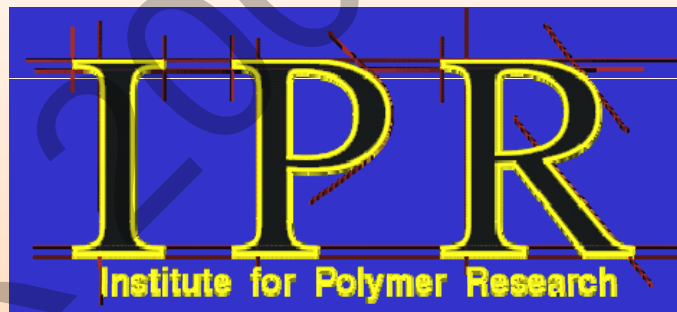


# Studies on chemical heterogeneity of multi-component polymers: Sequence Length Distributions



**Woosung Jung, T. A. Duever, A. Penlidis**

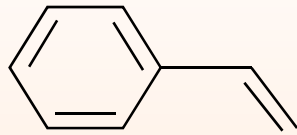
**Department of Chemical Engineering  
IPR annual symposium, University of Waterloo  
May 13, 2008**

# Outline

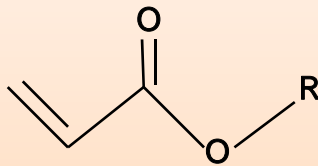
- **Introduction**
- **Copolymerization characteristics**
- **Macroscopic approach**
- **Microscopic approach**
- **Summary**

# Introduction

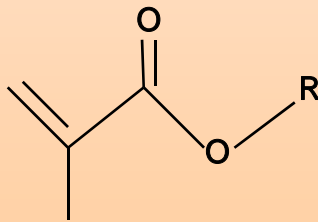
## - Multicomponent polymerization



M<sub>1</sub>



M<sub>2</sub>



M<sub>3</sub>

Monomer species

Propagation



Polymer chain

Composition  
& Arrangement

# Introduction

- **Multicomponent polymerization**
- **Competitive** reactions between same or different radical/monomer species
- Governed by **probabilistic** nature of reactions
- Numerous combinations of monomer species
- Macroscopic approach (Composition)
- Microscopic approach (SLD & Triad fraction)

# Copolymerization characteristics

## Model

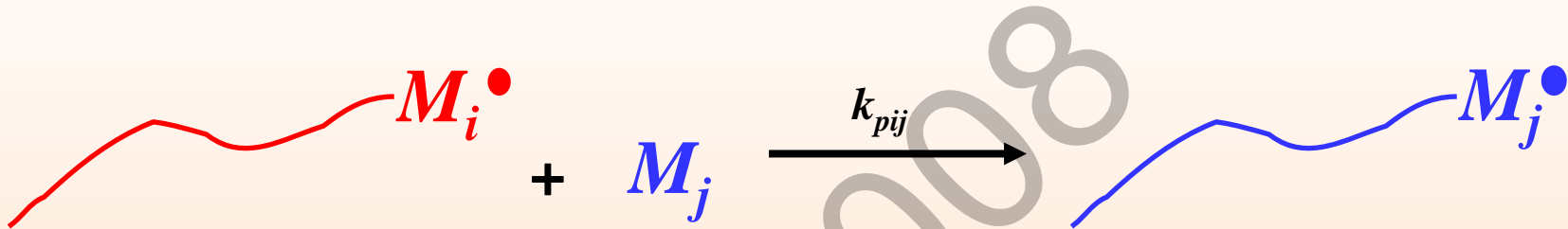
- Random (Bernoullian)
- Statistical (1<sup>st</sup>/2<sup>nd</sup> order Markov)

## Structures

- Alternating ( $-M_1M_2M_1M_2M_1M_2M_1M_2-$ )
- Block ( $-M_1M_1M_1M_1M_1M_2M_2M_2M_2M_1M_1-$ )
- Graft ( $-M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1-$ )  
|  
 $M_2M_2M_2M_2M_2-$

# Copolymerization characteristics

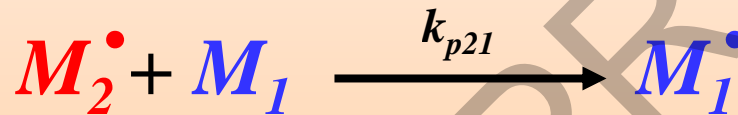
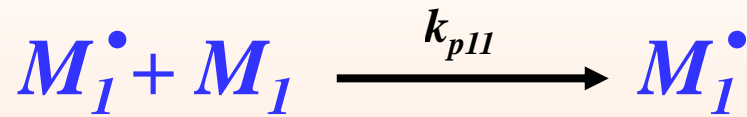
## - 1<sup>st</sup> order Markov (terminal) model



Reactivity of the propagating chain depends only on the monomer unit at **the growing end** and independent of chain composition.

# Copolymerization characteristics

## - 1<sup>st</sup> order Markov (terminal) model

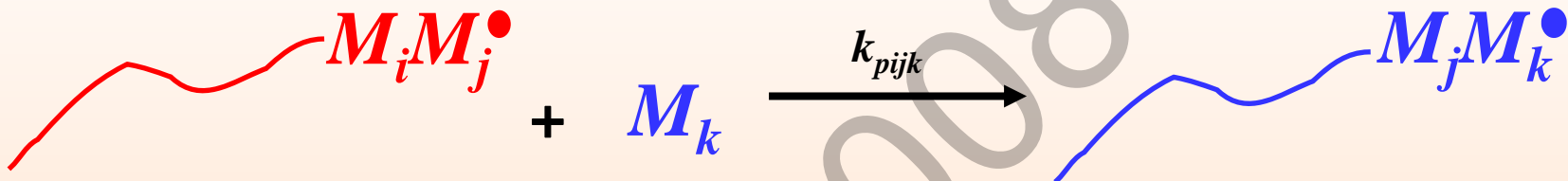


$$r_1 = \frac{k_{p11}}{k_{p12}}$$

$$r_2 = \frac{k_{p22}}{k_{p21}}$$

# Copolymerization characteristics

- 2<sup>nd</sup> order Markov (penultimate) model



Reactivity of the propagating chain is affected by **the last and the next-to-last** monomer units and independent of chain composition.

# Copolymerization characteristics

## - Reactivity ratios

- **Relative** rate of *homo-* to *cross-*propagation
- Estimated from experimental (**NMR**) data
- $r > 1$  : *homo*-propagation favored
- $r < 1$  : *cross*-propagation favored
- $r = 0$  : No *homo*-propagation (alternating)
- *Q-e* scheme, Hammett and Taft equation for starting values
- Determines **polymerization tendency**

# Macroscopic approach

## - Instantaneous composition

$$-\frac{d[M_i]}{dt} = \sum_{j=1}^N k_{pji} [R_j^\bullet] [M_i]$$

**Material balances**

$$k_{pij} [R_i^\bullet] [M_j] = k_{pji} [R_j^\bullet] [M_i]$$

**Steady-state hypothesis**

$$f_i = \frac{[M_i]}{\sum_{i=1}^N [M_i]}$$

**Monomer feed composition**

$$F_i = \frac{d[M_i]}{\sum_{i=1}^N d[M_i]}$$

**Instantaneous composition  
of multi-component polymer**

**N = 2: Mayo-Lewis**

**N = 3: Walling-Briggs**

# Macroscopic approach

## - Instantaneous composition

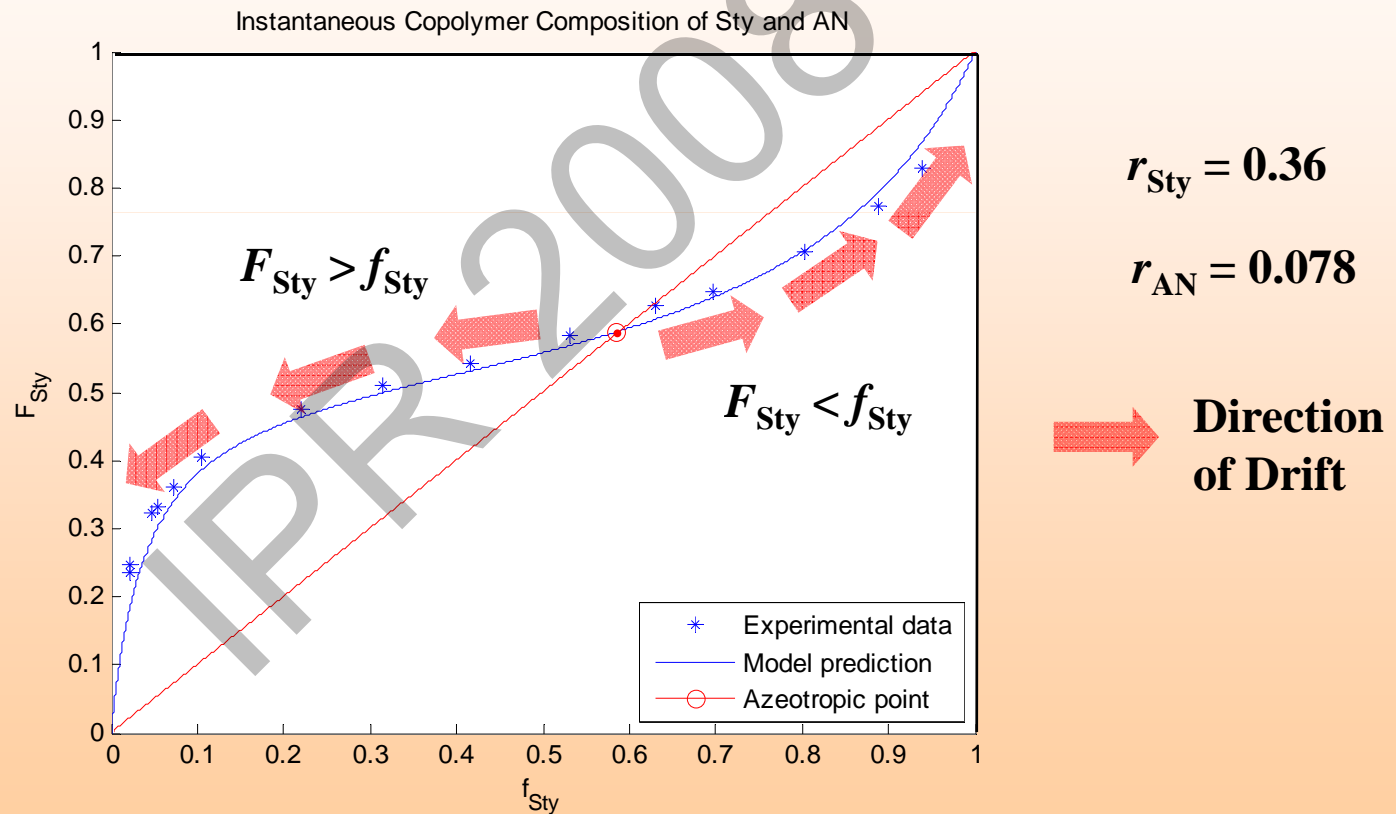


Figure 1. Simulation of **Styrene-Acrylonitrile** bulk *co*-polymerization  
T = 60°C (Experimental data from Hill *et al.*, 1982)

# Macroscopic approach

## - Instantaneous composition

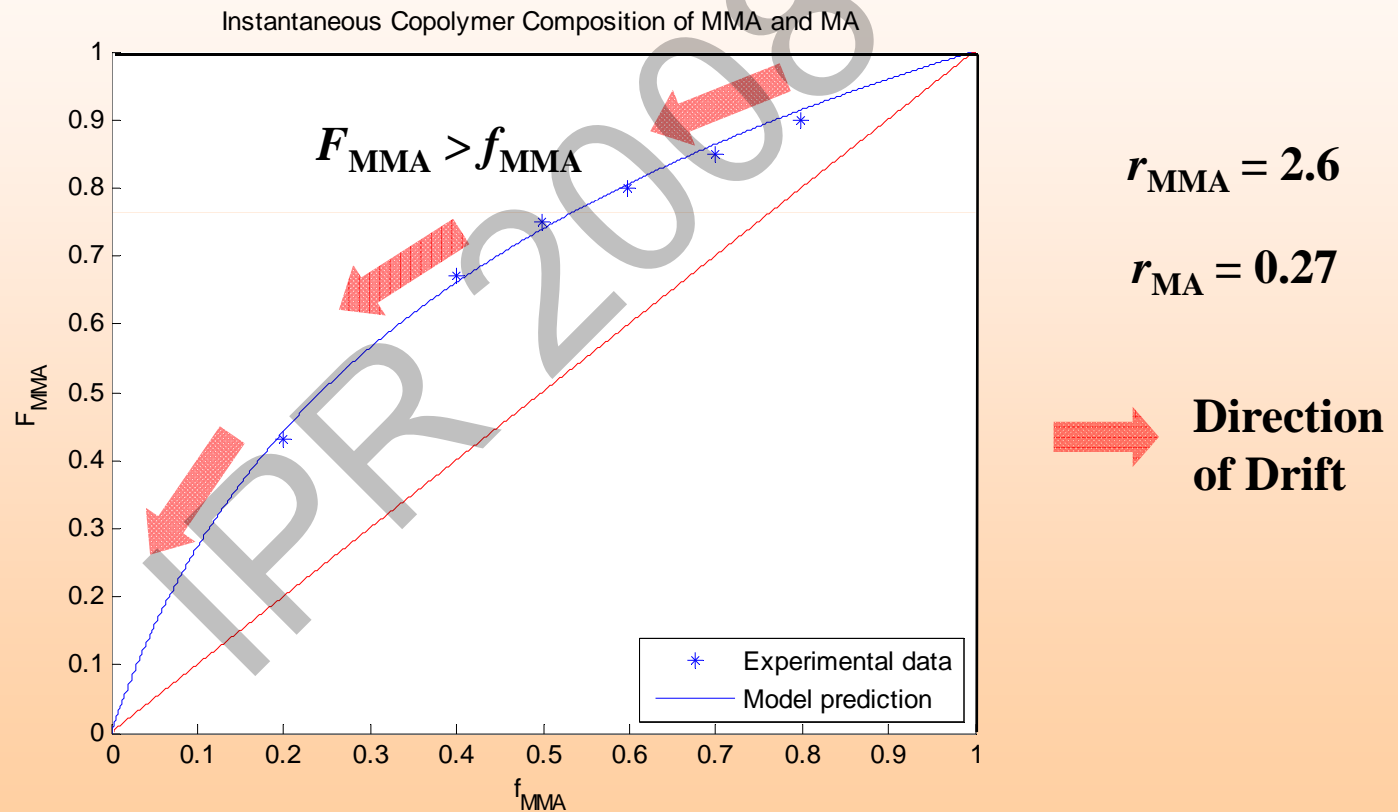


Figure 2. Simulation of **Methyl methacrylate-Methyl acrylate** bulk *co*-polymerization  
 $T = 50^{\circ}\text{C}$  (Experimental data from Kim and Harwood, 2002)

# Macroscopic approach

## - Cumulative (average) composition

$$\ln(1 - X) = \int_{f_{i0}}^{f_i} \frac{df_i}{F_i - f_i}$$

Skeist, Meyer-Lowry

$$X = \frac{[M]_0 - [M]}{[M]_0} = \frac{[P]}{[M] + [P]}$$

Conversion

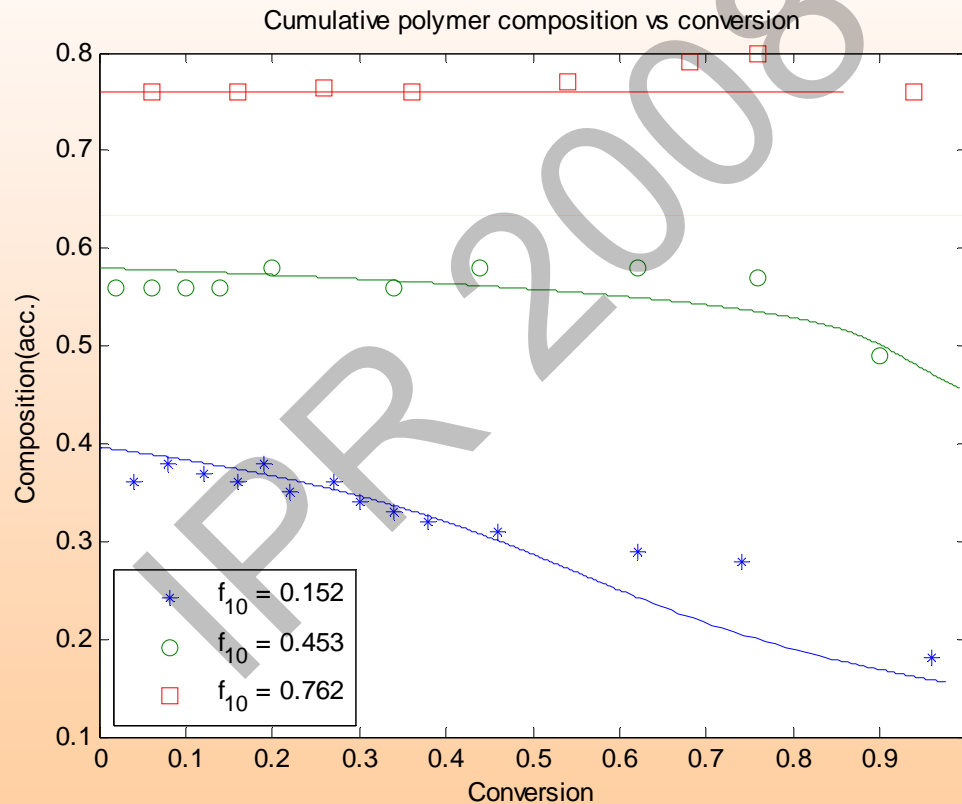
$$\bar{F}_i = \frac{[P_i]}{\sum_{i=1}^N [P_i]}$$

Cumulative composition  
of multi-component polymer

Composition changes during polymerization;  
**‘Composition drift’**

# Macroscopic approach

## - Cumulative composition drift



$$r_{\text{Sty}} = 0.717$$

$$r_{\text{EA}} = 0.128$$

Figure 3. Simulation of **Styrene-Ethyl acrylate** bulk *co*-polymerization  
T = 50°C (Experimental data from McManus and Penlidis, 1996)

# Macroscopic approach

## - Limitation

- Does not give information on monomer arrangements



*Block*



*Alternating*

- Different properties, same composition

$$F_{1, \text{Block}} - F_{1, \text{Alternating}} = 0.5$$

# Microscopic approach

## - Sequence Length Distribution (SLD)

- Shows intramolecular heterogeneity

$M_1M_1M_1M_1M_1M_2M_2M_2M_2M_2$

*Block*

$M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2$

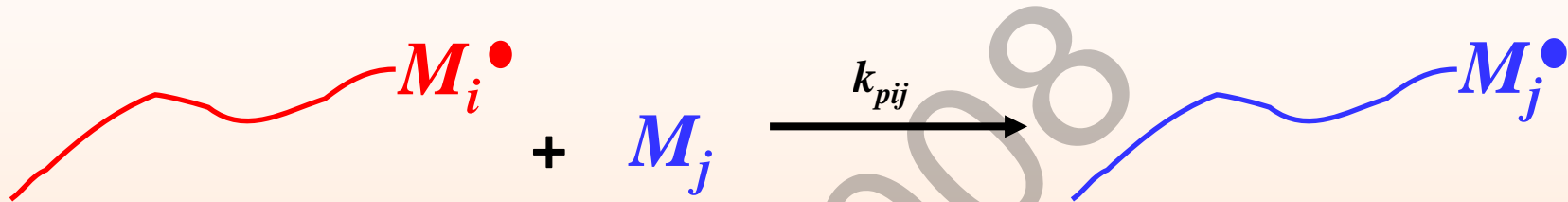
*Alternating*

Sequence length of  $M_{1, \text{Block}} = 5$

Sequence length of  $M_{1, \text{Alter.}} = 1$

# Microscopic approach

## - Sequence Length Distribution (SLD)



$$P_{ij} = \frac{k_{pij} [R_i^\bullet] [M_j]}{\sum_{j=1}^N k_{pij} [R_i^\bullet] [M_j]} = \frac{k_{pij} [M_j]}{\sum_{j=1}^N k_{pij} [M_j]} = \frac{k_{pij} f_j}{\sum_{j=1}^N k_{pij} f_j}$$

$$\sum_{j=1}^N P_{ij} = P_{ii} + \sum_{k=1}^N P_{ik} = 1 \quad (k \neq i)$$

Probability of reaction between **radical species  $i$**   
and **monomer species  $j$**

# Microscopic approach

## - Sequence Length Distribution (SLD)

$$N_{in} = P_{ii}^{n-1} \sum_{k=1}^N P_{ik}$$
$$= P_{ii}^{n-1} (1 - P_{ii}) \quad (k \neq i)$$

Probability of having  
***n* consecutive units**  
of monomer species *i*



$$N_{15} = (P_{11})^4 P_{12}$$

$$\sum_{n=1}^{\infty} N_{in} = \sum_{k=1}^N P_{ik} \left( \sum_{n=1}^{\infty} P_{ii}^{n-1} \right)$$
$$\approx \sum_{k=1}^N P_{ik} \frac{1}{1 - P_{ii}} = \frac{1 - P_{ii}}{1 - P_{ii}} = 1 \quad (k \neq i)$$

Long Chain Approximation

# Microscopic approach

## - Sequence Length Distribution (SLD)

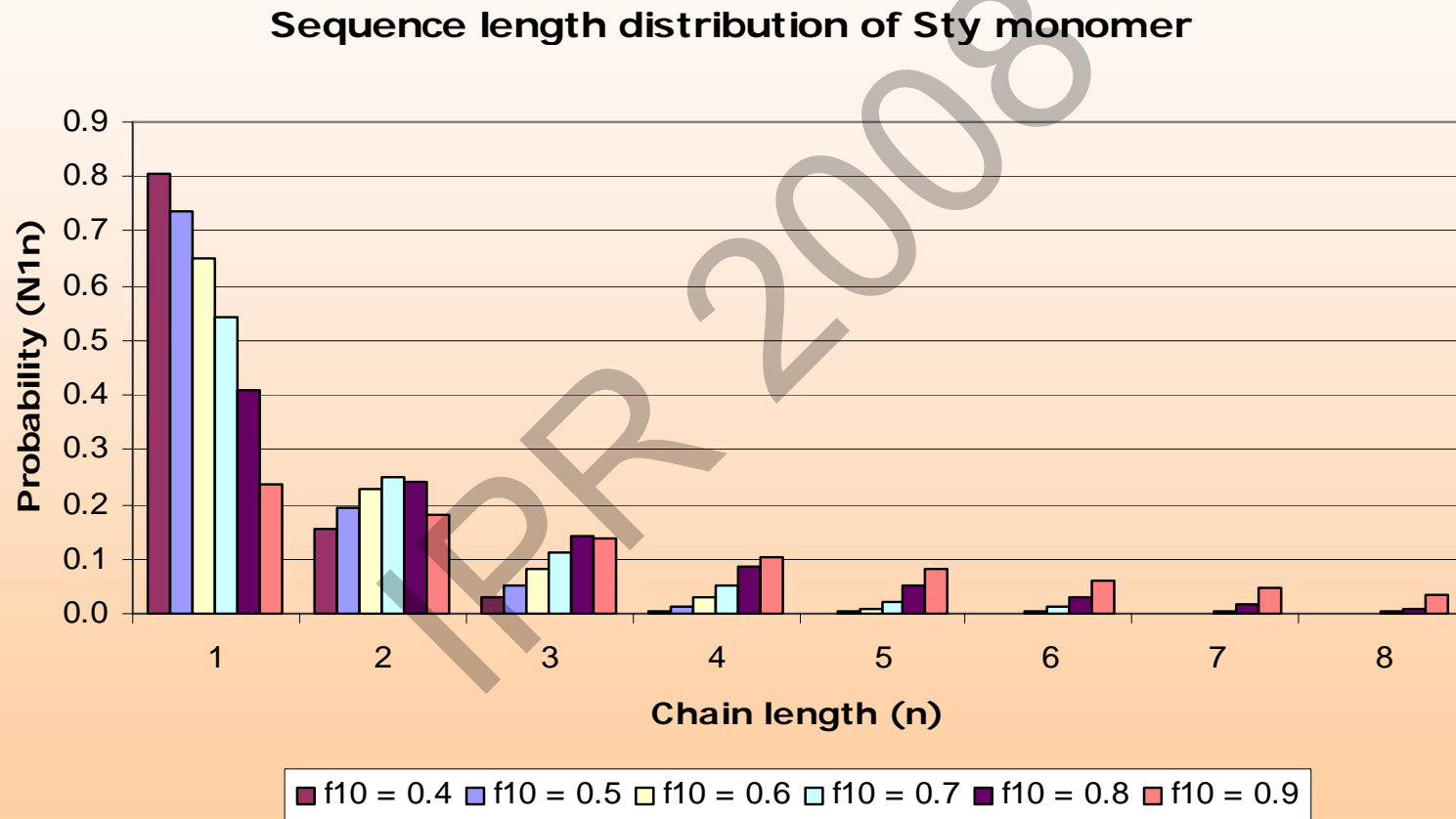


Figure 4. Sequence Length Distribution of Sty monomer in **Styrene-Acrylonitrile** *co*-polymer,  $T = 60^{\circ}\text{C}$

# Microscopic approach

## - Average Sequence Length

$$\bar{n}_i = \frac{\sum_{n=1}^{\infty} nN_{in}}{\sum_{n=1}^{\infty} N_{in}} = \sum_{n=1}^{\infty} nN_{in} = N_{i1} + 2N_{i2} + 3N_{i3} + \dots = \sum_{n=1}^{\infty} \{nP_{ii}^{n-1}(1 - P_{ii})\}$$

$$= \sum_{n=1}^{\infty} nP_{ii}^{n-1} - \sum_{n=1}^{\infty} nP_{ii}^n \approx \frac{1}{(1 - P_{ii})^2} - \frac{P_{ii}}{(1 - P_{ii})^2} = \frac{1}{1 - P_{ii}} = \frac{1}{\sum_{k=1}^N P_{ik}}$$

Instantaneous **number average** sequence length

# Microscopic approach

## - Average Sequence Length

$$\begin{aligned} \bar{w}_i &= \frac{\sum_{n=1}^{\infty} n^2 N_{in}}{\sum_{n=1}^{\infty} n N_{in}} = \frac{\sum_{n=1}^{\infty} n^2 N_{in}}{\bar{n}_i} = \sum_{k=1}^N P_{ik} \sum_{n=1}^{\infty} n^2 N_{in} = \left( \sum_{k=1}^N P_{ik} \right)^2 \sum_{n=1}^{\infty} n^2 P_{ii}^{n-1} \\ &= (1 - P_{ii})^2 \sum_{n=1}^{\infty} n^2 P_{ii}^{n-1} \approx (1 - P_{ii})^2 \frac{1 + P_{ii}}{(1 - P_{ii})^3} = \frac{1 + P_{ii}}{1 - P_{ii}} \end{aligned}$$

Instantaneous **weight average** sequence length

# Microscopic approach

## - Sequence Length Distribution (Ray)

$$\begin{aligned}\overline{N_{in, Ray}} &= \int_0^{X_i} N_{in} dX_i = \int_0^X N_{in} F_i dX \\ &= \int_0^X \left( P_{ii}^{n-1} \sum_{k=1}^N P_{ik} \right) F_i dX = \int_0^X \left\{ P_{ii}^{n-1} (1 - P_{ii}) \right\} F_i dX\end{aligned}$$

**Probability of having  $n$  consecutive units of monomer species  $i$  during polymerization**

# Microscopic approach

## - Sequence Length Distribution (HMP)

$$\begin{aligned} \overline{N}_{in,HMP} &= \frac{\int_0^{X_i} \left( \frac{N_{in}}{n_i} \right) dX_i}{\int_0^{X_i} \frac{dX_i}{n_i}} = \frac{\int_0^X \left( \frac{N_{in}}{n_i} \right) F_i dX}{\int_0^X \frac{F_i dX}{n_i}} = \frac{\int_0^X \left\{ P_{ii}^{n-1} \left( \sum_{k=1}^N P_{ik} \right)^2 \right\} F_i dX}{\int_0^X \left( \sum_{k=1}^N P_{ik} \right) F_i dX} \\ &= \frac{\int_0^X \left\{ P_{ii}^{n-1} (1 - P_{ii})^2 \right\} F_i dX}{\int_0^X (1 - P_{ii}) F_i dX}, \quad \sum_{n=1}^{\infty} \overline{N}_{in,HMP} = \frac{\int_0^X \left\{ \frac{1}{1 - P_{ii}} (1 - P_{ii})^2 \right\} F_i dX}{\int_0^X (1 - P_{ii}) F_i dX} = 1 \end{aligned}$$

**Probability of having  $n$  consecutive units of monomer species  $i$  during polymerization**

# Microscopic approach

## - Differences between Ray & HMP

- **Acc. Number average Sequence Length**

$$\frac{\int_0^x \frac{1}{(1-P_{ii})} F_i dX}{\int_0^x F_i dX}$$

**Ray**

$$\frac{\int_0^x F_i dX}{\int_0^x (1-P_{ii}) F_i dX}$$

**HMP**

- **Acc. Weight average Sequence Length**

$$\frac{\int_0^x \frac{1+P_{ii}}{(1-P_{ii})^2} F_i dX}{\int_0^x \frac{1}{1-P_{ii}} F_i dX}$$

**Ray**

$$\frac{\int_0^x \frac{1+P_{ii}}{1-P_{ii}} F_i dX}{\int_0^x F_i dX}$$

**HMP**

# Microscopic approach

## - Differences between Ray & HMP

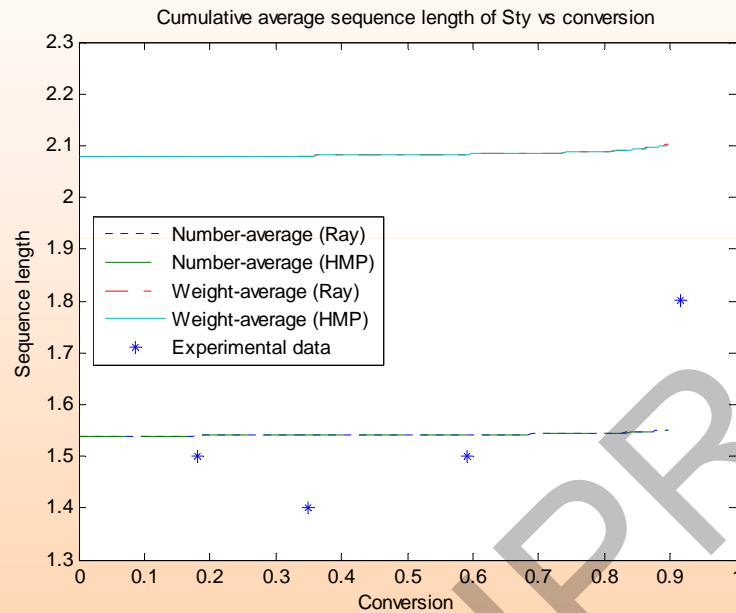


Figure 5.

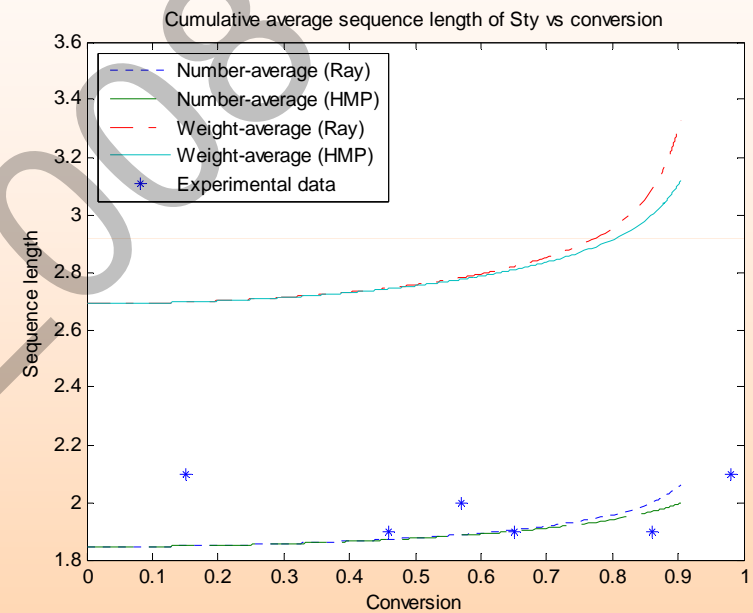


Figure 6.

Cumulative average sequence lengths of Sty in **Styrene-Acrylonitrile** *co*-polymer  
 $T = 60^{\circ}\text{C}$ ,  $[\text{AIBN}]_0 = 0.05 \text{ M}$ ,  $f_{\text{Sty}0} = 0.6$  (Fig. 5), and  $f_{\text{Sty}0} = 0.7$  (Fig. 6)  
(Number avg. sequence length experimental data from Garcia-Rubio *et al.*, 1985)

# Microscopic approach

## - Differences between Ray & HMP

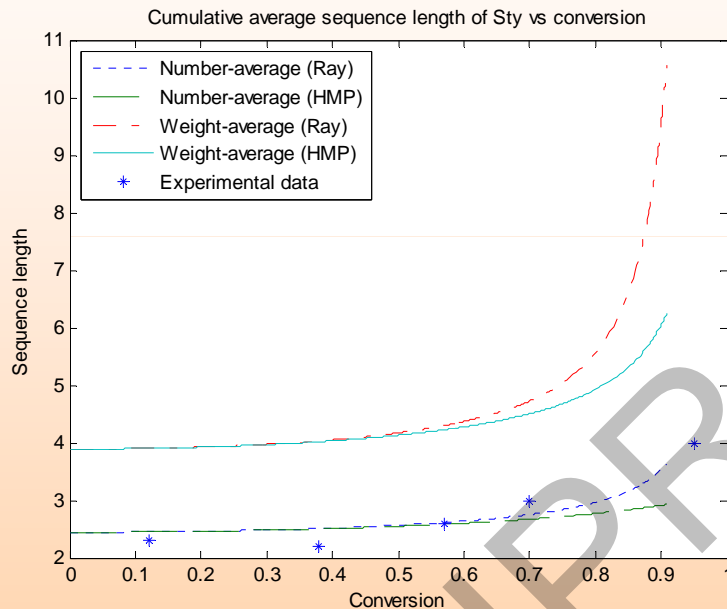


Figure 7.

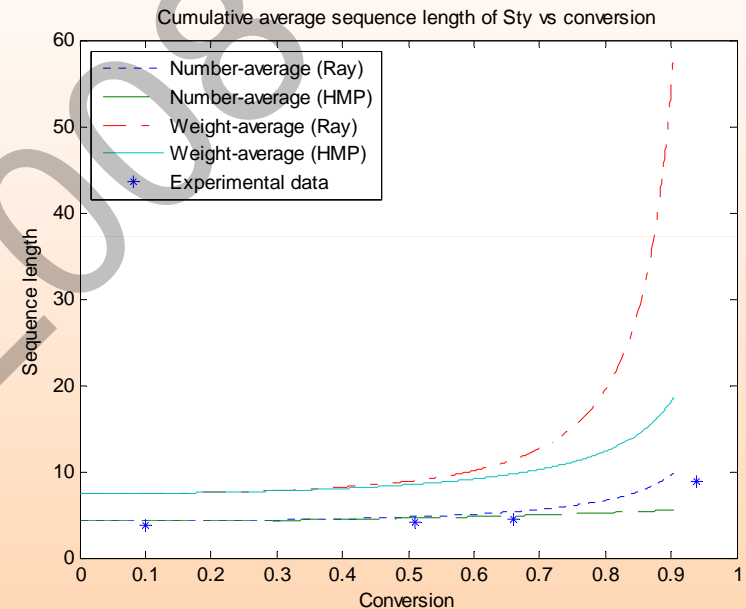


Figure 8.

Cumulative average sequence lengths of Sty in **Styrene-Acrylonitrile** *co*-polymer  
 $T = 60^{\circ}\text{C}$ ,  $[\text{AIBN}]_0 = 0.05 \text{ M}$ ,  $f_{\text{Sty}0} = 0.8$  (Fig. 7), and  $f_{\text{Sty}0} = 0.9$  (Fig. 8)  
(Number avg. sequence length experimental data from Garcia-Rubio *et al.*, 1985)

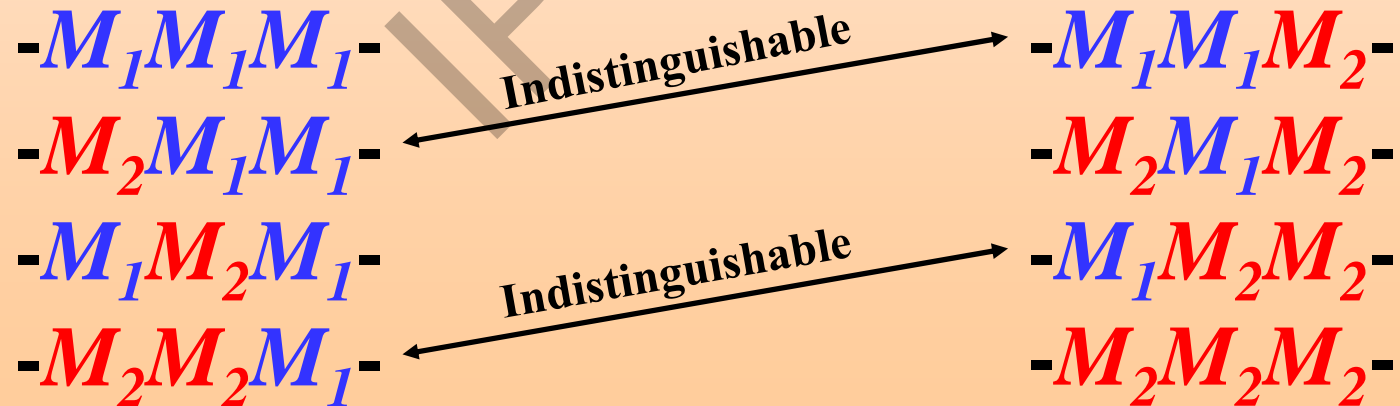
# Microscopic approach

## - Dyad/triad fractions

- Dyad fractions



- Triad fractions



# Microscopic approach

## - Triad fraction calculation

$$A_{iij} = P_{ii}^2 = \left( \frac{r_{ij} f_i}{f_j + r_{ij} f_i} \right)^2$$

$$A_{ijj} = A_{jii} = P_{ii} P_{ij} = P_{ii} (1 - P_{ii}) = \frac{r_{ij} f_i f_j}{(f_j + r_{ij} f_i)^2}$$

$$A_{jij} = P_{ij}^2 = \left( \frac{f_j}{f_j + r_{ij} f_i} \right)^2$$

$\sum$  (fractions centered on monomer  $i$ )

$$= A_{iij} + A_{ijj} + A_{jii} + A_{jij}$$

$$= P_{ii}^2 + 2P_{ii}P_{ij} + P_{ij}^2 = (P_{ii} + P_{ij})^2 = 1$$

**Triad fractions  
centered on  
monomer species  $i$**

# Microscopic approach

## - Triad fraction calculation

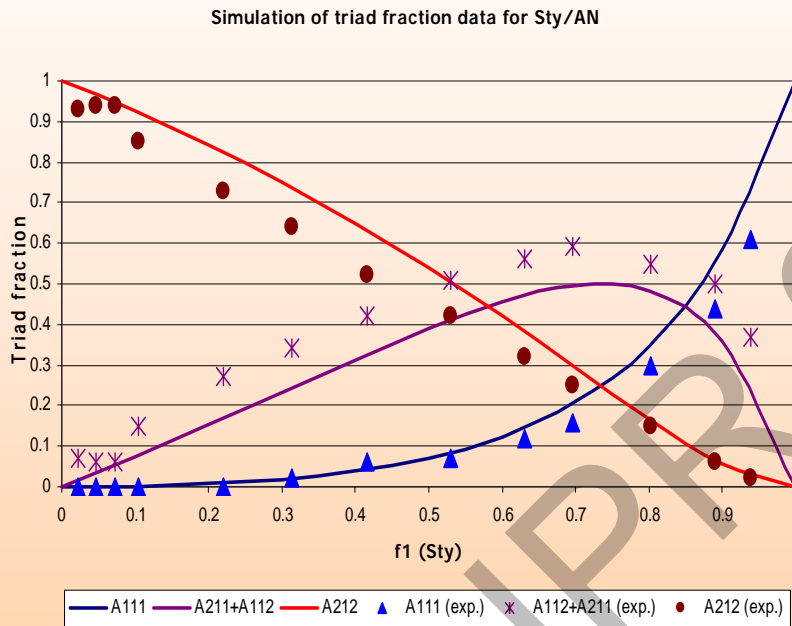


Figure 9.

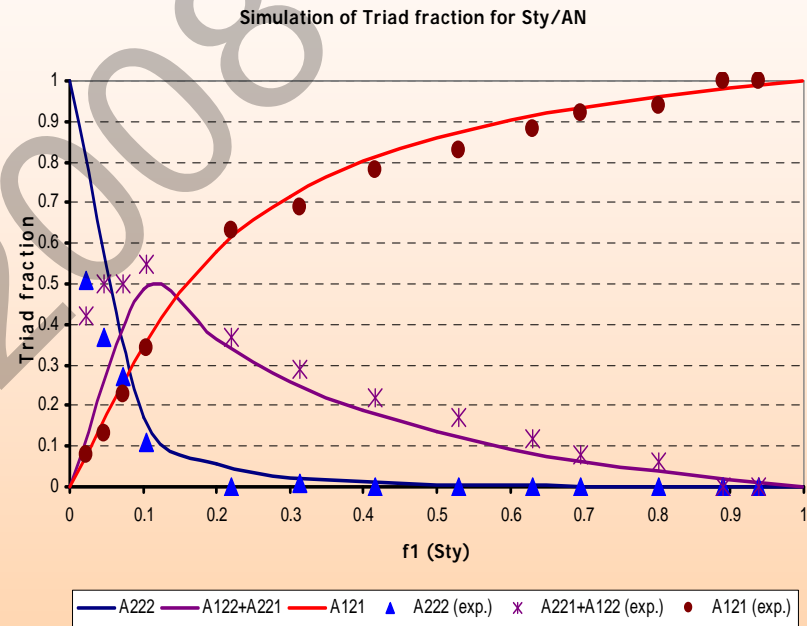


Figure 10.

Triad fraction calculation of **Styrene-Acrylonitrile** *co*-polymer  
 T = 60°C, Sty-centered (Fig. 9), and AN-centered (Fig. 10)  
 (Experimental data from Hill *et al.*, 1982)

# Microscopic approach - Triad fraction calculation

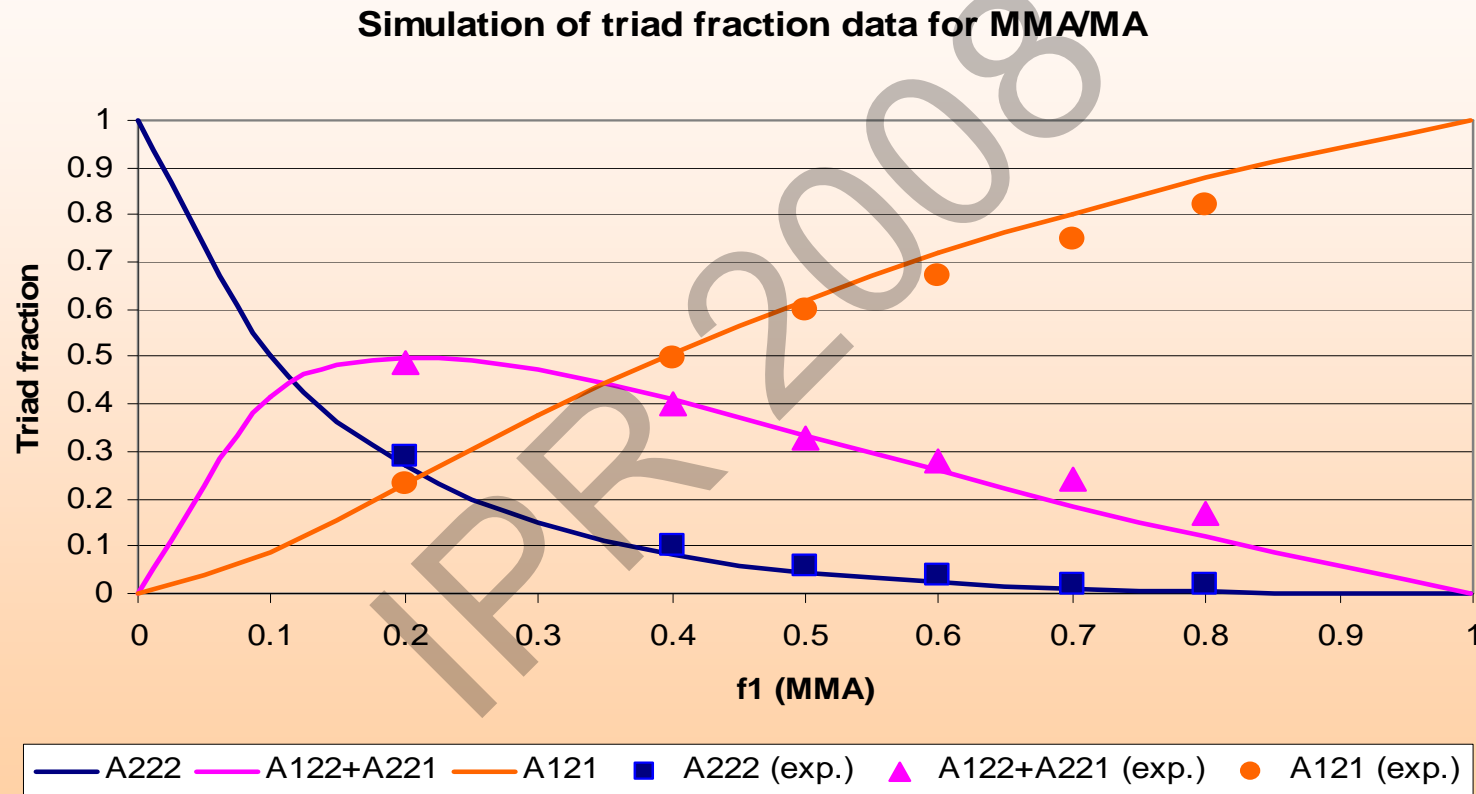


Figure 11. Triad fraction calculation of **Methyl methacrylate-Methyl acrylate** *co*-polymer  
T = 50°C, MA-centered (Experimental data from Kim and Harwood, 2002)

# Summary

- **Even with a limited number of monomers, a very large number of combinations**
- **Complicated multi-component system**
- **Lack of experimental data**

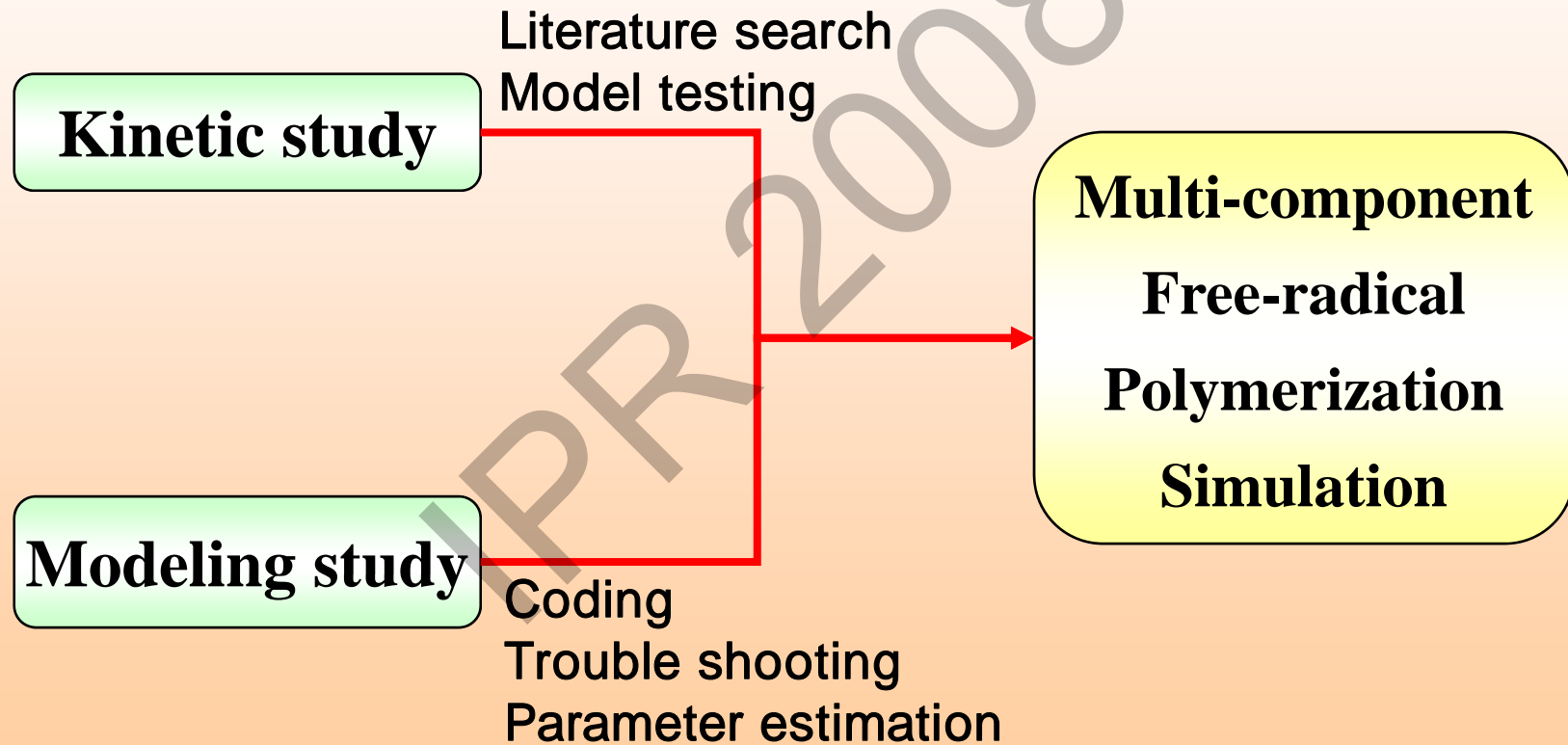
# Many Thanks to...

- *Prof. T. A. Duever*
- *Prof. A. Penlidis*
- **BASF SE**

**Questions?**

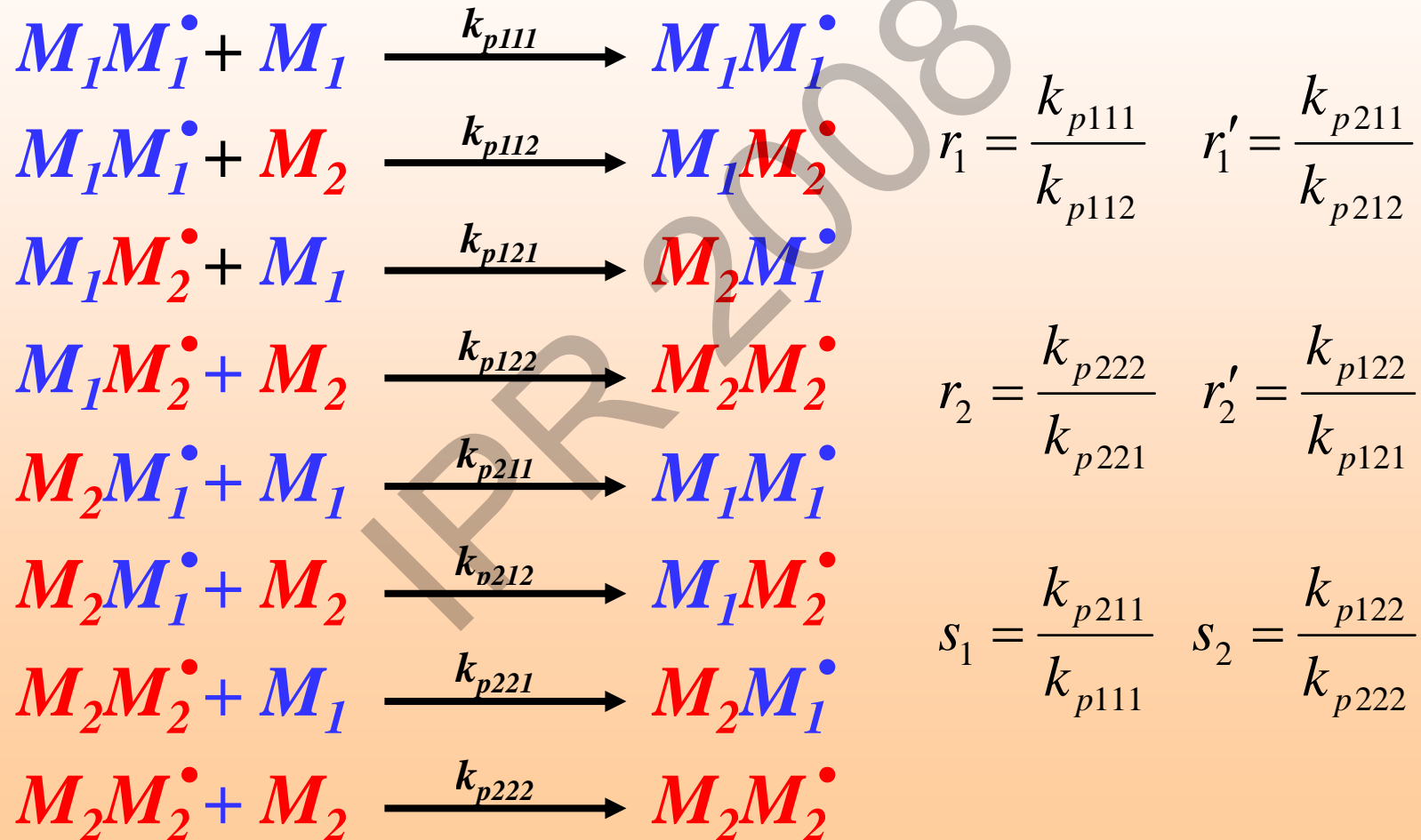
# Supplementaries

## - Simulation work



# Copolymerization characteristics

## - 2<sup>nd</sup> order Markov (penultimate) model



# Microscopic approach

## - Average Sequence Length (Ray)

$$\begin{aligned} \overline{N}_{i, Ray} &= \frac{\sum_{n=1}^{\infty} n \overline{N}_{in, Ray}}{\sum_{n=1}^{\infty} \overline{N}_{in, Ray}} = \frac{\int_0^X \left( \sum_{n=1}^{\infty} n P_{ii}^{n-1} \right) (1 - P_{ii}) F_i dX}{\int_0^X \left( \sum_{n=1}^{\infty} P_{ii}^{n-1} \right) (1 - P_{ii}) F_i dX} \\ &\approx \frac{\int_0^X \frac{1}{(1 - P_{ii})^2} (1 - P_{ii}) F_i dX}{\int_0^X \frac{1}{(1 - P_{ii})} (1 - P_{ii}) F_i dX} = \frac{\int_0^X \frac{1}{(1 - P_{ii})} F_i dX}{\int_0^X F_i dX} \end{aligned}$$

Cumulative **number average** sequence length

# Microscopic approach

## - Average Sequence Length (Ray)

$$\begin{aligned}\overline{W_{i, Ray}} &= \frac{\sum_{n=1}^{\infty} n^2 \overline{N_{in, Ray}}}{\sum_{n=1}^{\infty} n \overline{N_{in, Ray}}} = \frac{\int_0^X \left( \sum_{n=1}^{\infty} n^2 P_{ii}^{n-1} \right) (1 - P_{ii}) F_i dX}{\int_0^X \left( \sum_{n=1}^{\infty} n P_{ii}^{n-1} \right) (1 - P_{ii}) F_i dX} \\ &\approx \frac{\int_0^X \frac{1 + P_{ii}}{(1 - P_{ii})^3} (1 - P_{ii}) F_i dX}{\int_0^X \frac{1}{(1 - P_{ii})^2} (1 - P_{ii}) F_i dX} = \frac{\int_0^X \frac{1 + P_{ii}}{(1 - P_{ii})^2} F_i dX}{\int_0^X \frac{1}{1 - P_{ii}} F_i dX}\end{aligned}$$

Cumulative **weight average** sequence length

# Microscopic approach

## - Average Sequence Length (HMP)

$$\begin{aligned} \overline{N}_{i,HMP} &= \frac{\sum_{n=1}^{\infty} n \overline{N}_{in,HMP}}{\sum_{n=1}^{\infty} \overline{N}_{in,HMP}} = \frac{\int_0^X \left( \sum_{n=1}^{\infty} n P_{ii}^{n-1} \right) (1 - P_{ii})^2 F_i dX}{\int_0^X (1 - P_{ii}) F_i dX} \\ &\approx \frac{\int_0^X \frac{1}{(1 - P_{ii})^2} (1 - P_{ii})^2 F_i dX}{\int_0^X (1 - P_{ii}) F_i dX} = \frac{\int_0^X F_i dX}{\int_0^X (1 - P_{ii}) F_i dX} \end{aligned}$$

Cumulative **number average** sequence length

# Microscopic approach

## - Average Sequence Length (HMP)

$$\begin{aligned}
 \overline{W_{i,HMP}} &= \frac{\sum_{n=1}^{\infty} n^2 \overline{N_{in,HMP}}}{\sum_{n=1}^{\infty} n \overline{N_{in,HMP}}} = \frac{\sum_{n=1}^{\infty} n^2 \overline{N_{in,HMP}}}{\overline{N_{i,HMP}}} = \frac{\int_0^X \left( \sum_{n=1}^{\infty} n^2 P_{ii}^{n-1} \right) (1 - P_{ii})^2 F_i dX}{\overline{N_{i,HMP}} \int_0^X (1 - P_{ii}) F_i dX} \\
 &= \frac{\int_0^X \frac{1 + P_{ii}}{1 - P_{ii}} F_i dX}{\int_0^X (1 - P_{ii}) F_i dX} \\
 &\approx \frac{\int_0^X \frac{1 + P_{ii}}{(1 - P_{ii})^3} (1 - P_{ii})^2 F_i dX}{\overline{N_{i,HMP}} \int_0^X (1 - P_{ii}) F_i dX} = \frac{\int_0^X (1 + P_{ii}) F_i dX}{\int_0^X F_i dX} = \frac{\int_0^X \frac{1 + P_{ii}}{1 - P_{ii}} F_i dX}{\int_0^X F_i dX}
 \end{aligned}$$

Cumulative **weight average** sequence length

# Microscopic approach

## - Triad fractions

No. of Monomer Species	Distinguishable triads	Total possible triads
1 (homo-)	1	1
2 (co-)	6	8
3 (ter-)	18	27
4 (tetra-)	40	64
5 (penta-)	75	125
6 (hexa-)	126	216
7 (hepta-)	196	343
...	...	...
19	3610	6859
20	4200	8000