



The Use of Statistical Modeling and Chromatography to Characterize both Long Chain and Short Chain Branching in Polyolefins

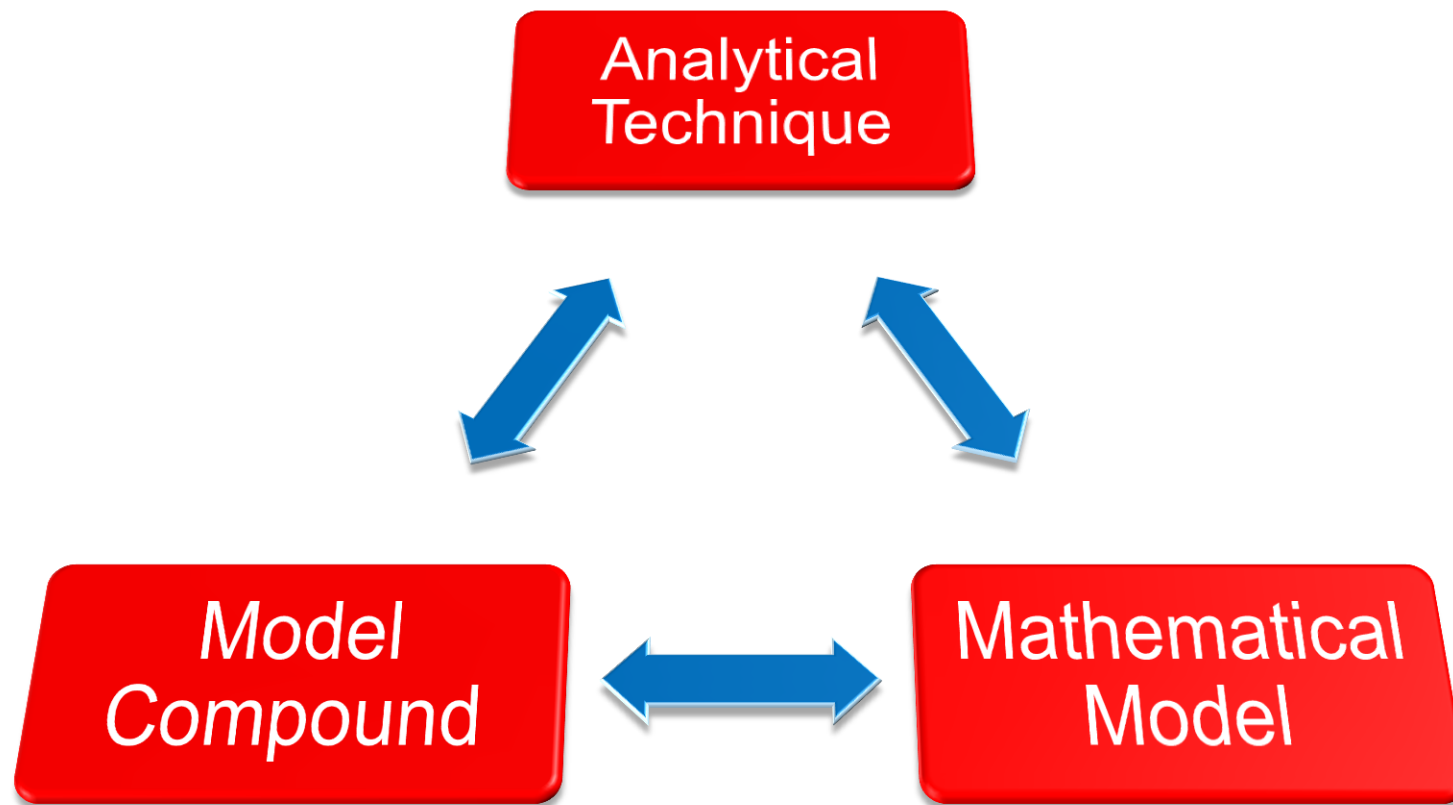
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- Mathematical Models
- Model Compounds
- GPC and Triple Detector GPC
- Examples
 - Linear Batch Reactor
 - Continuous Linear
 - LCB Continuous
 - SCBD Blends
- Conclusions

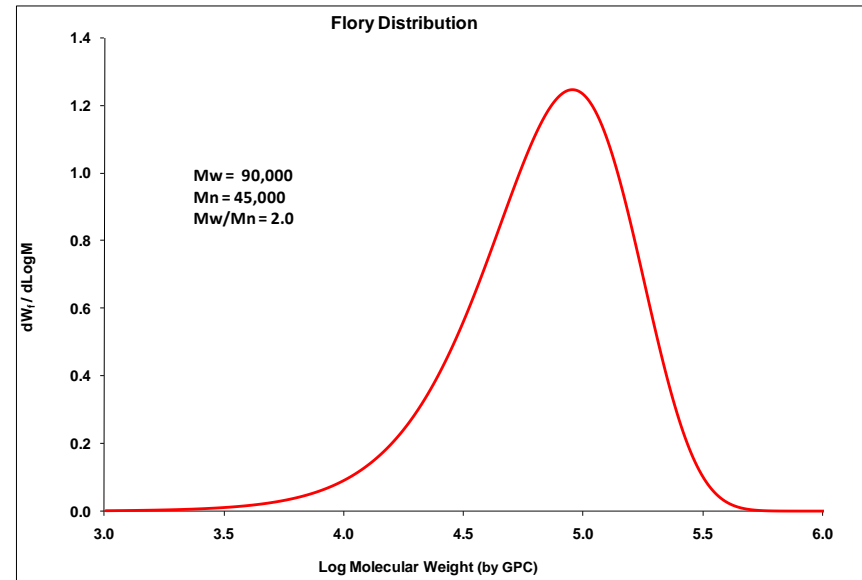
$$w_{\log MW} = 2.3026xMW^2\hat{\tau}^2 \exp(-MW\hat{\tau})$$

Where:

$w_{\log MW}$ = Molecular Weight Distribution

MW = Molecular Weight

$$\tau = \frac{1}{M_n}$$





$$f(r, n) = \frac{2}{(2n)!} r^{2n} \tau^{2n+1} \exp(-r\tau)$$

$f(r, n)$ = frequency distribution of chain lengths

r = chain length

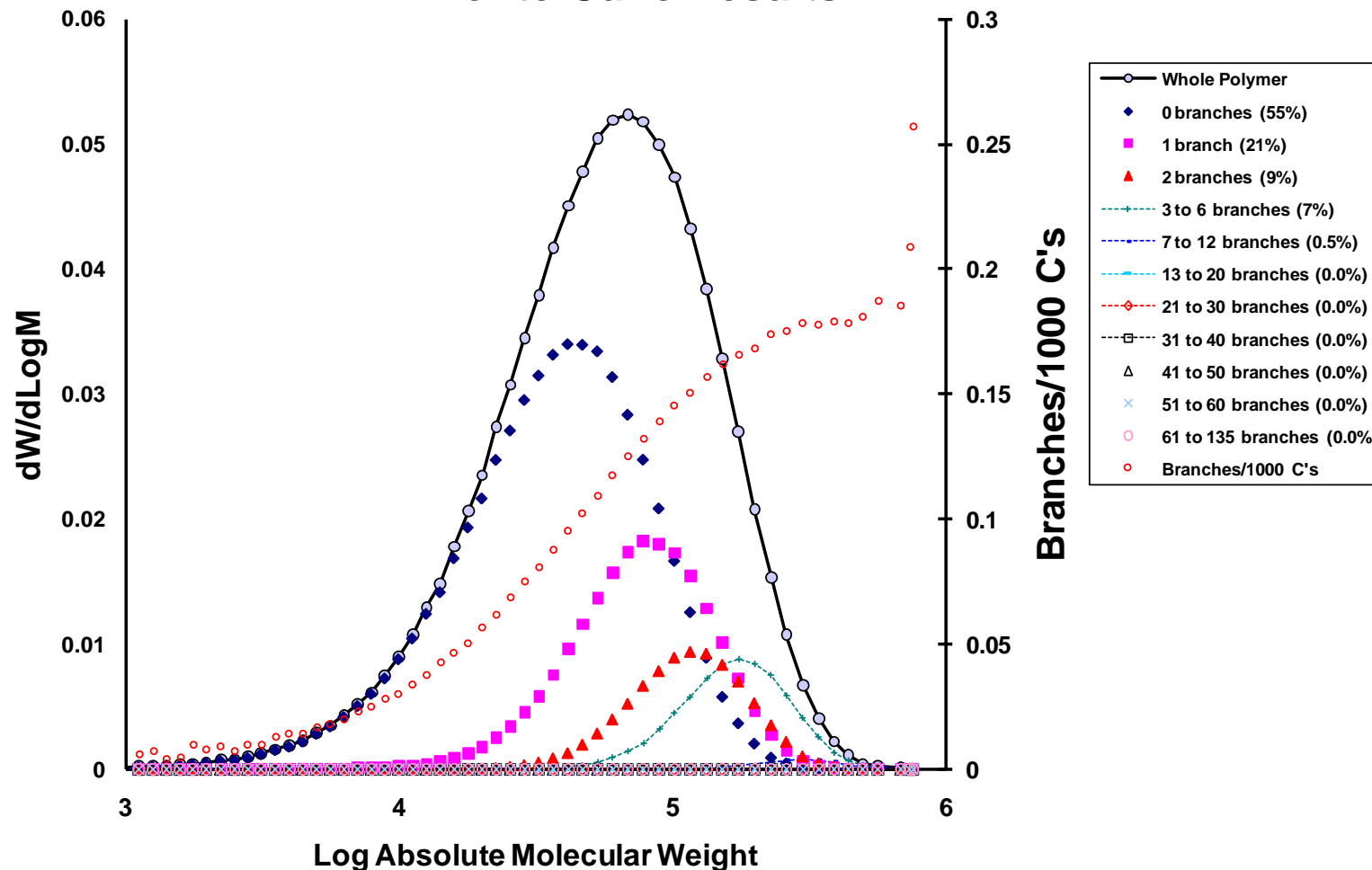
n = lcb/chain

τ = relates to propagation rate constant of vinyl terminated dead polymer and propagation rate constant for monomer

Model Results for 0.1 Branches/1,000 Carbons



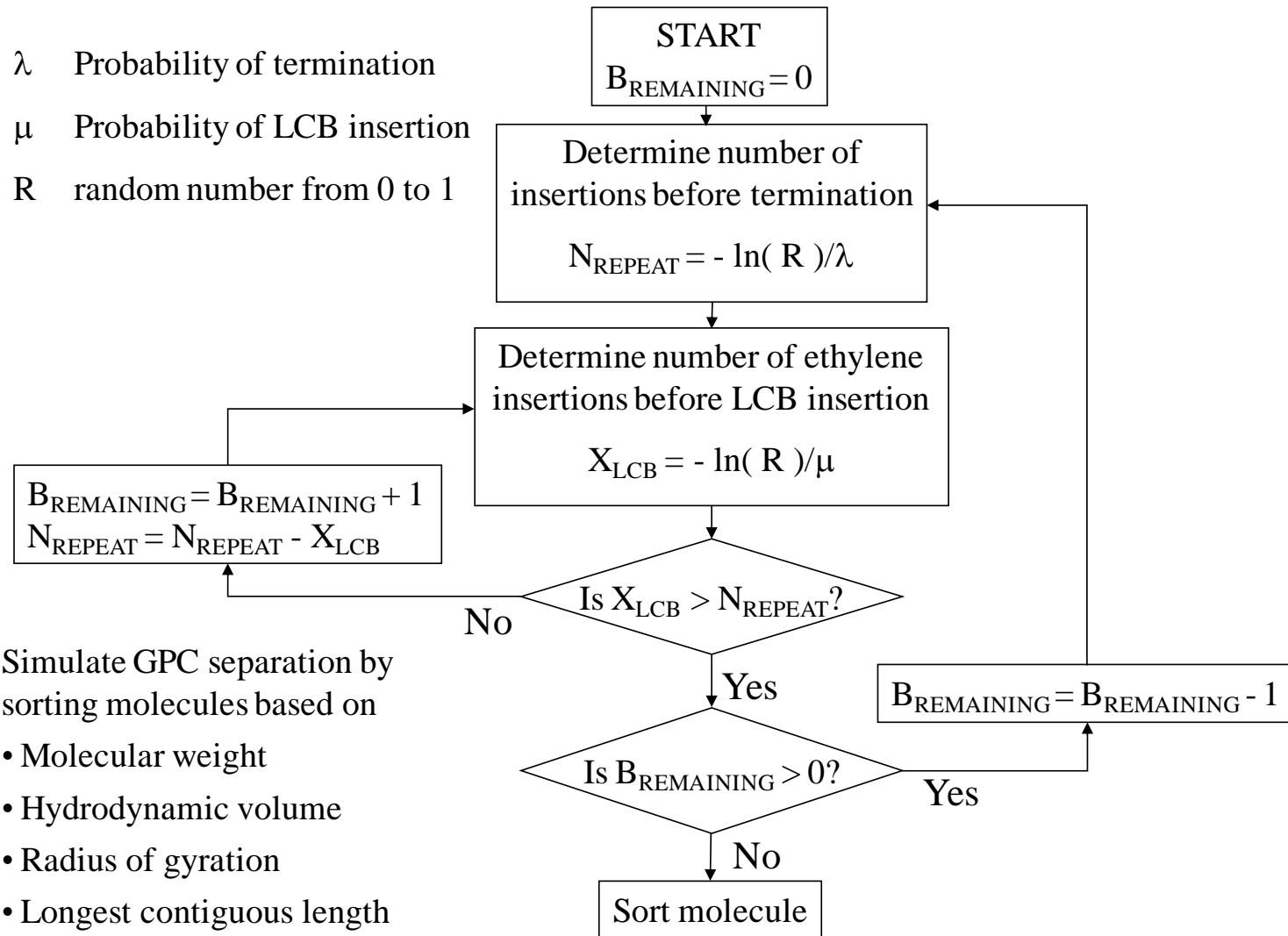
Monte-Carlo Results



Monte-Carlo Fractionation



- λ Probability of termination
- μ Probability of LCB insertion
- R random number from 0 to 1



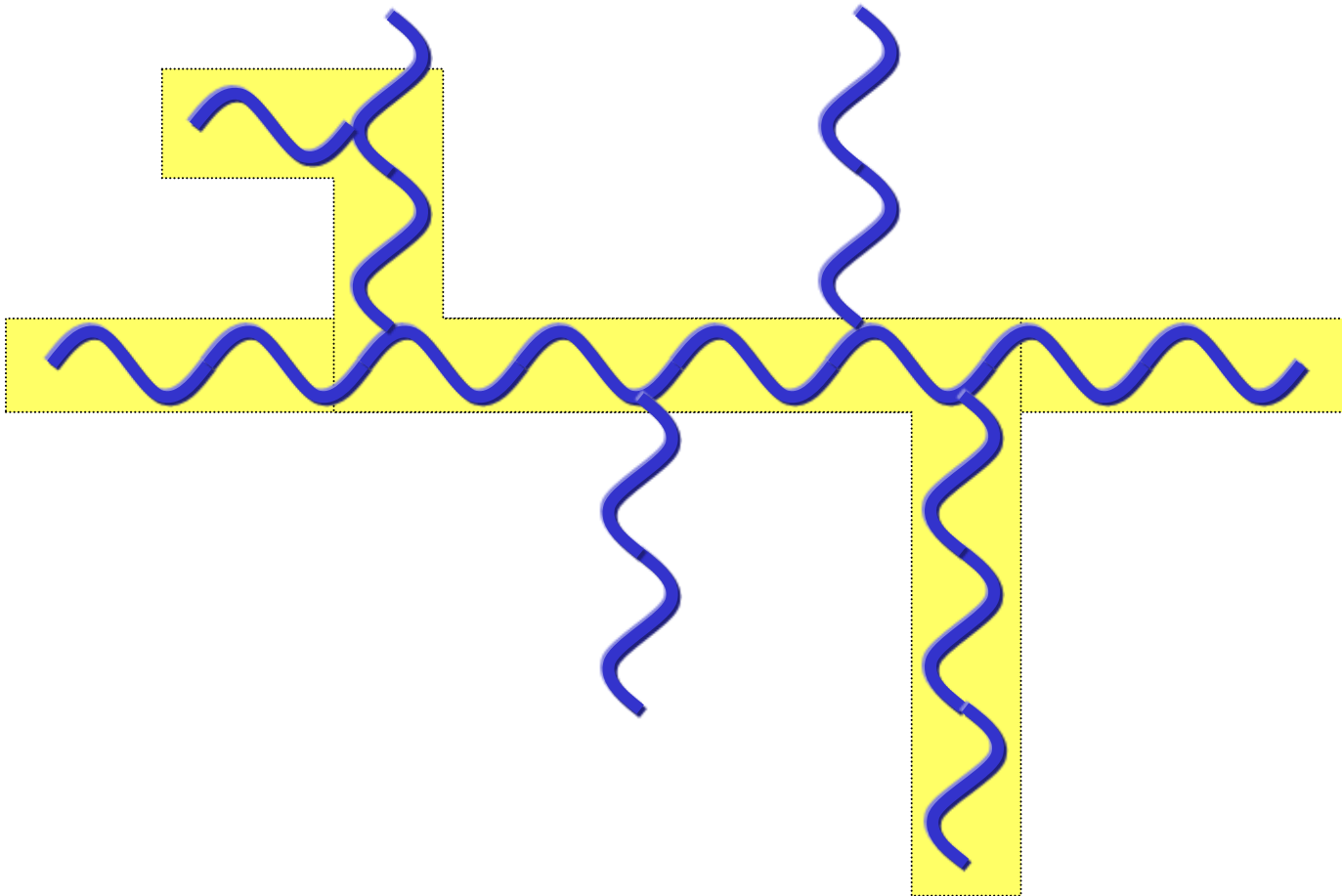
Simulate GPC separation by sorting molecules based on

- Molecular weight
- Hydrodynamic volume
- Radius of gyration
- Longest contiguous length

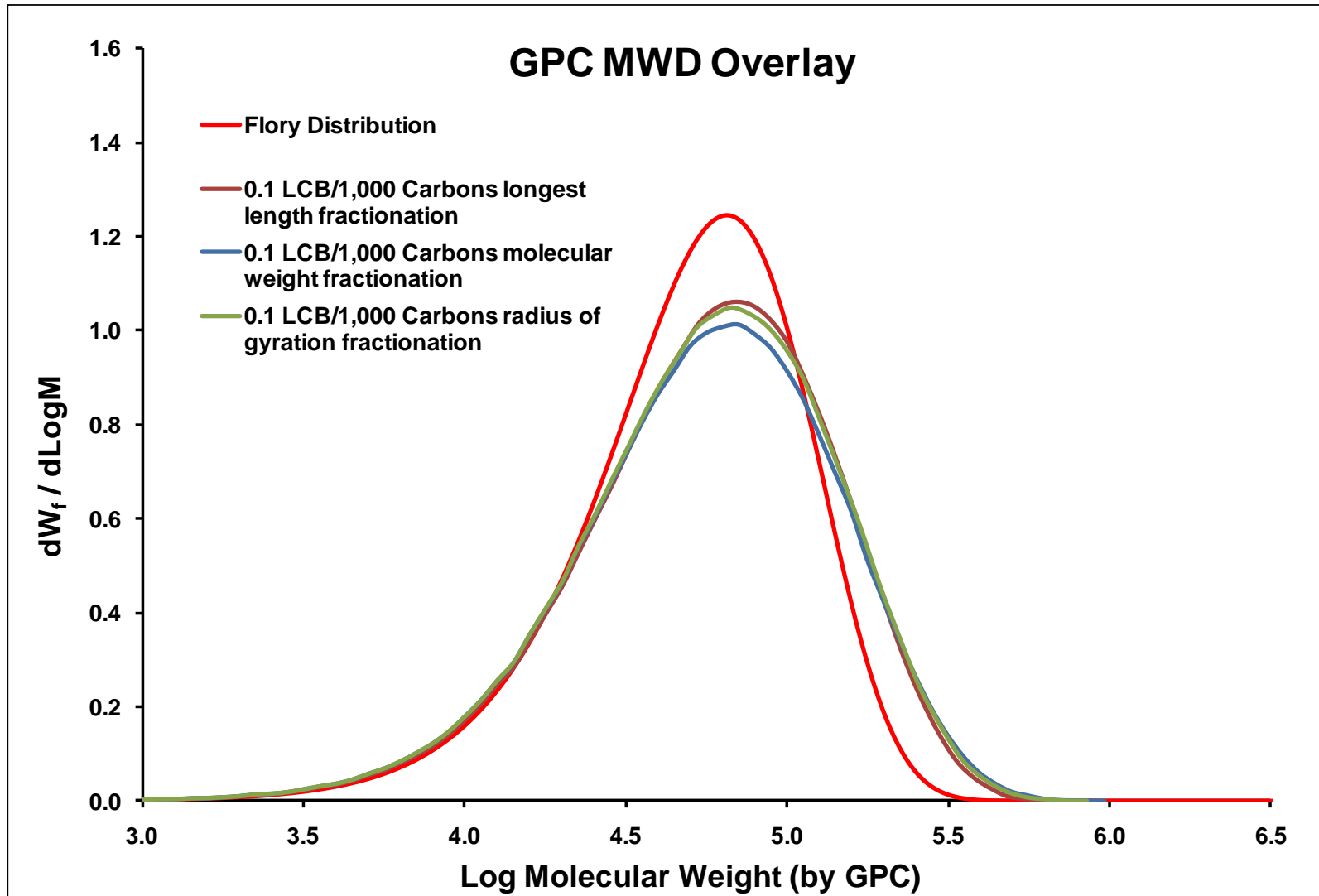
GPC Fractionation Process



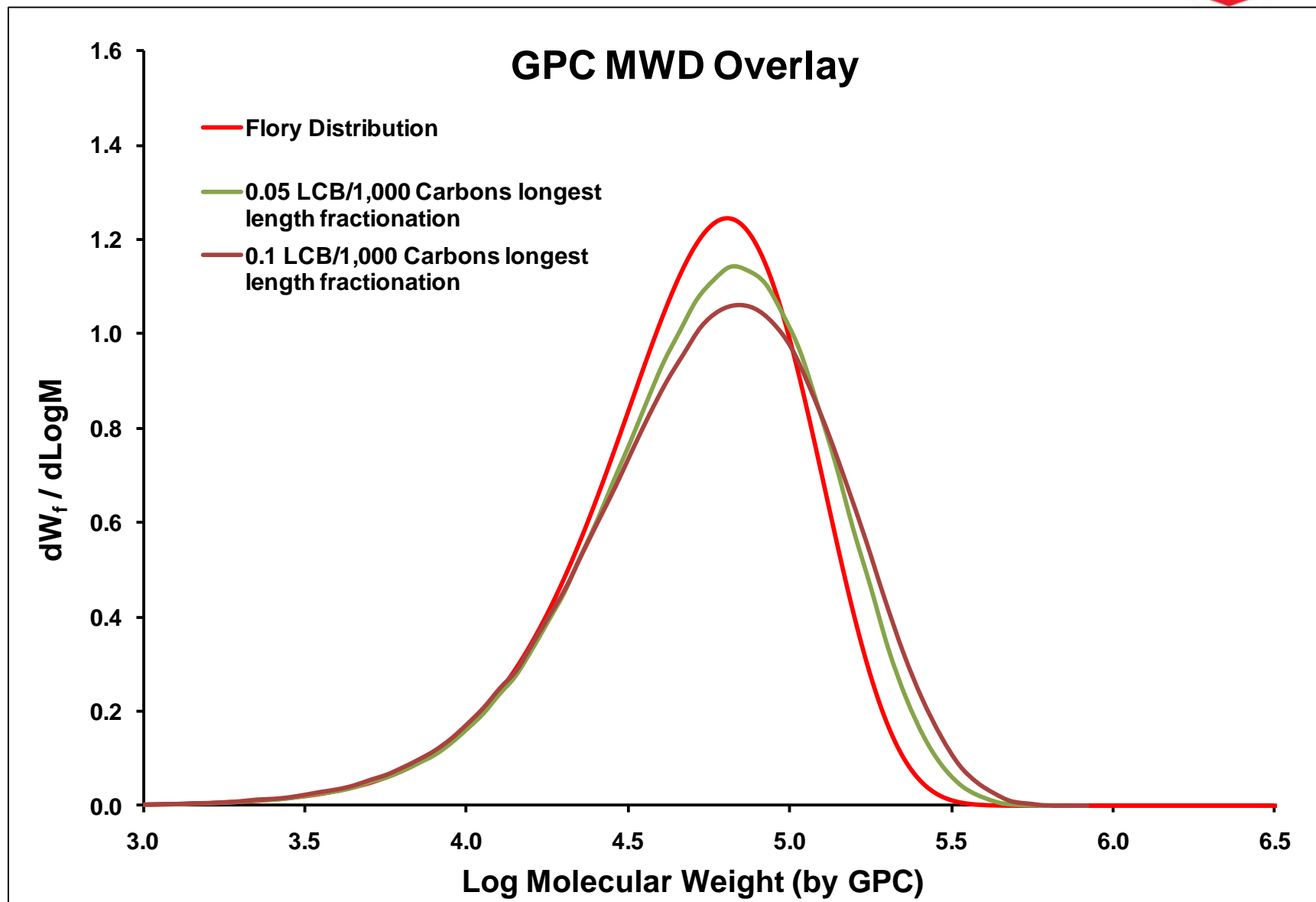
Does GPC sort by total chain length. . .
. . .or longest contiguous length?



Model Data for GPC Fractionation



Effect of LCB Level on Model MWD





$$g = \left[\left(1 + \frac{B_n}{7} \right)^{1/2} + \frac{4}{9} \frac{B_n}{\pi} \right]^{-1/2}$$

g = Zimm-Stockmayer Branching Factor

B_n = Branches per Number Average Molecular Weight

Branching Equations



$$g = \left[\frac{\langle R_g^2 \rangle_b}{\langle R_g^2 \rangle_l} \right]_M$$

$$g' = \left[\frac{[\eta]_b}{[\eta]_l} \right]_M$$

$$g' = g^\varepsilon$$

R_g^2 = radius of gyration squared

η = intrinsic viscosity

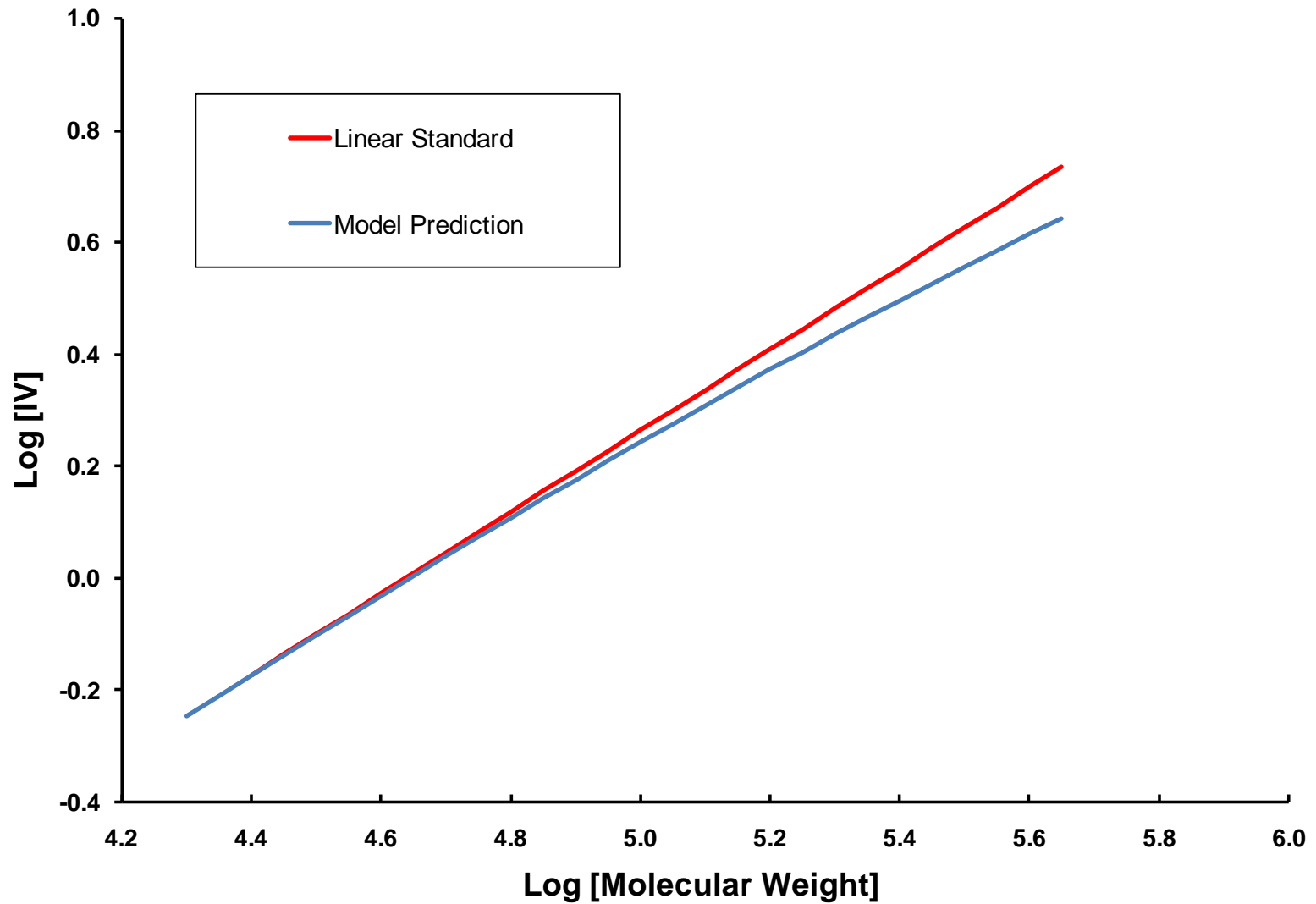
b = signifies branched molecules

l = signifies linear molecules

M = molecular weight

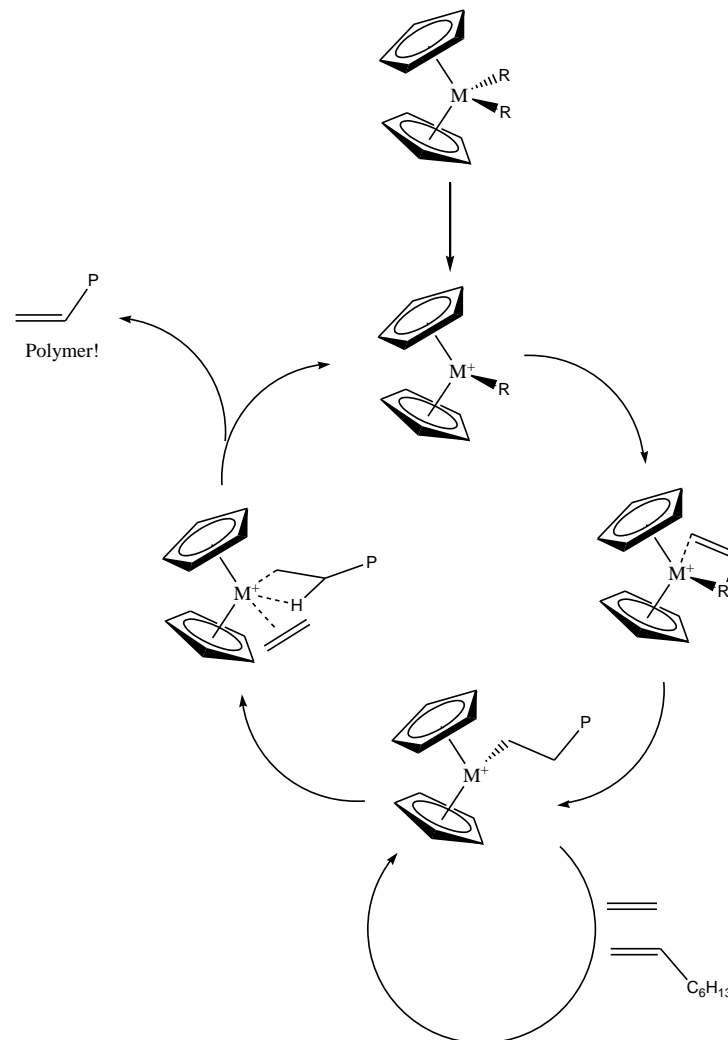
ε = determined experimentally to equal 0.5

Model Results for MH Plot of 0.1 Branches/1,000 Carbons



Batch or Continuous Process

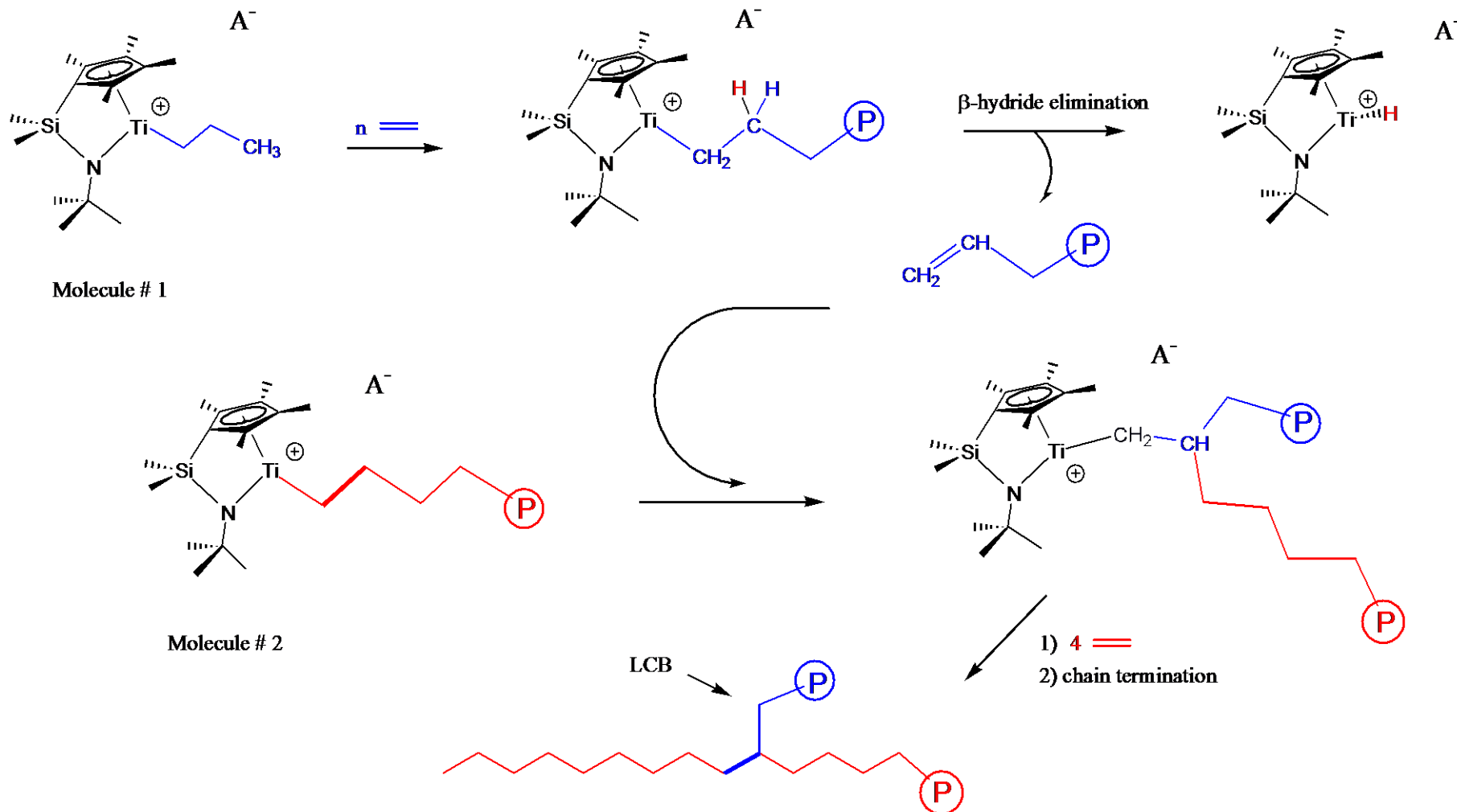
- **Activation:** create an olefin binding site.
- **Initiation:** the first monomer inserts.
- **Propagation:** monomers insert to build the chain.
 - » Molecular structure is constructed.
- **Termination:** A chain is released, and a new chain initiates.



Model Compounds – Polyethylene with LCB



Continuous Process



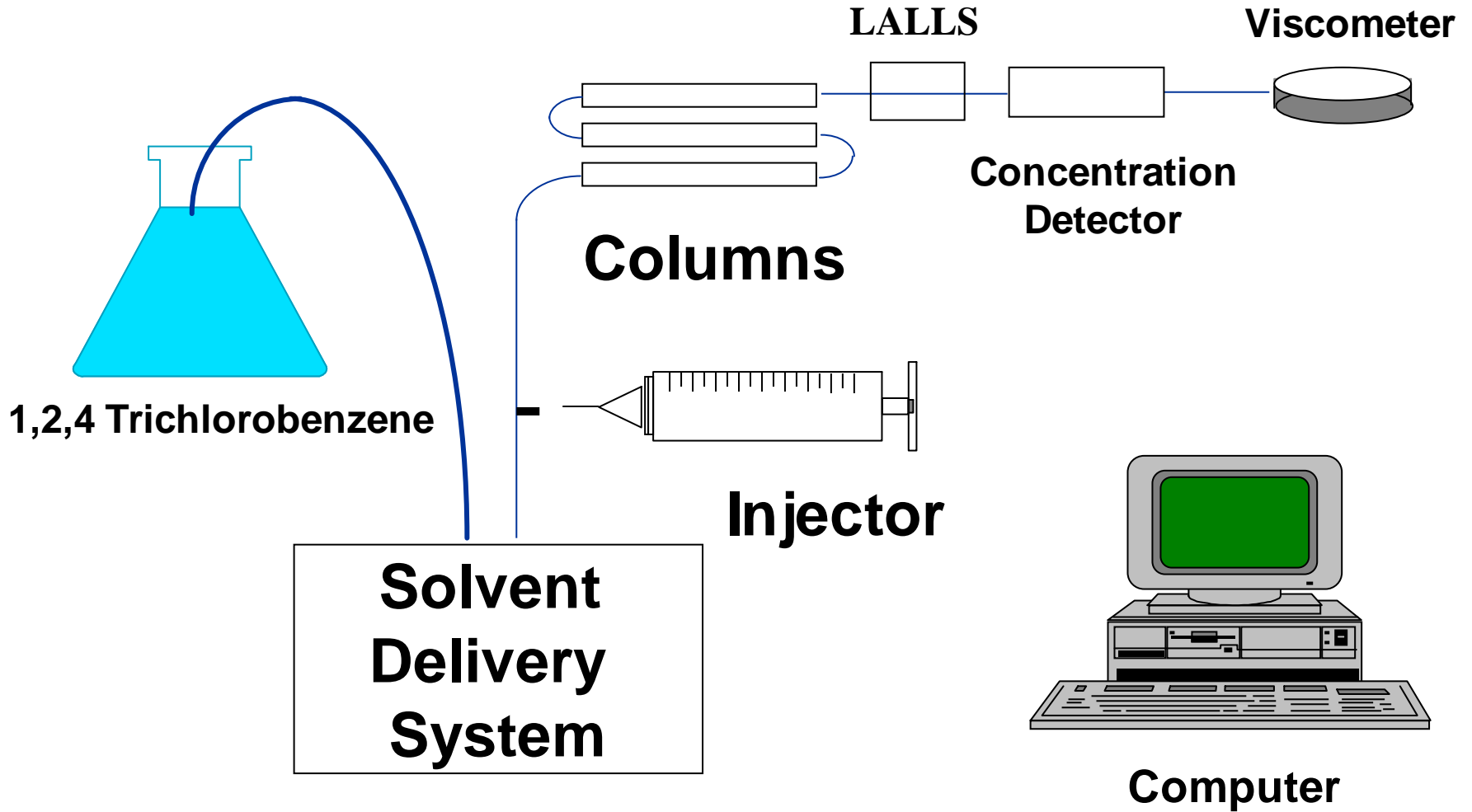
Molecular Weight and LCB Distribution Determination

Sample Description	Mn	Mw	Mw/Mn
Batch Reactor Sample A	24400	50900	2.09
Batch Reactor Sample B	41900	84000	2.00
Continuous Reactor Sample A	52700	105500	2.00
Continuous Reactor LCB Sample A	33700	79800	2.37

Comonomer Distribution Determination

Sample Description	Molecular Weight	MWD	Mole % Comonomer
Component A	~115000	2	1.3
Component B	~115000	2	0

Triple Detector GPC



GPC Analysis of Single Site Polymer MWD



Flory (Most Probable) MWD

$$\left[\frac{dW(M)}{dM} \right] = (M / M_n^2) \cdot \exp(-M / M_n)$$

$$\left[\frac{dW(\text{Log}M)}{d\text{Log}M} \right] = (M^2 / M_n^2) \cdot \exp(-M / M_n)$$

Converting to GPC elution curve $w(V)$

$$w(V) = \left[\frac{dW(V)}{dV} \right] = \left[\frac{dW(\text{Log}M)}{d\text{Log}M} \right] \cdot \left[\frac{d\text{Log}M}{dV} \right]$$

$$\text{where } \left[\frac{d\text{Log}M}{dV} \right] = \text{slope GPC calibration}$$

GPC Modeling Using Tung's Axial Dispersion Equation*

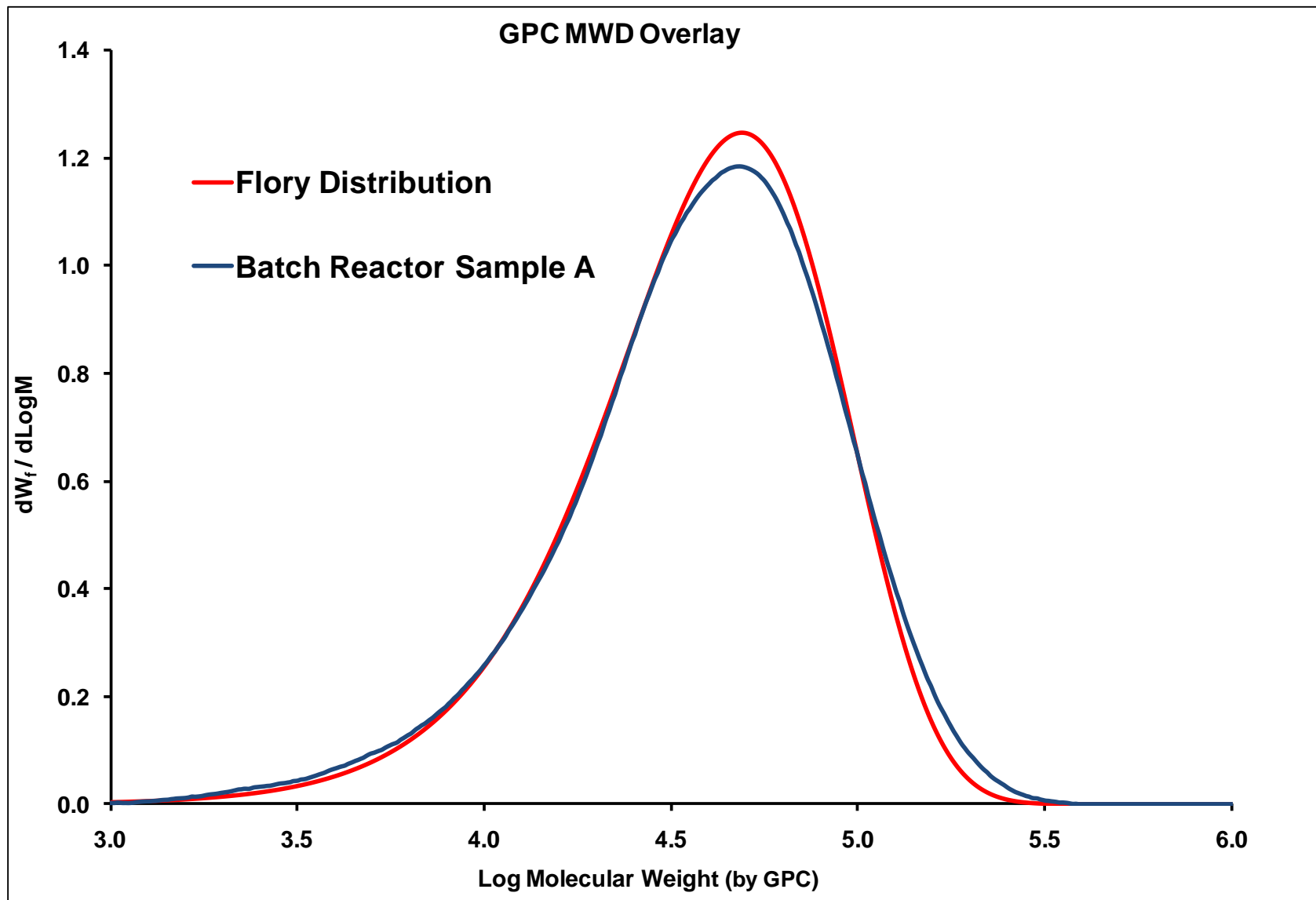
Model Prediction of GPC Curve Convolutd with Axial Dispersion

$$F(V) = \int w(y) \cdot G(V - y) dy \quad \text{where, } G(V - y) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(V-y)^2/2\sigma^2}$$

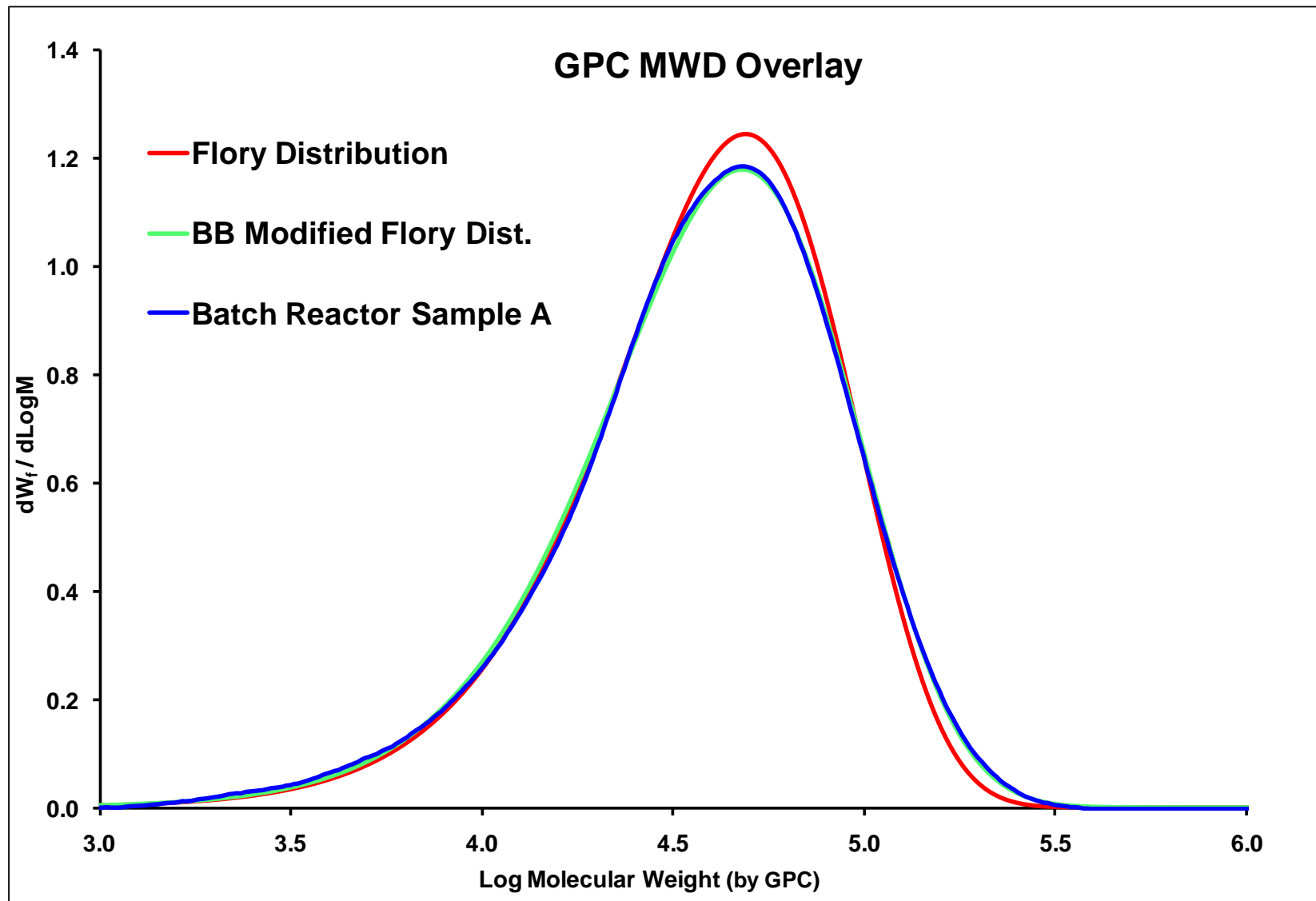
where, σ = Gaussian axial dispersion standard deviation

* L. H. Tung, J. C. Moore, G. W. Knight, J. Appl. Polym. Sci. Vol. 10, 1261 (1966)

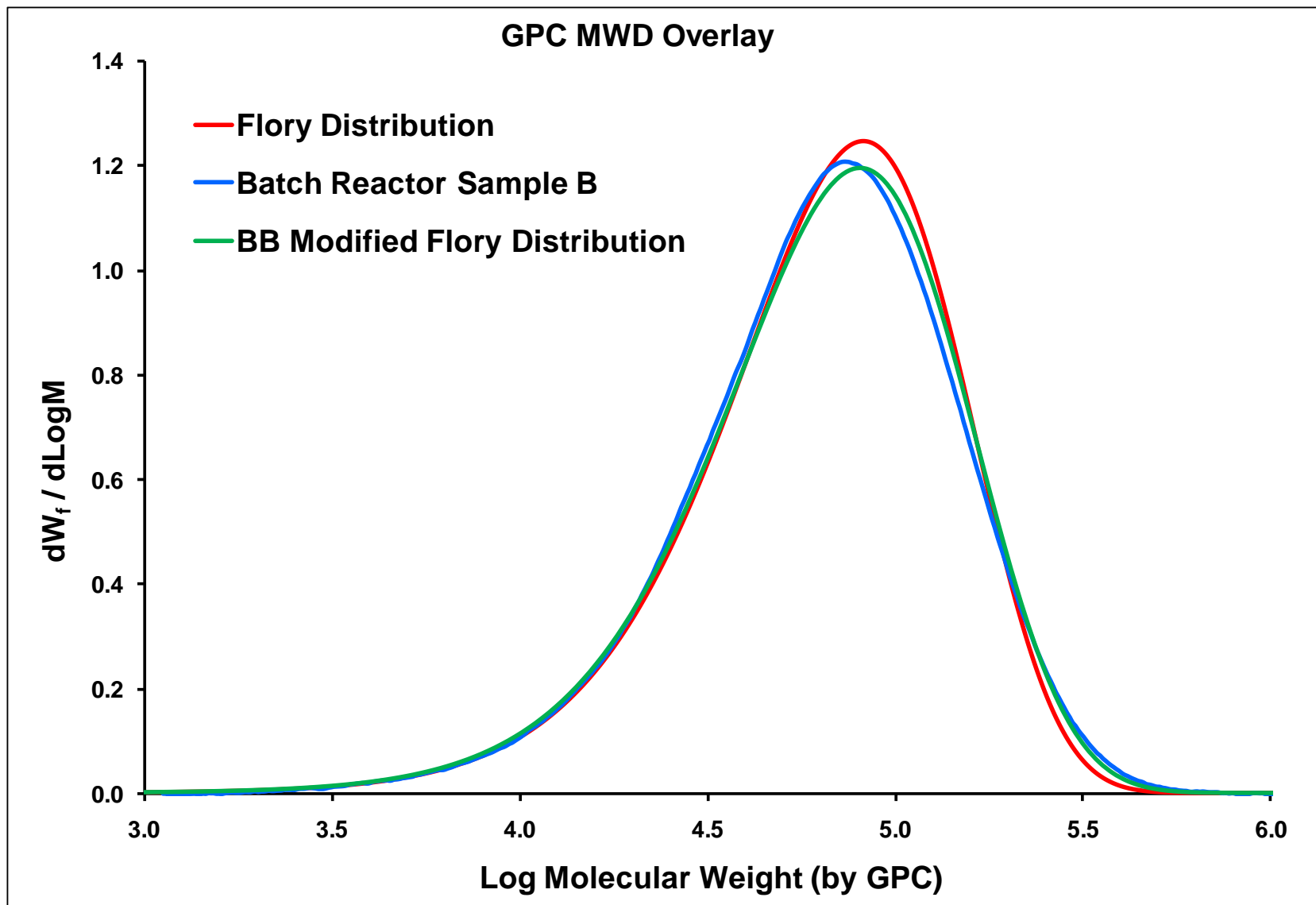
Flory Distribution Versus Measured Distribution



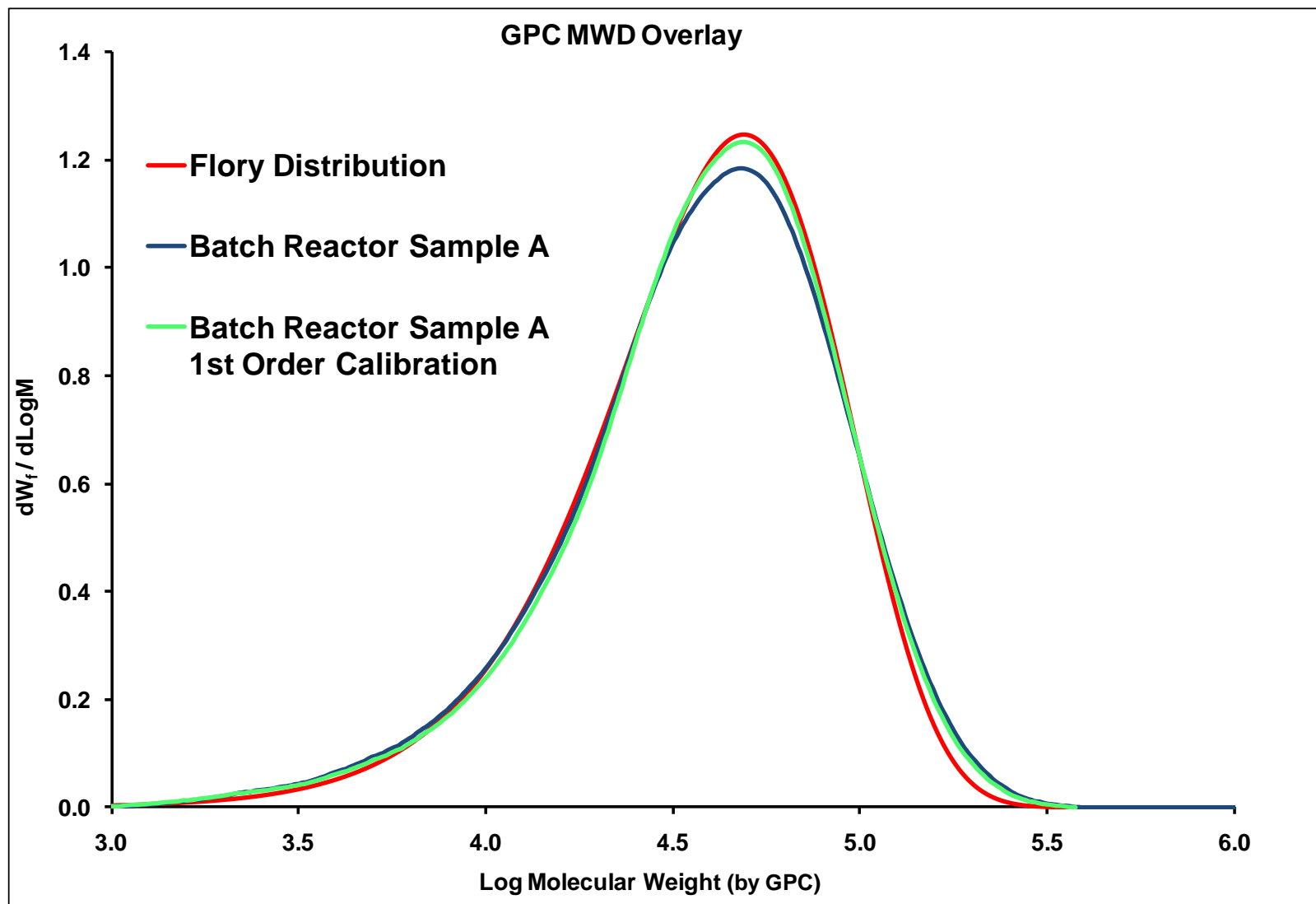
BB Modified Flory Distribution Versus Batch Reactor Sample #2



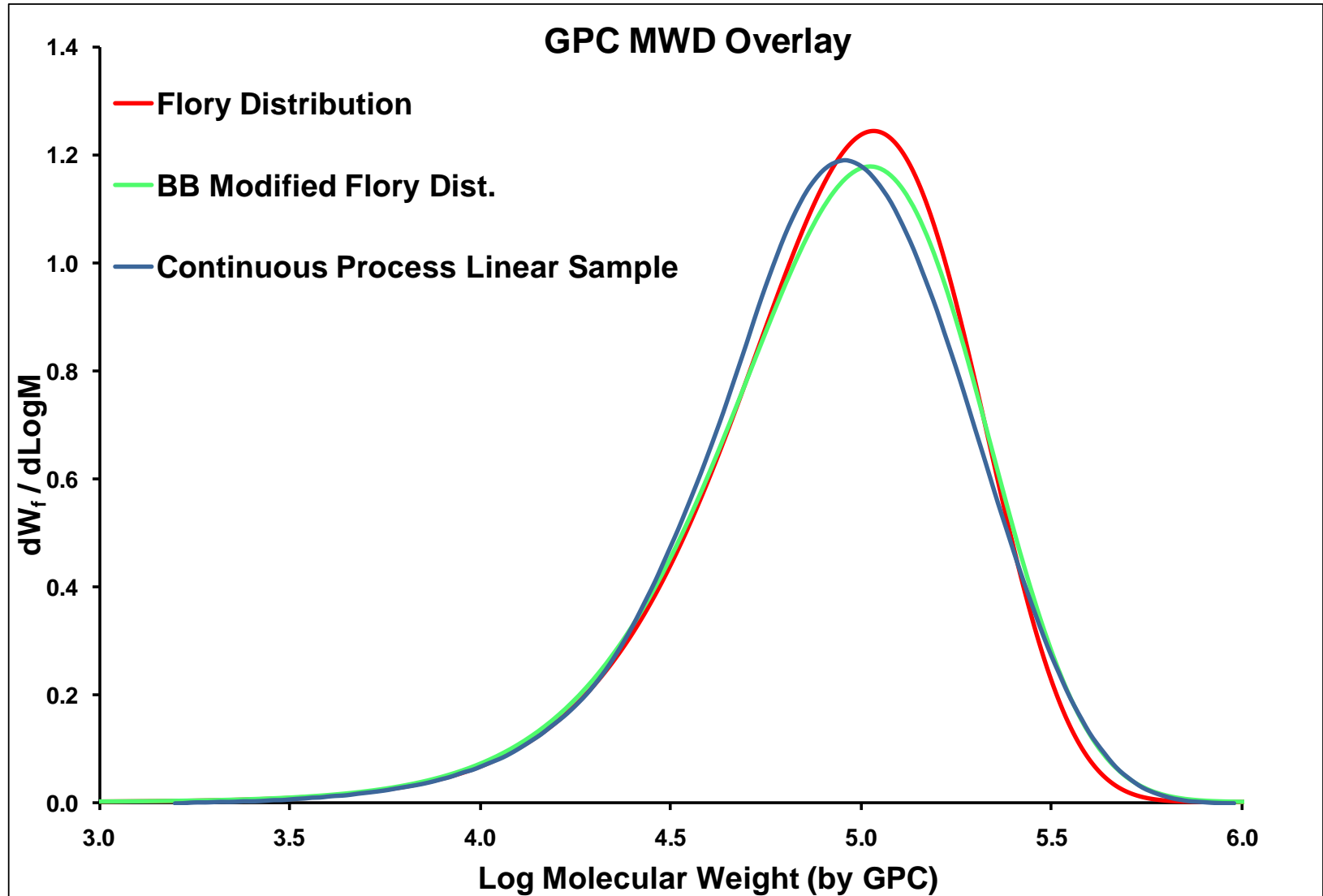
Batch Reactor Sample B – Model Versus Real Data



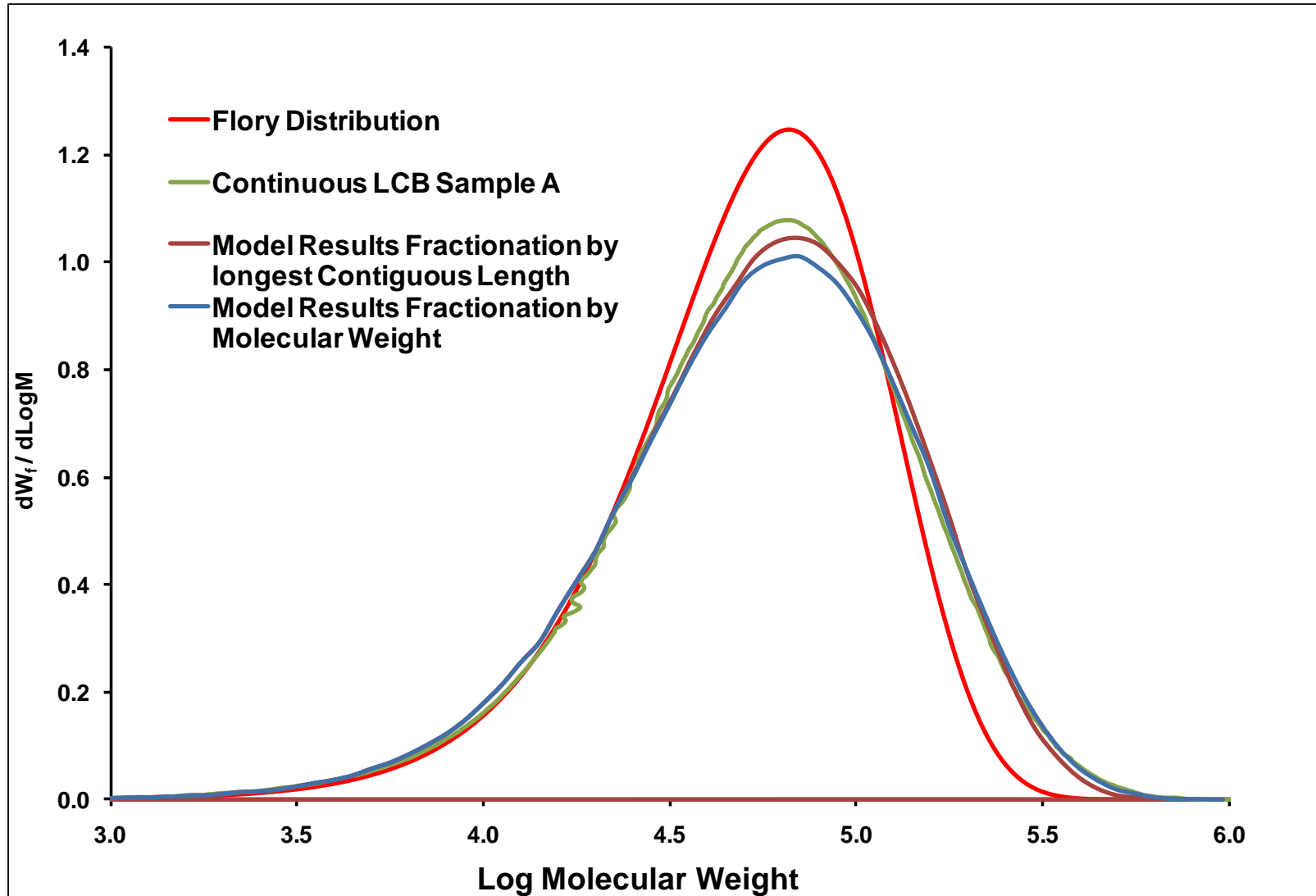
Flory Versus Batch for 1st Order and 5th Order Fit



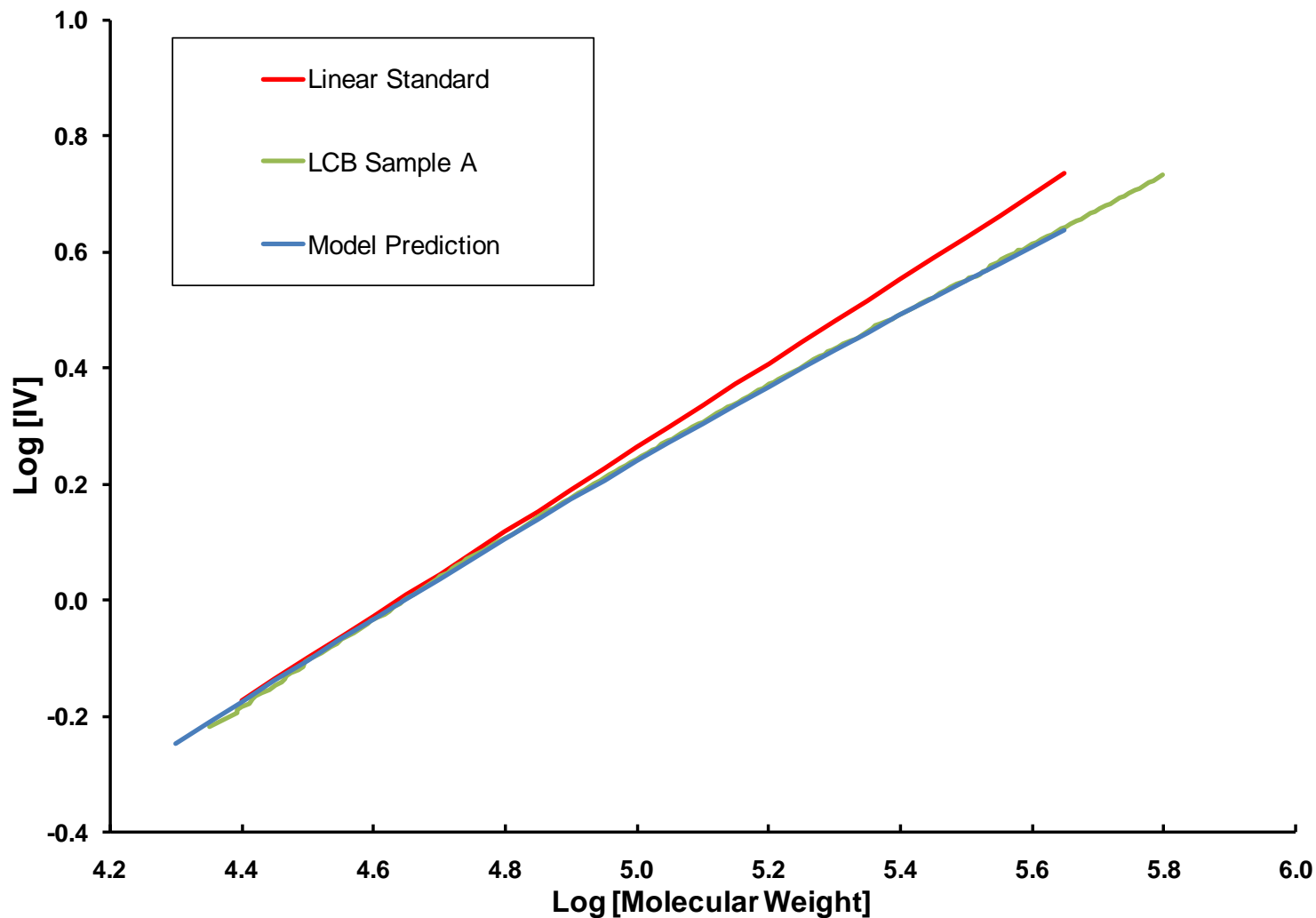
Continuous Process Linear Versus Model



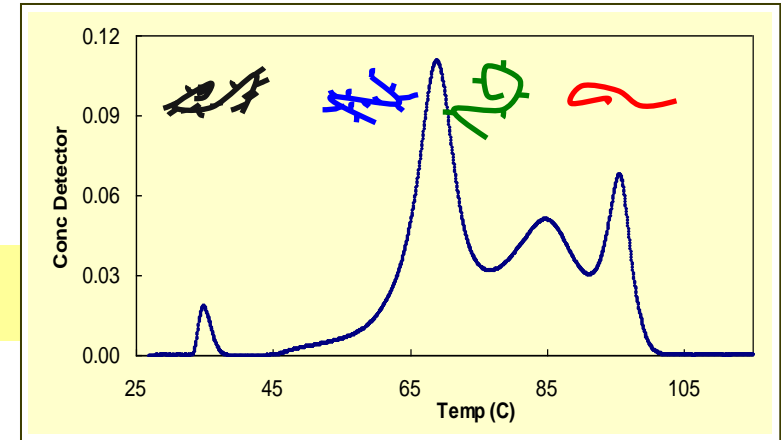
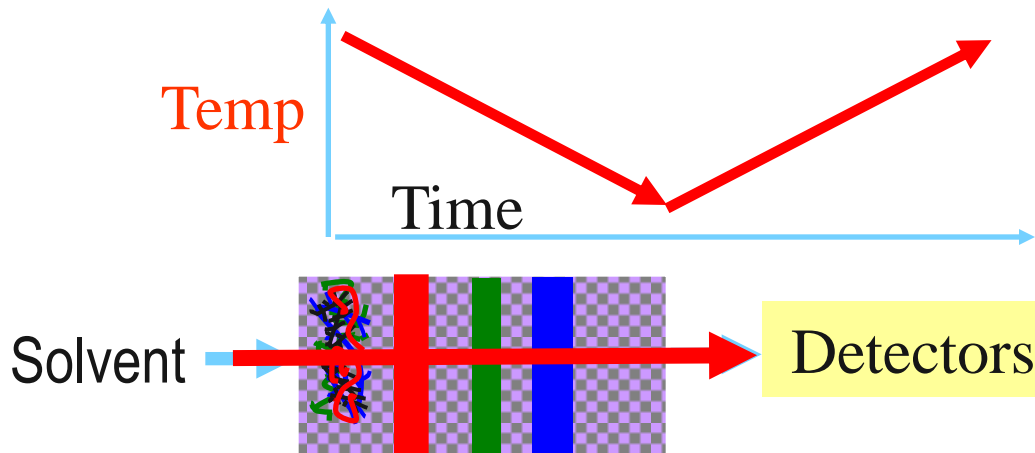
Continuous LCB Sample A Versus Model Results



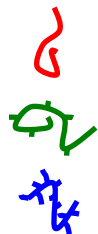
Mark-Houwink Plot Linear versus Model Versus LCB Sample A



Crystallization Elution Fractionation (CEF)



Dynamic Crystallization On Column



Linear
 Minimally Branched
 Highly Branched
 Non-crystallizable chains

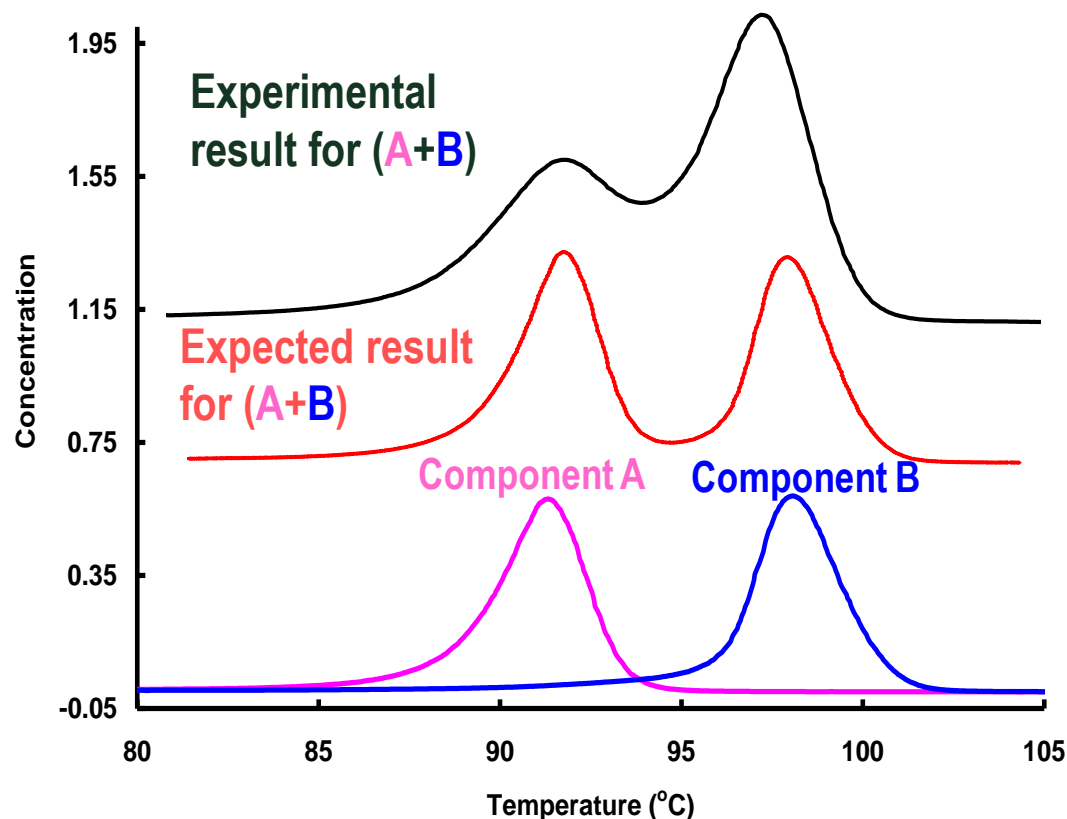
Advantages of CEF:

- Fast – 45 minutes
- Very reproducible
- Commercially available instrument

Disadvantages of CEF:

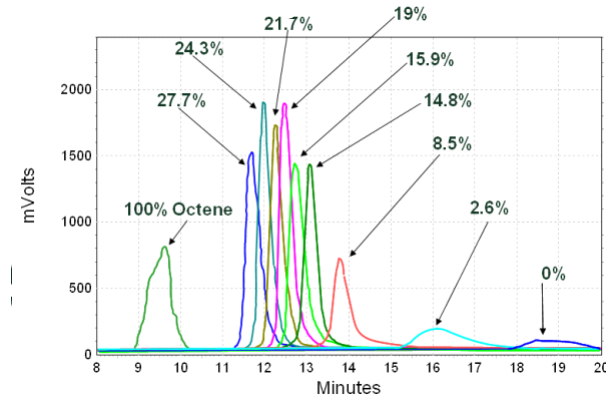
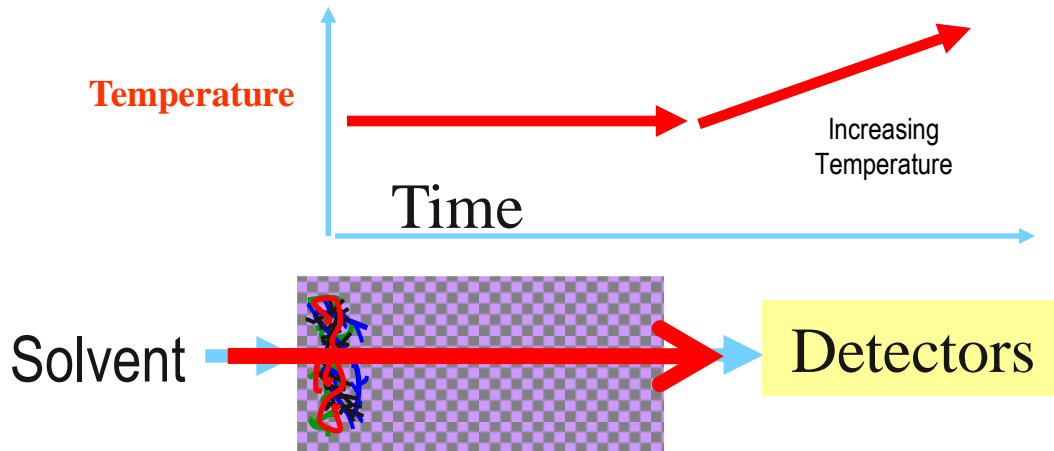
- Co-crystallization
- Can't fractionate amorphous polymer

Cocrystallization Complicates SCBD Analysis

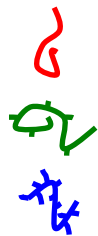


- Limits resolution
- Causes composition inaccuracy

High Temperature Liquid Chromatography (HT-LC)



Interaction with column



Linear
Minimally Branched
Highly Branched
Amorphous chains

- Advantages of HT-LC:
- No Co-Crystallization Effects
 - Fractionates amorphous polyolefins

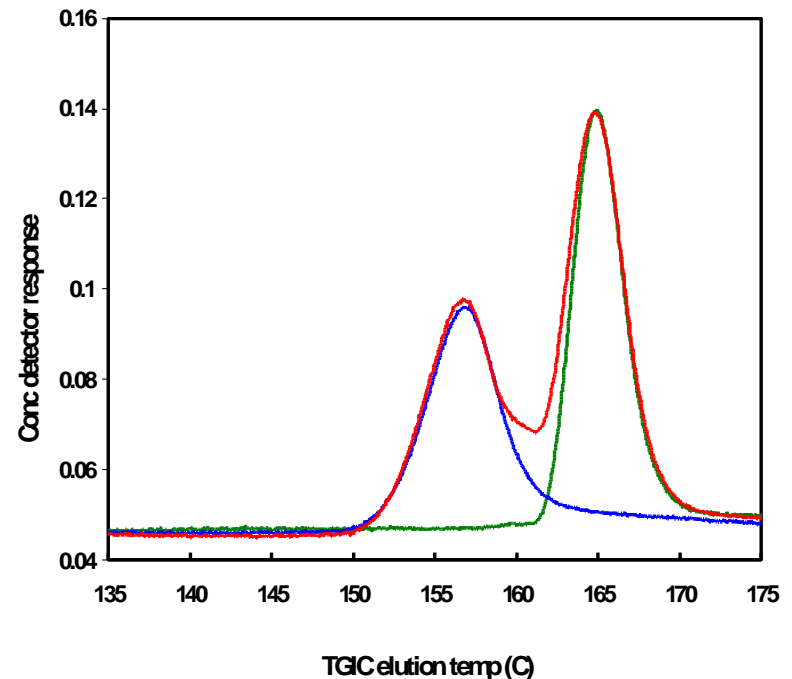
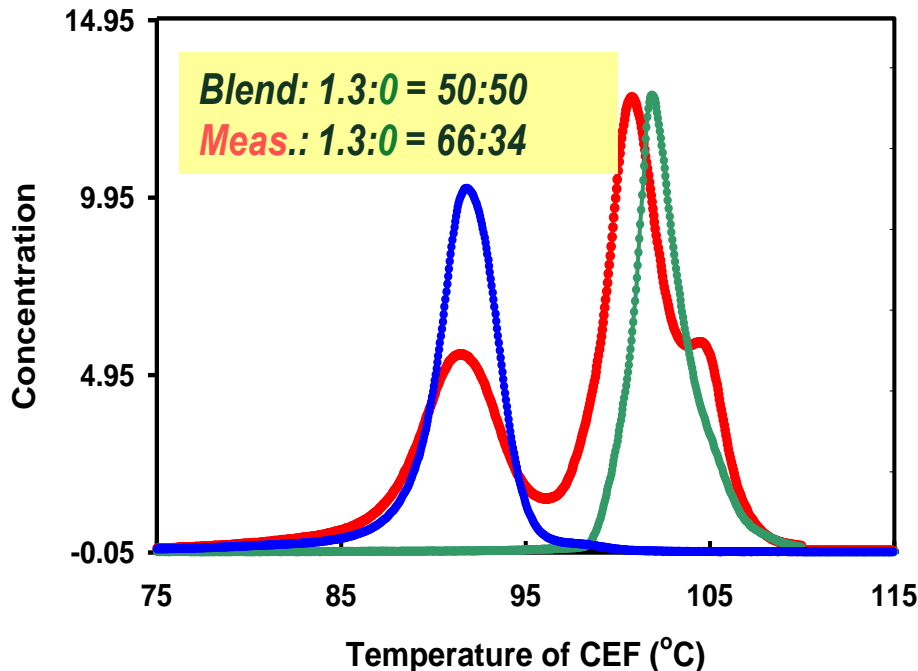
TGIC eliminates cocrystallization



Blend of 0 mol% octene with 1.3 mol% octene (both 1MI)

CEF observed cocrystallization

TGIC did not observe cocrystallization



- Composition accuracy with TGIC will improve the ability to verify product design and develop structure –property relationship.

- Batch reactor samples with minor adjustments for Band Broadening generally match GPC molecular weight distribution results.
- The use of model compounds can be a very sensitive way to tell how well your GPC is functioning.
- Model results for LCB Sample A match best with molecular weight fractionation model.
- The use of the Zimm-Stockmayer model works well in predicting the Mark-Houwink relationship for Continuous LCB Sample A.
- The HT-LC method offers the potential to finally be able to supply correct comonomer distributions which can greatly improve our ability to model comonomer distributions.

Acknowledgements



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