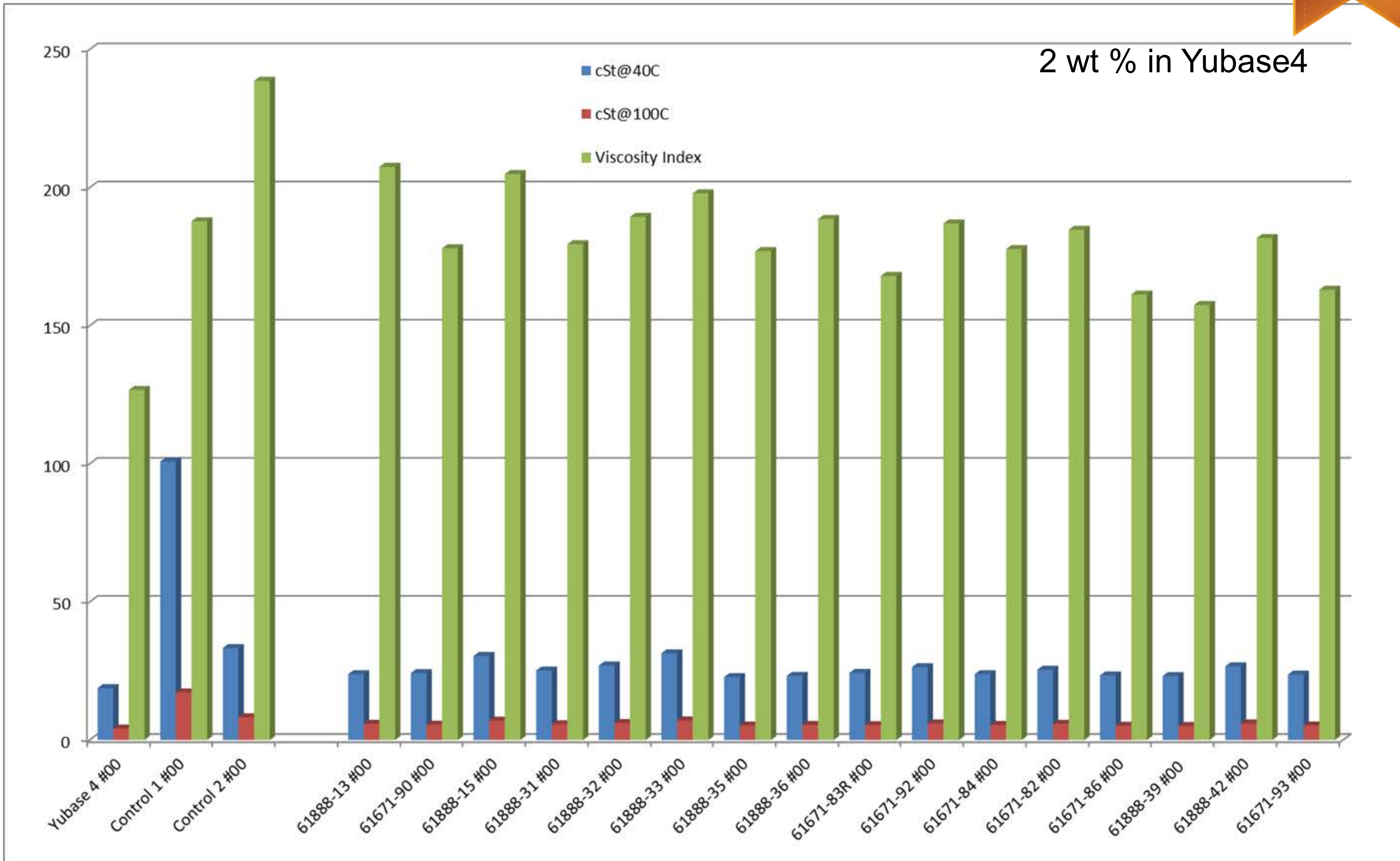
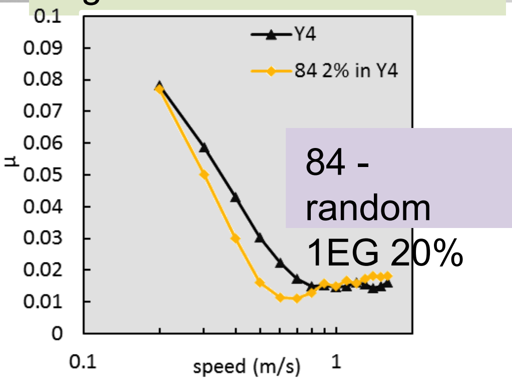
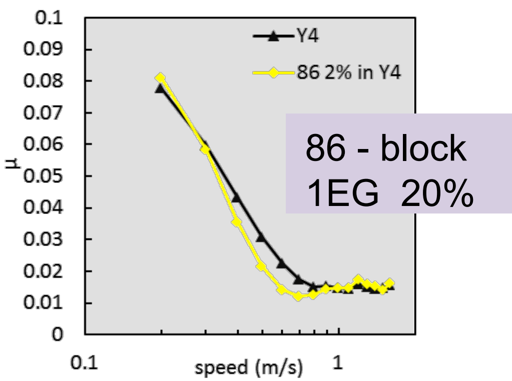
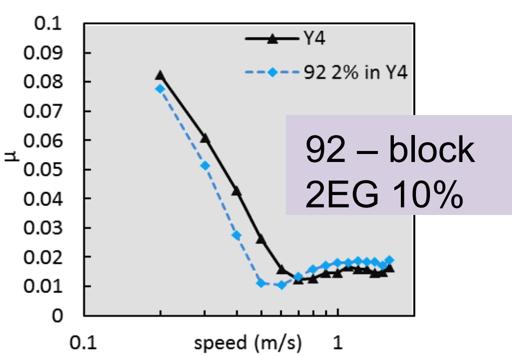


Effect of Polarity on Friction

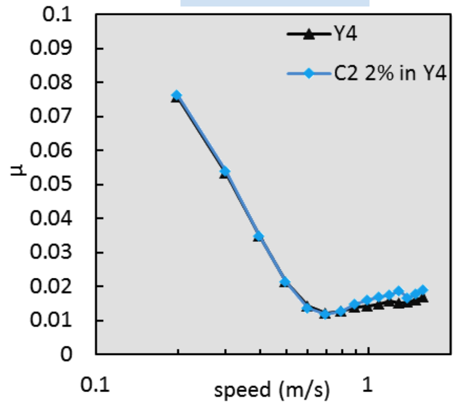
Significant friction benefit







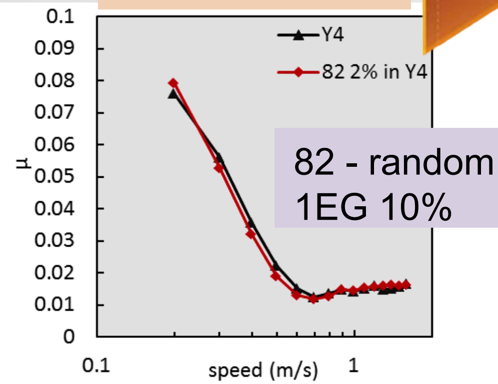
Control 2

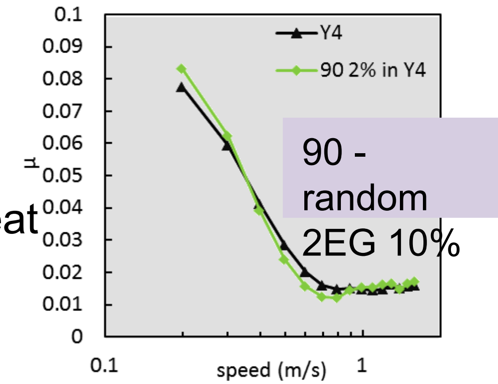


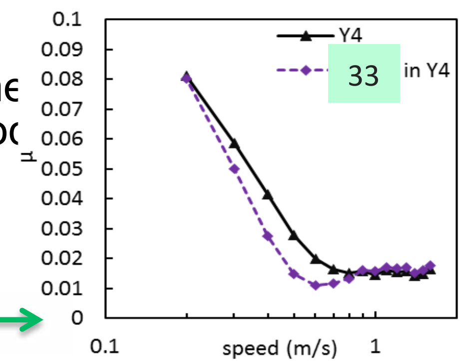
- In the depths of our understanding, these are great data
- A 20% polar co-monomer composition sufficient to see friction benefits
- The topology of the co-polyme is important: as expected, bloc is better than random if low amount of polar monomer is used

Scale-up candidate

No friction benefit







Effect of Topology on Viscosity

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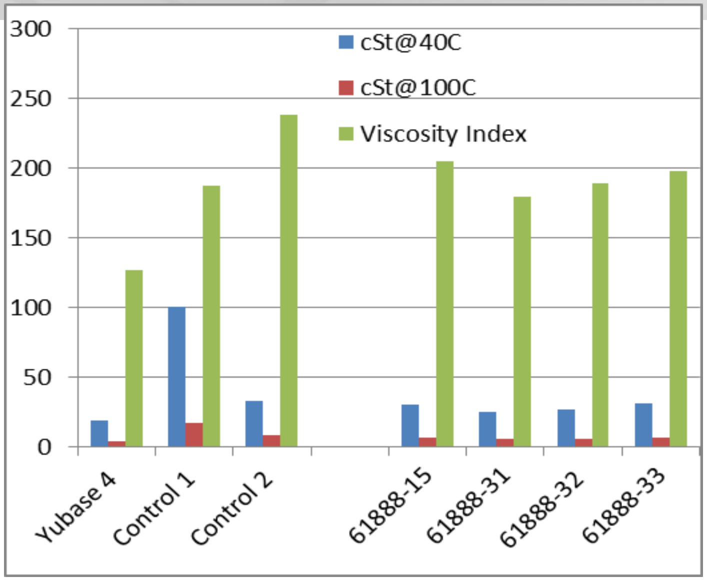


Structural differences that control topology

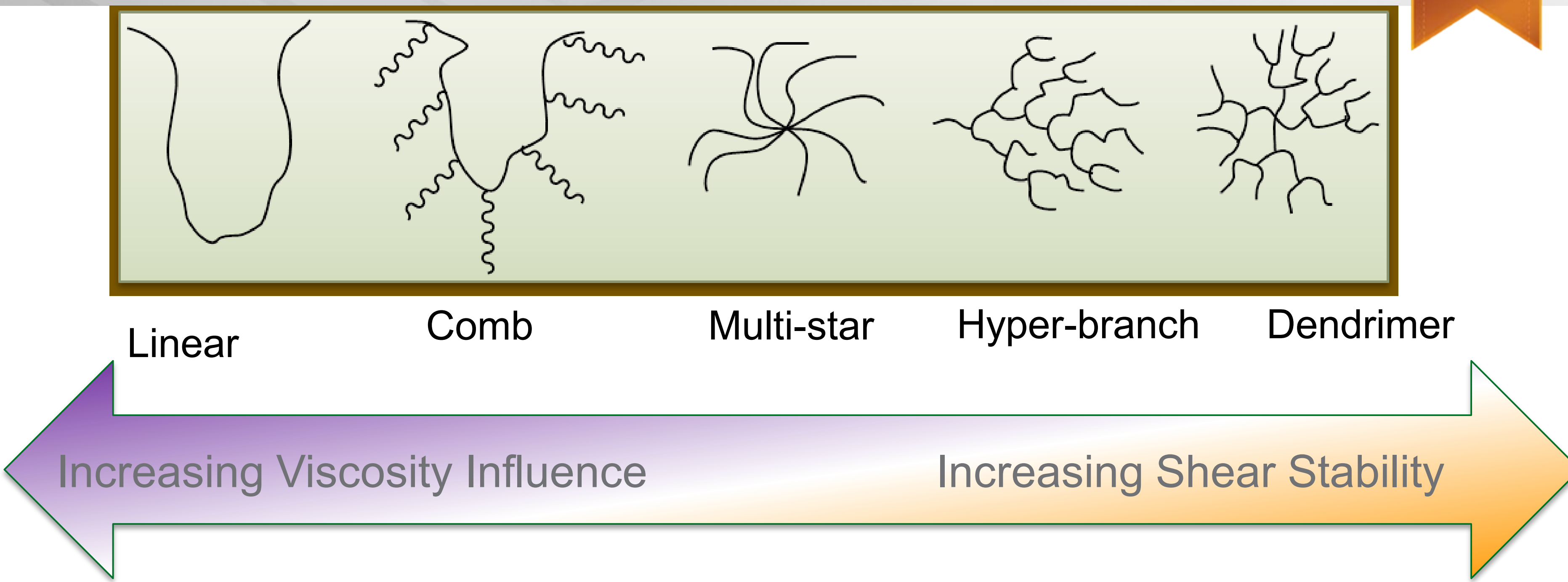
- Little to no influence on VI
- No trend observed

#15: $\bar{M}_n^{\ app}$ = 128 kDa
#31: $\bar{M}_n^{\ app}$ = 174 kDa
#32: $\bar{M}_n^{\ app}$ = 271 kDa
#33: $\bar{M}_n^{\ app}$ = 171 kDa

- Lowest Molecular weight analog has the highest VI
- No trend observed

$\bar{M}_n$: number-average molar mass

Polymer Architectures



- Molecular weight and architecture play significant roles in the design of viscosity modifiers
- Non-linear polymers
  - Less-explored as viscosity modifiers
  - Provide a shear benefit over linear architectures
  - Provide more structural handles to introduce polar groups into the molecular design