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

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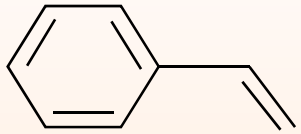
Outline

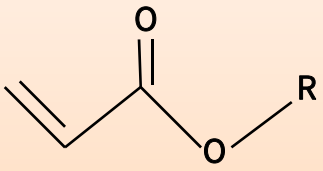
- **Introduction**
- **Copolymerization characteristics**
- **Macroscopic approach**
- **Microscopic approach**
- **Summary**

Introduction

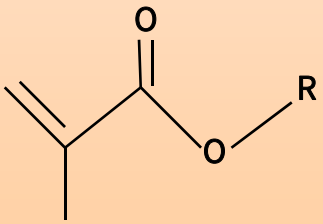
- Multicomponent polymerization



M_1



M_2



M_3

Monomer species

Propagation

$-M_1M_2M_1M_3-\ldots$

$\ldots-M_2M_3M_1M_1-$

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 (1st/2nd order Markov)**

Structures

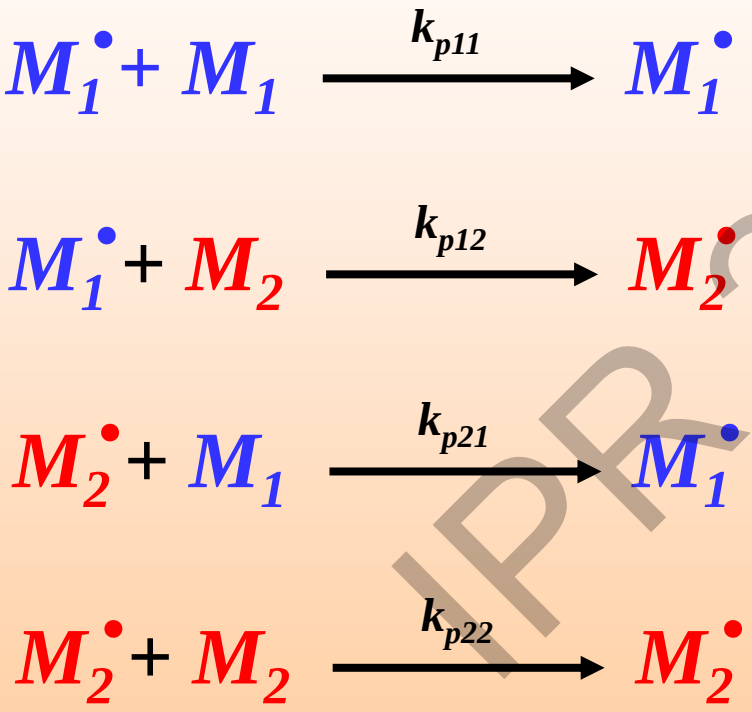
- **Alternating (-$M_1M_2M_1M_2M_1M_2M_1M_2$-)**
- **Block (-$M_1M_1M_1M_1M_1M_2M_2M_2M_2M_1M_1$-)**
- **Graft (-$M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1$-)**

$M_2M_2M_2M_2M_2$-

Copolymerization characteristics
- 1st order Markov (terminal) model

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

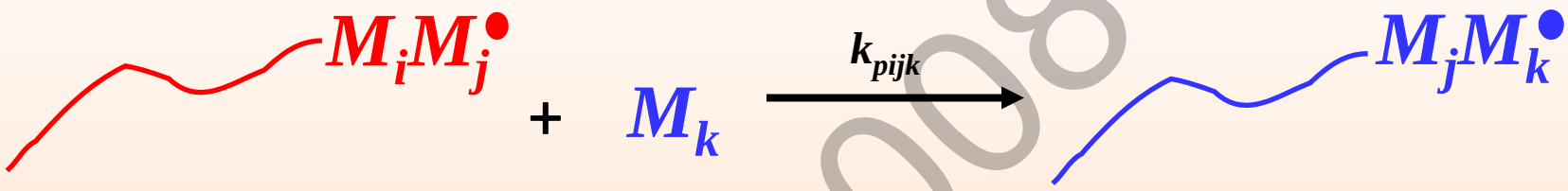
Copolymerization characteristics
- 1st order Markov (terminal) model



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

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

Copolymerization characteristics
- 2nd 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, Hammet 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

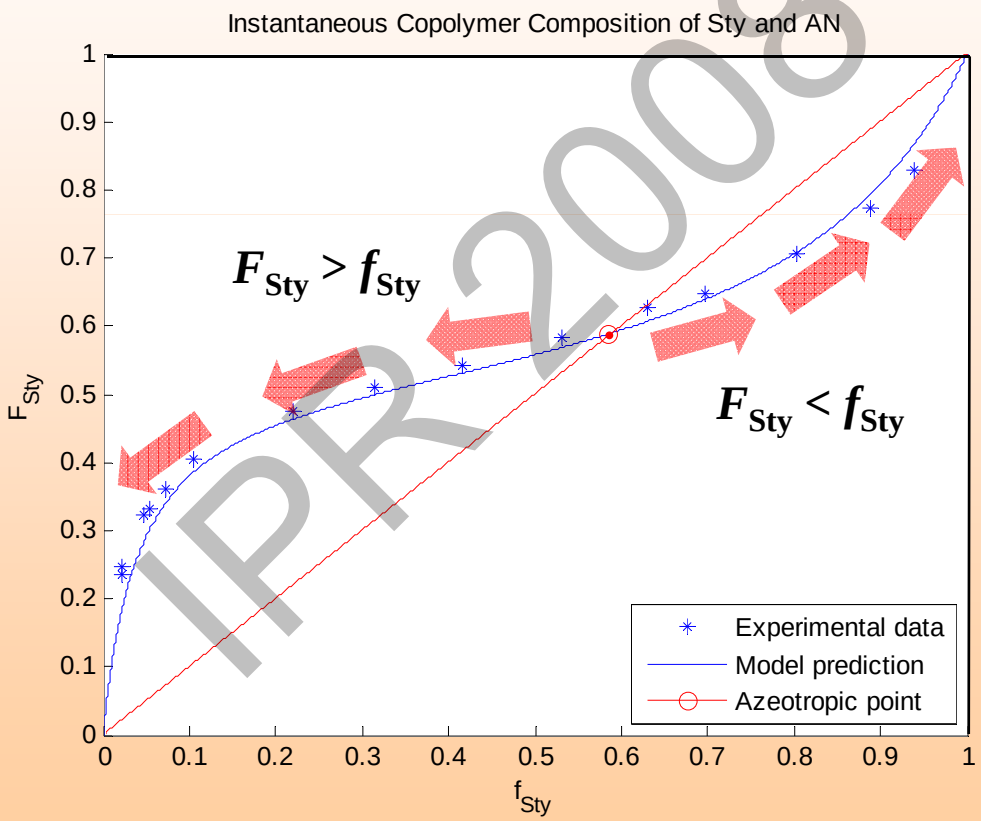
$$f_i = \frac{[M_i]}{\sum_{i=1}^{N}[M_i]}$$

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



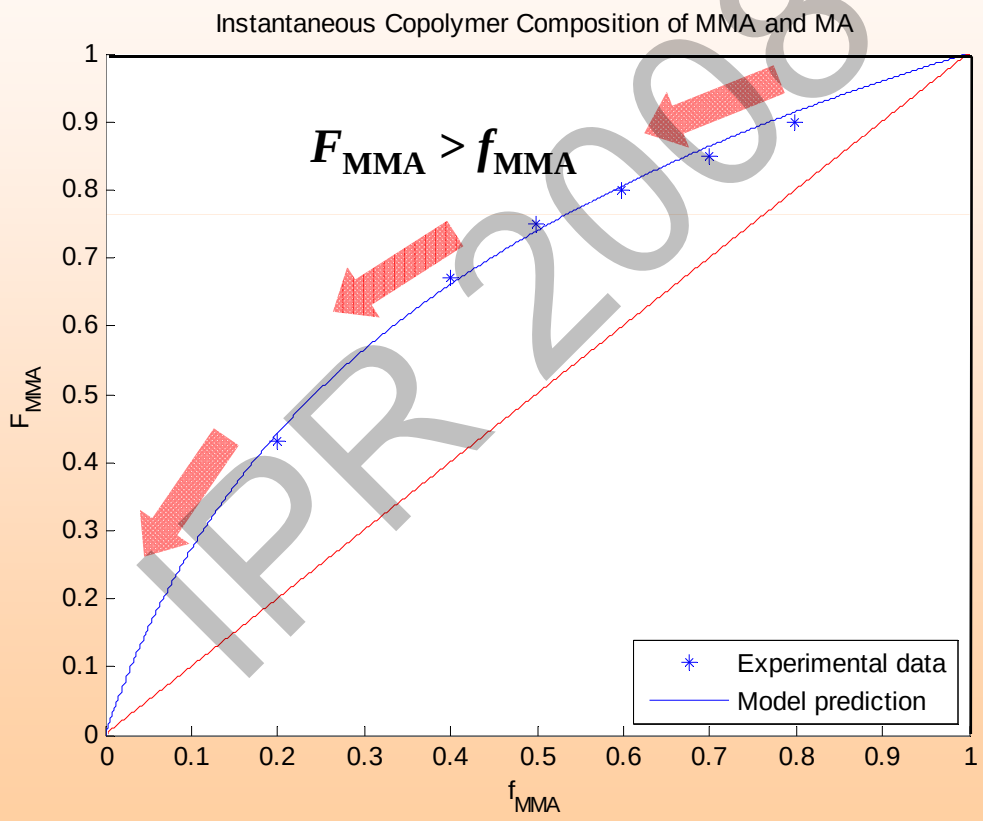
$r_{Sty} = 0.36$

$r_{AN} = 0.078$

Direction of Drift

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

Macroscopic approach
- Instantaneous composition



$r_{MMA} = 2.6$

$r_{MA} = 0.27$

Direction of Drift

Figure 2. Simulation of Methyl methacrylate-Methyl acrylate bulk *co*-polymerization T = 50℃ (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

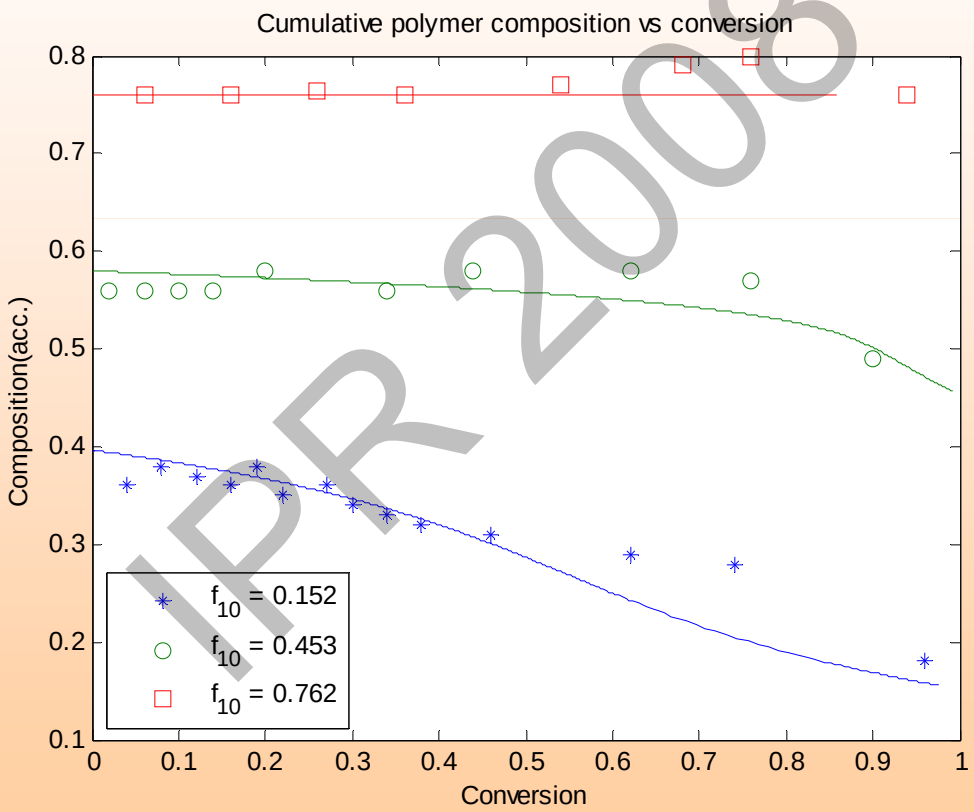
$$\overline{F_i} = \frac{[P_i]}{\sum_{i=1}^{N}[P_i]}$$

Cumulative composition of multi-component polymer

Composition changes during polymerization;

‘Composition drift’

Macroscopic approach
- Cumulative composition drift



$r_{Sty} = 0.717$

$r_{EA} = 0.128$

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

Macroscopic approach
- Limitation

- **Does not give information on monomer arrangements**

$M_1M_1M_1M_1M_1M_2M_2M_2M_2M_2$ ***Block***

$M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2$ ***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 $M_{1,\ Block} = 5$

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

Microscopic approach
- Sequence Length Distribution (SLD)

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

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

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

Microscopic approach

- Sequence Length Distribution (SLD)

$$N_{in} = P_{ii}^{n-1} \sum_{k=1}^{N} P_{ik}$$

$$= P_{ii}^{n-1}\left(1 - P_{ii}\right) \qquad (k \neq i)$$

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

$$-M_1M_1M_1M_1M_1M_2-$$

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

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

Long Chain Approximation

$$\approx \sum_{k=1}^{N} P_{ik} \frac{1}{1 - P_{ii}} = \frac{1 - P_{ii}}{1 - P_{ii}} = 1 \qquad (k \neq i)$$

Microscopic approach
- Sequence Length Distribution (SLD)

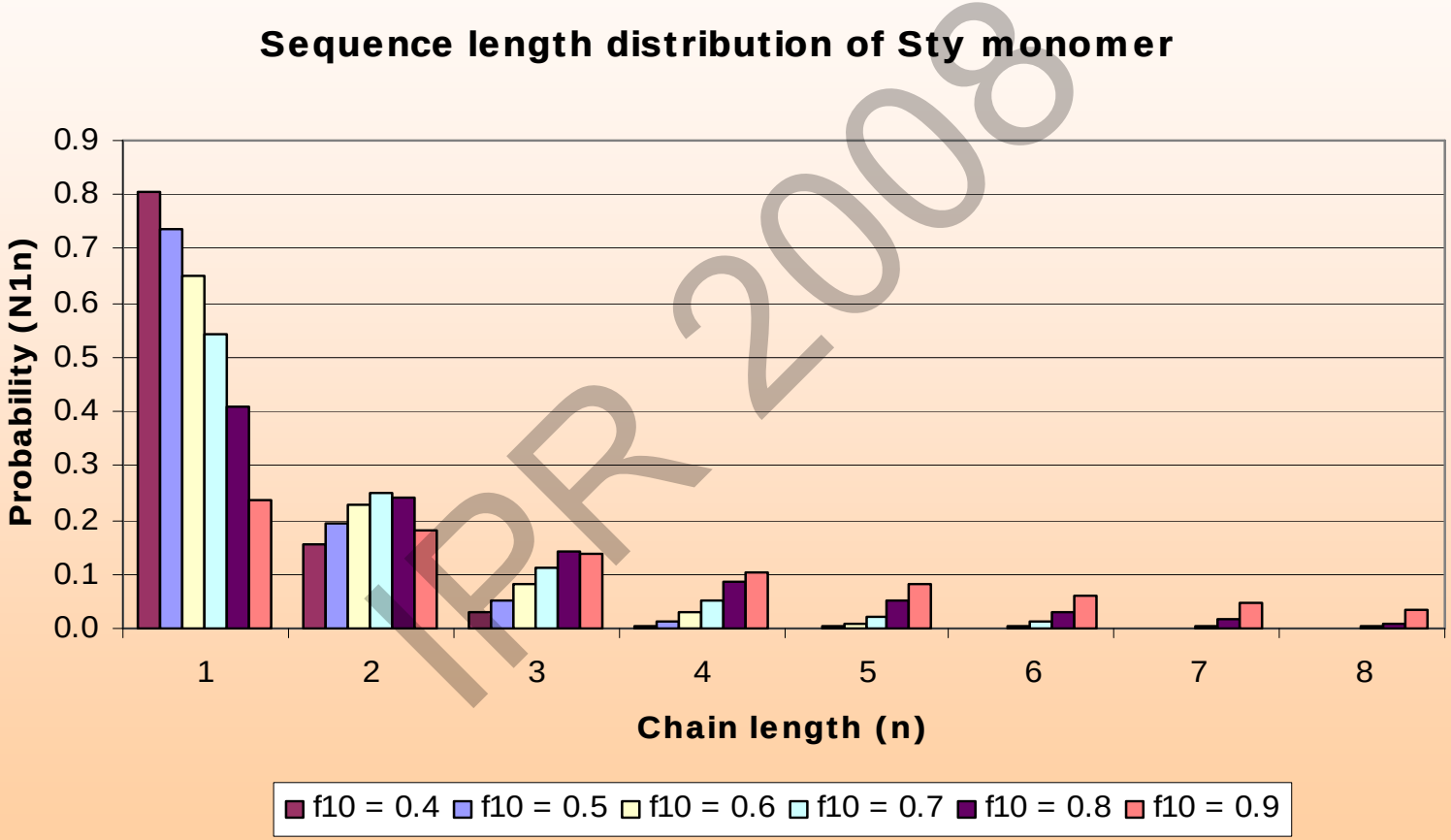


Figure 4. Sequence Length Distribution of Sty monomer in Styrene-Acrylonitrile *co*-polymer, T = 60℃

Microscopic approach

- Average Sequence Length

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

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

Instantaneous number average sequence length

Microscopic approach

- Average Sequence Length

$$\overline{w_i} = \frac{\sum_{n=1}^{\infty} n^2 N_{in}}{\sum_{n=1}^{\infty} n N_{in}} = \frac{\sum_{n=1}^{\infty} n^2 N_{in}}{\overline{n_i}} = \sum_{k=1}^{N} P_{ik} \sum_{n=1}^{\infty} n^2 N_{in} = \left(\sum_{k=1}^{N} P_{ik} \right)^2 \sum_{n=1}^{\infty} n^2 P_{ii}^{n-1}$$

$$= (1 - P_{ii})^2 \sum_{n=1}^{\infty} n^2 P_{ii}^{n-1} \approx (1 - P_{ii})^2 \frac{1 + P_{ii}}{(1 - P_{ii})^3} = \frac{1 + P_{ii}}{1 - P_{ii}}$$

Instantaneous weight average sequence length

Microscopic approach

- Sequence Length Distribution (Ray)

$$\overline{N_{in,Ray}} = \int_0^{X_i} N_{in}\, dX_i = \int_0^{X} N_{in} F_i\, dX$$

$$= \int_0^{X} \left(P_{ii}^{n-1} \sum_{k=1}^{N} P_{ik} \right) F_i\, dX = \int_0^{X} \left\{ P_{ii}^{n-1} \left(1 - P_{ii}\right) \right\} F_i\, dX$$

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

Microscopic approach
- Sequence Length Distribution (HMP)

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

$$= \frac{\int_0^{X} \left\{ P_{ii}^{n-1} (1-P_{ii})^2 \right\} F_i dX}{\int_0^{X} (1-P_{ii}) F_i dX}, \qquad \sum_{n=1}^{\infty} \overline{N_{in,HMP}} = \frac{\int_0^{X} \left\{ \frac{1}{1-P_{ii}} (1-P_{ii})^2 \right\} F_i dX}{\int_0^{X} (1-P_{ii}) F_i dX} = 1$$

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

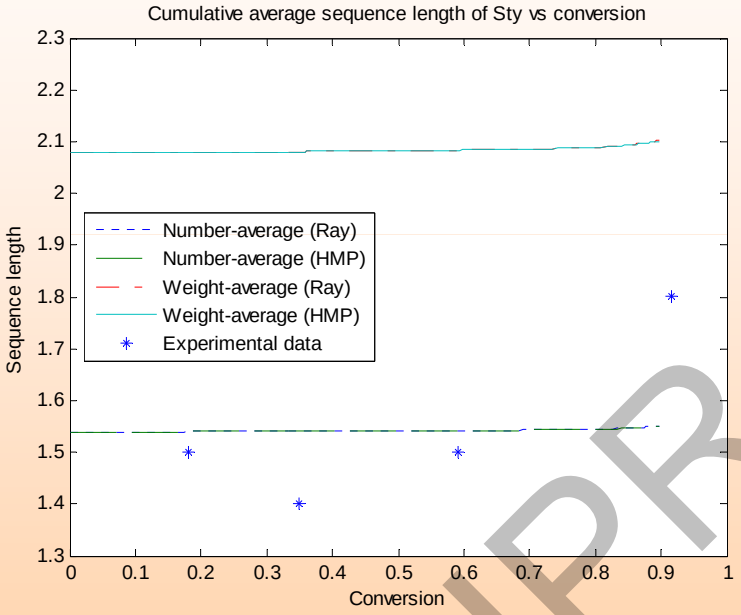


Figure 5.

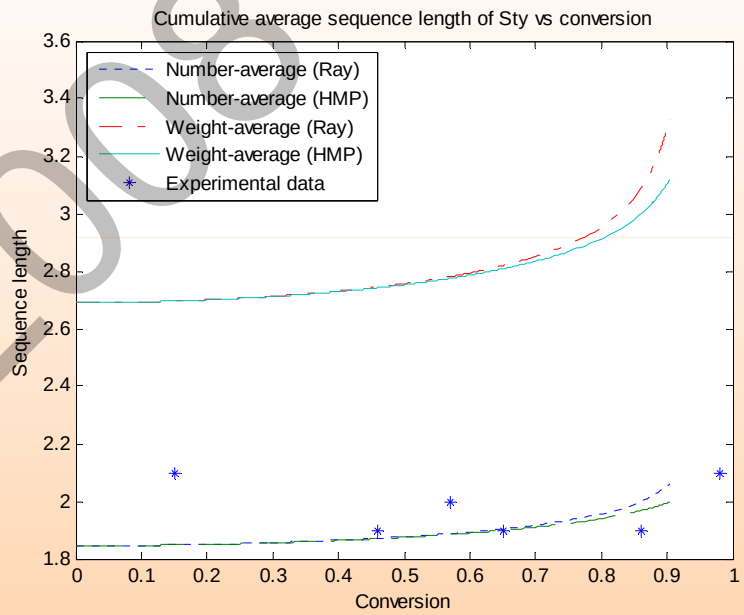


Figure 6.

Cumulative average sequence lengths of Sty in Styrene-Acrylonitrile *co*-polymer
T = 60°C, $[AIBN]_0$ = 0.05 M, f_{Sty0} = 0.6 (Fig. 5), and f_{Sty0} = 0.7 (Fig. 6)
(Number avg. sequence length experimental data from Garcia-Rubio *et al.*, 1985)

Microscopic approach
- Differences between Ray & HMP

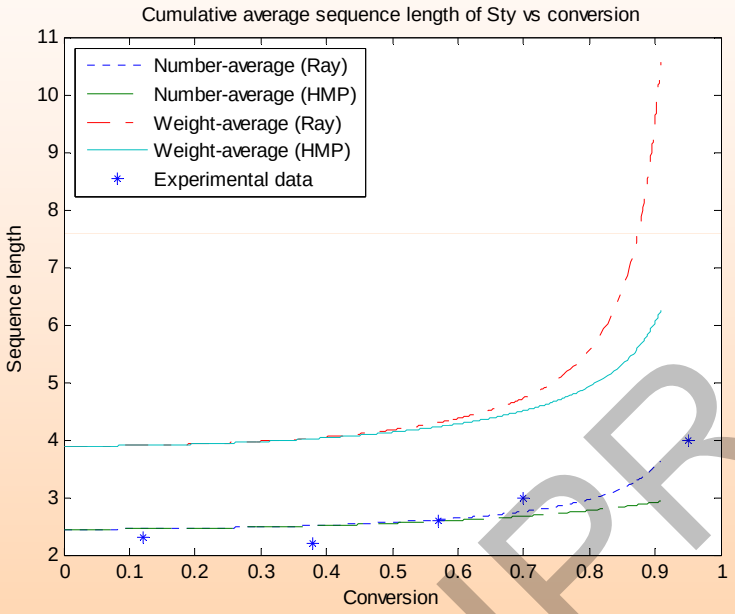


Figure 7.

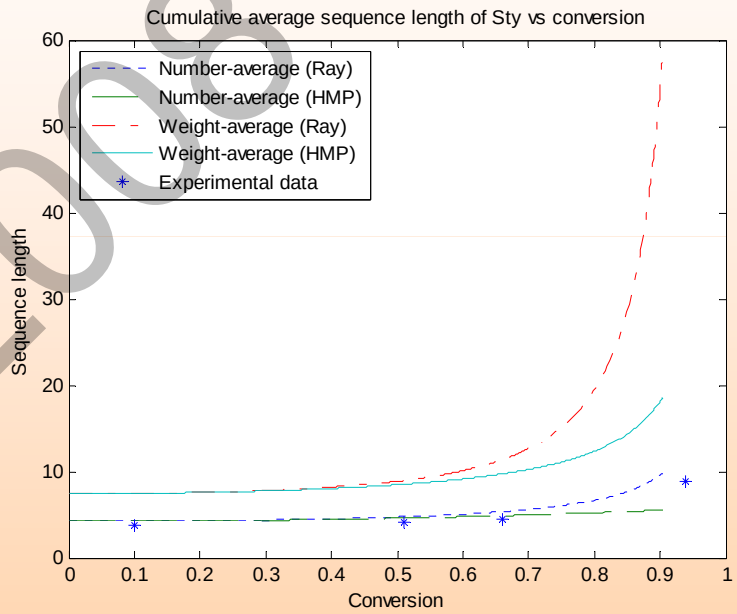


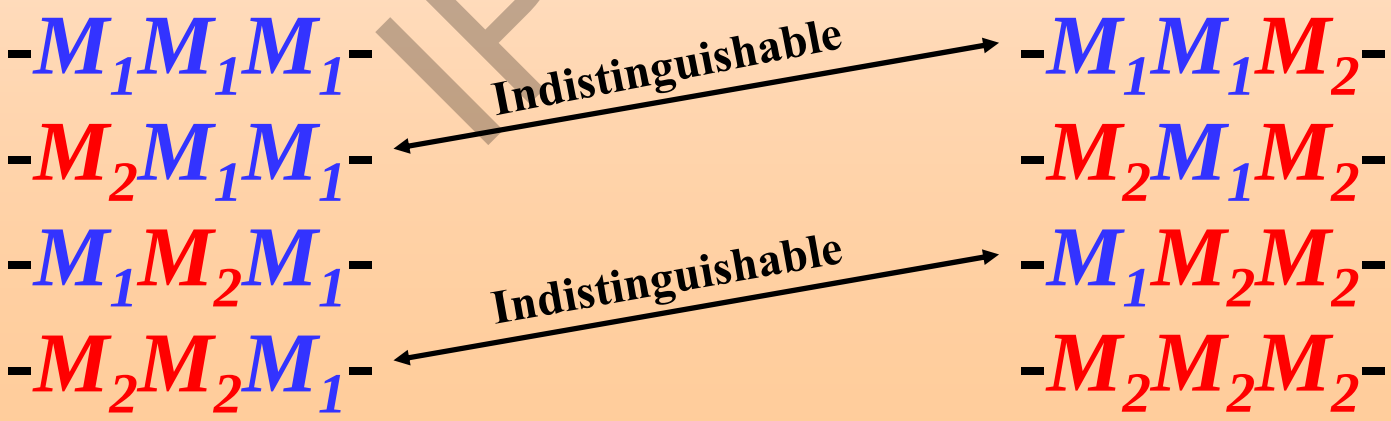
Figure 8.

Cumulative average sequence lengths of Sty in Styrene-Acrylonitrile *co*-polymer
T = 60℃, $[AIBN]_0$ = 0.05 M, f_{Sty0} = 0.8 (Fig. 7), and f_{Sty0} = 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

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

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

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

Triad fractions centered on monomer species *i*

$$\sum (\textit{fractions centered on monomer } i)$$
$$= A_{iii} + A_{iij} + A_{jii} + A_{jij}$$
$$= P_{ii}^2 + 2P_{ii}P_{ij} + P_{ij}^2 = (P_{ii} + P_{ij})^2 = 1$$

Microscopic approach
- Triad fraction calculation

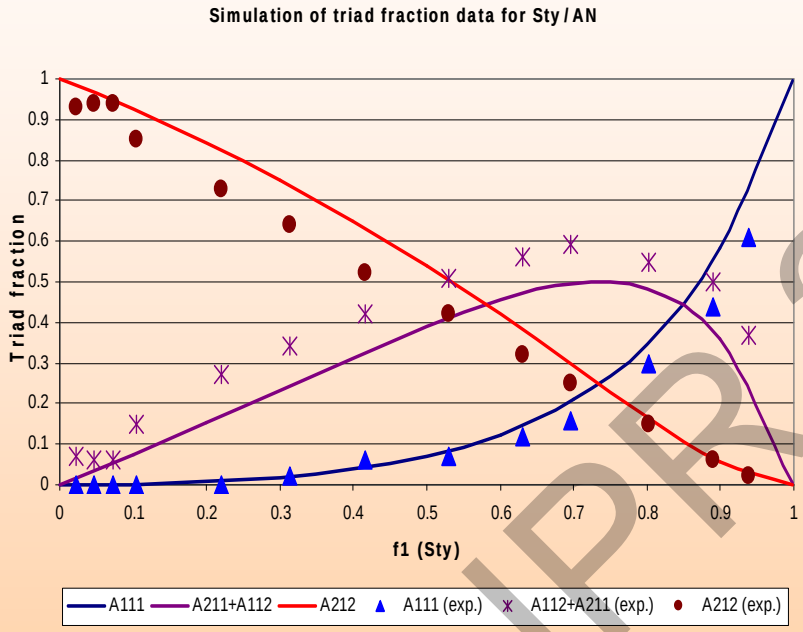


Figure 9.

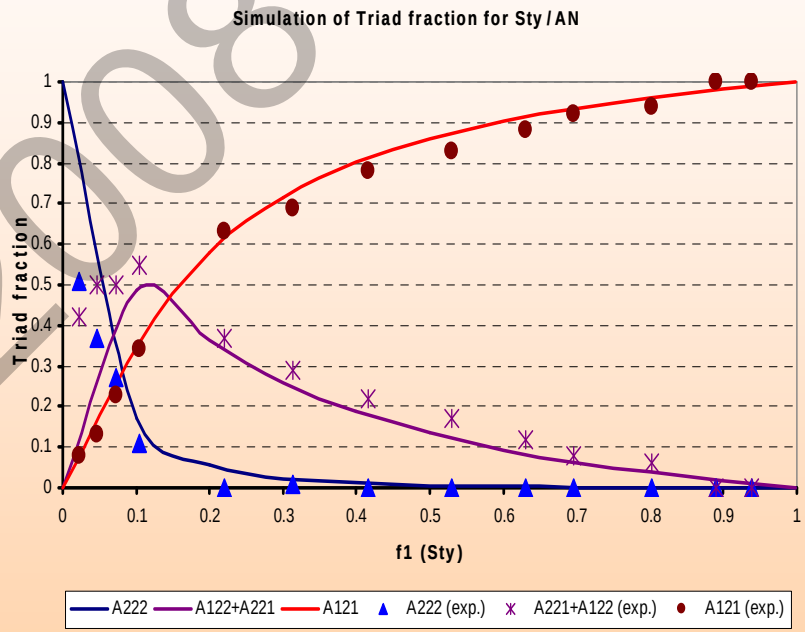


Figure 10.

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

Microscopic approach
- Triad fraction calculation

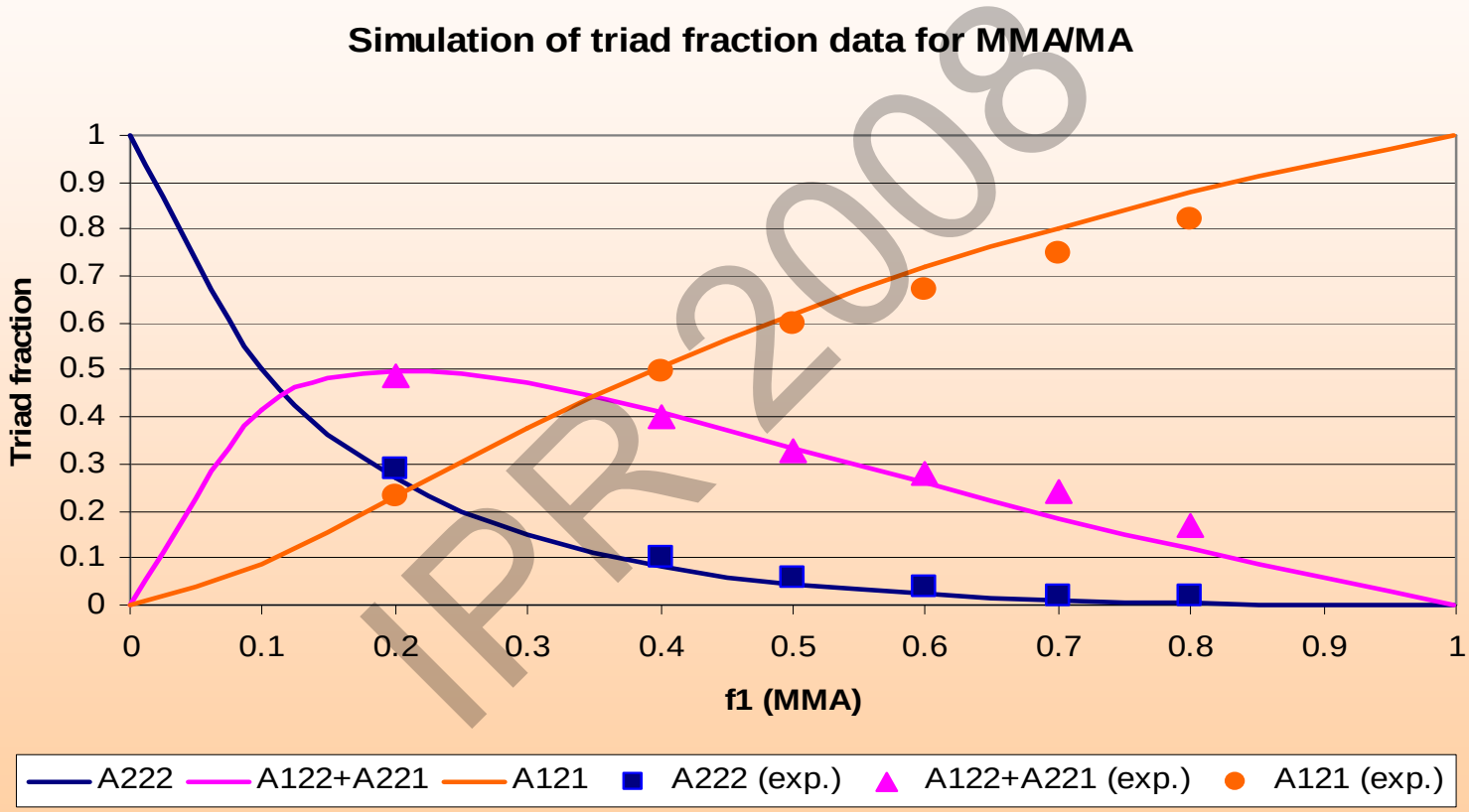


Figure 11. Triad fraction calculation of Methyl methacrylate-Methyl acrylate *co*-polymer T = 50℃, MA-centered (Experimental data from Kim and Harwood, 2002)

Summary

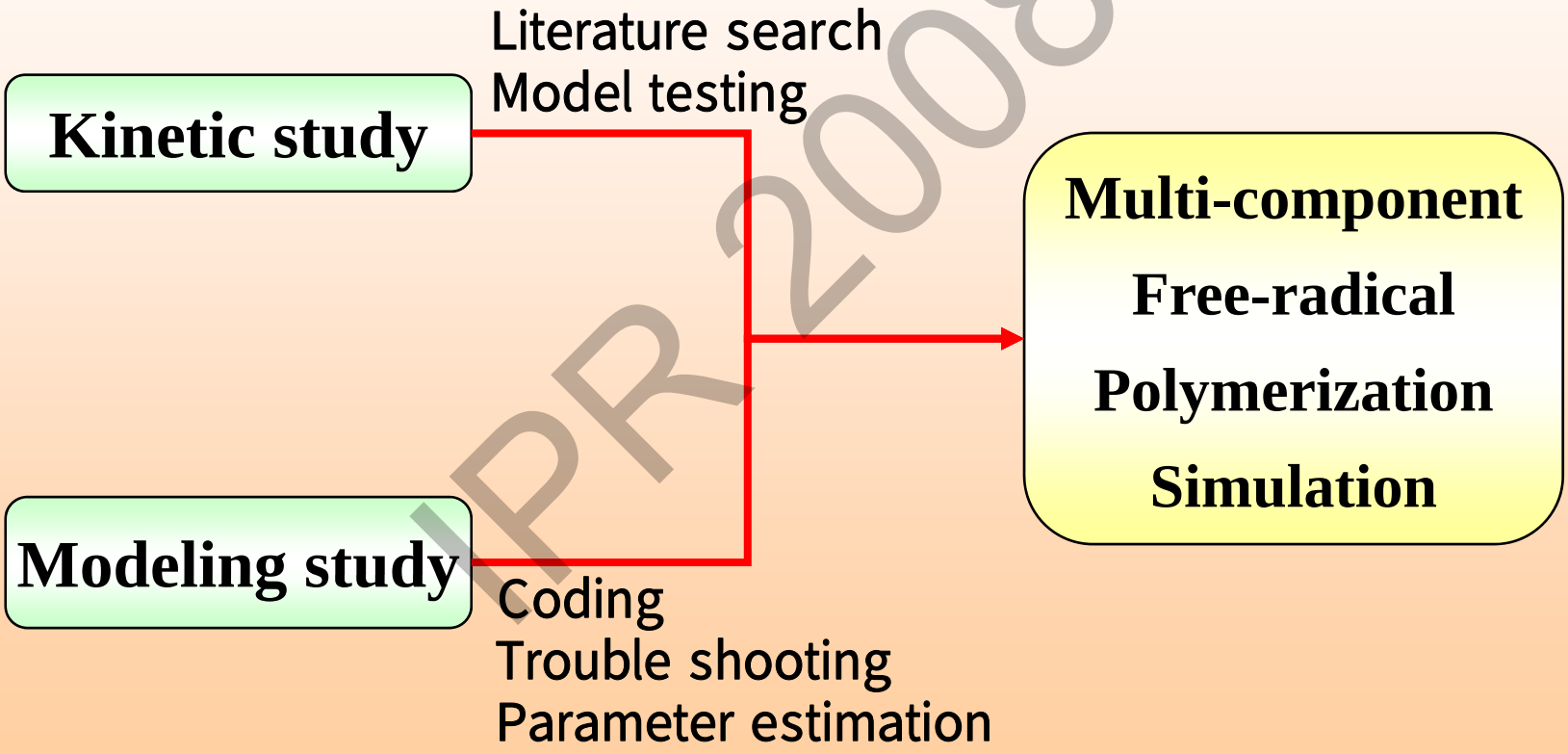
- **Even with a limited number of monomers, a very large number of combinations**
- **Complicated multi-component system**
- **Lack of experimental data**

Many Thanks to…

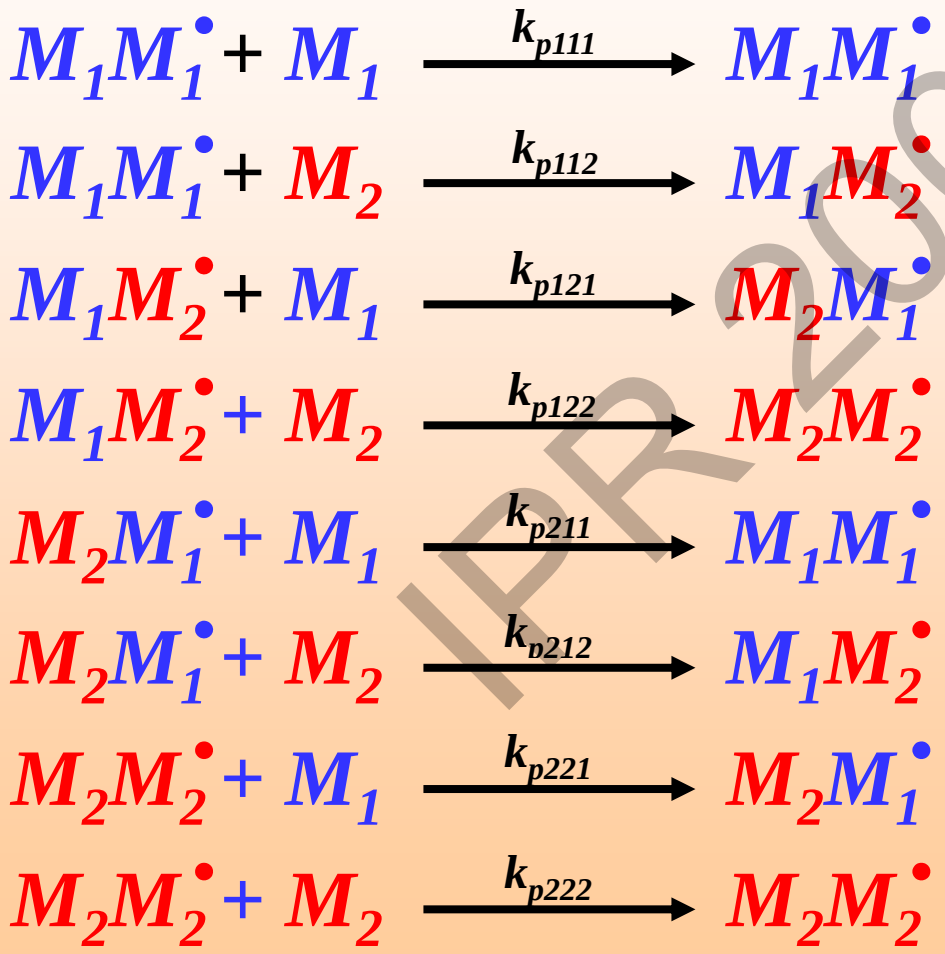
- ***Prof.*** **T. A. Duever**
- ***Prof.*** **A. Penlidis**
- **BASF SE**

Questions?

Supplementaries
- Simulation work



Copolymerization characteristics
- 2nd order Markov (penultimate) model



$$r_1 = \frac{k_{p111}}{k_{p112}} \qquad r_1' = \frac{k_{p211}}{k_{p212}}$$

$$r_2 = \frac{k_{p222}}{k_{p221}} \qquad r_2' = \frac{k_{p122}}{k_{p121}}$$

$$s_1 = \frac{k_{p211}}{k_{p111}} \qquad s_2 = \frac{k_{p122}}{k_{p222}}$$

Microscopic approach

- Average Sequence Length (Ray)

$$\overline{N_{i,Ray}} = \frac{\sum_{n=1}^{\infty} n\,\overline{N_{in,Ray}}}{\sum_{n=1}^{\infty} \overline{N_{in,Ray}}} = \frac{\int_0^X \left(\sum_{n=1}^{\infty} n P_{ii}^{n-1} \right) (1-P_{ii}) F_i dX}{\int_0^X \left(\sum_{n=1}^{\infty} P_{ii}^{n-1} \right) (1-P_{ii}) F_i dX}$$

$$\approx \frac{\int_0^X \frac{1}{(1-P_{ii})^2} (1-P_{ii}) F_i dX}{\int_0^X \frac{1}{(1-P_{ii})} (1-P_{ii}) F_i dX} = \frac{\int_0^X \frac{1}{(1-P_{ii})} F_i dX}{\int_0^X F_i dX}$$

Cumulative number average sequence length

Microscopic approach

- Average Sequence Length (Ray)

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

$$\approx \frac{\int_0^X \frac{1+P_{ii}}{(1-P_{ii})^3} (1-P_{ii}) F_i dX}{\int_0^X \frac{1}{(1-P_{ii})^2} (1-P_{ii}) F_i dX} = \frac{\int_0^X \frac{1+P_{ii}}{(1-P_{ii})^2} F_i dX}{\int_0^X \frac{1}{1-P_{ii}} F_i dX}$$

Cumulative weight average sequence length

Microscopic approach

- Average Sequence Length (HMP)

$$\overline{N_{i,HMP}} = \frac{\sum_{n=1}^{\infty} n\,\overline{N_{in,HMP}}}{\sum_{n=1}^{\infty} \overline{N_{in,HMP}}} = \frac{\int_0^X \left(\sum_{n=1}^{\infty} n P_{ii}^{n-1} \right) (1-P_{ii})^2 F_i dX}{\int_0^X (1-P_{ii}) F_i dX}$$

$$\approx \frac{\int_0^X \frac{1}{(1-P_{ii})^2} (1-P_{ii})^2 F_i dX}{\int_0^X (1-P_{ii}) F_i dX} = \frac{\int_0^X F_i dX}{\int_0^X (1-P_{ii}) F_i dX}$$

Cumulative number average sequence length

Microscopic approach

- Average Sequence Length (HMP)

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

$$\approx \frac{\int_0^X \frac{1+P_{ii}}{(1-P_{ii})^3} (1-P_{ii})^2 F_i dX}{\overline{N_{i,HMP}} \int_0^X (1-P_{ii}) F_i dX} = \frac{\int_0^X \frac{1+P_{ii}}{1-P_{ii}} F_i dX}{\int_0^X F_i dX} = \frac{\int_0^X \frac{1+P_{ii}}{1-P_{ii}} F_i dX}{\int_0^X (1-P_{ii}) F_i dX}$$

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