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# Detailed Modelling of LLDPE Structure: Kinetics-Microstructure-Properties Relationship

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## Abstract

The research project targets to study the polymerization mechanisms of olefins using coordination catalysts to produce high quality polymers. The macromolecular architecture depends on the type of polymerization mechanism, the chemical nature of the monomers, the physical state of the reacting system and the type of reactor configuration. The molecular and morphological properties of a polymer product strongly influence its physical, thermal, chemical, rheological, mechanical properties as well as the end-use applications. A comprehensive mathematical model will be developed using Monte Carlo simulation to describe the mechanism of polymerization and to predict the polymer molecular structure in terms of molecular weight, chemical composition and topology. This technique has also been reported in the literature to be able to describe accurately the structure of polymer based on knowledge obtained from polymerization kinetics or polymer characterization. This work will expand the use of Monte Carlo simulation to address non-steady state problems. In industrial polymerization processes important variables affecting the polymerization mechanism may change or fluctuate, therefore affecting the structure of the final polymer.

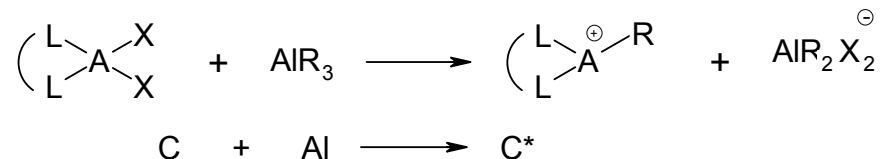
# Metallocene & Coordination Mechanisms of Olefin Polymerization



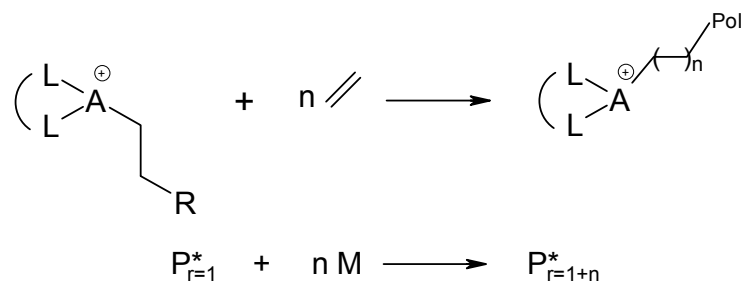
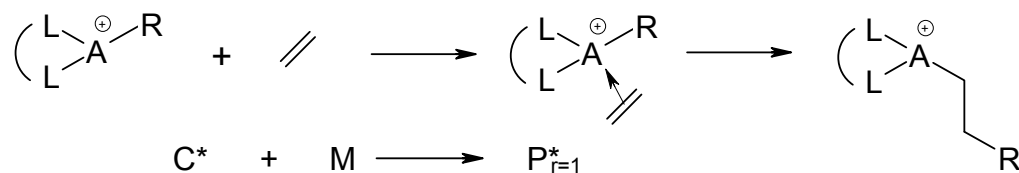
The active site in coordination catalysts for olefin polymerization is a transition metal surrounded by ligands. The catalytic properties depend on the fine tuning between the transition metal and ligands in terms of geometry and electronic character. In most cases the active site is produced by the activation of a complex called pre-catalyst, or catalyst precursor. Polymerization with coordination catalysts proceeds via two main steps: monomer coordination to the active site and monomer insertion into the growing polymer chain. Prior to insertion, the double bond in the olefin monomer coordinates to the coordination vacancy of the transition metal. After the olefin is inserted into the growing polymer chain, another olefin monomer can coordinate to the vacant site. In the case of copolymerization, there is a competition between the comonomers to coordinate to the active sites and to be inserted into the growing polymer chains. Different rates of coordination and insertion of comonomers determine the final chemical composition of the copolymer chain. Several chain transfer mechanisms are operative in coordination polymerization. The type of termination reaction determines the chemical group bound to the active site and the terminal chemical group in the polymer chain.

# Coordination Mechanism Equations

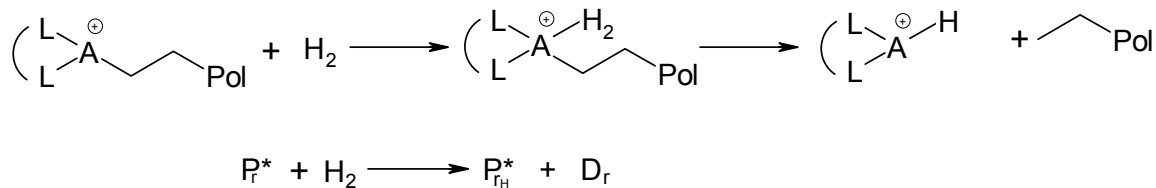
Catalyst activation by reaction of pre-catalyst and cocatalyst



Monomer coordination and insertion



Chain termination mechanisms, transfer to hydrogen



A = transition metal center (Ti, Zr, Ni, ...)

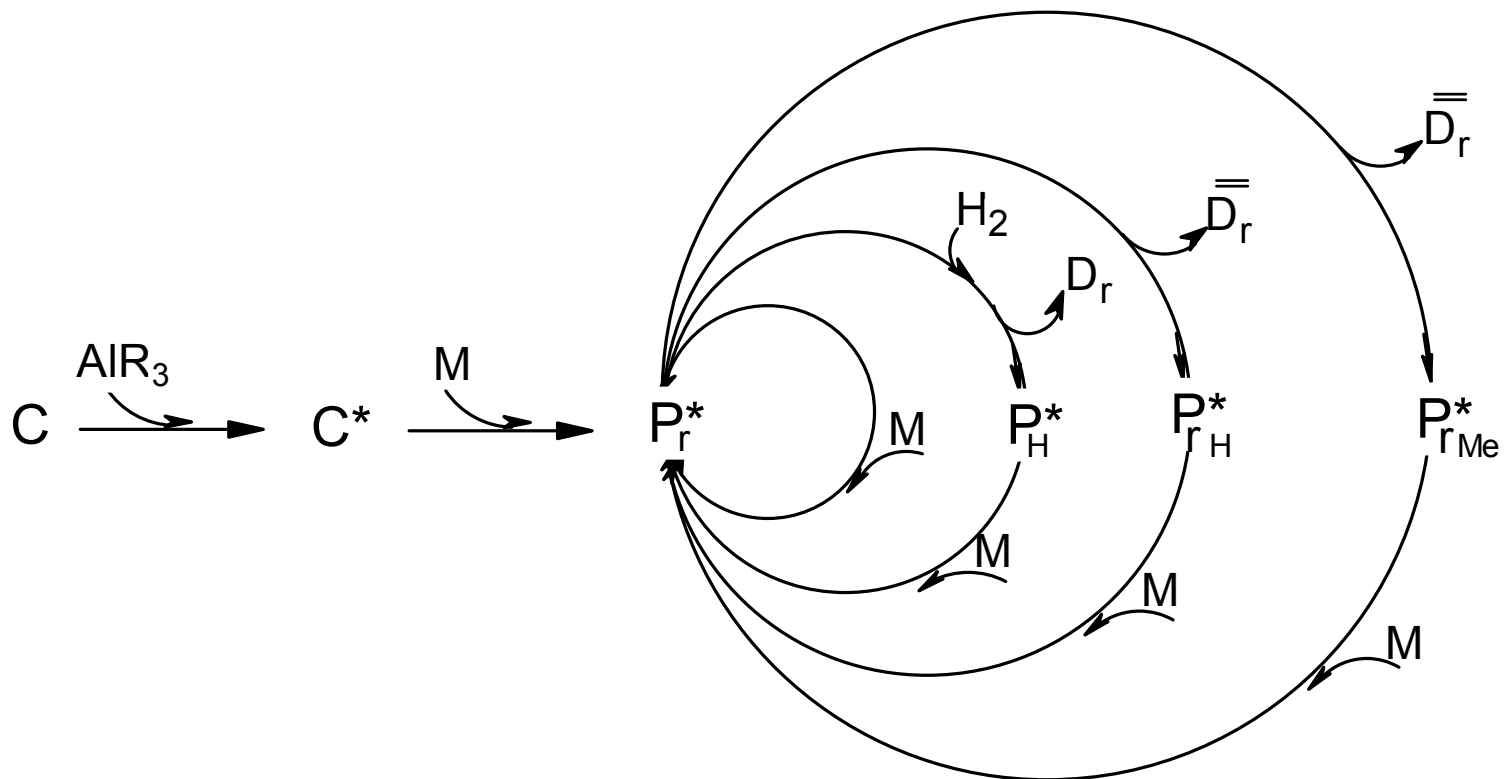
L = ligands

X = halogen (Cl, Br)

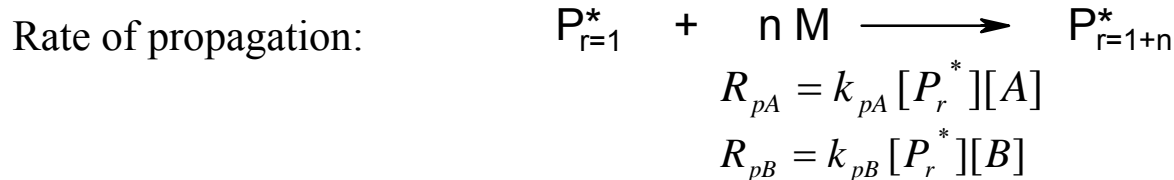
AlR<sub>3</sub> = alkylaluminum cocatalyst

R = alkyl group (methyl, ethyl)

# Catalytic cycle for polymerization



# Copolymerization Kinetic Equations



We relate the number average chain length to the propagation and termination rates using the following equation:

$$\bar{r}_n = \frac{R_p}{R_t}$$

The chain length is related to the molecular weight by the molar mass of the monomer unit and the probability of chain propagation  $P_p$  is related to the number-average chain length  $\bar{r}_n$  by:

$$P_p = \frac{R_p}{R_p + R_t} = \frac{(k_{pA} [P_r^*][A] + k_{pB} [P_r^*][B])}{(k_{pA} [P_r^*][A] + k_{pB} [P_r^*][B]) + (k_{tA} [P_r^*] + k_{tB} [P_r^*])}$$

$$P_p = \frac{R_p}{R_p + R_t} = \frac{1}{1 + \frac{R_t}{R_p}} = \frac{1}{1 + \frac{1}{\bar{r}_n}} \approx 1 - \frac{1}{\bar{r}_n}$$

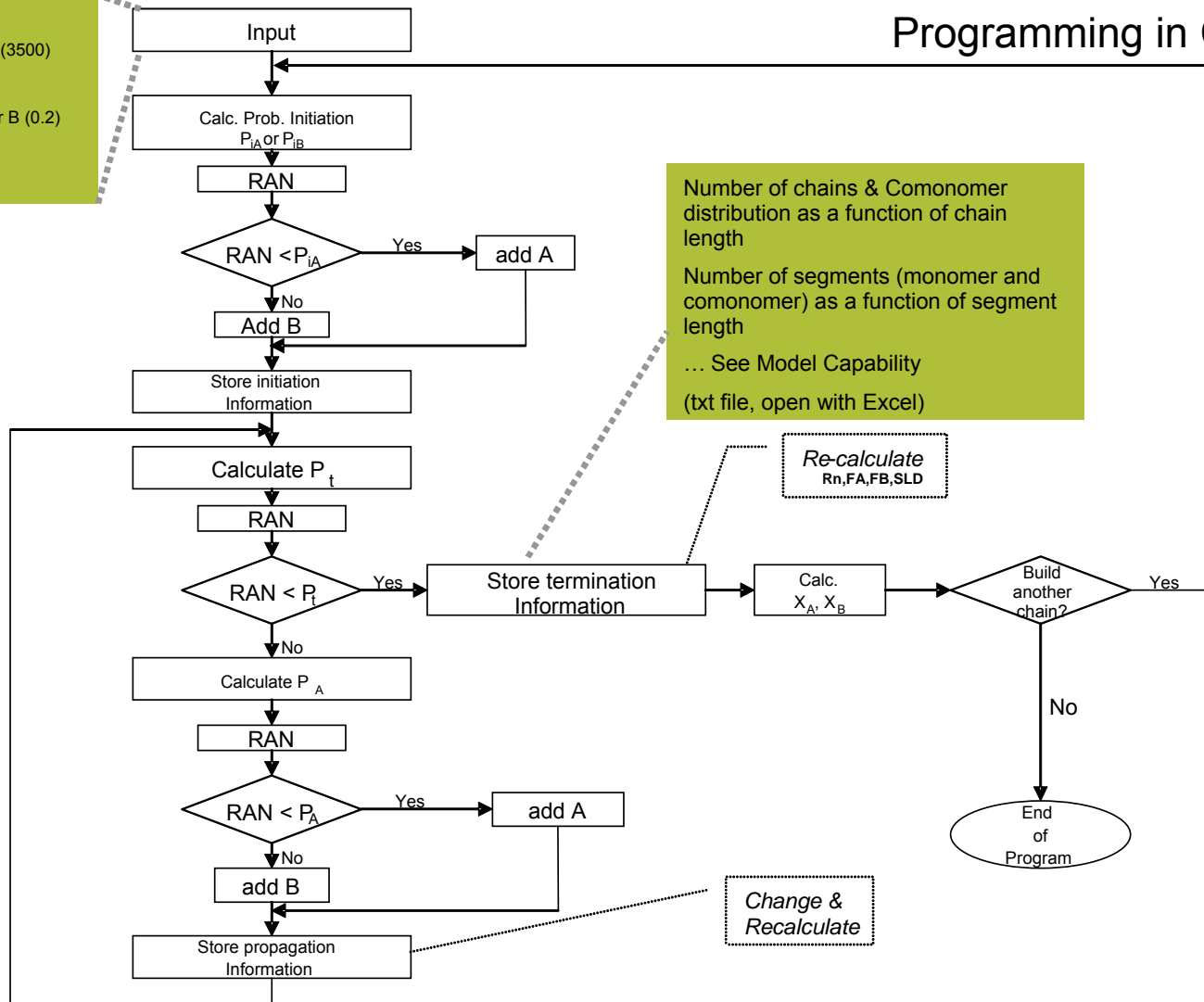
# Copolymerization Schematic Flow Chart



Programming in C++

Number of chains (1000000)  
 Number average chain length (3500)  
 Class (200)  
 Probability of adding monomer B (0.2)  
 Random number seed ( -1)  
 File name ( 25 character)

Number of chains & Comonomer distribution as a function of chain length  
 Number of segments (monomer and comonomer) as a function of segment length  
 ... See Model Capability  
 (txt file, open with Excel)



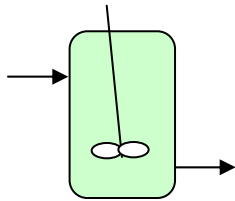
# Model Capabilities



- $M_n$ ,  $M_w$ ,  $M_z$ , PDI
- Chain Length Distribution,  $rn$  (molecular weight)
- Average Comonomer Composition (FB)
- Comonomer Composition Distribution  $FB=f(rn)$
- Monomer Segments Distribution  $A1-A20=f(rn)$
- Comonomer Segments Distribution  $B1-B20=f(rn)$
- Triads Distribution AAA, AAB\_BAA, BBA\_ABB, BAB, ABA, BBB= $f(rn)$
- Distribution of Segment Length for Monomer A and Monomer B



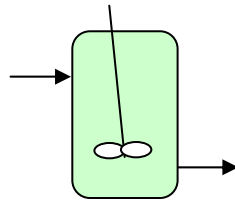
## 250k Chains Produced in Each Reactor then Mixed to give 1000k Chains with Changing $rn$ & FB



Reactor 1  
(250k chains)

**$rn = 1007$**

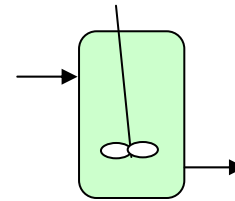
**FB = 5%**



Reactor 2  
(250k chains)

**$rn = 3001$**

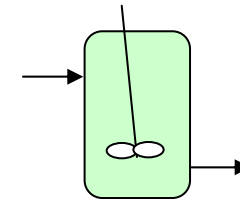
**FB = 4%**



Reactor 3  
(250k chains)

**$rn = 5004$**

**FB = 3%**

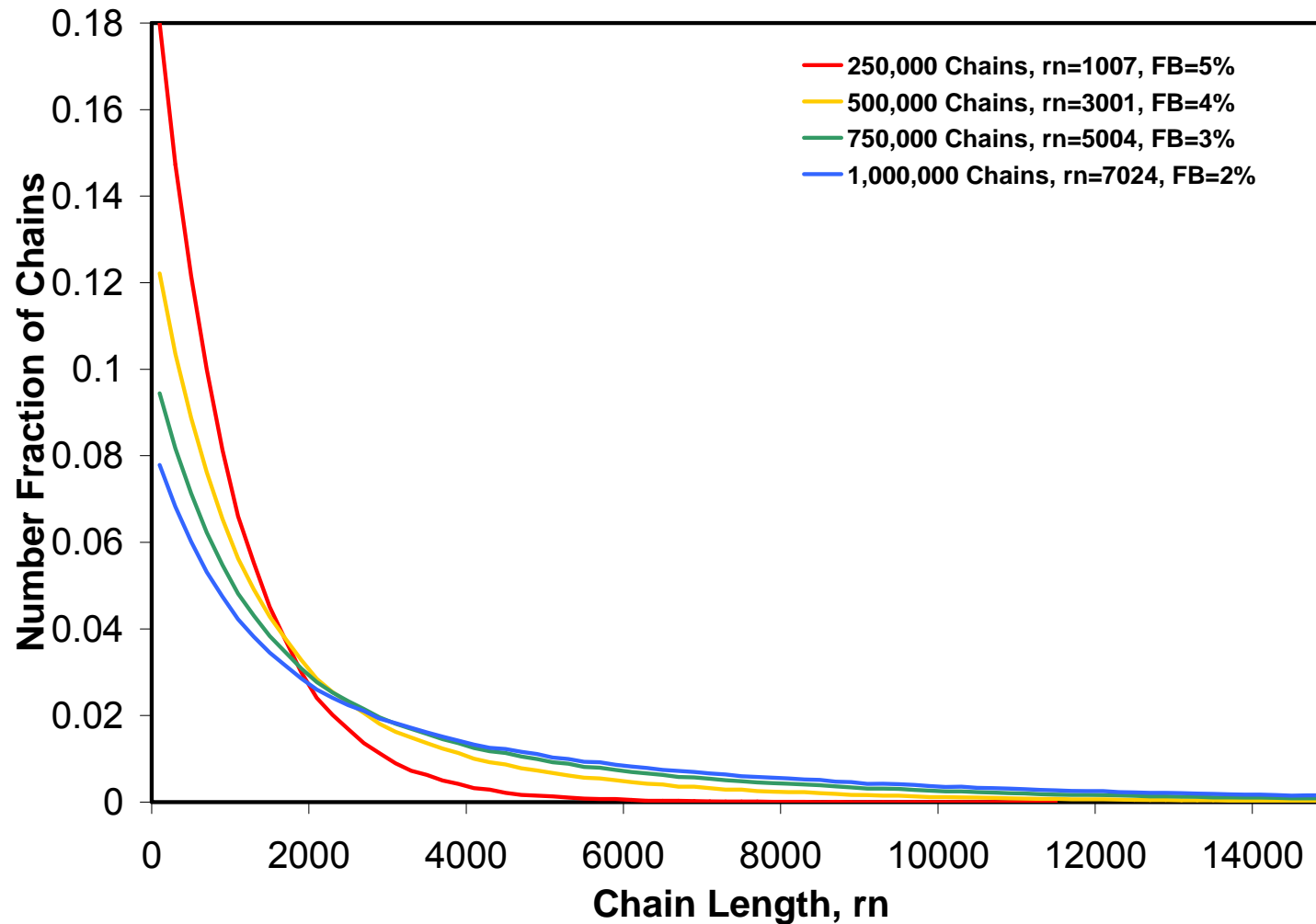


Reactor 4  
(250k chains)

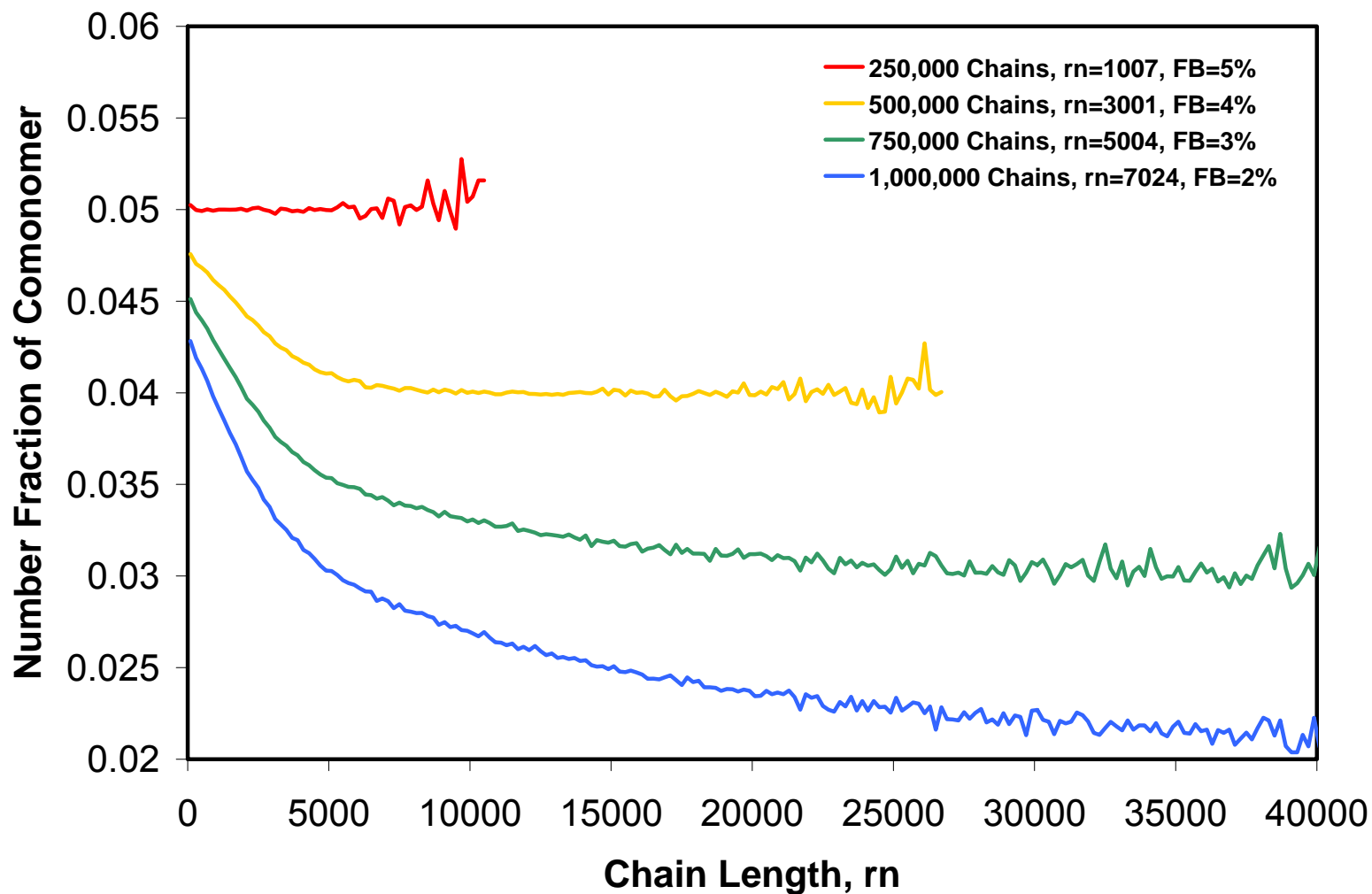
**$rn = 7024$**

**FB = 2%**

# Number Fraction of Chains Vs Chain Length, $rn$ (Mixing from 250k to 1000k Chains, Changing $rn$ , FB)

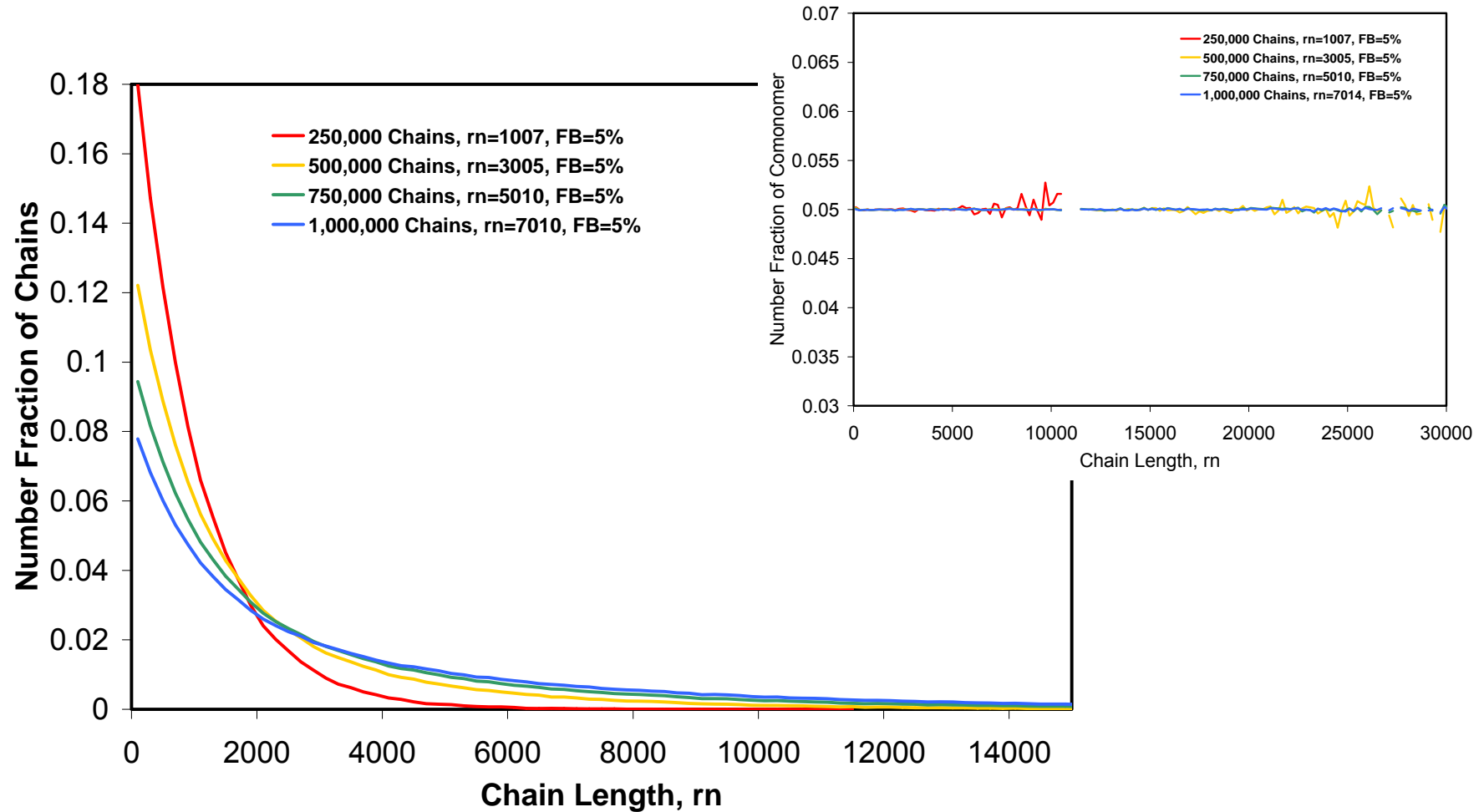


## Number Fraction of Comonomer Vs Chain Length, $rn$ (Mixing from 250k to 1000k Chains, Changing $rn$ , FB)



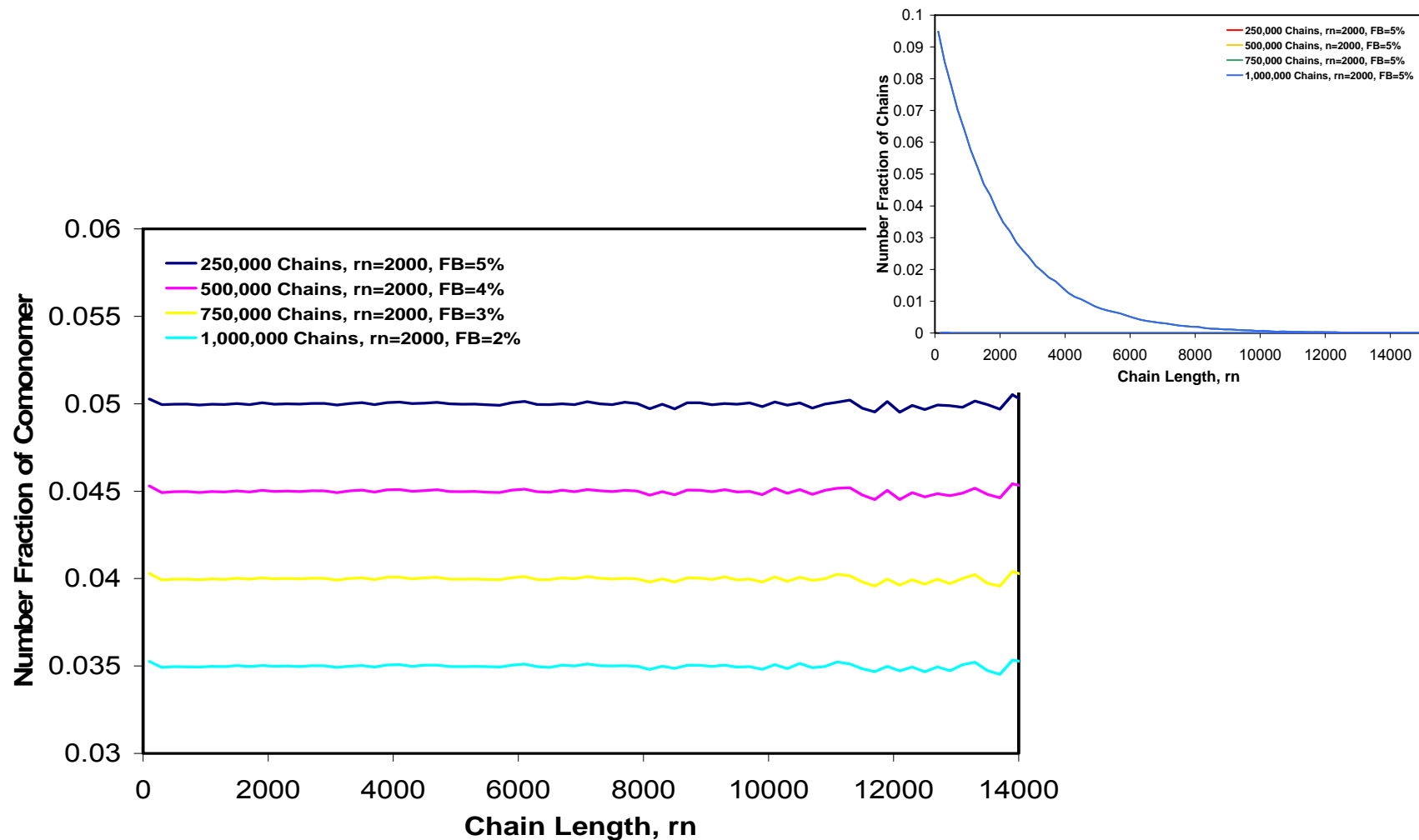
# Number Fraction of Chains Vs Chain Length, $rn$ & Comonomer Distribution

(Mixing from 250k to 1000k Chains, Changing  $rn$ , Const. FB)

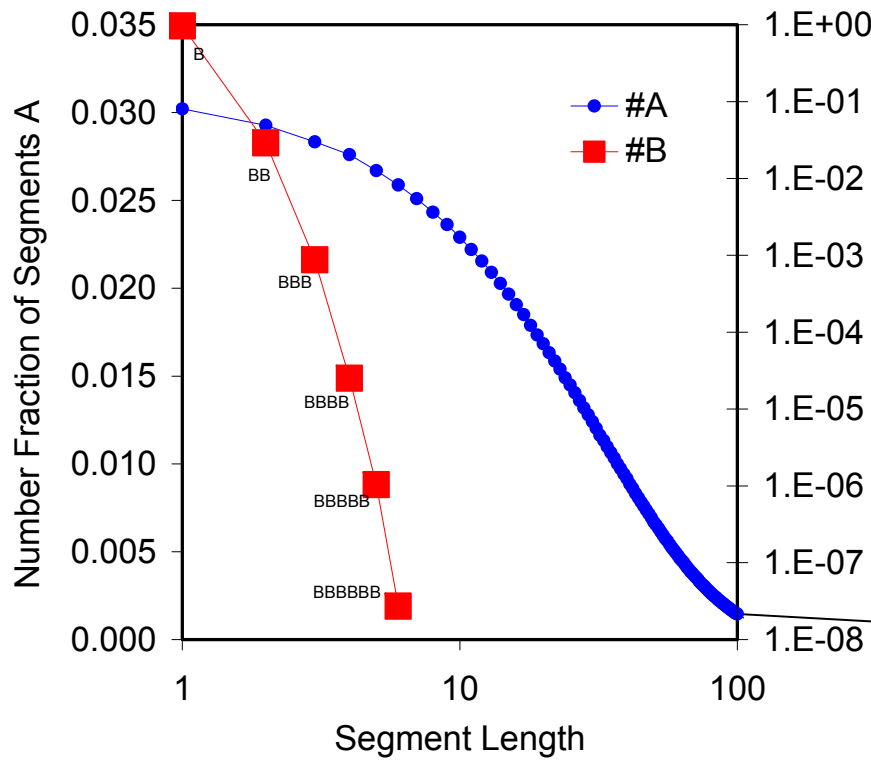


# Number Fraction of Chains Vs Chain Length, $rn$ & Comonomer Distribution

(Mixing from 250k to 1000k Chains, Const.  $rn$ , Changing FB)



# Segment Length Distribution, $rn=5004$ , $FB=3\%$



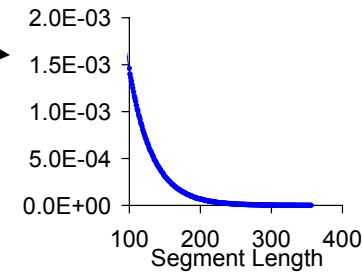
AAABBAABAABBBA



$(A)_n$

Segment < 20 monomer units will not crystallize

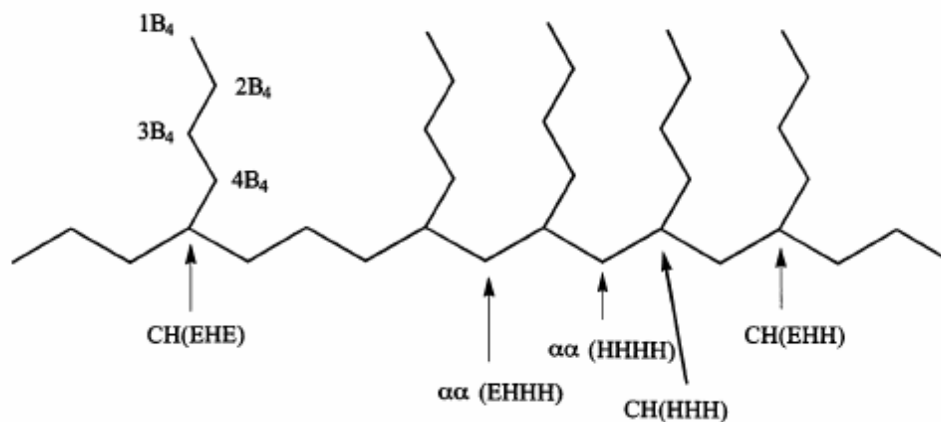
$$\sum_{n=1}^{n=20} A_n$$



## Nomenclature and $^{13}\text{C}$ Chemical Shift Assignments

Nuclear Magnetic Resonance spectroscopy is a very powerful technique for polymer characterization that can be used to determine branching, the sequence of comonomer units in the copolymer chain. The Greek letters are used to denote the positions of a given backbone carbon site relative to methine carbons and side-chain carbons (“B” for branch) are labeled using the format  $n\text{B}_m$ , where  $m$  represents the length of the side chain and  $n$  refers to the position of the carbon in question, as counted from the *end* of the side chain.

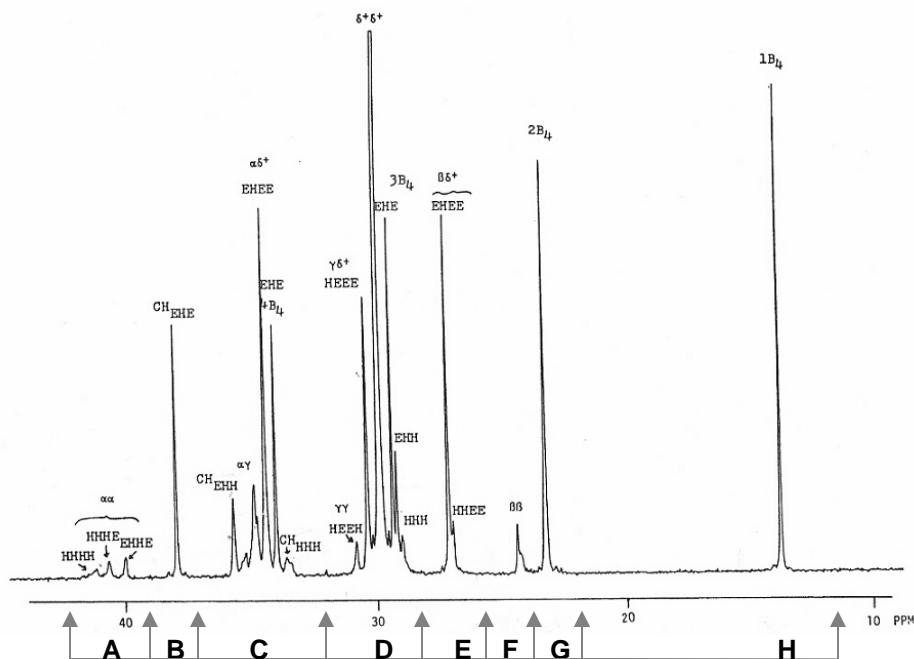
*introduced by Randall and by Carman and Wilkes and later extended by others.*



*Seger, M.; Maciel, G. 2004, Analytical Chemistry, Vol. 76, No. 19, 5734-5747*

In the production of Linear Low Density Polyethylene 1-Hexene is considered to be an important commercial comonomer (monomer **B** in our general model would be in this case indicated by **H** and monomer **A** would be replaced by **E** for Ethylene monomers)

# Chemical Shifts Assignments



Carbon-13 NMR Spectrum of ethylene-1-hexene copolymer at 125°C in 1,2,4-trichlorobenzene  
Randall, J., 1989, *Macromol, Chem., Phys.*, 201-317

Chemical Shift ppm, TMS		Carbon Assignment	Sequence Assignment
TCB	TCE-d2		
41.4		$\alpha\alpha$	HHHH (mmm)
40.86		$\alpha\alpha$	HHHE+EHHH (mm)
40.18		$\alpha\alpha$	EHHE (m)
38.13	38.22	Methine	EHE
35.85	35.92	Methine	EHH+HHE (m)
35.37		$4B_4$	HHH (mm)
35	35.1	$\alpha\gamma$	HHEH+HEHH (mm)
		$\alpha\gamma$	EHEH+HEHE (m)
34.9	35.02	$\alpha\delta^+$	HHEE+EEHH
		$4B_4$	EHH+HHE (mm)
34.54	34.62	$\alpha\delta^+$	EHEE+EEHE
34.13	34.21	$4B_4$	EHE
33.57		Methine	HHH (mm)
30.94	30.94	$\gamma\gamma$	HEEH
30.47	30.48	$\gamma\delta^+$	HEEE+EEEH
29.98	29.98	$\delta^+\delta^+$	(EEE) <i>n</i>
29.51	29.58	$3B_4$	EHE
29.34	29.41	$3B_4$	EHH+HHE (m)
29.18	29.24	$3B_4$	HHH (mm)
27.28	27.31	$\beta\delta^+$	EHEE+EEHE
27.09	27.13	$\beta\delta^+$	HHEE+EEHH (m)
23.37	23.39	$2B_4$	EHE+EHH+HHE+HHH
14.12	14.21	Methyl	EHE+EHH+HHE+HHH

Carbon-13 Chemical Shift Assignments at 50.3 MHz for Ethylene-1-Hexene Copolymers Containing Principally Isotactic 1-Hexene Sequences and No Inverted 1-Hexene Repeat Units. The Samples Were Prepared at 10% by Weight in 1,2,4-Trichlorobenzene (TBC) with Perdeuterobenzene Added and at 15% by Weight in Tetrachloroethane- $d_2$  (TCE- $d_2$ ). The Spectra Were Obtained at 125 °C. The  $\delta^+\delta^+$  Peak is Set at 29.98 ppm with Respect to an Internal Tetramethylsilane Standard

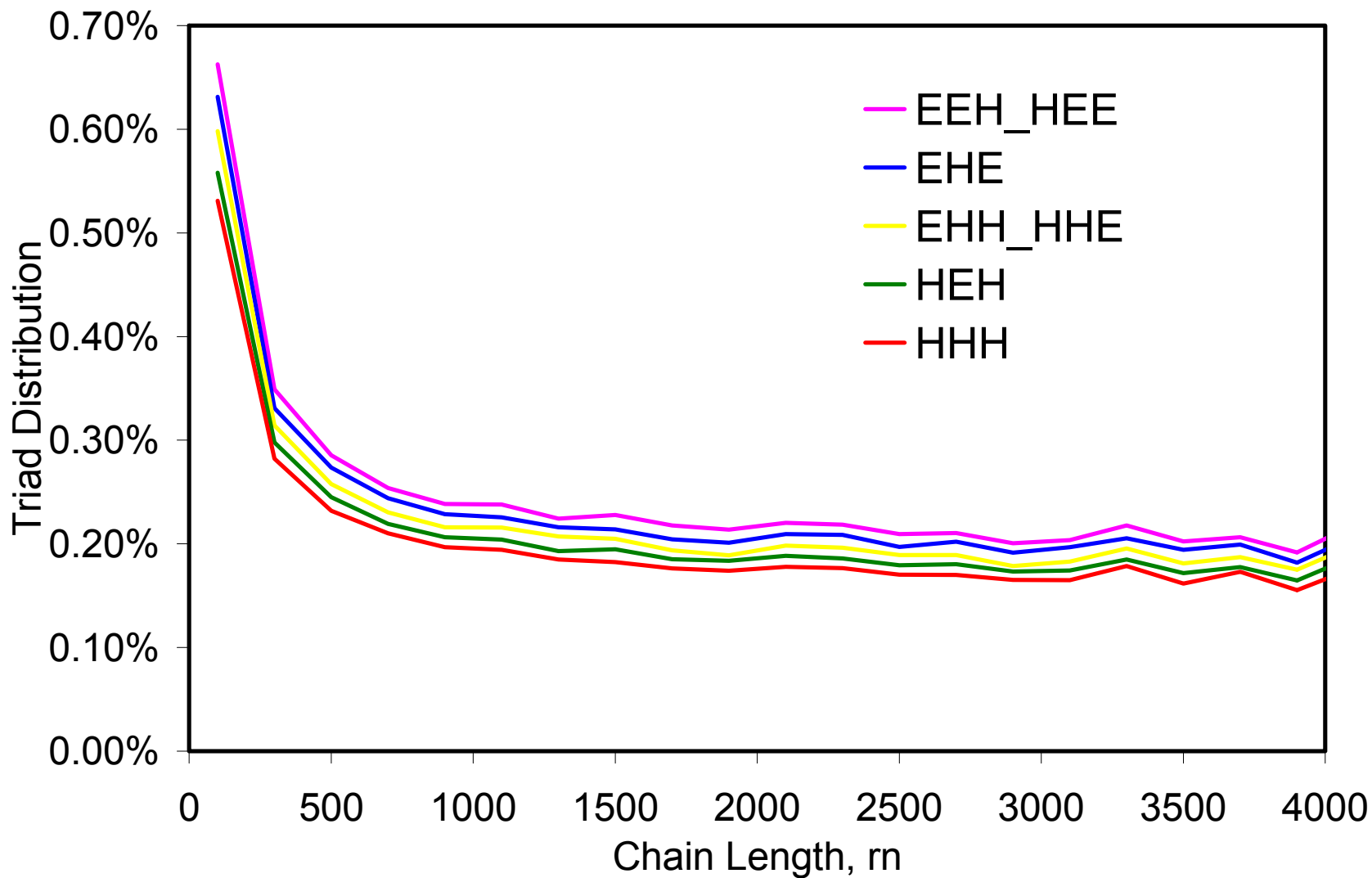


# Tabulated Intensity Equations



Region	Range (ppm)		Contributing Carbons	Intensity Equation
	from	to		
A	39.5	42	$\alpha\alpha$ , Methylene	$TA = k( HHH + (1/2) [ HHE+EHH ] )$
B	38.1		(Methine) <sub>EHE</sub>	$TB = k( EHE )$
C	33	36	(Methine) <sub>EHH+HHE</sub> , (Methine) <sub>HHH</sub> , 4B <sub>4</sub> , $\alpha\gamma$ , $\alpha\delta$	$TC = k( EHE + 2[ EHH+HHE ] + 2HHH + 2HEH + [ HEE+EEH ] )$
D	28.5	31	$\delta^+\delta^+$ , 3B <sub>4</sub> , $\gamma\gamma$ , $\gamma\delta^+$	$TD = k( 2EEE + (1/2) [ HEE + EEH ] + EHE + EHH+HHE + HHH )$
E	26.5	27.5	$\beta\delta^+$	$TE = k( HEE+EEH )$
F	24	25	$\beta\beta$	$TF = k( HEH )$
G	23.4		2B <sub>4</sub>	$TG = k( EHE + EHH+HHE + HHH )$
H	14.1		1B <sub>4</sub>	$TH = k( EHE + EHH+HHE + HHH )$

# Triad Distribution, $rn=1007$ , $FB=5\%$



## Conclusions

- The model was able to predict the number fraction of chains produced for a certain chain length.
- In case of copolymerization the fraction of monomer B incorporated in the polymer chain was not dependant on the size of the chain, in agreement with the polymerization mechanism.
- Information for model can obtained by polymer analysis or through the reaction kinetics.
- The probability of propagation is calculated from the reaction kinetics.
- From the probability of propagation we can find the number average chain length.

## Future Work

- The model will have the ability to determine the monomer sequence distribution.
- The reaction rate constants are dependant on the reactor temperature according to Arrhenius equation.
- The new value of the propagation rate constant is given by the following equation
$$k_p = k_{p,o} \cdot e^{-E_{Act,p} / RT}$$
- Temperature fluctuation in the reactor will generate different average chain lengths.
- Compositional Drift will affect the amount of comonomer incorporation, where the amount of comonomer incorporation will be affected by the chain lengths produced.
- This work will expand the use of Monte Carlo simulation to address non-steady state problems.

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