



Evidences of Long-Chain Branching in Ziegler-Natta Polyethylene Resins

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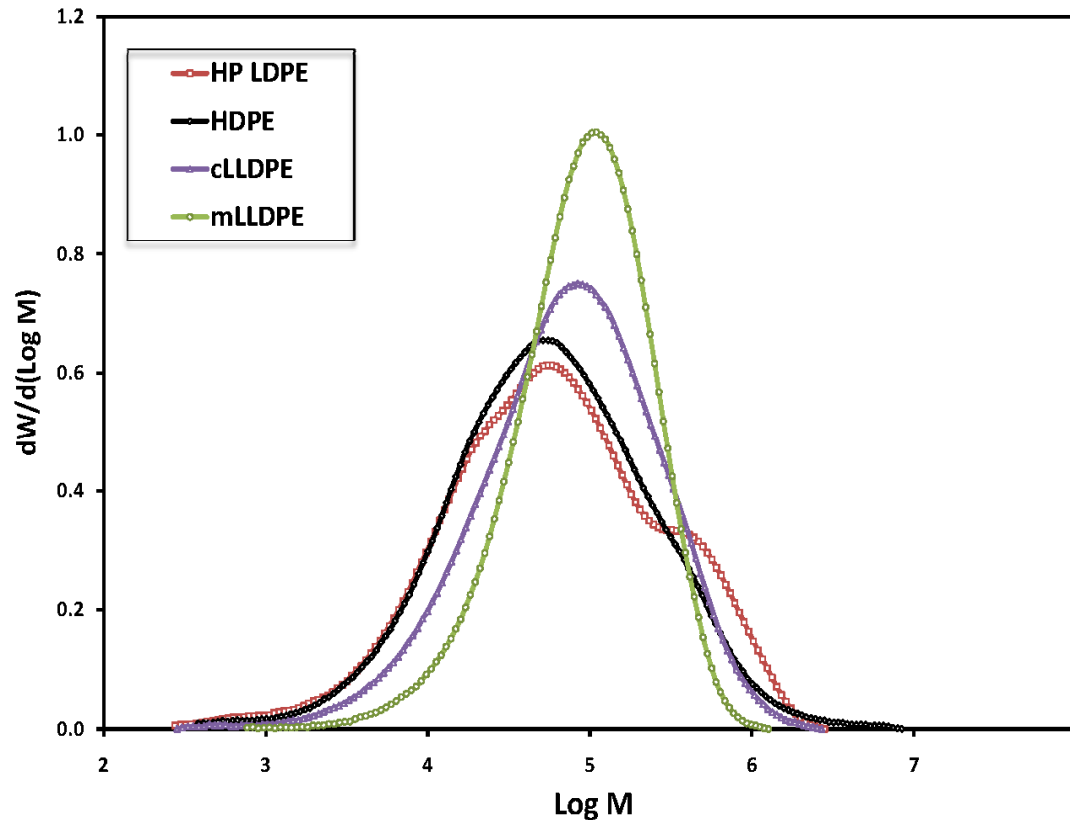
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Outline

- Introduction
 - LCB in LDPE, HDPE, and mPE
 - LCB in Z-N PE resins??
- SEC-MALS Studies
- Fractionation Studies
- Root-cause of Elution Anomaly
- Conclusions

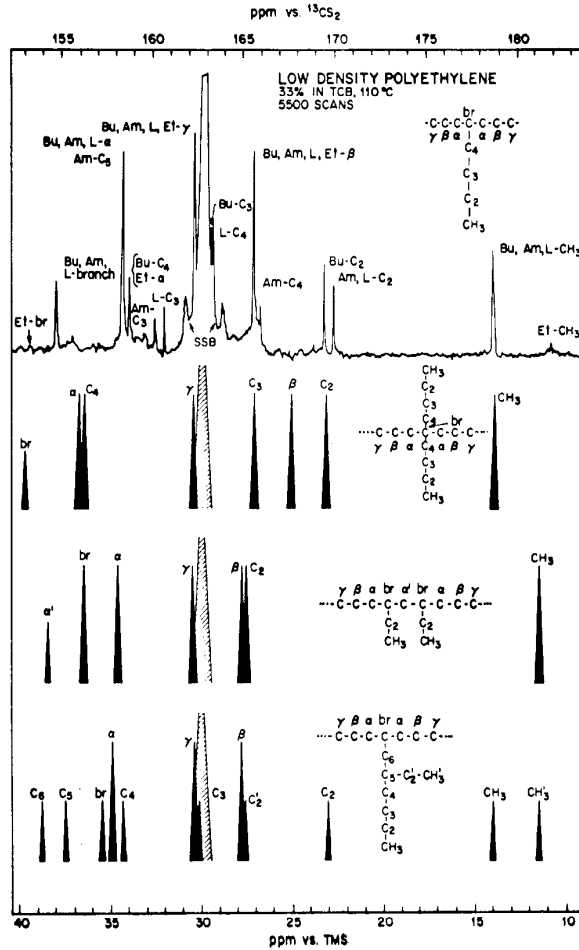
Polyethylene Types



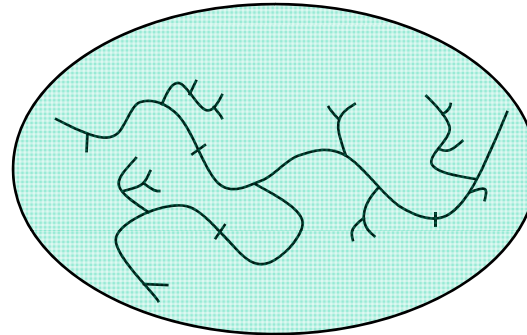
- LDPE
 - Free radical @ high pressure
- HDPE
 - Phillips Cr catalyst
- cLLDPE
 - Z-N catalyst
- mPE
 - Metallocene and other “single” site catalysts

Many reports of LCB in LDPE, HDPE and mPE in the literature,
but very few reports on LCB in Z-N resins

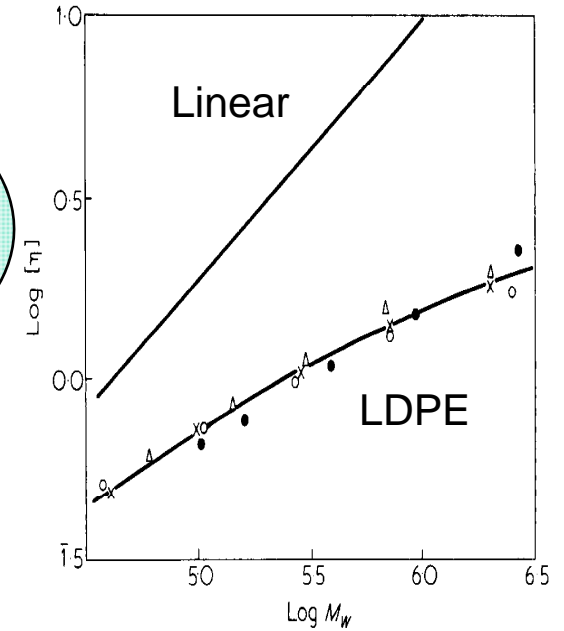
LCB in HP LDPE



Bovey et al., *Macromolecules*, **1975**, 9, 76



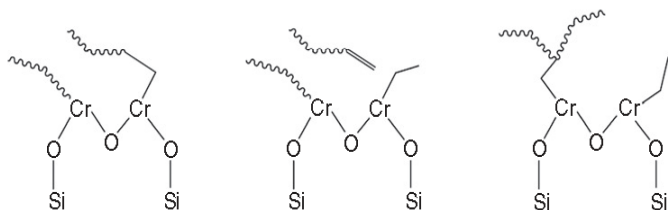
LDPE



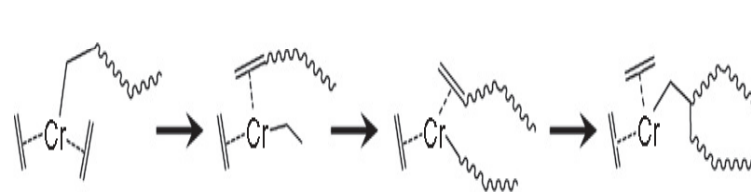
Gianotti et al, *Polymer*, **1980**, 21, 1087

- “Back-biting” mechanism to form LCB (Roedel, *JACS*, **1953**, 75, 6110)
- Branching on branches
- High flow activation energy (Romanini, Savadori, Gianotti, *Polymer*, **1980**, 21, 1092)
- Strain hardening effect (Yamaguchi, Takahashi, *Polymer*, **2001**, 42, 8663)

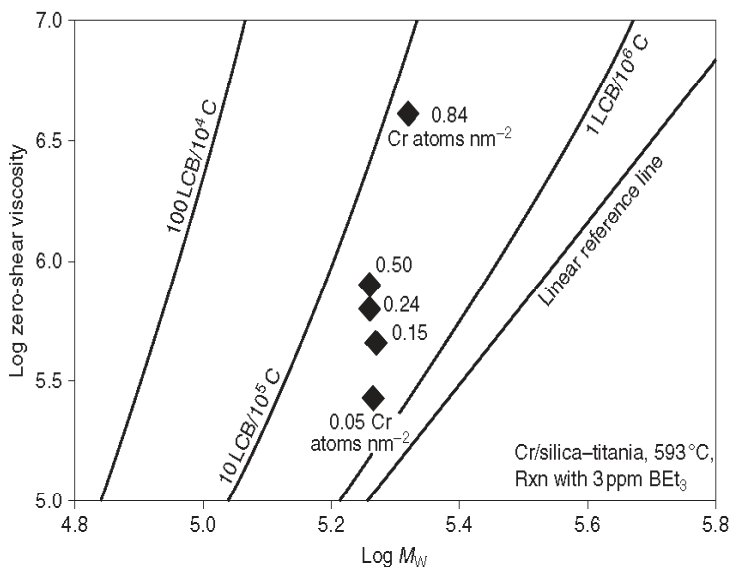
LCB in Cr-PE



Intermolecular mechanism



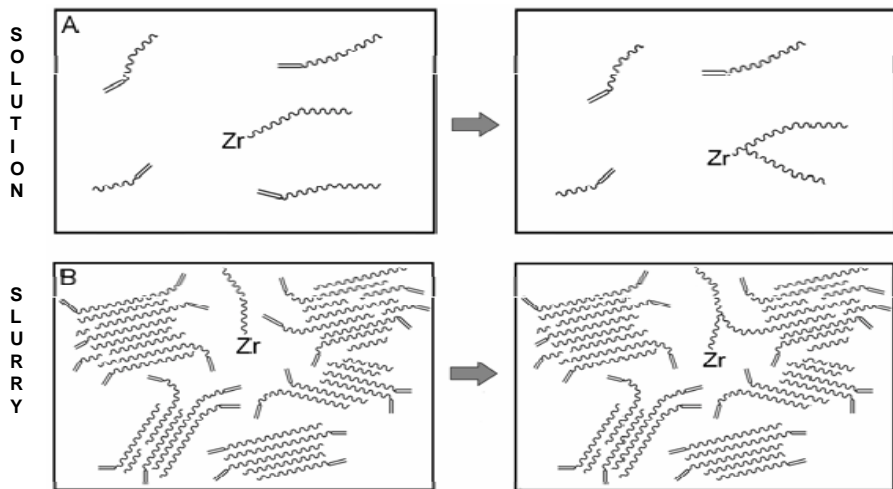
Intramolecular mechanism



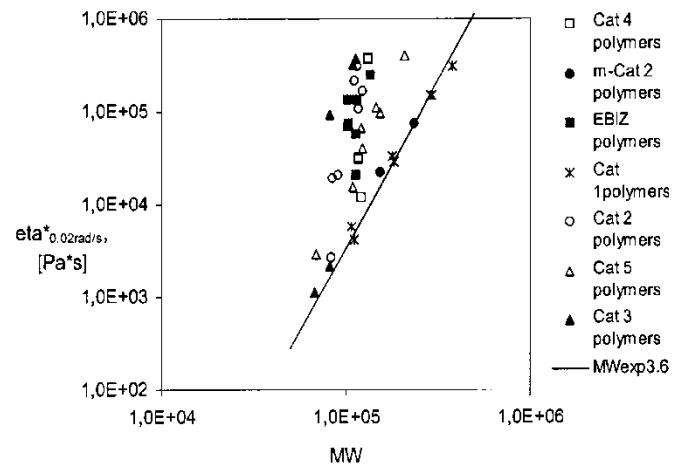
McDaniel, *Adv. Catal.*, **1985**, 33, 47 & **2010**, 53, 123

- LCB in HPPE mostly studied via rheology
 - Significantly increased zero-shear viscosity with the presence of very small amount of LCB
 - Elevated flow activation energy
- Little or no chromatographic evidences until recently
(DesLauriers, Tso, Yu, Rohlfing, McDaniel, *Appl. Catal. A*, **2010**, 388, 102)

LCB in m-PE



Yang, Jensen, McDaniel, *Macromolecules*, **2010**, 43, 8836



Malmberg et al., *Macromolecules*, **1999**, 32, 6687

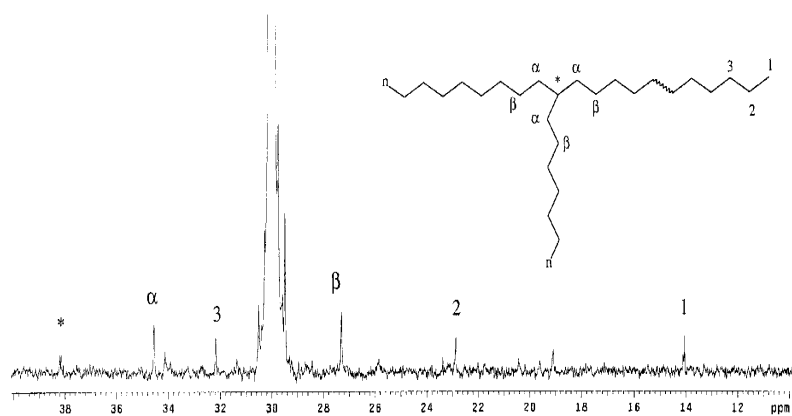
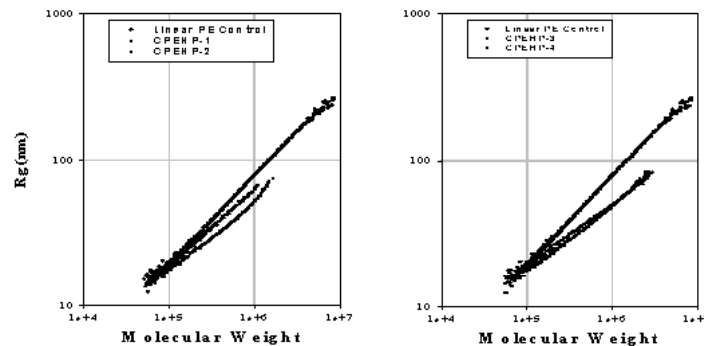


Figure 3. ¹³C NMR spectrum of sample B5 (in 10 mm NMR tube, number of transients accumulated 12 000).

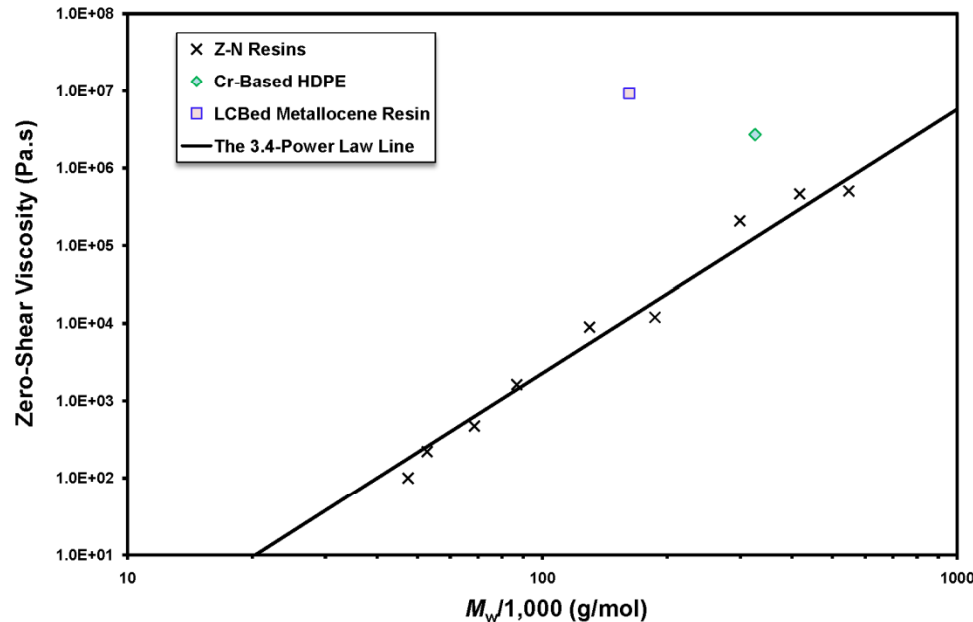
Malmberg et al., *Macromolecules*, **1998**, 31, 8448



Yu, Rohlfing, Hawley, Deslauriers, *Polym. Prepr.*, **2003**, 44(2), 50



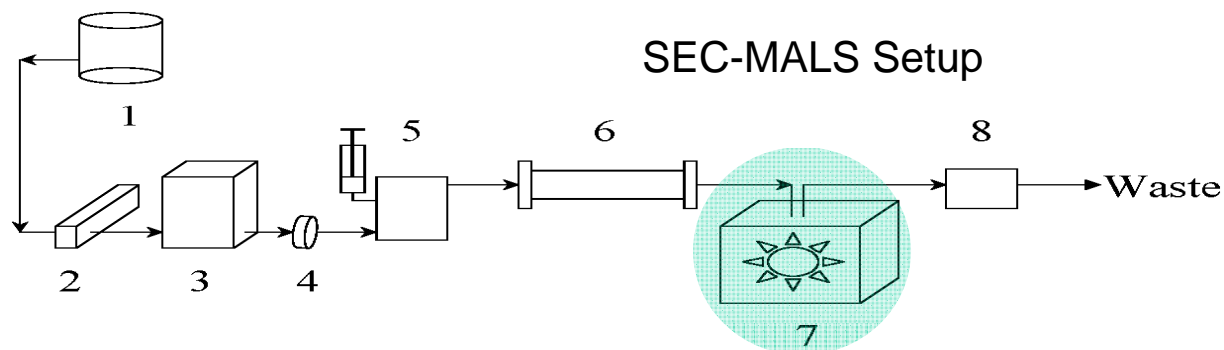
LCB in Z-N PE Resins??



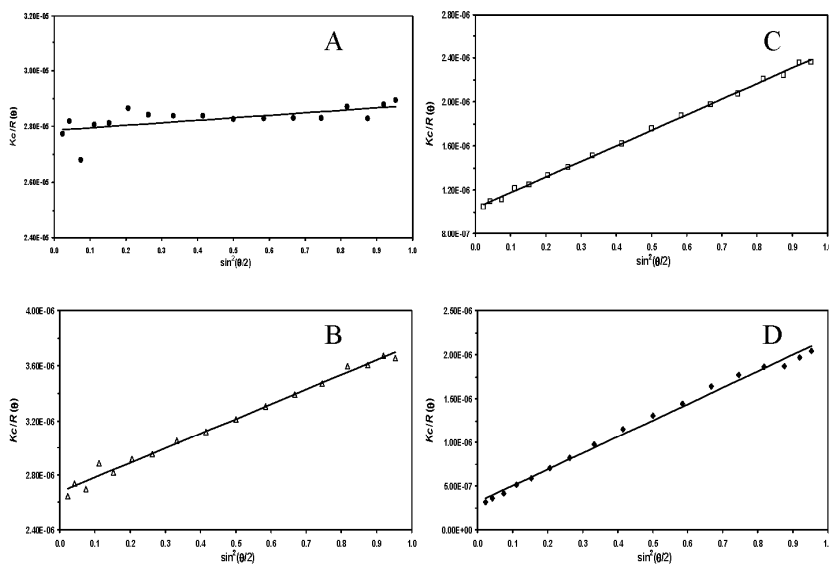
- Zero-shear viscosities of Z-N resins largely on the Arnett line
- Largely unelevated flow-activation energies
- No LCB observed by NMR

- Very low level of vinyl end-group in Z-N PE samples
 - Which led to the beliefs that Z-N catalysts do not undergo β -hydride elimination to produce the vinyl end-group necessary for macromer reinsertion, forming LCB
- Z-N resins sometimes used as linear controls in rheological tests (!)

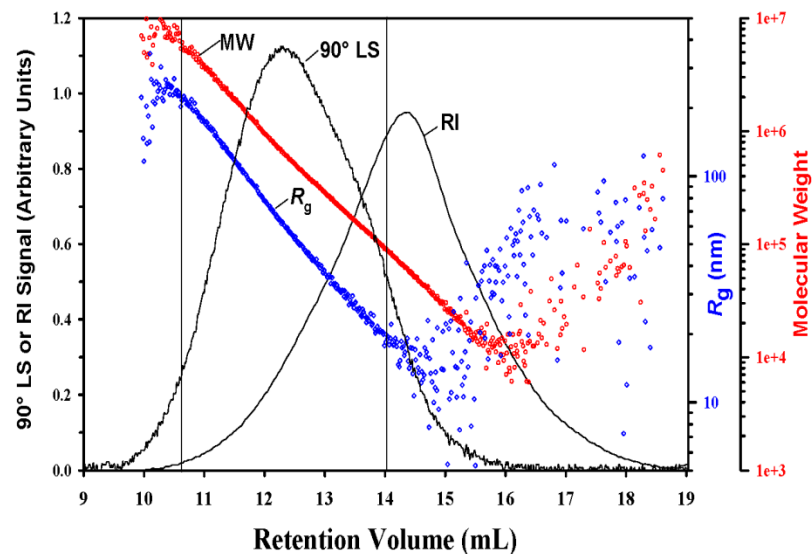
SEC-MALS



- | | | |
|----------------------|------------------|----------------|
| 1. Solvent Reservoir | 2. Degasser | 3. Pump |
| 4. In-line Filter | 5. Injector | 6. Column Bank |
| 7. MALS | 8. Refractometer | |

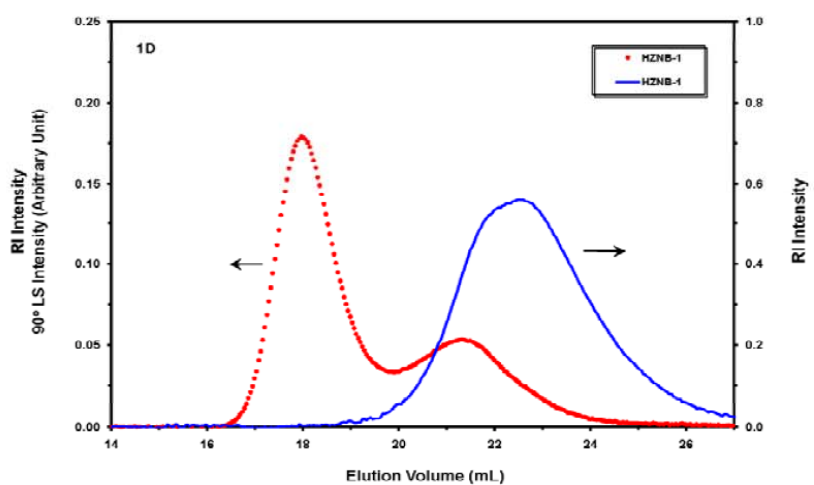
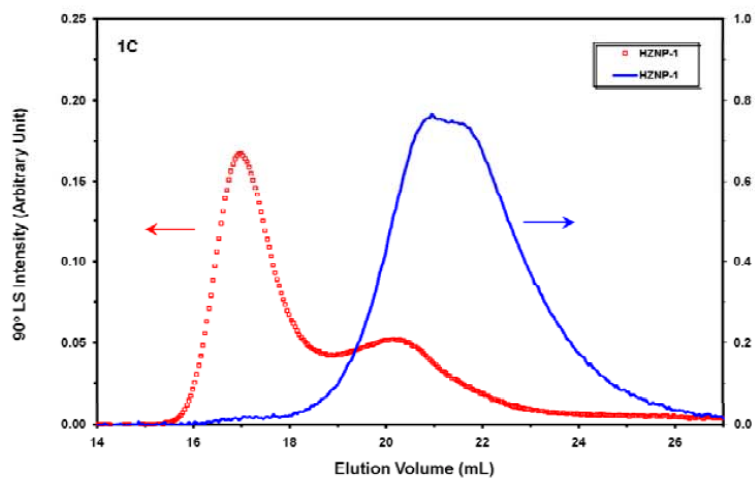
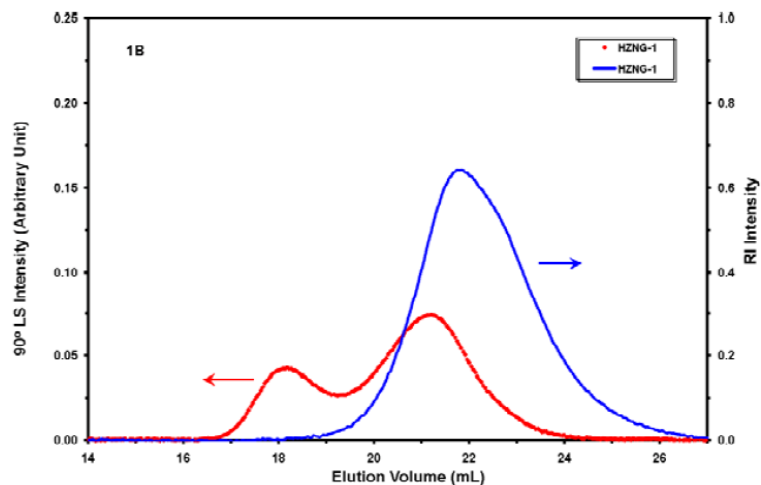
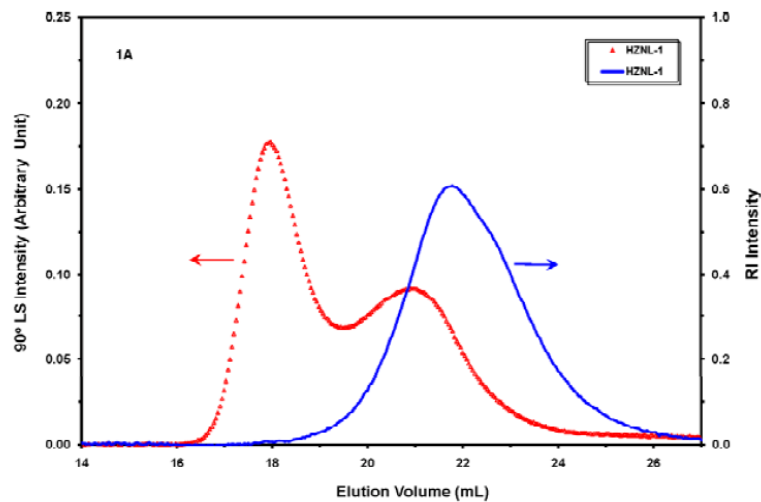


Debye Plots

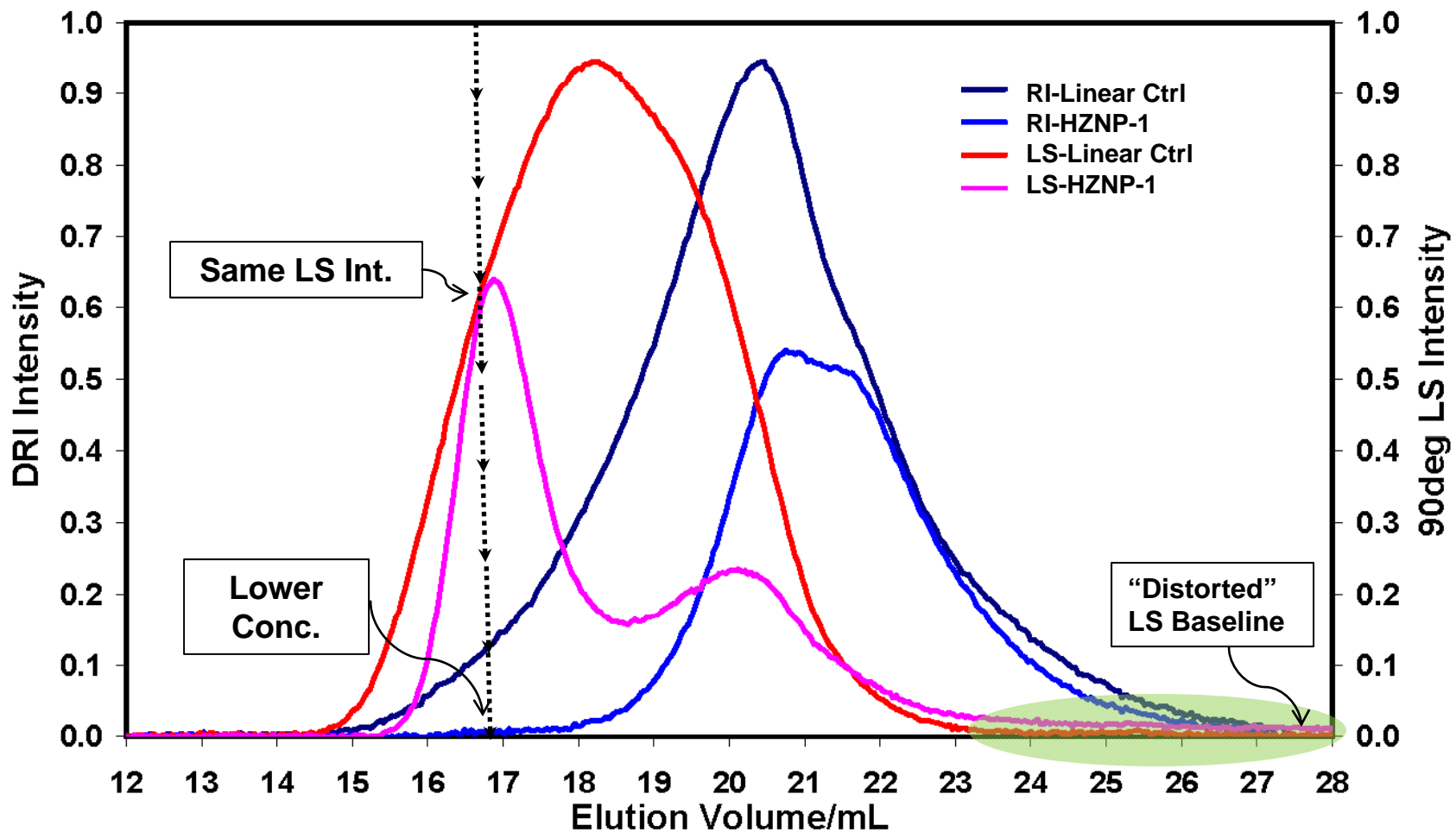


Yu, DesLauriers, Rohlfing, *Polymer*, 2005, 46, 5165

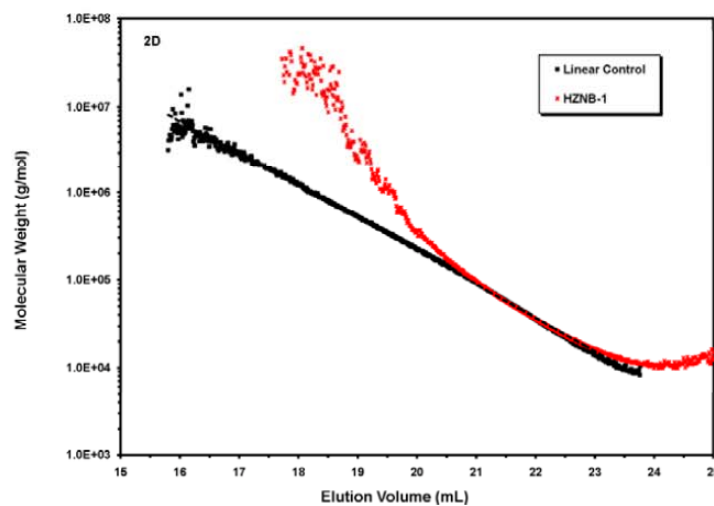
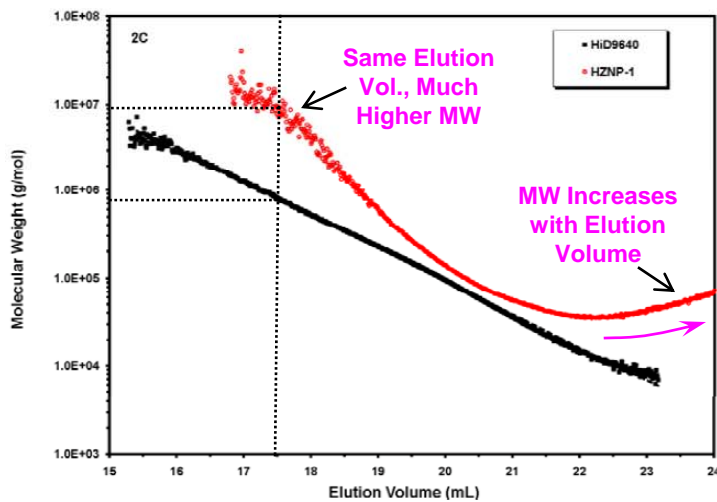
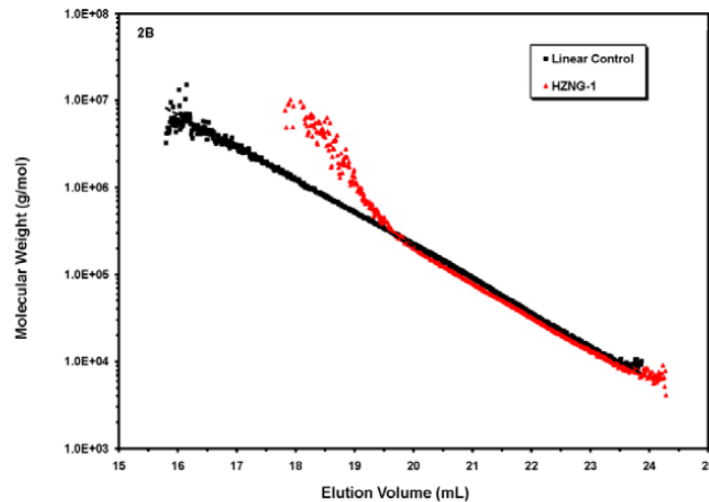
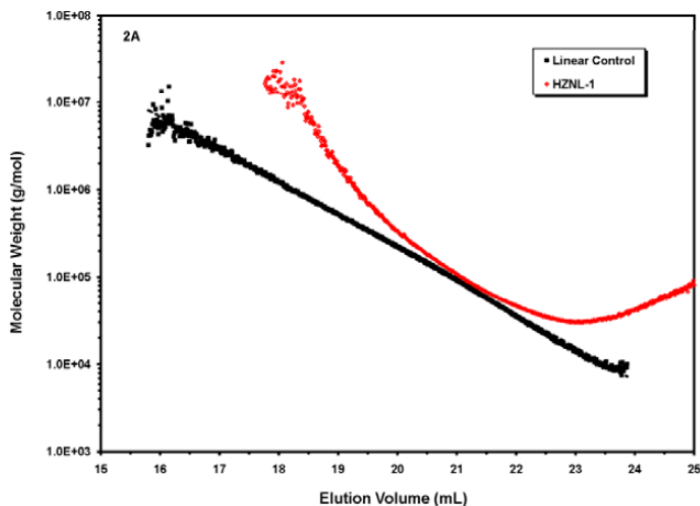
SEC-MALS of Z-N Homopolymers



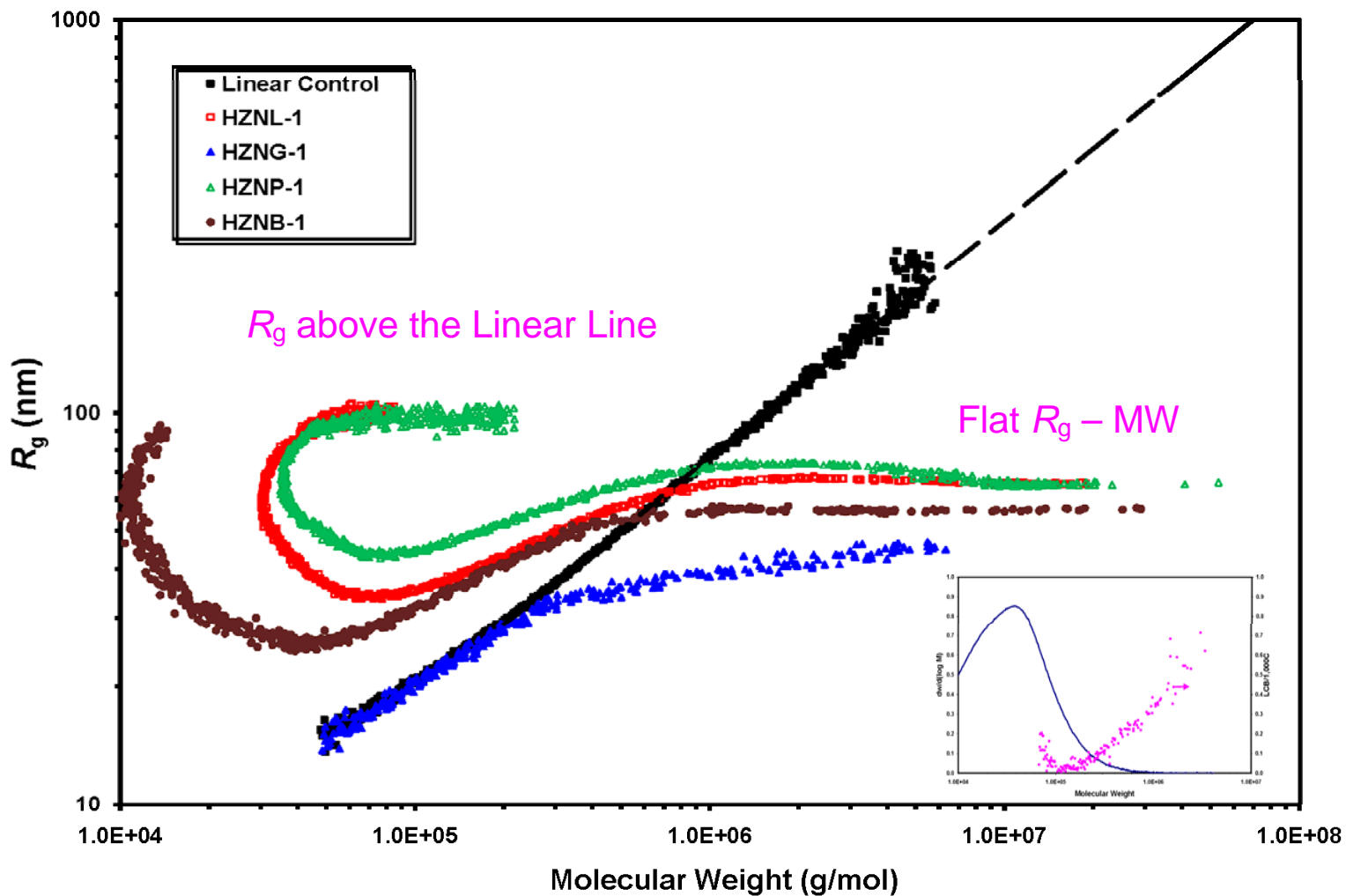
SEC-MALS of Z-N Homopolymers



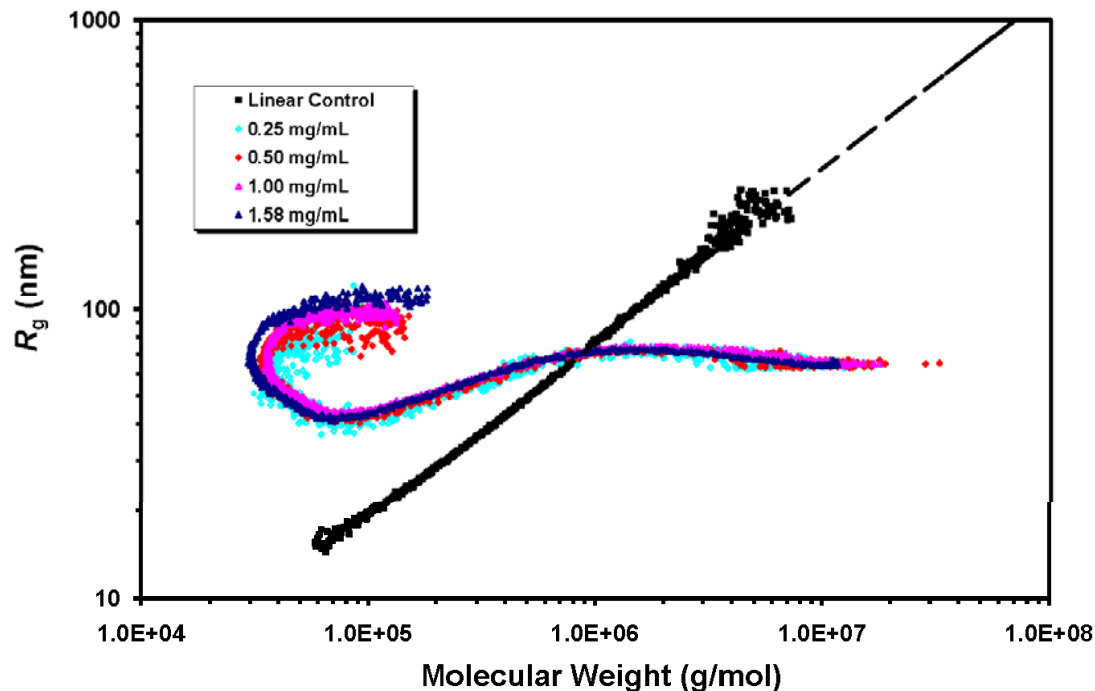
SEC-MALS of Z-N Homopolymers



SEC-MALS of Z-N Homopolymers



SEC-MALS of Z-N Homopolymers



- R_g -MW plot unaffected by diluting polymer solutions
- R_g -MW plot unchanged after being treated with acidic solutions
- Same R_g -MW plot observed for freshly made Z-N homopolymers

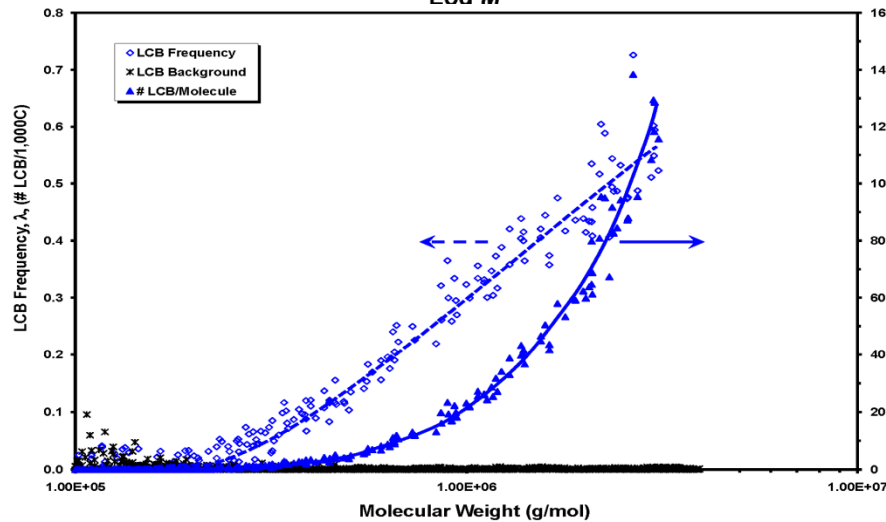
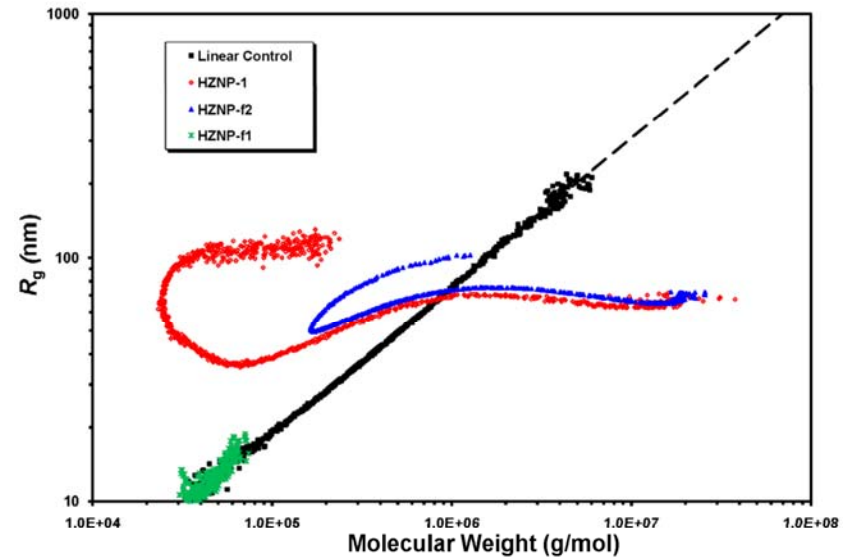
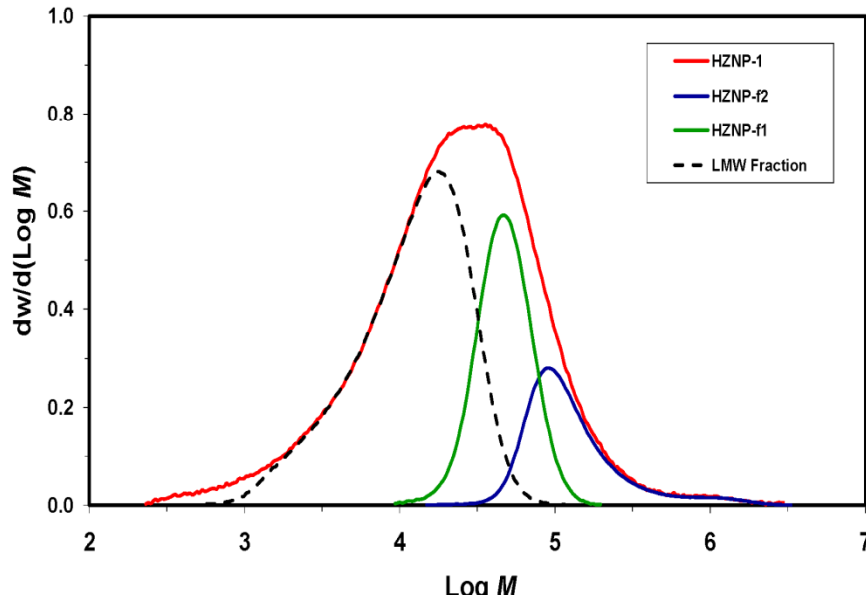
- Elution behavior inherent property of this Z-N homopolymer
- These Z-N homopolymers contain components that have compact structures, i.e. long-chain branched, or perhaps hyperbranched structures



Fractionation Studies

- Using two fractionation techniques
 - Solvent-gradient fractionation (SGF)
 - Polymer separated by molecular weight
 - No interaction between polymer and the packing material (i.e. stainless steel)
 - Preparative SEC column fractionation
 - Polymer separated by hydrodynamic volume
 - Potential interaction between eluting polymer and the column packing material (i.e. poly(styrene-co-divinylbenzene))
- To concentrate LCB in some fractions in order to see rheologic effect

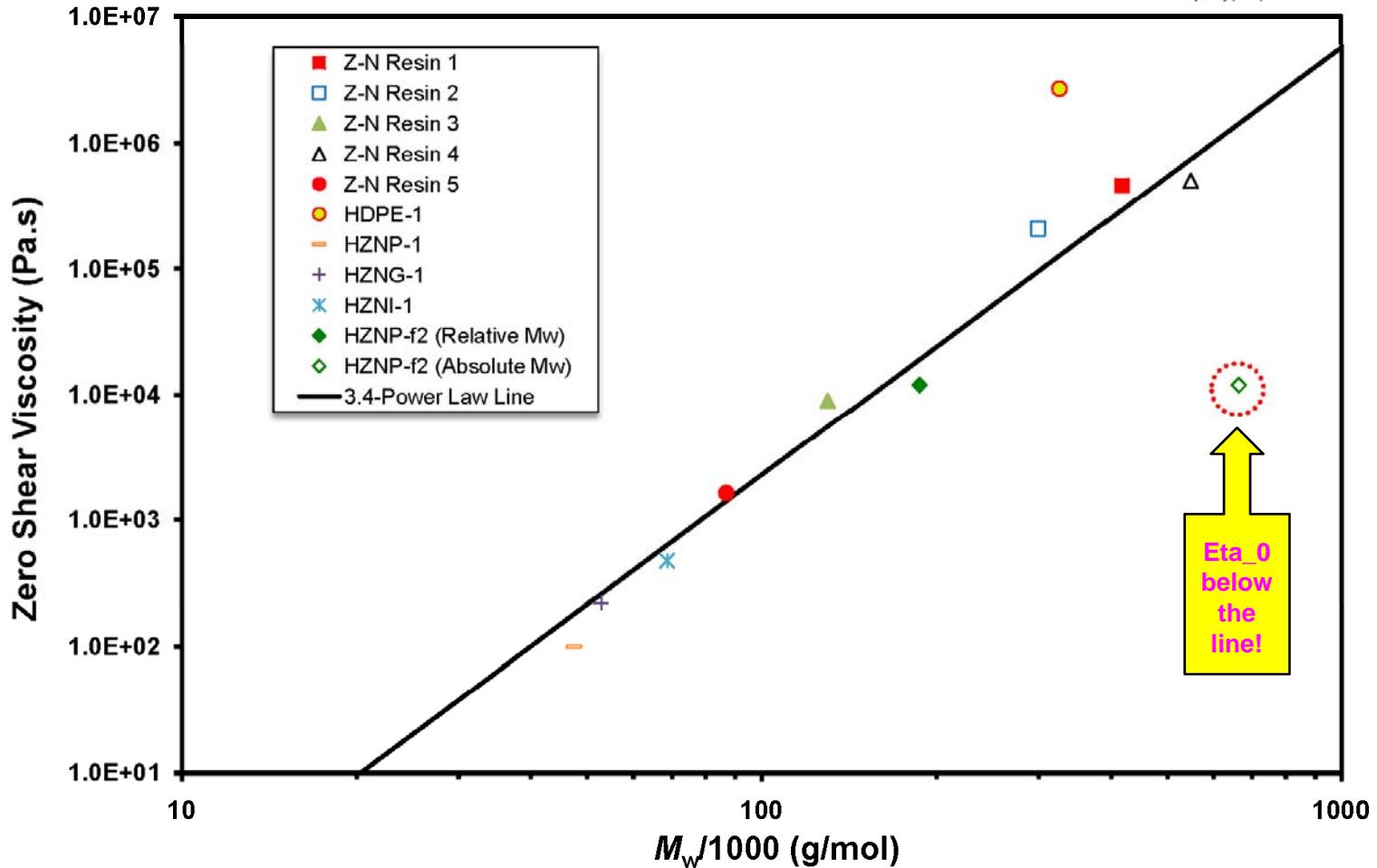
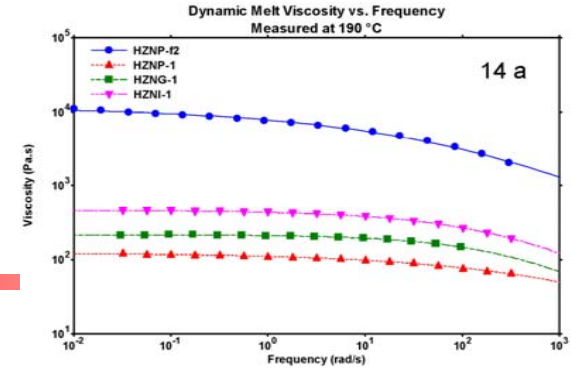
SGF Fractions



- LCBed components are located at the high MW end and concentrated in the high MW fraction
- Low MW fractions essentially linear
- LCB level at the highest MWD end where R_g is least affected by the delayed elution is at or above 0.5 LCB/1,000 TC

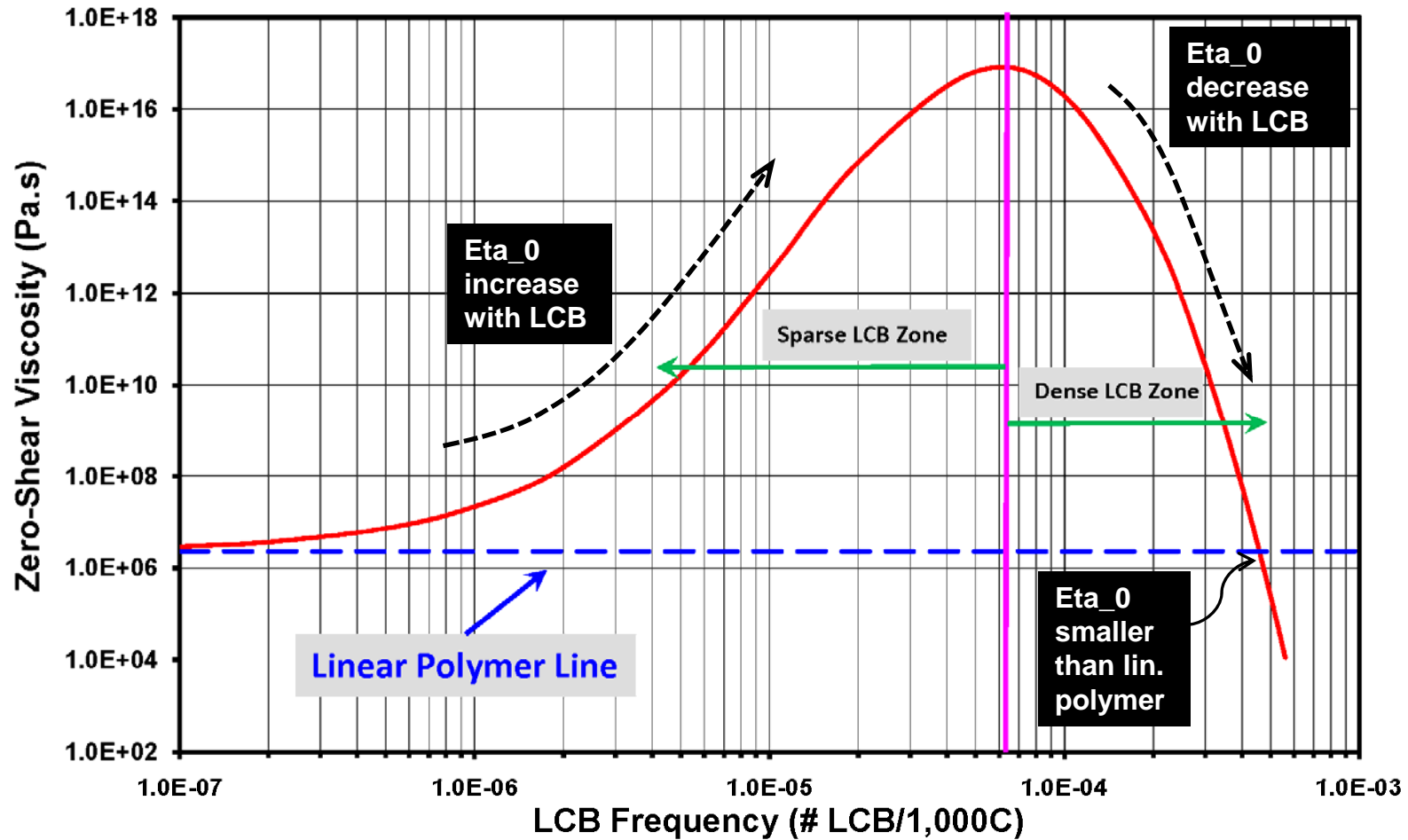


Rheology of Z-N Polymers & Fractions

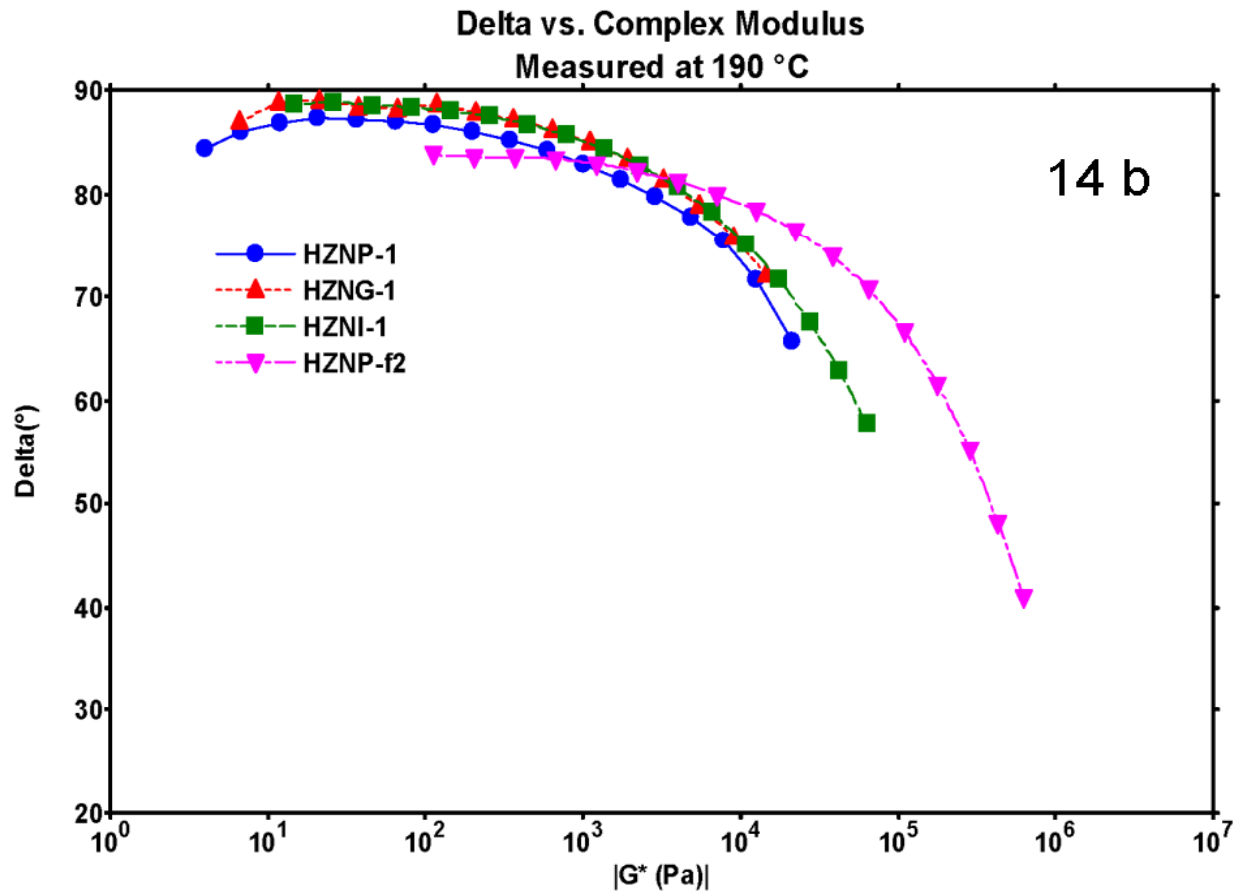




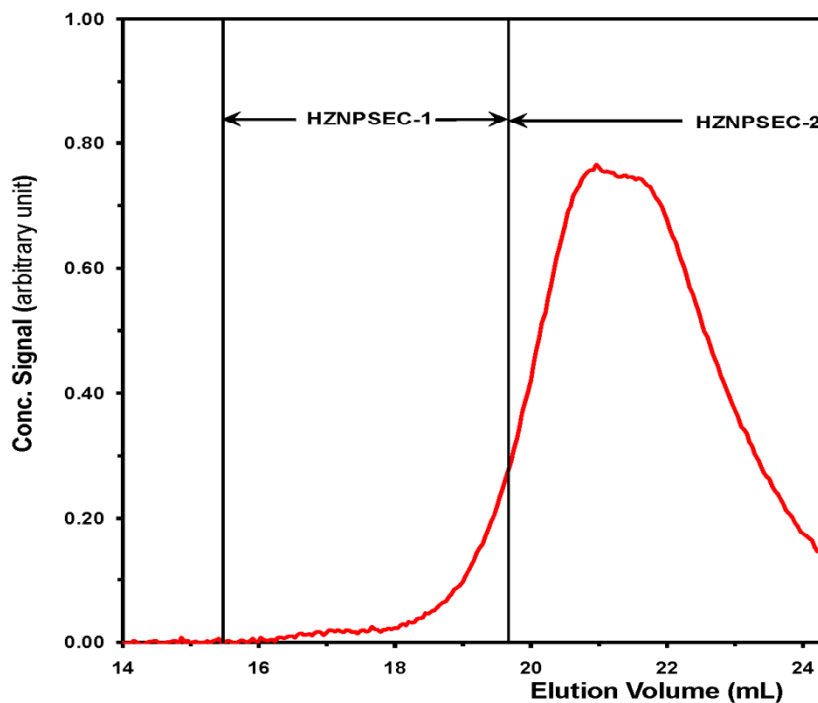
Janzen-Colby Model Simulation



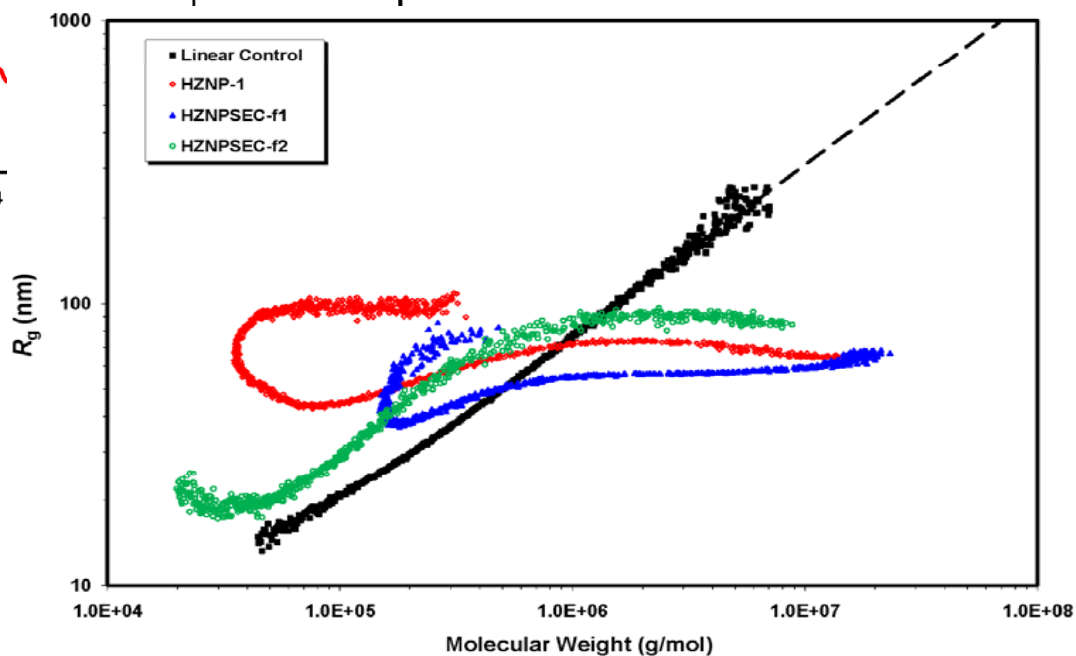
van Gorp-Palman Plot



Preparative SEC Column Fractions

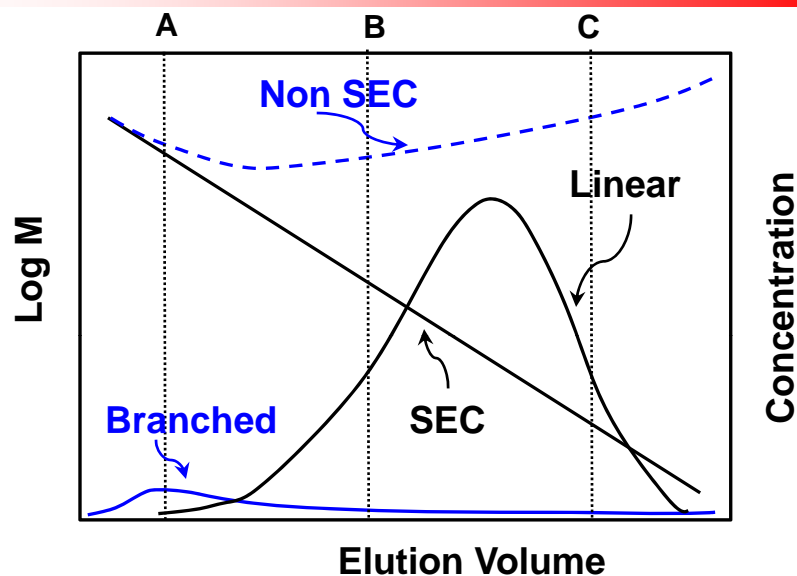


- Both of the high MW and low MW fractions contain LCBed components
- LCBed components have delayed elution on SEC columns



Root-cause of Elution Anomaly

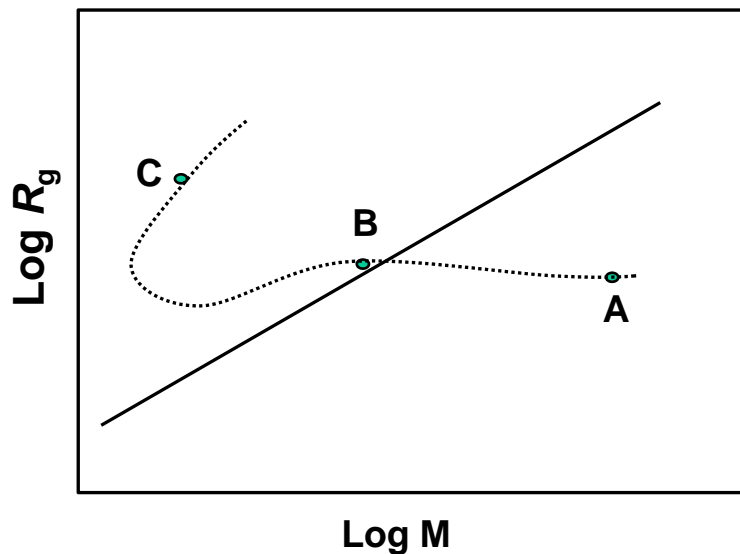
The elution anomaly is caused by the delayed elution of highly branched, high MW components.



$$M_w = \frac{\sum c_i M_i}{\sum c_i}$$

$$R_{g.z} = \sqrt{\frac{\sum c_i M_i R_{g.i}^2}{\sum c_i M_i}}$$

$$R_g = K M_i^\alpha$$



- MALS measures weight-average molecular weight (M_w) but z-average radius of gyration ($R_{g.z}$)
- When a SEC slice is polydispersed, the measured (or the apparent) $R_{g.z}$ is heavily biased towards larger R_g components. The larger the polydispersity of the slice, the larger the apparent $R_{g.z}$.



Conclusions

- Long-chain branches (LCB), perhaps hyperbranches, are observed in all Z-N homopolymers studied
- LCBs are concentrated in the high MW end while the rest of the polymers appear to be essentially linear
- Some LCBed macromolecules appear to have strong interaction with SEC packing material, causing delayed elution, and consequently, resulting in anomalous elution behavior in SEC-MALS
- LCBed species in these Z-N homopolymers appear to have poor entanglement with their neighbors in the melts, perhaps due to their hyperbranched nature



Acknowledgements

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THANK YOU!