Project 1: Controlling Polymer Rheological Properties Using Long-Chain Branching

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Proposed Budget: $150,000/year; In Kind Support ORNL $40,000/year; NIST $40,000/year

Project Duration: 4 years

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Outcomes/Deliverables

- Inference of long-chain branching structures from rheological, neutron scattering, SEC, and other measurements.
- Development of computer software for inference of long-chain branching structure from characterization data and catalyst information
- Inference of nonlinear rheology and processing characteristics from branching structure
- Tools for optimization of branching

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Impact

- Improved ability to design and control polymer processing properties
- Ability to infer likely branching characteristics from rheology
- Understanding of complex catalyst systems and resolution of some longstanding debates over molecular structure in certain resin systems

Supplementary Material

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Industrial Relevance

"The flow behavior ('rheology') [of polymers] is *enormously* sensitive to LCB [long chain branching] concentrations far too low to be detectable by spectroscopic (NMR, IR) or chromatographic (SEC) techniques. Thus polyethylene manufacturers are often faced with 'processability' issues that depend directly upon polymer properties that are not explainable with spectroscopic or chromatographic characterization data. Rheological characterization becomes the method of last resort, but when the rheological data are in hand, we often still wonder what molecular structures gave rise to those results."

Janzen and Colby, J. Molecular Structure, 1999

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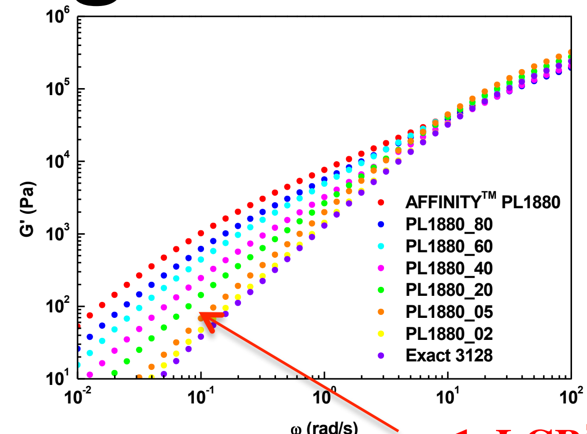
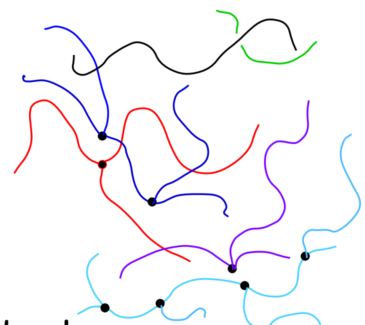
Rheology, Processing and Long-Chain Branching

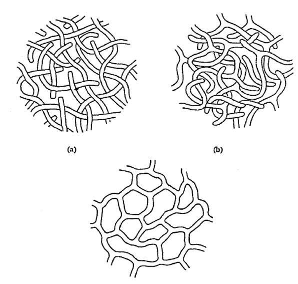


<1 LCB's per million carbons significantly affects rheology!



branched polymers

branched thread-like micelles



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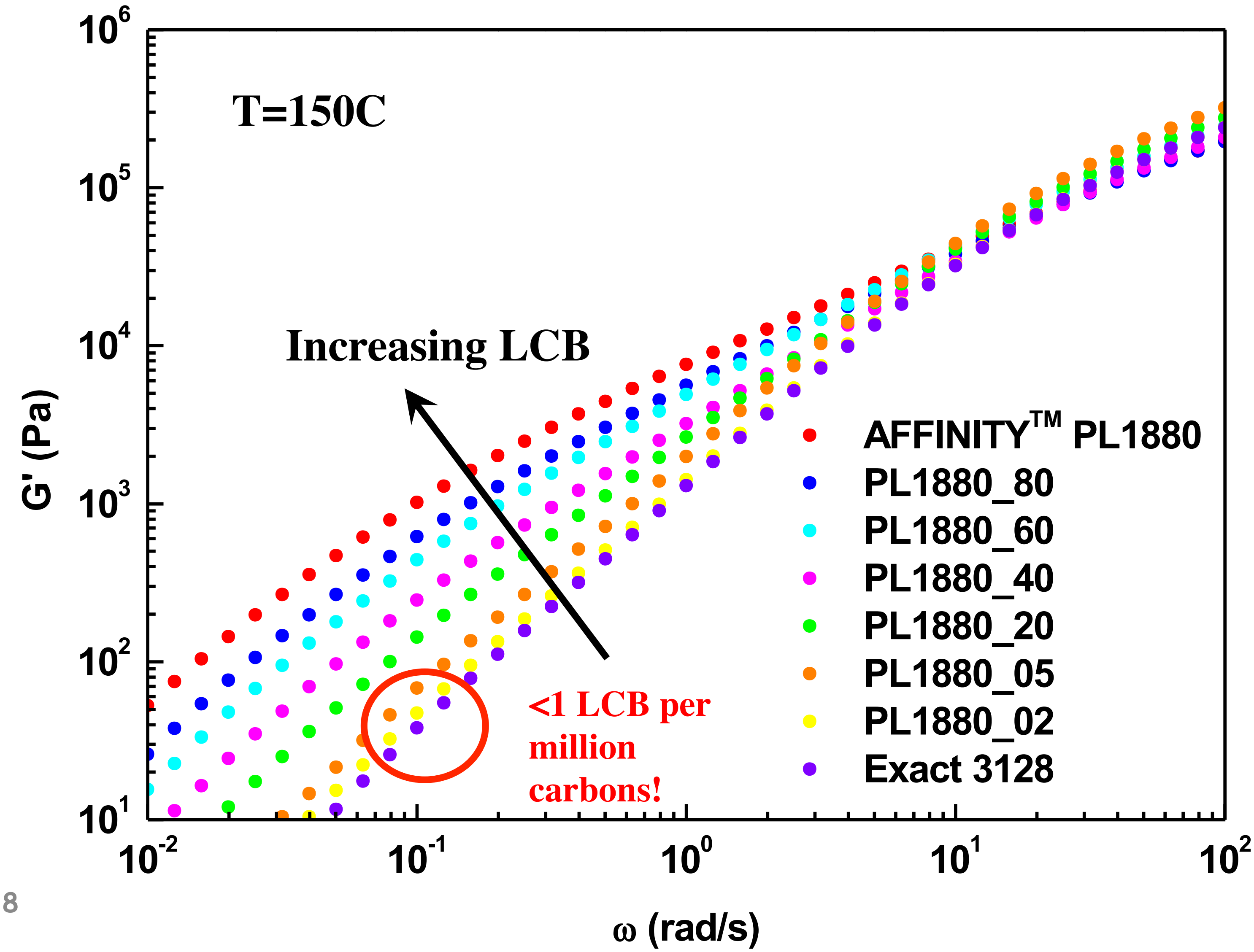
Blends of Linear Exact 3128 and Branched PL1880 Polyolefins

Sample name	AFFINITY™ PL1880 (branched)	Exact 3128 (linear)	LCB (n/1000C)	n_c	M_w (kg/mol)
AFFINITY™ PL 1880	100%	0%	0.0177	0.0482	116
PL1880_80	80%	20%	0.0142	0.0502	116
PL1880_60	60%	40%	0.0106	0.0521	116
PL1880_40	40%	60%	0.00709	0.0541	116
PL1880_20	20%	80%	0.00355	0.0560	115
PL1880_05	5%	95%	0.000887	0.0575	115
PL1880_02	2%	98%	0.000355	0.0578	115
Exact 3128	100%	0%	0	0.0580	115

X.Chen, C. Costeux, R. Larson. J. of Rheology 54(6) 1185-1206, 2010

Rheology of Blends of Linear Exact 3128 and Branched PL1880 Polyolefins



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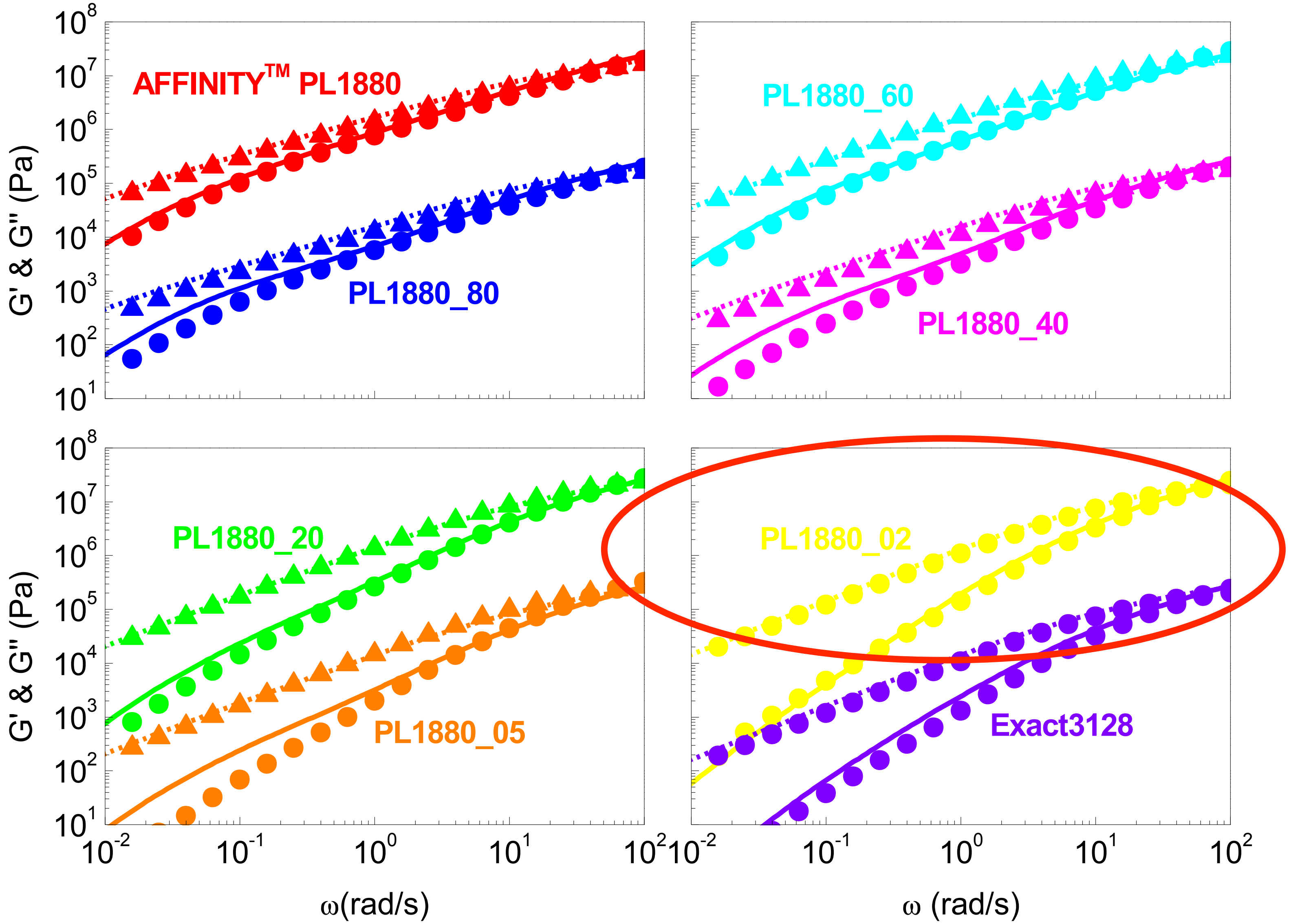
A Priori Predictions of Commercial Branched Polymer Rheology with Levels of LCB down to one Branch per Million Backbone Carbons



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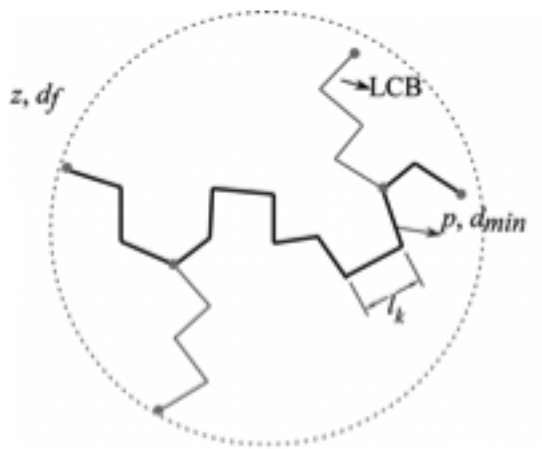
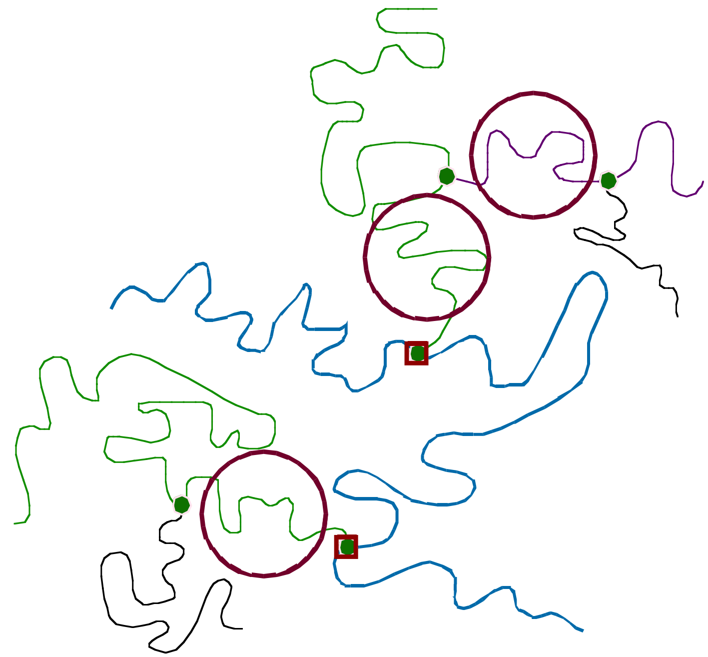
Small-Angle Neutron Scattering





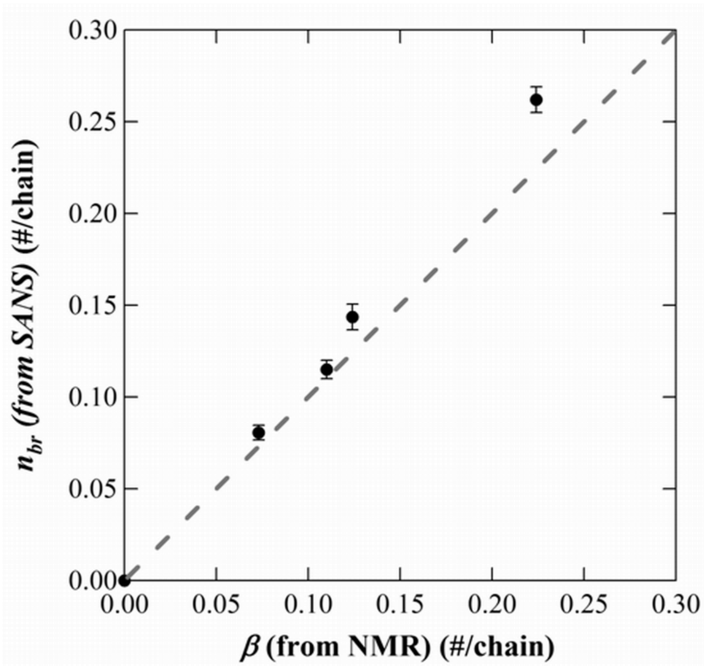
$$n_{br} = \frac{z^{[(5/2d_f)-(3/2c)]+[1-(1/c)]} - 1}{2}$$

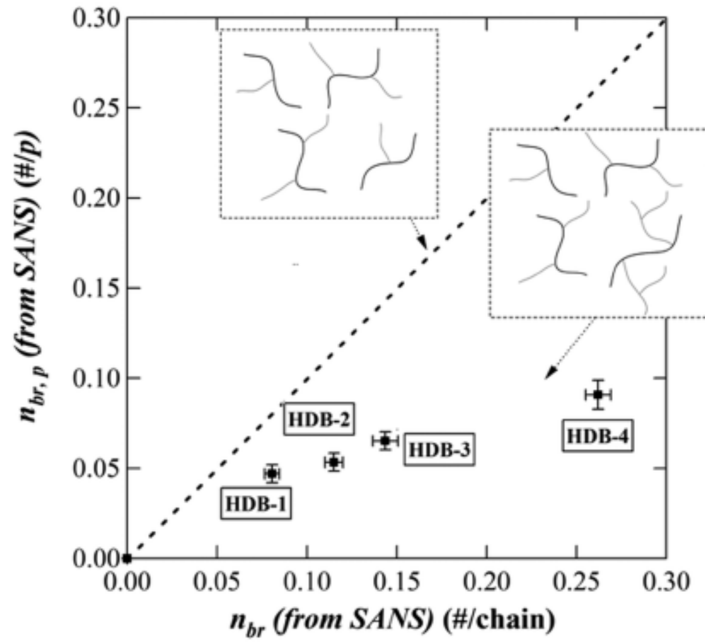
$$n_{br,p} = \left[p^{(1/d_{\min})-(3/5)}\right]^{5/2} - 1$$

$$n_i = n_{br} - n_{br,p}$$

Branch content of metallocene polyethylene **Ramachandran R, Beaucage G, Kulkarni AS, McFaddin D, Merrick-Mack J, Galiatsatos V** ***Macromolecules*****, 42** 4746-4750 (2009).

Metallocene Resins





Branch content of metallocene polyethylene **Ramachandran R, Beaucage G, Kulkarni AS, McFaddin D, Merrick-Mack J, Galiatsatos V *Macromolecules*, 42** 4746-4750 (2009).

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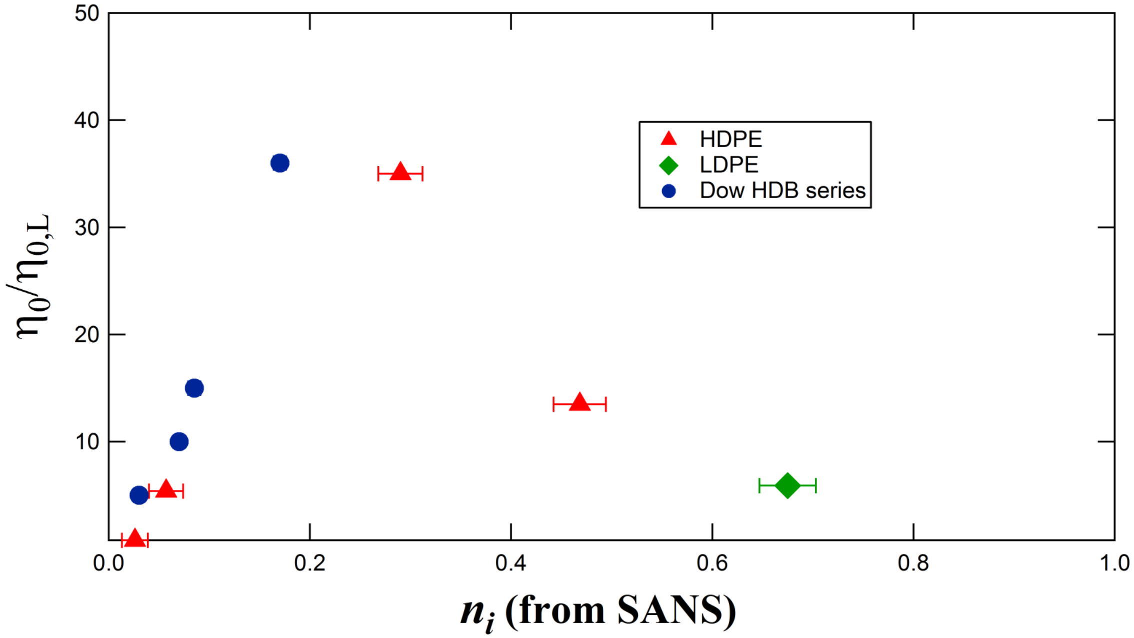
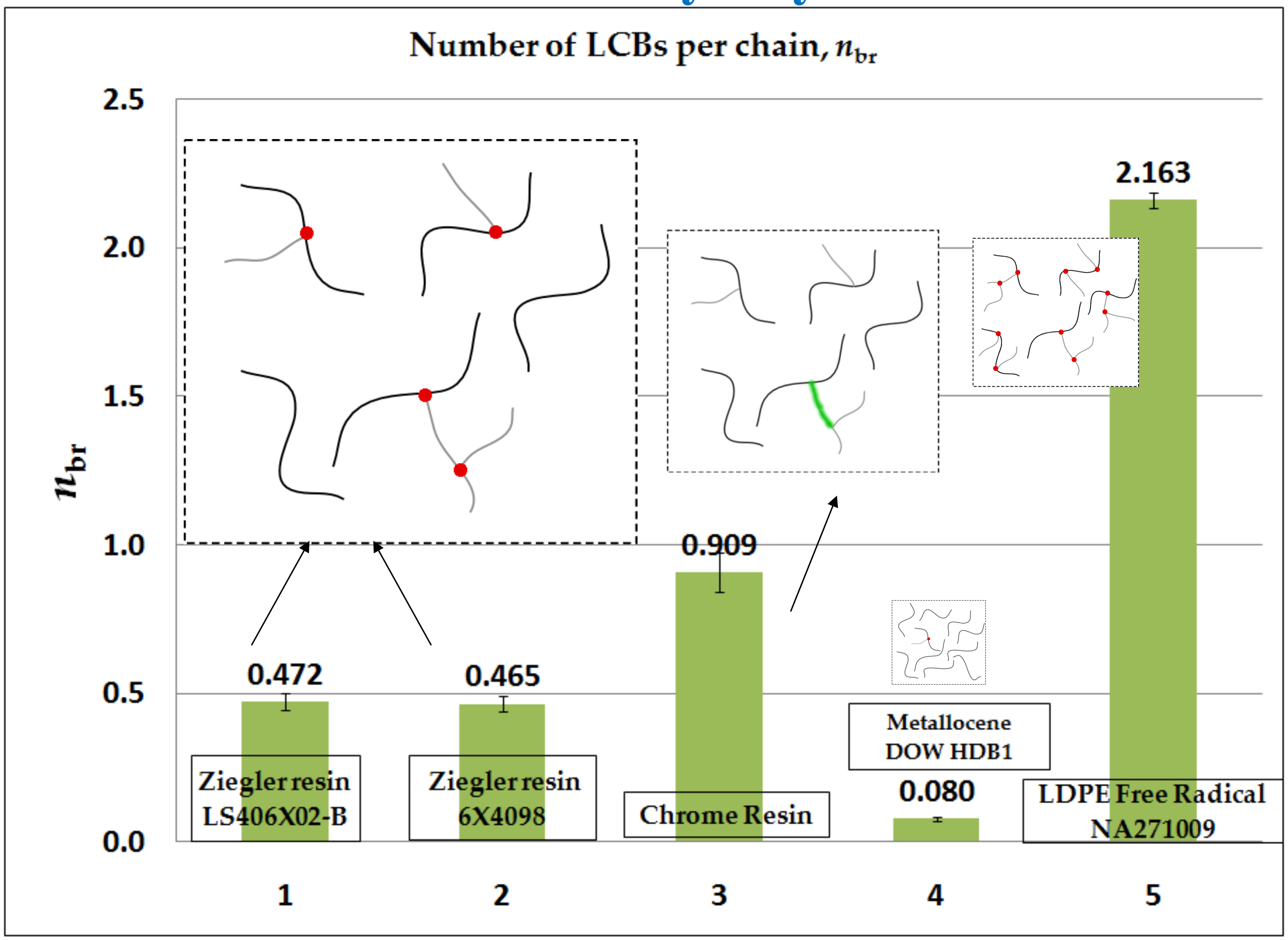
Zero-shear viscosity enhancement vs. Hyperbranch content (Polyethylene)



- Costeux, S.; Wood-Adams, P.; Beigzadeh, D., *Macromolecules* **2002,** *35* (7), 2514-2528.
- Ramachandran, R.; Beaucage, G.; Kulkarni, A. S.; McFaddin, D.; Merrick-Mack, J.; Galiatsatos, V., Branch Content of Metallocene Polyethylene. *Macromolecules* **2009,** *42* (13), 4746-4750.

Branches per Chain
Compare Catalysts

Effect of catalyst systems



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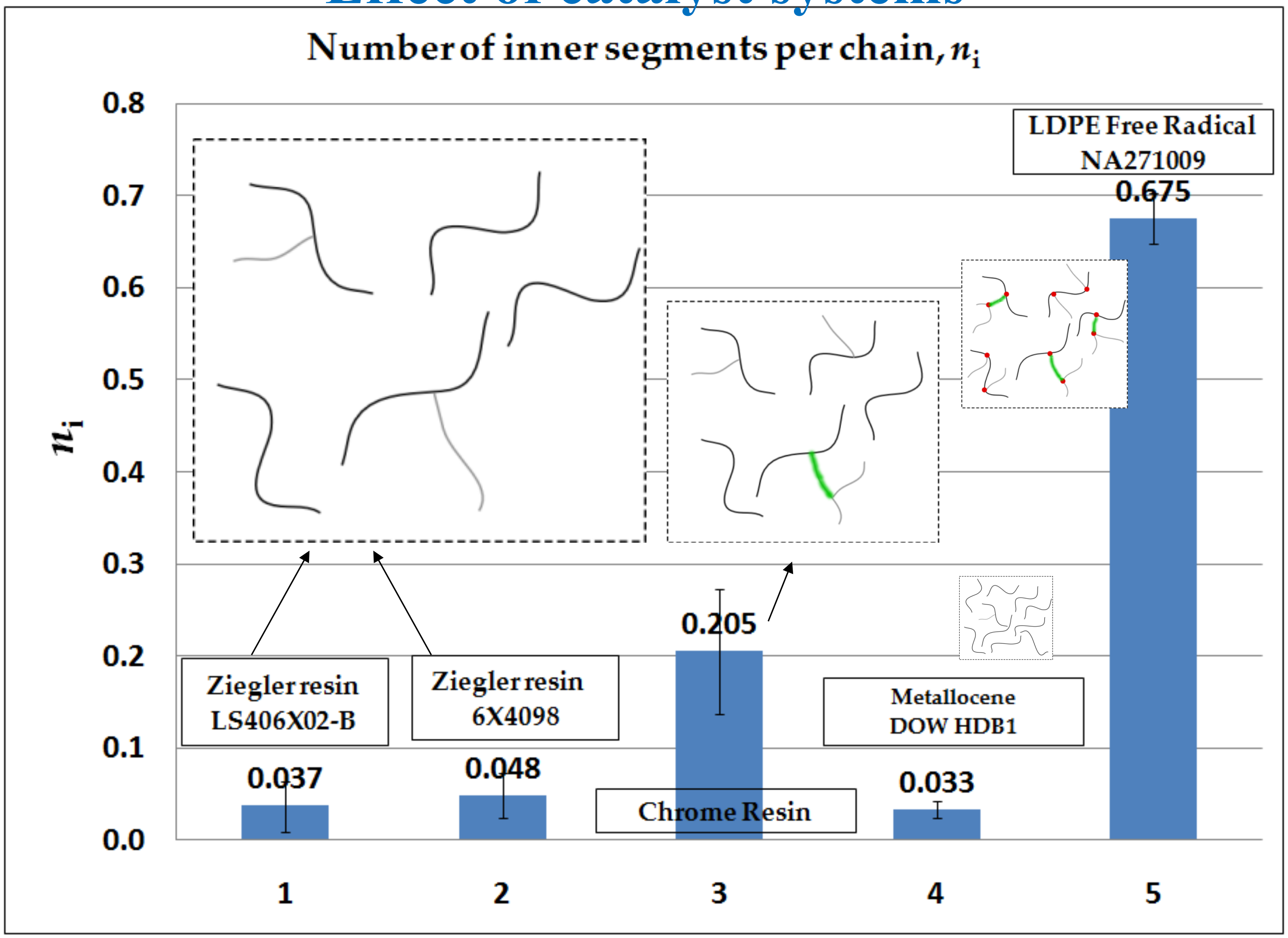
Hyperbranch Content Compare Catalysts

Effect of catalyst systems



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Proposed Work

-Scaling Method: Beaucage has developed a new method for the quantification of macromolecular topology, that can be used to analyze small-angle scattering data. The method yields unique parameterization of the average branch length, number of inner segments (branch on branch or hyperbranch content) and quantitative (with error bars) measures of the number of branches, mole fraction branches as well as a number of other parameters.

-Linear Rheology: We propose to combine this new method with methods developed in the Larson group for inferring branching structures from linear rheology data and catalyst reaction pathways to improve determination of branching structures in polymers of industrial importance.

-Non-Linear Rheology: This will be combined with predictions of nonlinear rheology to determine how to tailor branching levels to obtain optimal processing behavior.