# MODELING OLEFIN POLYMERIZATION USING MONTE CARLO SIMULATION: DETAILED COMONOMER DISTRIBUTION



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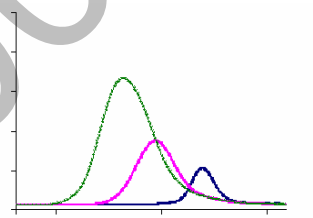
# Objectives

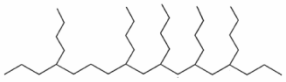
- To build a Monte Carlo model to describe the polymerization mechanisms of olefin copolymerization using single-site coordination catalyst

- To predict detailed polymer microstructure:
  - The complete chain length distribution;
  - Polydispersity;



  - Average comonomer (B) composition FB;
  - Comonomer composition distribution as function of chain length;
  - Monomer (A) and comonomer (B) segment length distribution as function of chain length;

  - Average triads distribution;
  - Triad distribution as a function of chain length;



# Introduction

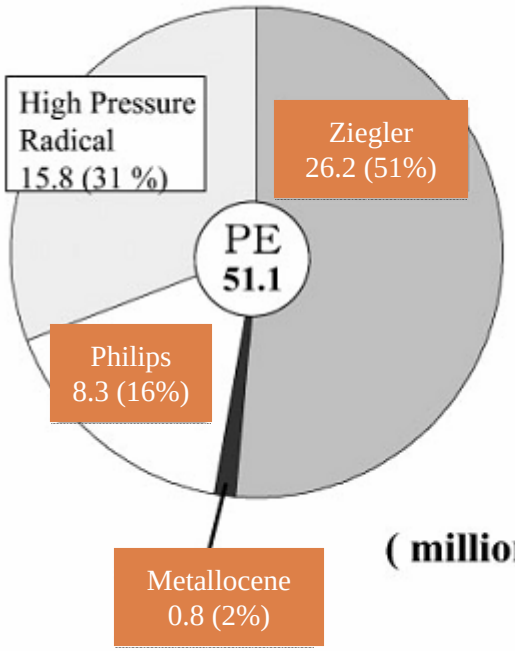
## *Stochastic Modeling & Monte Carlo Simulation*

- Monte Carlo modeling is a convenient method of modeling polymer reaction mechanism and is widely used in polymerization systems (use of probabilities)
- It is useful specially when analytical solutions are not available

## *Polyolefins*

- The basic properties of PE $(-CH_2CH_2-)_n$ are determined by the molecular structure
- Depends on degree of crystallinity, degree of polymerization, average molar mass and molar mass distribution

# n Catalysts




Catalysts for global PE production (Kashiwa, 2004)

n catalyst types available commercially in

| | | Characteristics |
|---|---|---|
| | | Narrow molecular weight distribution<br>Co-catalyst required<br>Hydrogen as chain transfer agent |
| Ziegler | Titanium | • Relatively narrow molecular weight distribution<br>• Aluminum alkyl co-catalyst required<br>• Hydrogen is used for molecular weight control |
| Phillips | Chromium | • Relatively broad molecular weight distribution<br>• Co-catalyst not required<br>• Hydrogen is not used for molecular weight control |

# Copolymer-Kinetic Equations-Probabilities Calculations

Rate of Propagation:

$$P^*_{r=1} + n\,M \longrightarrow P^*_{r=1+n}$$

$$R_{pA} = k_{pA}[P_r^*][A]$$

$$R_{pB} = k_{pB}[P_r^*][B]$$

Rate of Termination:

$$P_r^* \longrightarrow P_H^* + \overline{\overline{D}}_r$$

$$R_{tA} = k_{tA}[P_r^*]$$

$$R_{tB} = k_{tB}[P_r^*]$$

The probability of propagation:

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

Knowing that, the number average chain length:

$$r_n = \frac{R_p}{R_t} = \frac{(R_{pA}+R_{pB})}{(R_{tA}+R_{tB})}$$

# Copolymer-Kinetic Equations-Probabilities Calculations



The probability of propagation is related to the number-average chain length:

$$P_p = \frac{R_p}{R_p + R_t} = \frac{1}{1 + \frac{R_t}{R_p}} = \frac{1}{1 + \frac{1}{r_n}} \approx 1 - \frac{1}{r_n}$$

And, the probability of chain termination is related to the number-average chain length by:

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

$$P_t = \frac{R_t}{R_p + R_t} = \frac{1}{\frac{R_p}{R_t} + 1} = \frac{1}{r_n + 1} \approx \frac{1}{r_n}$$

# Copolymerization Schematic Flow Chart

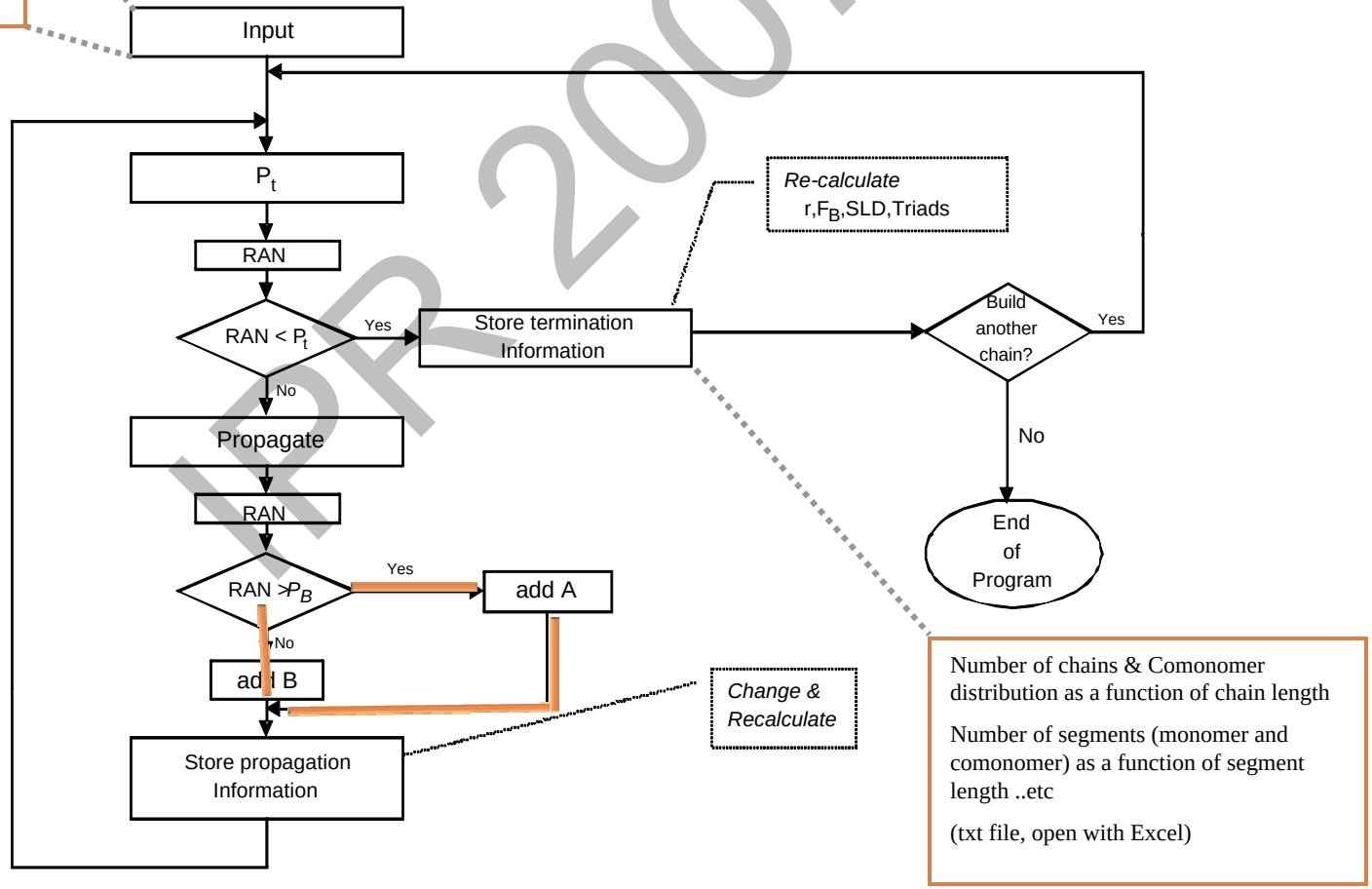
Number of chains (1000000)

Number average chain length (3500)

Probability of adding monomer B (0.2)

Random number seed (-1)

$AABAA(A)_n\ B(B)_n$

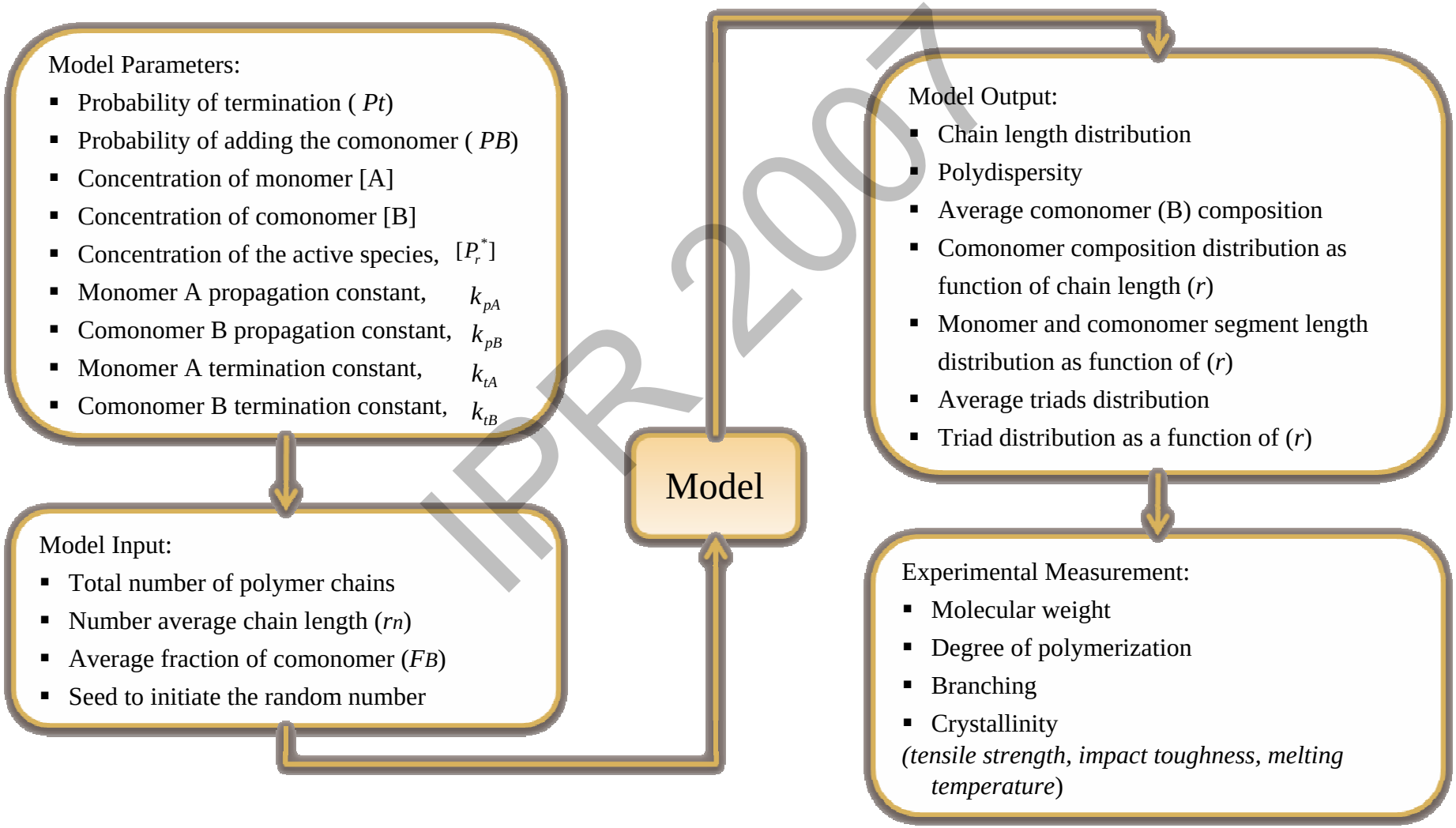



Number of chains & Comonomer distribution as a function of chain length

Number of segments (monomer and comonomer) as a function of segment length ..etc

(txt file, open with Excel)

# Simulation Model Inputs-Outputs

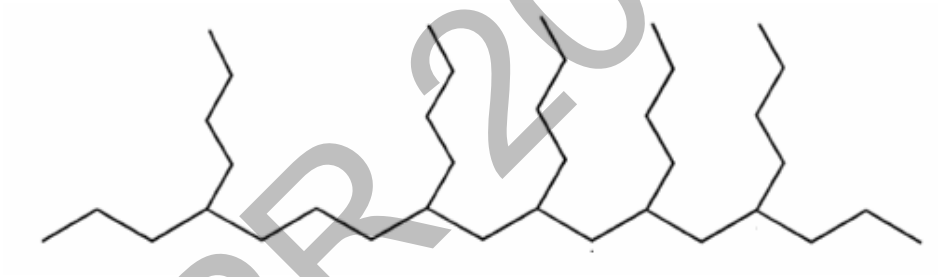


# Triads Relative Intensities of $^{13}$C-NMR Spectra

## Nomenclature and $^{13}$C-NMR Chemical Shift Assignments

Nuclear Magnetic Resonance spectroscopy is a very powerful technique for polymer characterization

..ABABBBBA...



A B A B B B B A



A = ethylene
B = 1-hexene

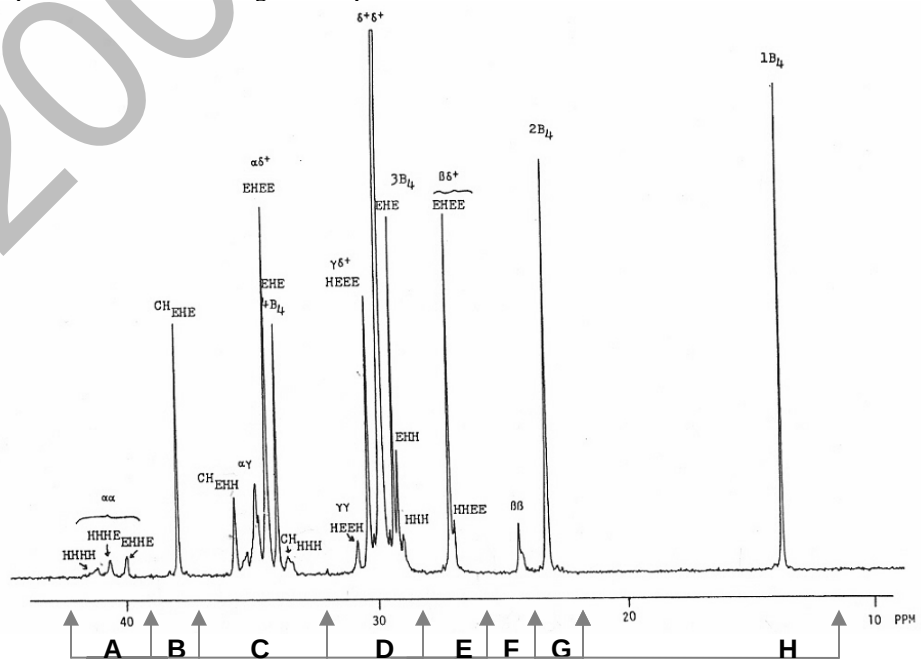
LLDPE = Linear Low Density Polyethylene

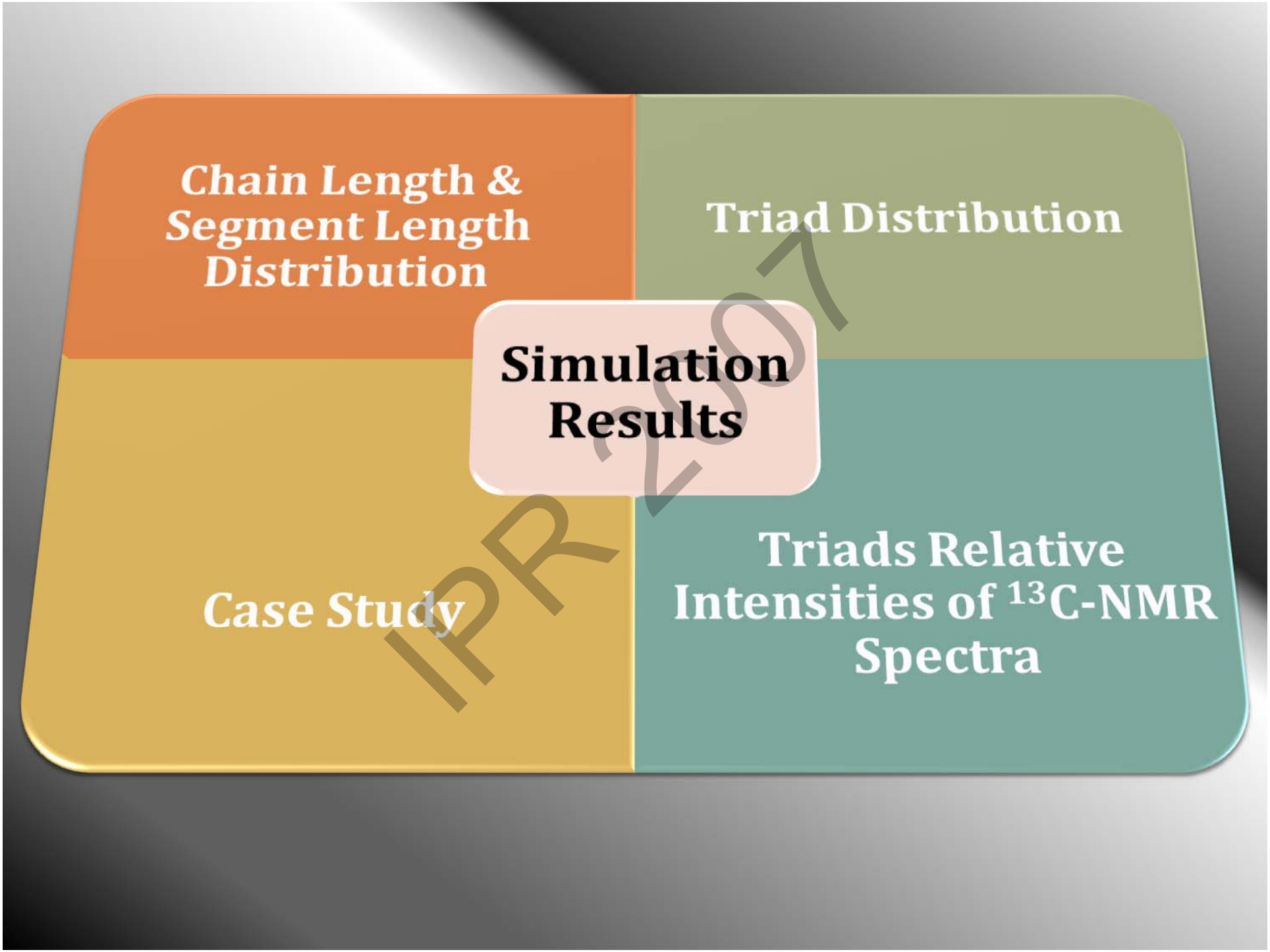
# Tabulated Intensity Equations Chemical Shifts Assignments



Calculated intensities with respective chemical shift assignments ($r_n$ =1008 and $F_B$= 5%)

| | Range (ppm) | | |
|---|---|---|---|
| Region | from | to | Contributing Carbons |
| A | 39.5 | 42 | αα, Methylene |
| B | 38.1 | | $(Methine)_{EHE}$ |
| C | 33 | 36 | $(Methine)_{EHH+HHE}$, $(Methine)_{HHH}$, $4B_4$, αγ, αδ |
| D | 28.5 | 31 | $\delta^+\delta^+$, $3B_4$ , γγ, $\gamma\delta^+$ |
| E | 26.5 | 27.5 | $\beta\delta^+$ |
| F | 24 | 25 | ββ |
| G | 23.4 | | $2B_4$ |
| H | 14.1 | | $1B_4$ |



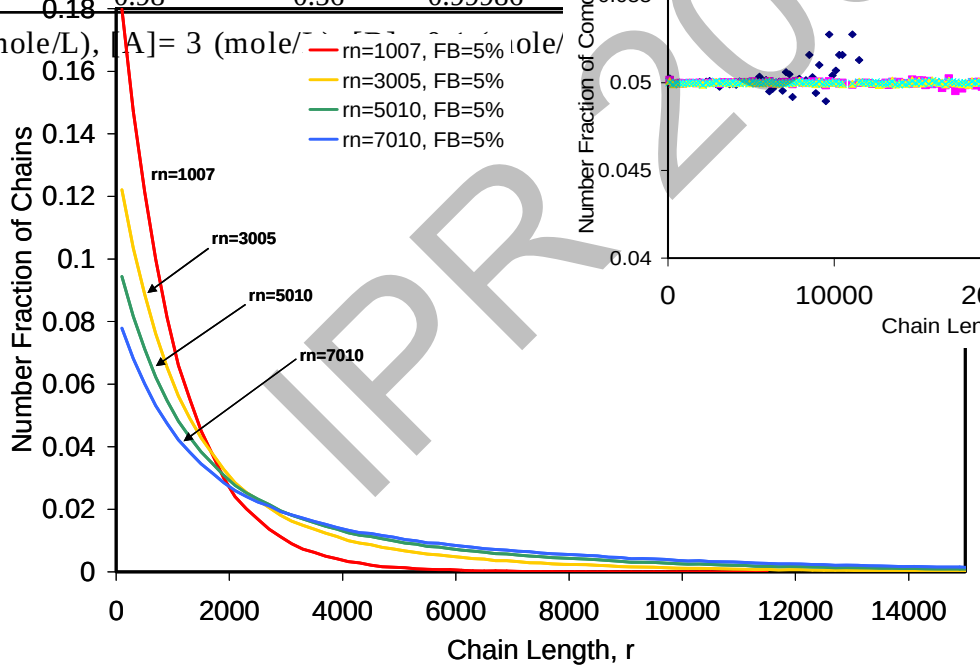

Chain Length & Segment Length Distribution
Triad Distribution
Simulation Results
Case Study
Triads Relative Intensities of $^{13}$C-NMR Spectra

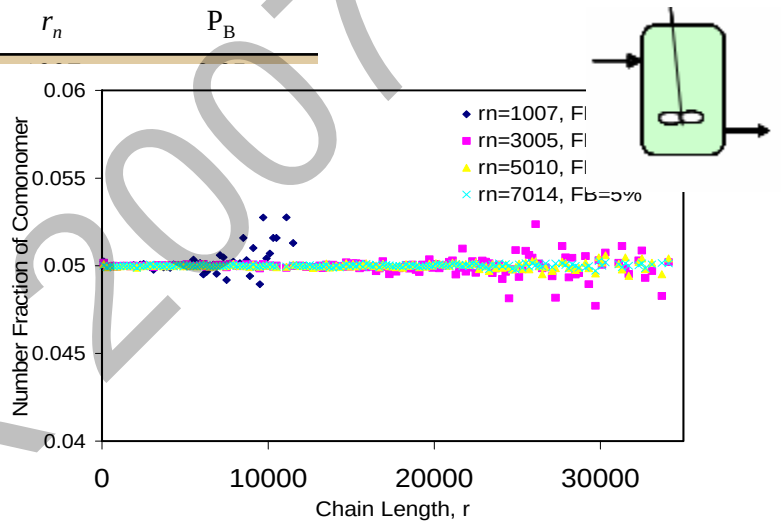
# Number Fraction of Chains as a Function of Chain Length and Comonomer Distribution

Four different simulations scenarios

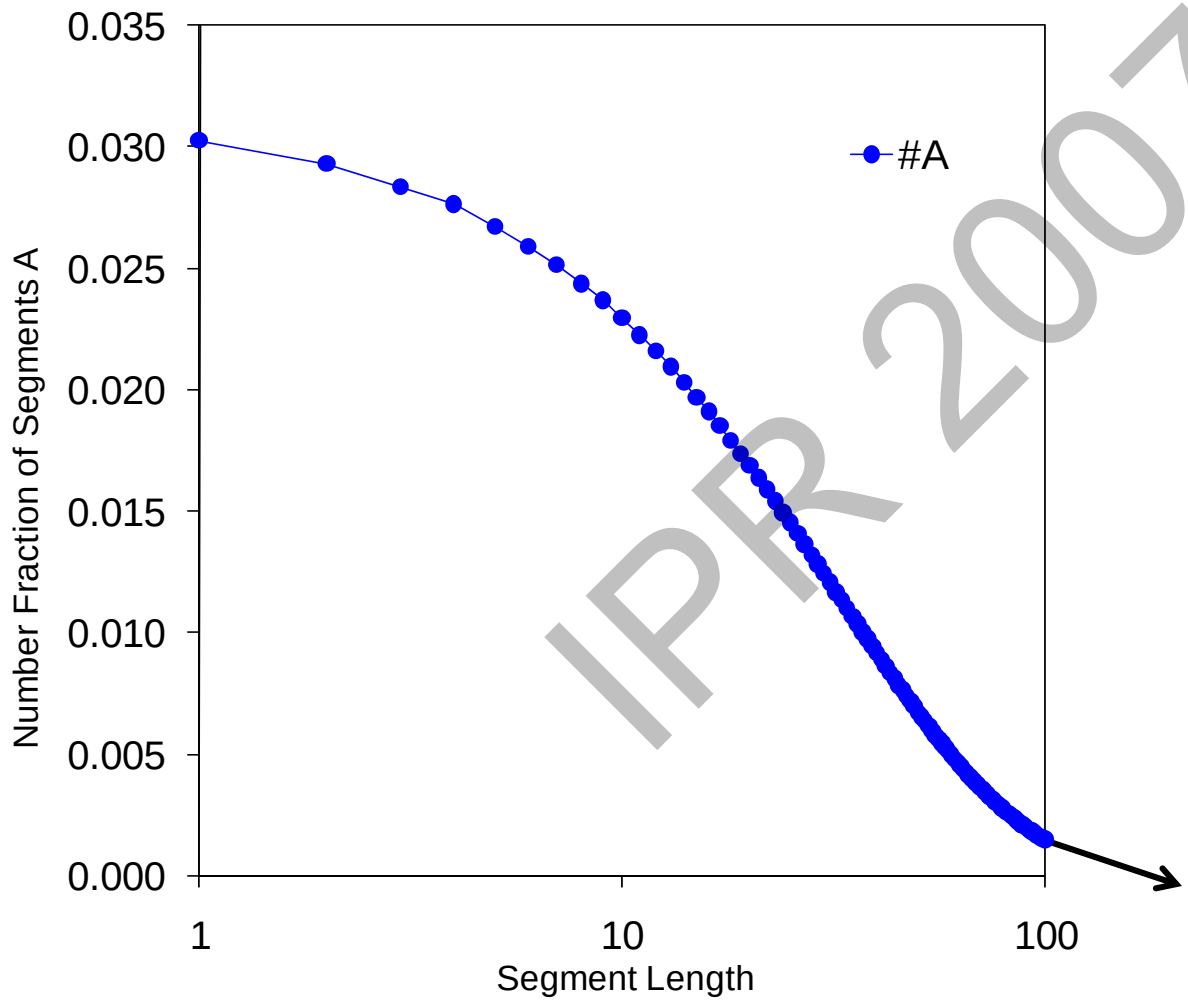
| $k_{pA}$ (L/mole.s) | $k_{pB}$ (L/mole.s) | $k_{tA}$ (L/mole.s) | $k_{tB}$ (L/mole.s) | *Pp* | $r_n$ | $P_B$ |
|---|---|---|---|---|---|---|
| 1210 | 1910 | 2.70 | 1.10 | 0.99901 | | |
| 2150 | 3395 | 1.35 | 0.91 | 0.99967 | | |
| 3220 | 5080 | 1.23 | 0.80 | 0.99980 | | |
| 3420 | 5340 | 0.98 | 0.56 | 0.99986 | | |

$[Pr^*]=10 \times 10^{-6}$ (mole/L), [A]= 3 (mole/[illegible]ole/ comonomer B



# Fraction of Monomer Segment Length, $A_n$ ($r_n$=5004, $F_B$=3%)





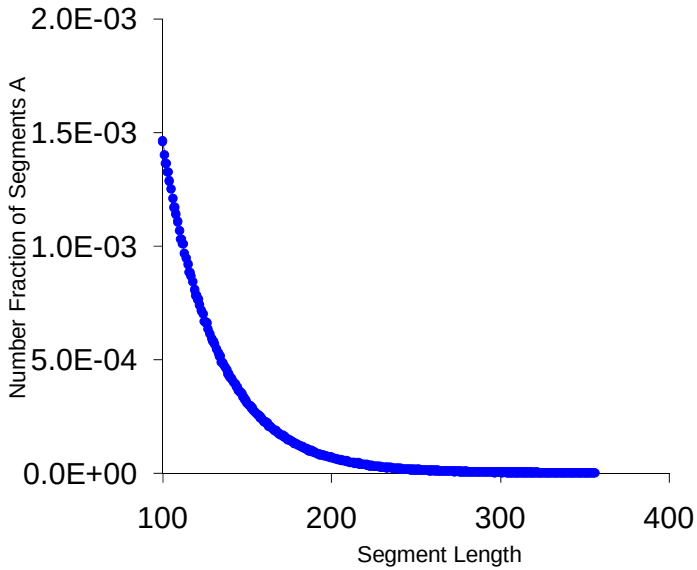

Monomer A Segment Length = 3

**AAABBAAABAABBBA**

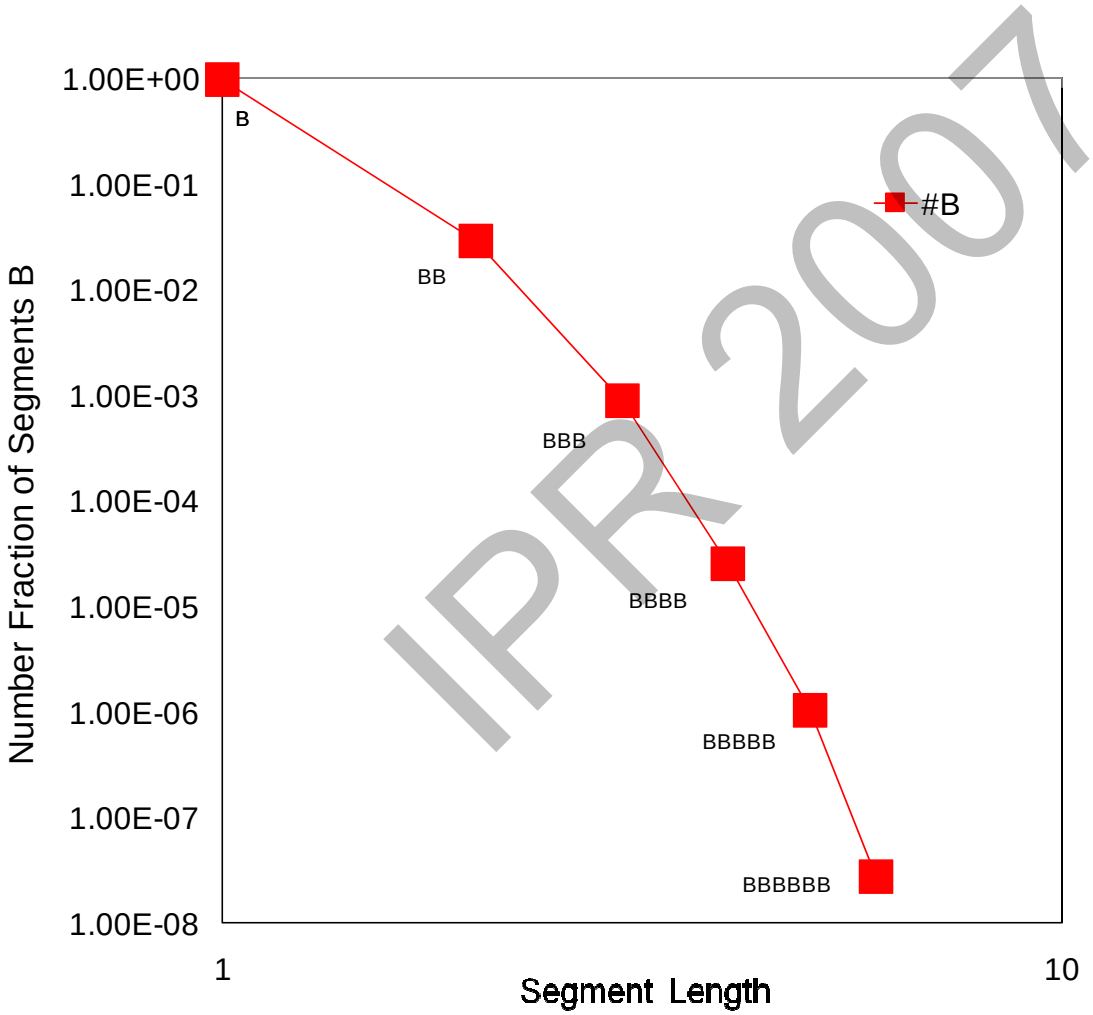
$(A)_n$

Segment < 20 monomer units will not crystallize

(Haag et. al.,2003)



# Fraction of Comonomer Segment Length $B_n$ ($r_n$=5004, $F_B$=3%)

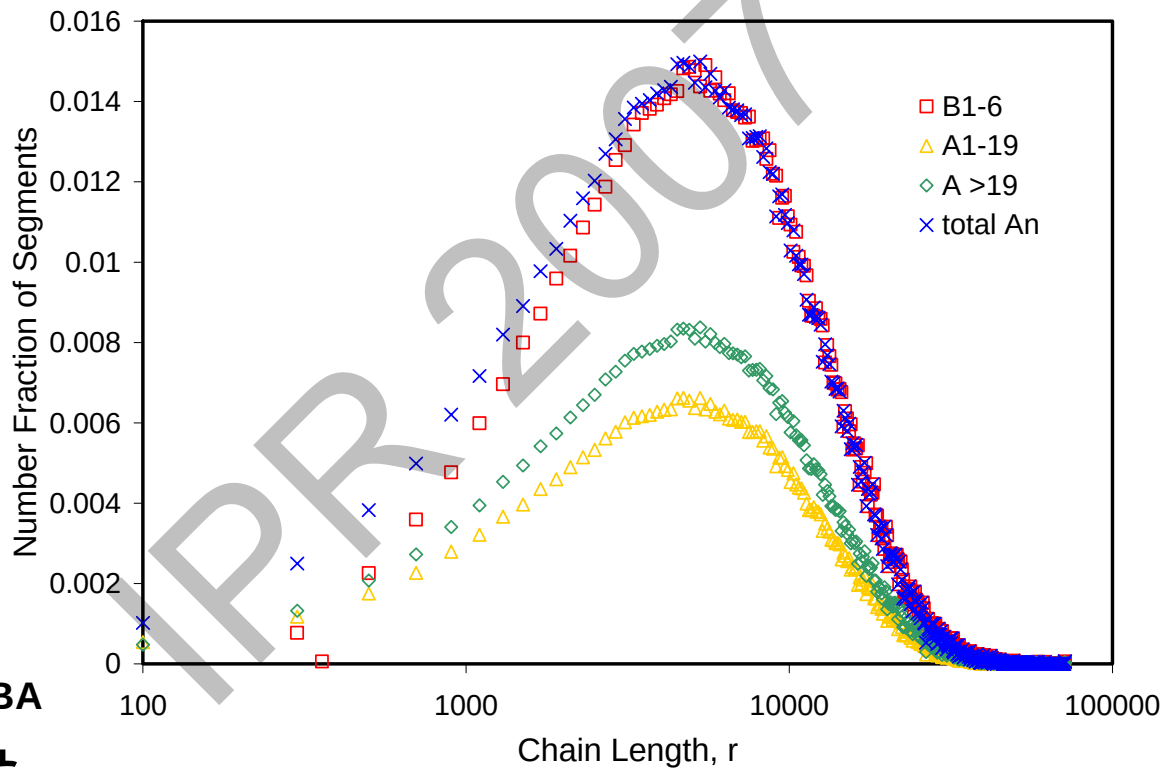





Monomer B Segment Length = 2

**AAABBAAABAABBBA**

# Distribution of Segments $B_{1\text{-}6}$, $A_{1\text{-}19}$, $A_{>19}$ and total $A_n$ as a Function of Chain Length ($r_n$=5004, $F_B$=3%)





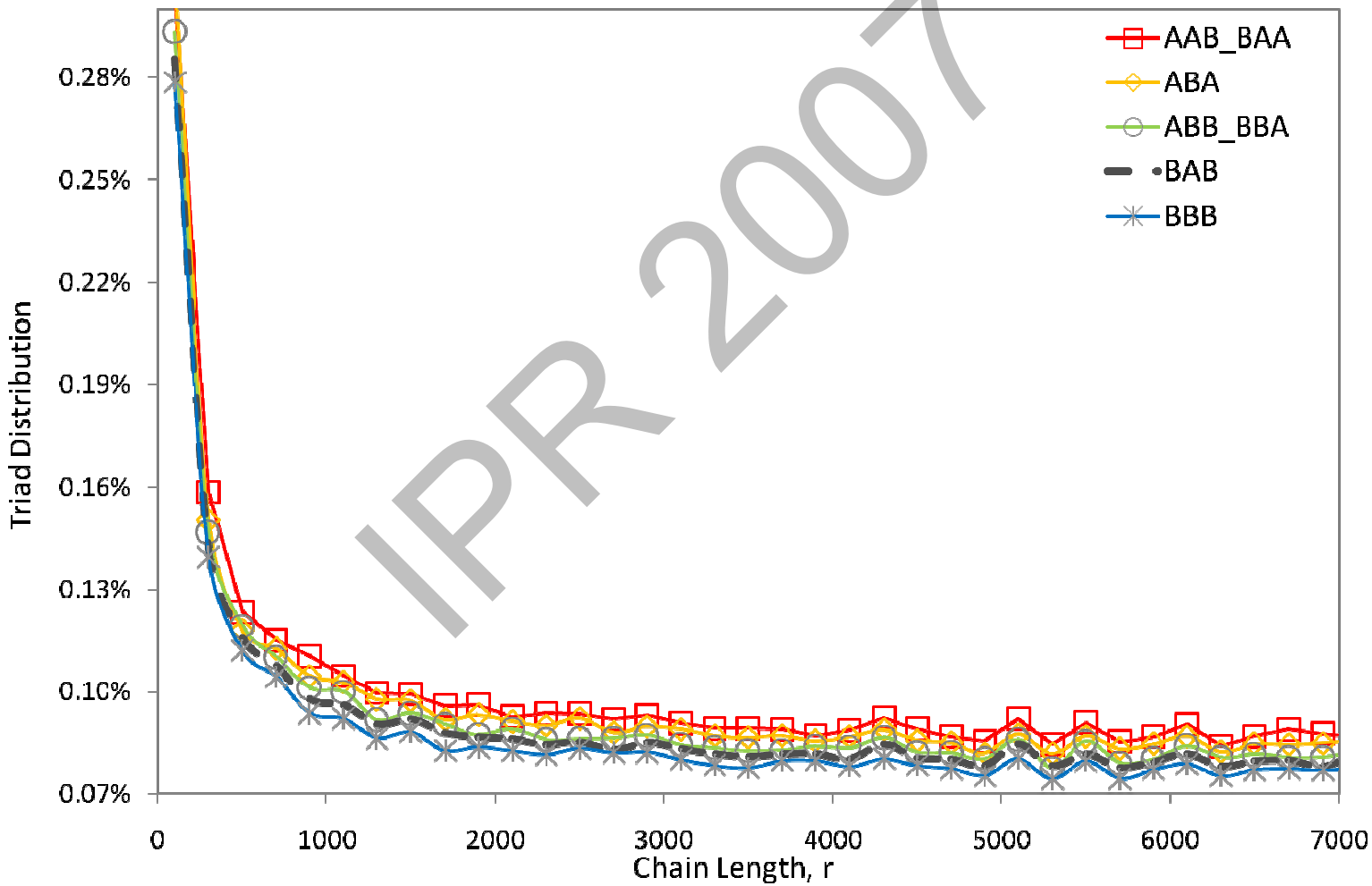

**AAABBAAABAABBBA**

$(A)_n$

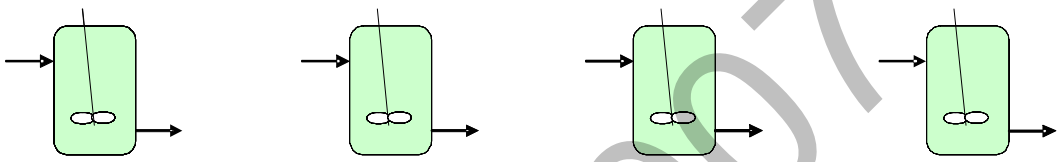
Segment < 20 monomer units will not crystallize

(Haag et. al.,2003)

# Triad Distribution as a Function of Chain Length ($r_n$=5004, $F_B$=3%)



# Case Study



| Reactor 1 (250k chains) | Reactor 2 (250k chains) | Reactor 3 (250k chains) | Reactor 4 (250k chains) |
|---|---|---|---|
| $r_n$ = 1008 | $r_n$ = 3001 | $r_n$ = 5004 | $r_n$ = 7024 |
| $F_B$ = 5% | $F_B$ = 4% | $F_B$ = 3% | $F_B$ = 2% |

Kinetic parameters used in the case study (representing four different reactor conditions)

| | $k_{pA}$ (L/mole.s) | $k_{pB}$ (L/mole.s) | $k_{tA}$ (L/mole.s) | $k_{tB}$ (L/mole.s) | $P_t$ | $P_p$ | $r_n$ | $P_B$ |
|---|---|---|---|---|---|---|---|---|
| $R_1$ | 1210 | 1910 | 2.70 | 1.10 | 0.00099 | 0.99901 | 1008 | 0.05 |
| $R_2$ | 2160 | 2700 | 1.25 | 1.00 | 0.00033 | 0.99967 | 3001 | 0.04 |
| $R_3$ | 2200 | 2040 | 0.79 | 0.57 | 0.00020 | 0.99980 | 5004 | 0.03 |
| $R_4$ | 3900 | 2390 | 0.92 | 0.78 | 0.00014 | 0.99986 | 7024 | 0.02 |

$[Pr^*]=10 \times 10^{-6}$ (mole/L), [A]= 3 (mole/L), [B]= 0.1 (mole/L)

# Case Study

Effect of product mixing from reactor1 to reactor 4 on the polymer parameters

| | $r_n$ | $r_w$ | PDI | $F_B$ |
|---|---|---|---|---|
| $R_1$ | 1008 | 2001 | 1.98 | 5.0% |
| $R_1$+$R_2$ | 2006 | 4994 | 2.49 | 4.5% |
| $R_1$+$R_2$+$R_3$ | 3007 | 7777 | 2.59 | 4.0% |
| $R_1$+$R_2$+$R_3$+$R_4$ | 4009 | 10513 | 2.62 | 3.5% |

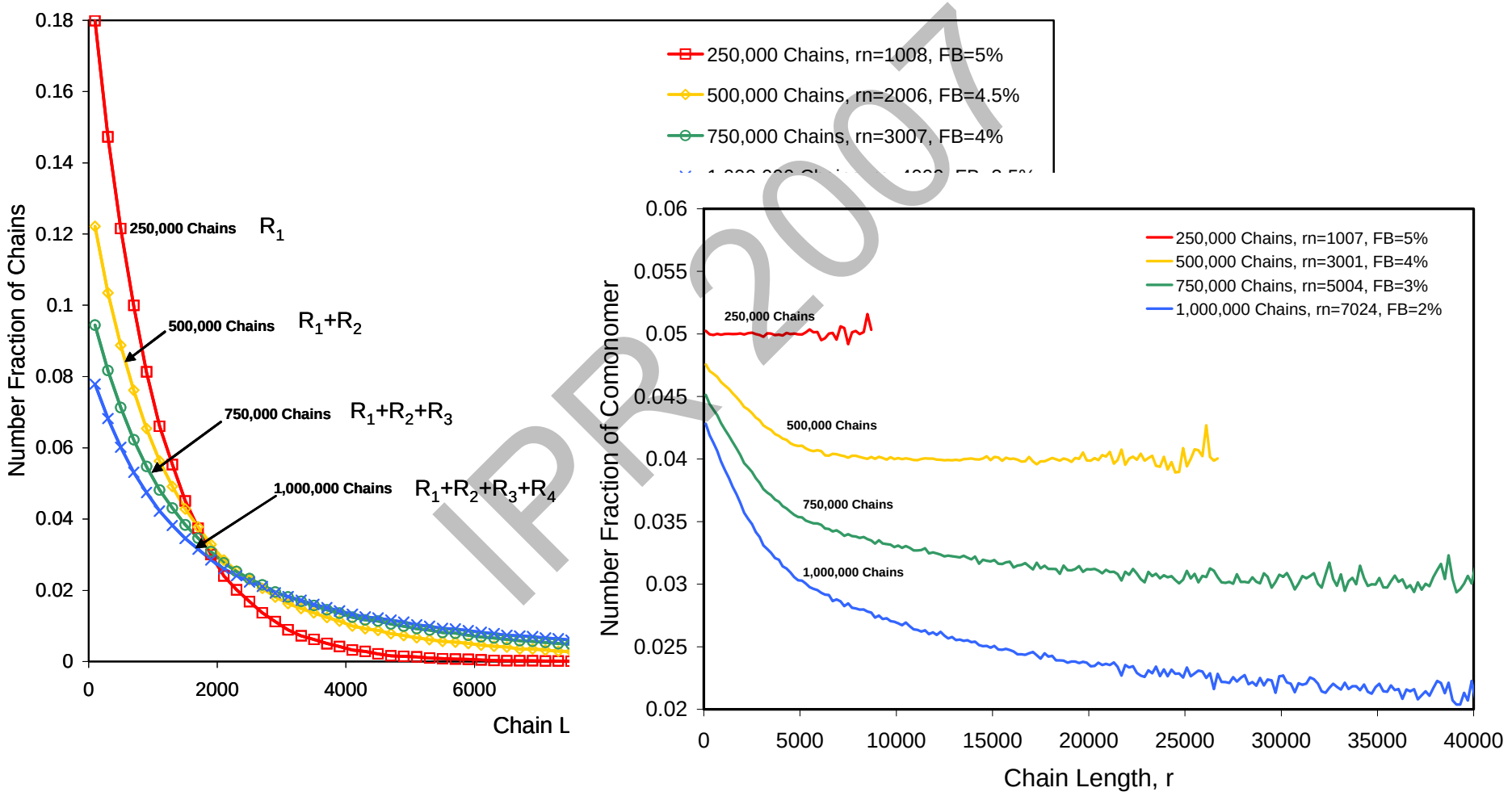
Kinetic parameters used in the case study after mixing (representing the products with $r_n$= 1008 to 4009 for mixed product from reactor 1 to reactor 4)

| | $k_{pA}$ (L/mole.s) | $k_{pB}$ (L/mole.s) | $k_{tA}$ (L/mole.s) | $k_{tB}$ (L/mole.s) | $P_t$ | $P_p$ | $r_n$ | $P_B$ |
|---|---|---|---|---|---|---|---|---|
| $R_1$ | 1210 | 1910 | 2.70 | 1.10 | 0.00099 | 0.99901 | 1008 | 0.05 |
| $R_1$+$R_2$ | 1100 | 1550 | 0.92 | 0.80 | 0.00050 | 0.99950 | 2006 | 0.045 |
| $R_1$+$R_2$+$R_3$ | 1308 | 1650 | 0.79 | 0.57 | 0.00033 | 0.99967 | 3007 | 0.04 |
| $R_1$+$R_2$+$R_3$+$R_4$ | 2220 | 2400 | 0.94 | 0.78 | 0.00025 | 0.99975 | 4009 | 0.035 |

$[Pr^*]=10\ \ 10^{-6}$ (mole/L), [A]= 3 (mole/L), [B]= 0.1 (mole/L)

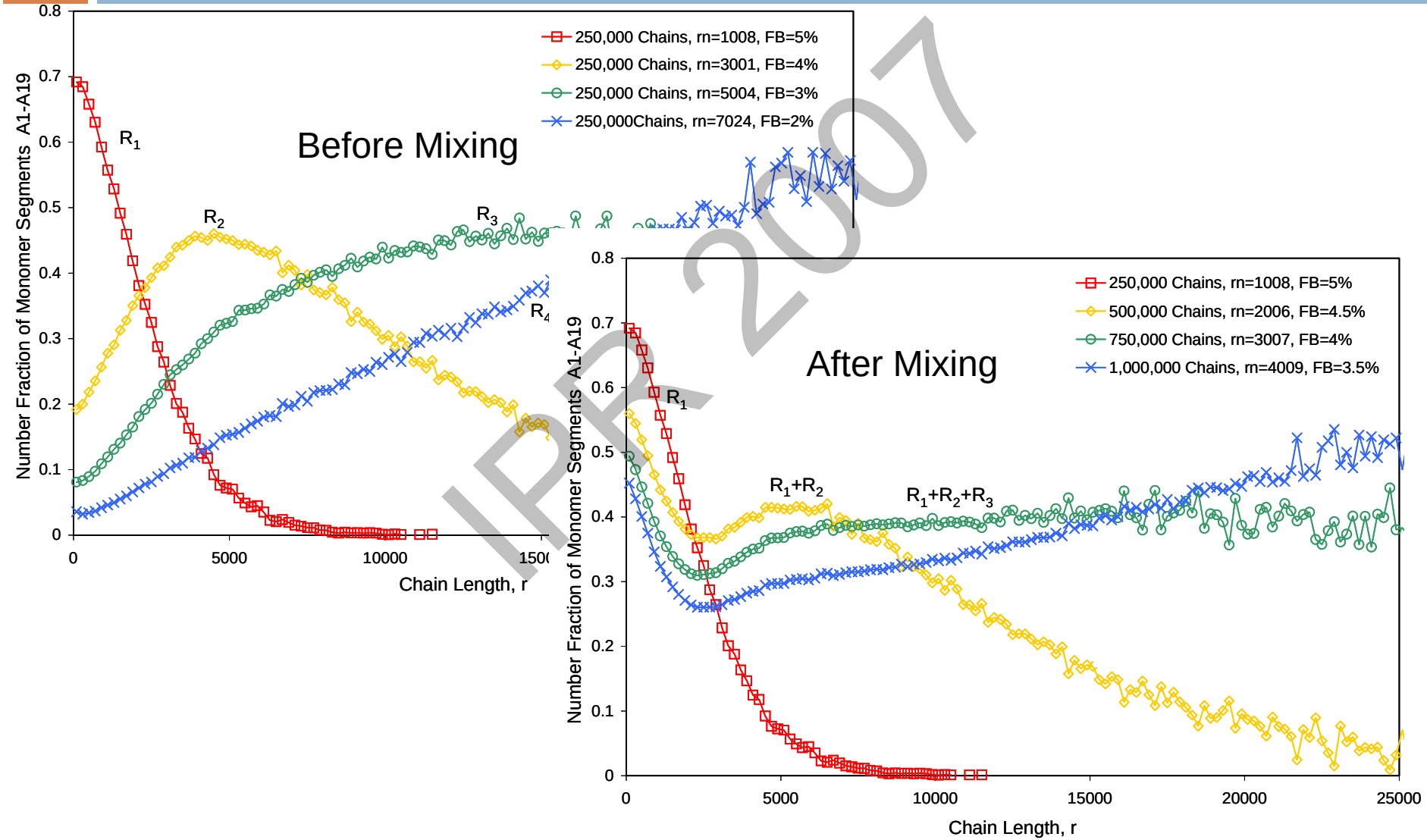
# Case Study

From reactor 1 with 250,000 chains to reactor 4 with 1,000,000 chains



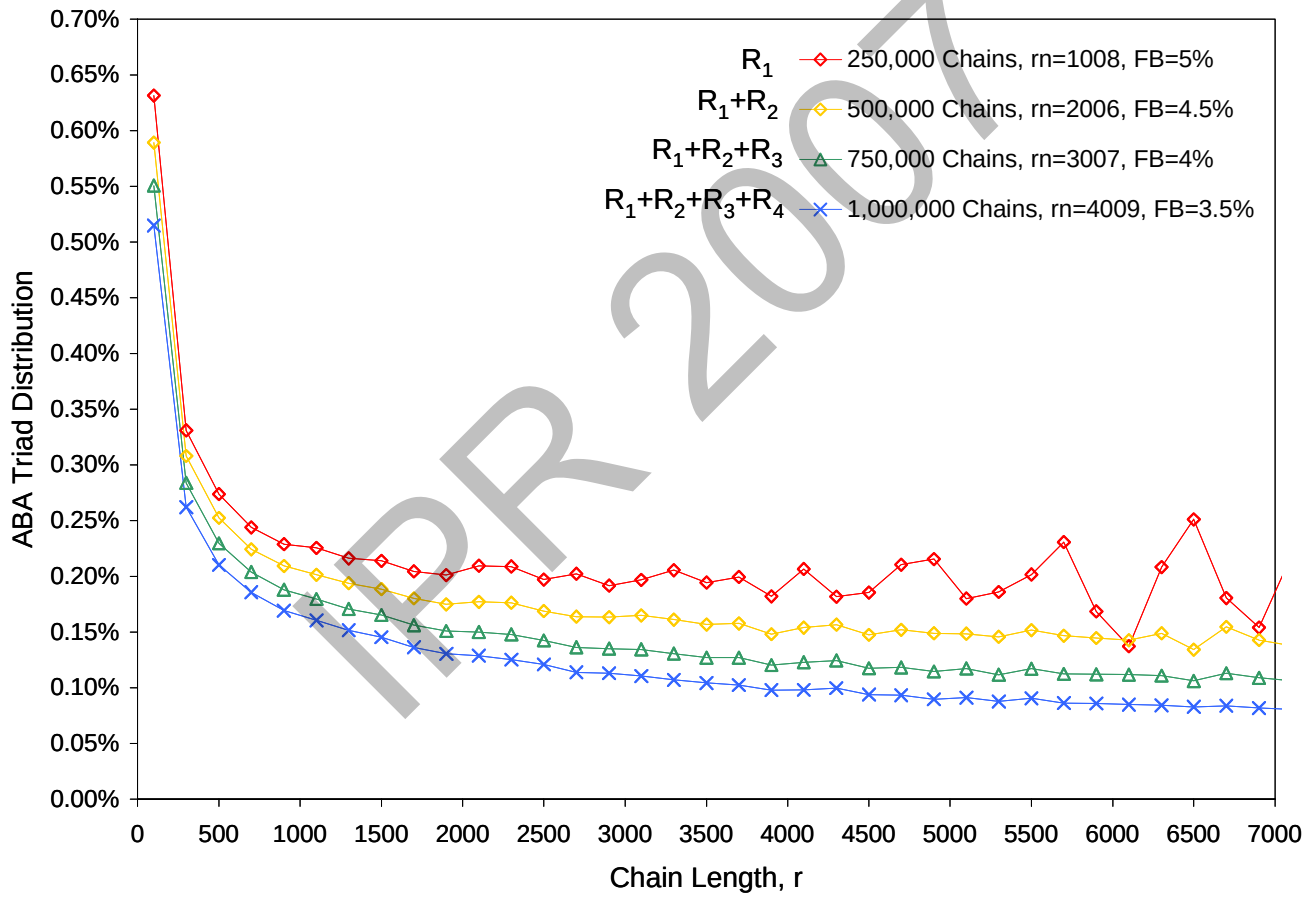
# Case Study

Number fraction of monomer segments for $A_1$ to $A_{19}$ from reactor 1 with 250,000 chains to reactor 4 with 1,000,000 chains as function of chain length



# Case Study

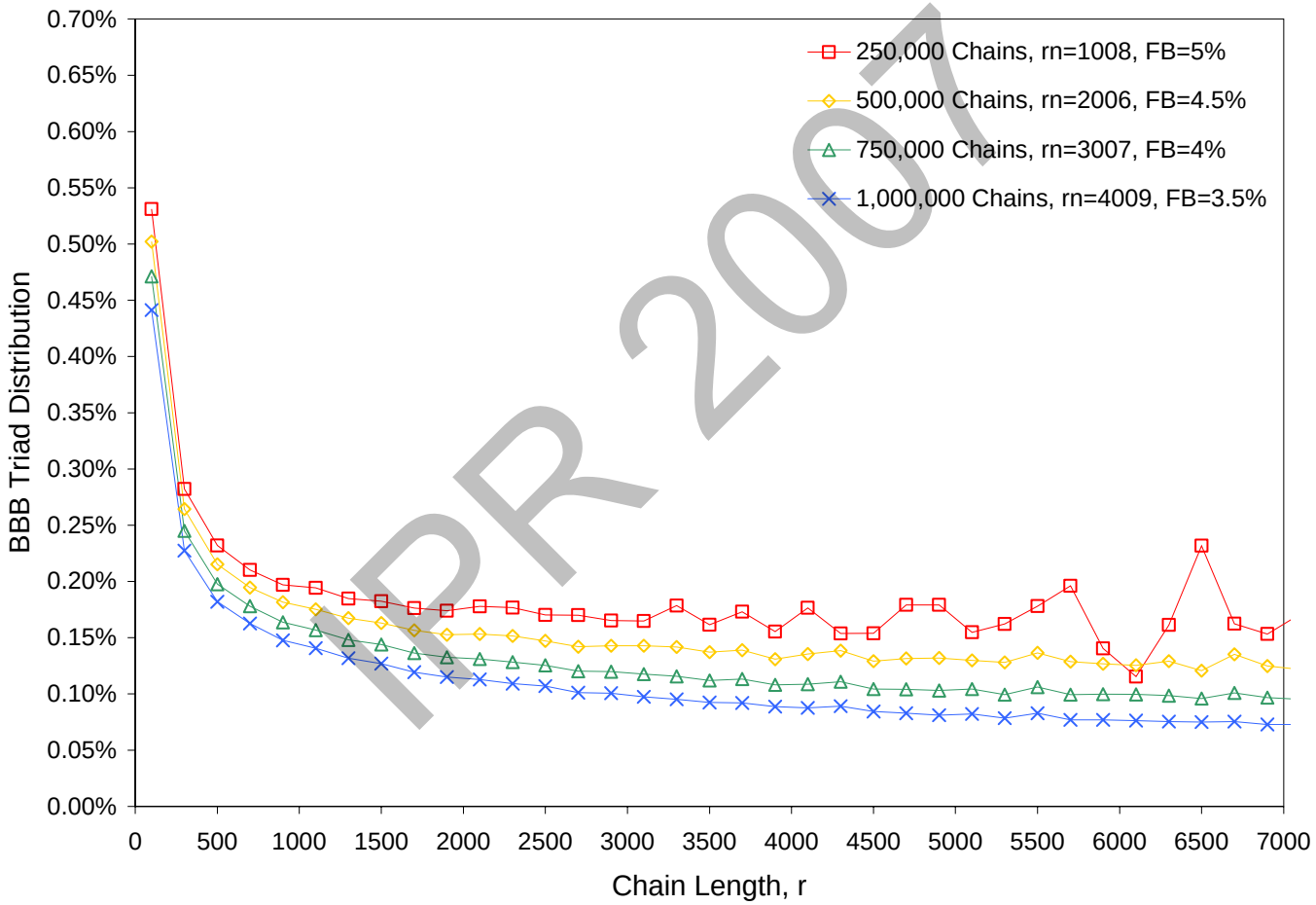
## *Triad Distribution*






ABA triad distribution from reactor 1 with 250,000 chains to reactor 4 with 1,000,000 chains as function of chain length (varying $r_n$, $F_B$)

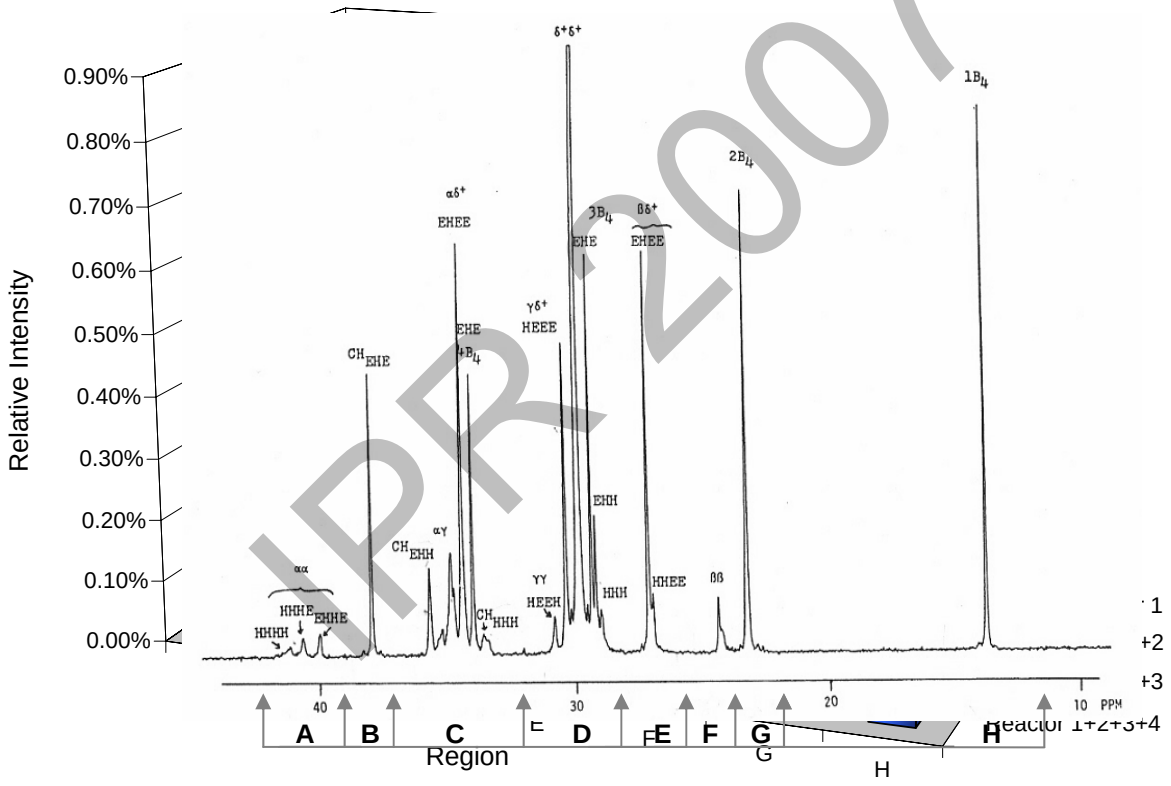
# Case Study





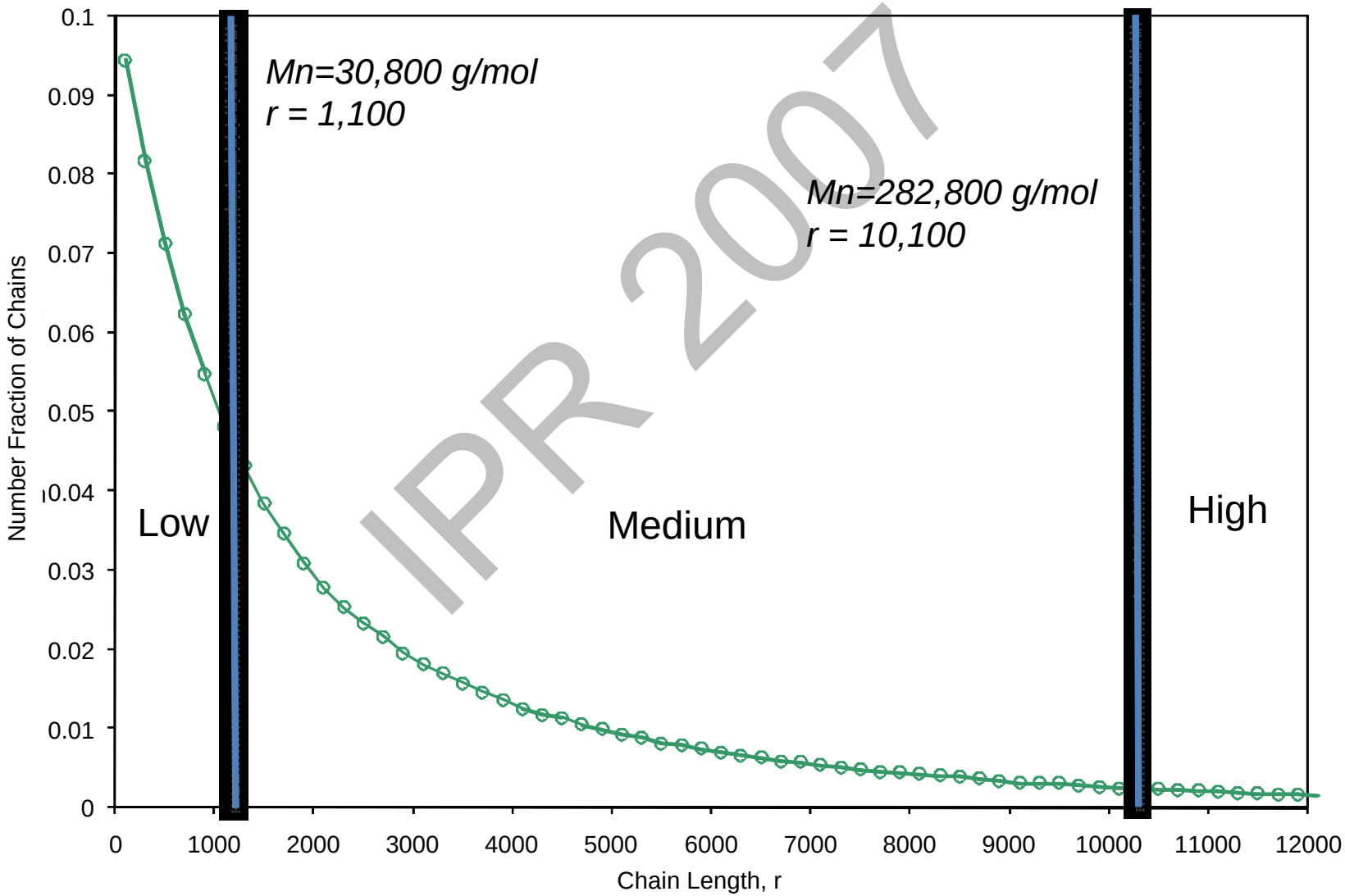

BBB triad distribution from reactor 1 with 250,000 chains to reactor 4 with 1,000,000 chains as function of chain length (varying $r_n$, $F_B$)

# Triads Relative Intensities




The relative intensities of $^{13}$C-NMR spectra for the branching regions

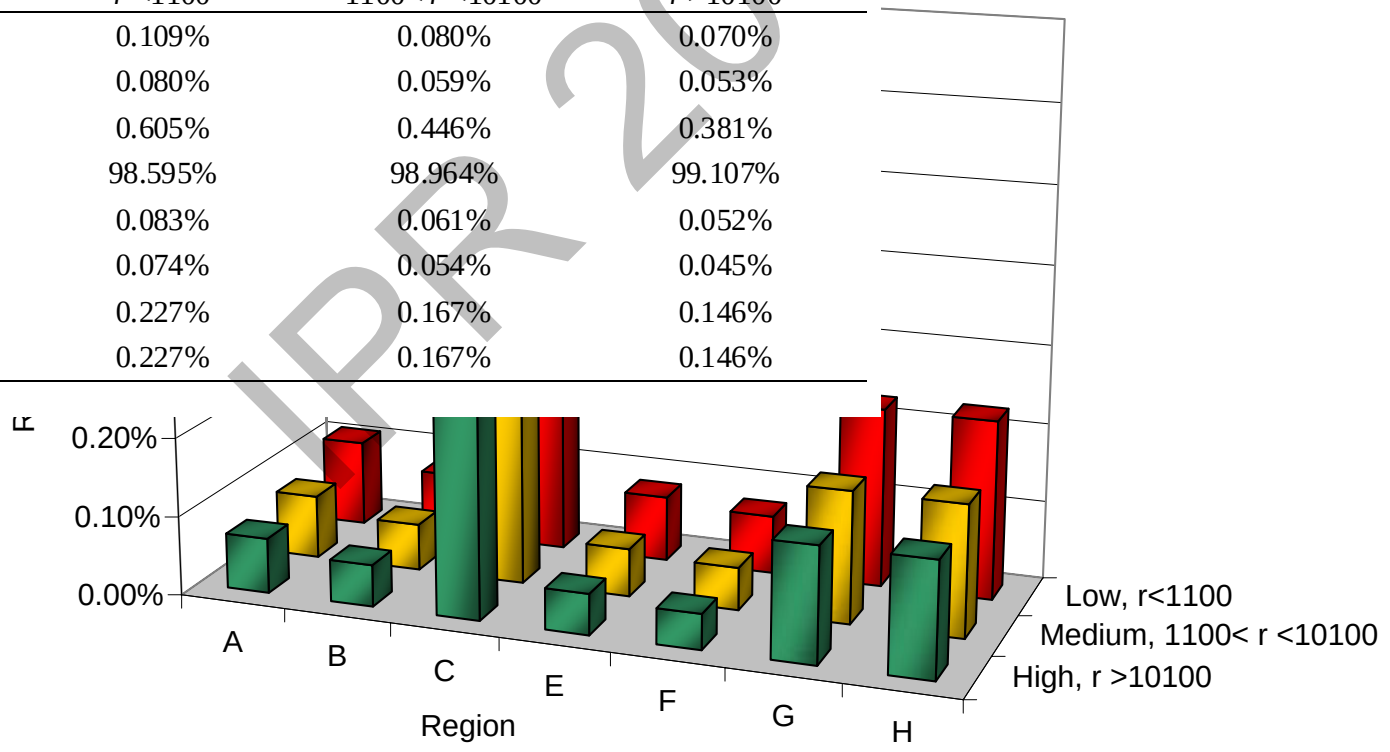
# Fractionated Chain Length Population



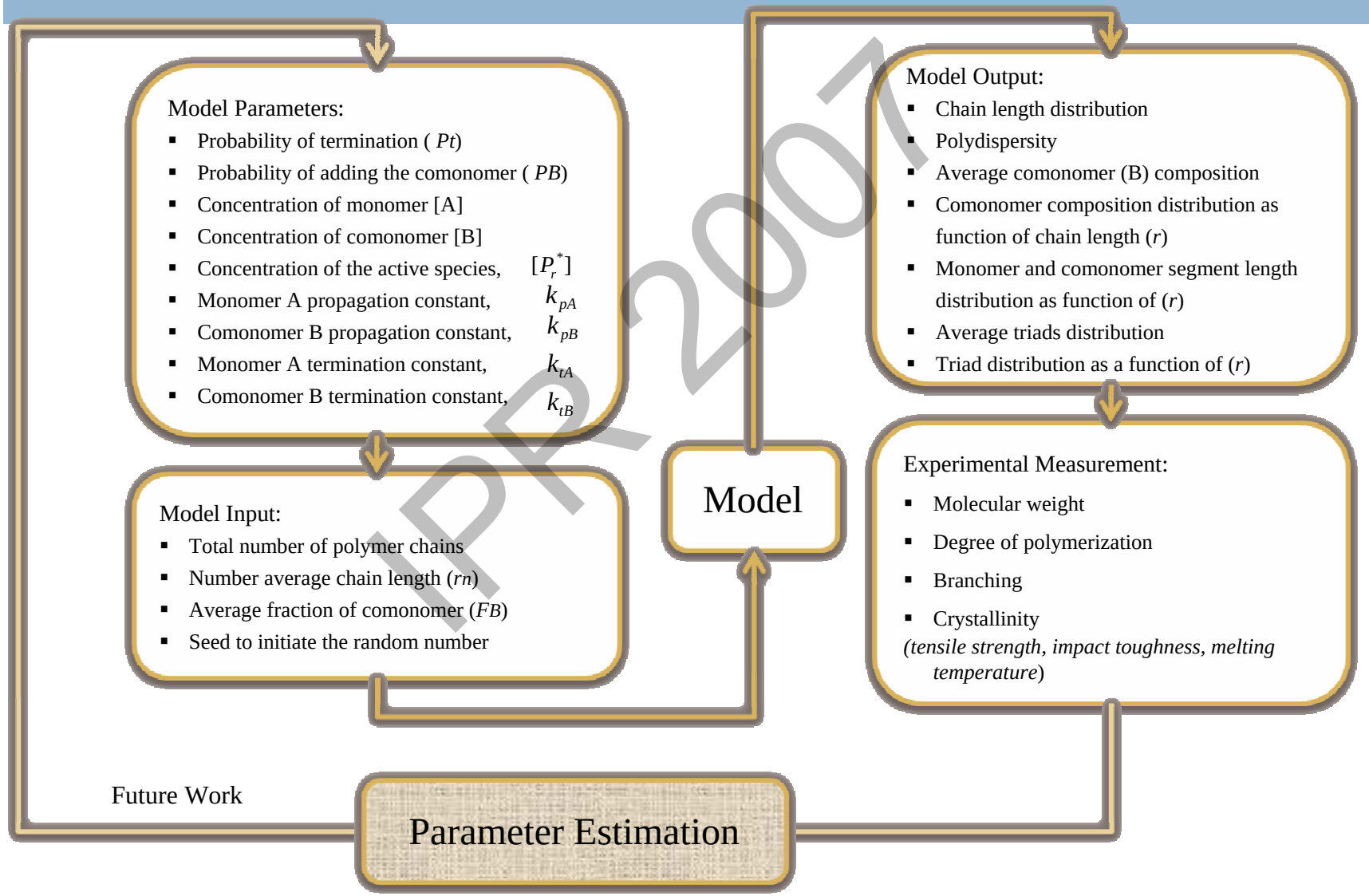
# Triads Relative Intensities

Table-7 Fractionated population classes for the relative intensities with respective regions of reactor 4 after mixing the products from reactor 1 to 4 ($R_1$+$R_2$+ $R_3$+ $R_4$) according to chain length ($r$)

| Region | Low<br>$r$ <1100 | Medium<br>1100< $r$ <10100 | High<br>$r$ >10100 |
|---|---|---|---|
| A | 0.109% | 0.080% | 0.070% |
| B | 0.080% | 0.059% | 0.053% |
| C | 0.605% | 0.446% | 0.381% |
| D | 98.595% | 98.964% | 99.107% |
| E | 0.083% | 0.061% | 0.052% |
| F | 0.074% | 0.054% | 0.045% |
| G | 0.227% | 0.167% | 0.146% |
| H | 0.227% | 0.167% | 0.146% |



# Future Research Work



# Conclusions

- The comprehensive Monte Carlo model which is developed and tested in this research work was able to describe the detailed comonomer distribution in the copolymerization of ethylene-α-olefins.
- For copolymerization, the model was able to predict chain length and comonomer sequence distribution with great detail.
- In the case of copolymerization the fraction of monomer B incorporated in the polymer chain was not dependant on the size of the chain, which is in agreement with the polymerization mechanism.
- The input information for running the model can be obtained from experimental polymer analysis or through the reaction kinetics.

# Conclusions

- The input information is used to calculate model probabilities that are then used to determine each event of the polymerization mechanism.
- The model demonstrated great ability in predicting the detailed segment length distribution as a function of chain length, as well as the relative intensity for the peaks of the $^{13}$C-NMR.
- This is a powerful tool to explore the chemical composition of the polymer in more detail.
- Knowing the segment lengths and triads distribution as a function of chain length is an advantage that allows us to study the polymerization mechanism and the properties of the polymer.