

Chemical Engineering 160/260
Polymer Science and Engineering

**Lecture 7 - Statistics of Chain
Copolymerization**

January 31, 2001

Objectives

- To determine the **compositional relationships** between lower and higher order sequences of units in a two-component copolymer.
- To evaluate the **conditional probability** in terms of the simple probabilities of occurrence of sequences of different orders.
- To demonstrate how probability theory may be used to develop information about **“local” structure in copolymers**, e.g, average sequence length.

Outline

- Relationships between simple and conditional probability
- Evaluation of microstructure
 - ◆ Markovian statistics
 - ◆ Bernoullian or random statistics
 - ◆ Terminal model
 - ◆ Penultimate model
 - ◆ Departure from random statistics
 - ◆ Number fraction of sequences of A units
 - ◆ Number average length of A or B runs

Definitions of Probability

Simple probability:

$$P\{A\} = \frac{N_A}{N}$$

The **simple probability** of event A occurring is just the relative fraction of A events compared to the total number of events.

Conditional probability:

$$P\{B / A\} = \frac{N_{AB}}{N_A}$$
$$P\{B / A\} = \frac{P\{AB\}}{P\{A\}}$$

The **conditional probability** of event B occurring given that A has preceded it is just the ratio of the number of compound AB events to the number of simple A events.

Relationships Between Lower and Higher Order Sequences: Monad/Diad

$$P_1\{A\} + P_2\{B\} = 1 \quad \text{Monad mole fractions sum to 1.}$$

Consider successor/predecessor relations:

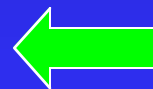
$$P_1\{A\} = P_2\{A\underline{A}\} + P_2\{A\underline{B}\} = P_2\{\underline{A}A\} + P_2\{\underline{B}A\}$$



$$P_1\{B\} = P_2\{B\underline{B}\} + P_2\{B\underline{A}\} = P_2\{\underline{B}B\} + P_2\{\underline{A}B\}$$



$$P_2\{AB\} = P_2\{BA\}$$



This is the Principle of Microscopic Reversibility.

Consider diad mole fractions:

$$P_2\{AA\} + 2P_2\{AB\} + P_2\{BB\} = 1$$

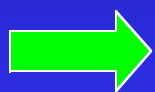
Relationship Between Lower and Higher Order Sequences: Diad/Triad

$$P_2\{AA\} = P_3\{AA\underline{A}\} + P_3\{AAB\underline{B}\} = P_3\{\underline{A}AA\} + P_3\{BAA\}$$

$$P_2\{AB\} = P_3\{ABA\underline{A}\} + P_3\{ABB\underline{B}\} = P_3\{\underline{A}AB\} + P_3\{BAB\}$$

$$P_2\{BA\} = P_3\{BAA\underline{A}\} + P_3\{BAB\underline{B}\} = P_3\{\underline{A}BA\} + P_3\{BBA\}$$

$$P_2\{BB\} = P_3\{BBA\underline{A}\} + P_3\{BBB\underline{B}\} = P_3\{\underline{A}BB\} + P_3\{BBB\}$$



$$P_3\{AAB\} = P_3\{BAA\}$$

$$P_3\{BBA\} = P_3\{ABB\}$$

microscopic reversibility
(equal to mirror image)

Consider triad mole fractions:

$$P_3\{AAA\} + P_3\{ABA\} + 2P_3\{AAB\} + 2P_3\{BBA\} + P_3\{BAB\} + P_3\{BBB\} = 1$$

Conditional and Simple Probabilities

Conditional probability:

$$P\{X_{n+1} / X_1 X_2 \perp X_n\}$$

Simple probability:

$$P_2\{AA\} = P_1\{A\}P\{A / A\}$$

$$P_2\{BA\} = P_1\{B\}P\{A / B\}$$

$$P_3\{AAA\} = P_1\{A\}P\{A / A\}P\{A / AA\}$$

$$P_3\{BAA\} = P_1\{B\}P\{A / B\}P\{A / BA\}$$

Conditional Probability in Terms of Ratios of Simple Probabilities

$$P\{A / A\} = \frac{P_2\{AA\}}{P_1\{A\}}$$

$$P\{A / B\} = \frac{P_2\{BA\}}{P_1\{B\}}$$

$$P\{B / A\} = \frac{P_2\{AB\}}{P_1\{A\}}$$

$$P\{B / B\} = \frac{P_2\{BB\}}{P_1\{B\}}$$

Monad fractions may be determined from **elemental analysis**.

Diad, triad, tetrad, and pentad fractions may be determined from **NMR**.

Conditional Probability in Terms of Ratios of Simple Probabilities

$$P\{A / AA\} = \frac{P_3\{AAA\}}{P_2\{AA\}}$$

$$P\{A / BA\} = \frac{P_3\{BAA\}}{P_2\{BA\}}$$

$$P\{A / AB\} = \frac{P_3\{ABA\}}{P_2\{AB\}}$$

$$P\{A / BB\} = \frac{P_3\{BBA\}}{P_2\{BB\}}$$

$$P\{B / AA\} = \frac{P_3\{AAB\}}{P_2\{AA\}}$$

$$P\{B / BA\} = \frac{P_3\{BAB\}}{P_2\{BA\}}$$

$$P\{B / AB\} = \frac{P_3\{ABB\}}{P_2\{AB\}}$$

$$P\{B / BB\} = \frac{P_3\{BBB\}}{P_2\{BB\}}$$

Use NMR to determine all triad and diad fractions.

Probability Sums

$$P\{A / A\} + P\{B / A\} = 1$$

$$P\{A / B\} + P\{B / B\} = 1$$

$$P\{A / AA\} + P\{B / AA\} = 1$$

$$P\{A / AB\} + P\{B / AB\} = 1$$

$$P\{A / BA\} + P\{B / BA\} = 1$$

$$P\{A / BB\} + P\{B / BB\} = 1$$

Conditional Probability of Different Orders

If the probability of finding a particular sequence of n units depended upon every one of the preceding $(n-1)$ units, the **number fraction** of the n -unit sequence would be:

$$P_n\{A^n\} = P_1\{A\}P\{A/A\}P\{A/AA\} \dots P\{A/A^{n-1}\}$$

If the “local” chemical interactions only influence reactivity over a sequence length of k units, the **number fraction** of the n -unit sequence would be:

$$P_n\{A^n\} = P_1\{A^k\}P\{A/A^k\}^{n-k}$$

Conditional Probability of Different Orders

The number fraction of a sequence of n units for a k th order Markovian process is given by:

$$P_n\{A^n\} = P_1\{A^k\}P\{A / A^k\}^{n-k}$$

Zero-order Markovian statistics:

(Bernoulian or random statistics)

$$k = 0 \quad \rightarrow \quad P_n\{A^n\} = (P_1\{A\})^n$$

First-order Markovian statistics:

(Terminal model)

$$k = 1 \quad \rightarrow \quad P_n\{A^n\} = P_1\{A\}(P\{A / A\})^{n-1}$$

Second-order Markovian statistics:

(Penultimate model)

$$k = 2 \quad \rightarrow \quad P_n\{A^n\} = P_2\{AA\}(P\{A / AA\})^{n-2}$$

Example: the sequence ABABA

Bernoullian statistics (random model):

$$P_5\{ABABA\} = P_1\{A\}P_1\{B\}P_1\{A\}P_1\{B\}P_1\{A\}$$

$$P_5\{ABABA\} = (P_1\{A\})^3(P_1\{B\})^2$$

First-order Markovian statistics (terminal model):

$$P_5\{ABABA\} = P_1\{A\}P\{B/A\}P\{A/B\}P\{B/A\}P\{A/B\}$$

$$P_5\{ABABA\} = P_1\{A\}(P\{B/A\})^2(P\{A/B\})^2$$

Second-order Markovian statistics (penultimate model):

$$P_5\{ABABA\} = P_2\{AB\}P\{A/AB\}P\{B/BA\}P\{A/AB\}$$

$$P_5\{ABABA\} = P_2\{AB\}(P\{A/AB\})^2 P\{B/BA\}$$

A Measure of the Departure from Random Statistics

$$\chi = \frac{P_2\{AB\}}{P_1\{A\}P_1\{B\}}$$

$$\chi = 1$$

Completely random copolymer

$$\chi > 1$$

Copolymer with an alternating tendency

$$\chi = 2$$

Completely alternating copolymer

$$\chi < 1$$

Copolymer with a “blocking” tendency

$$\chi = 0$$

Completely block copolymer

Number Fraction of Sequences of A Units

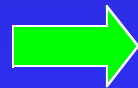
$$N_A(n) = \frac{P_{n+2}\{BA_nB\}}{\sum_1^{\infty} P_{n+2}\{BA_nB\}}$$

Sequences of A units must be preceded and succeeded by at least one B unit.

$$\sum_1^{\infty} P_{n+2}\{BA_nB\} = P_3\{B\underline{A}B\} + P_4\{BA\underline{A}B\} + P_5\{BAA\underline{A}B\} + \dots$$

$$\sum_1^{\infty} P_{n+2}\{BA_nB\} = P_2\{AB\}$$

All possible contributions from AB diads will be included in the sum.



$$N_A(n) = \frac{P_{n+2}\{BA_nB\}}{P_2\{AB\}}$$

For example,

$$N_A(3) = \frac{P_5\{BAAAB\}}{P_2\{AB\}}$$

Number Average Length of A or B Runs

$$\bar{l}_A = \frac{\sum_{n=1}^{\infty} n N_A(n)}{\sum_{n=1}^{\infty} N_A(n)}$$

Use the number distribution function for the sequence length to evaluate the average length.

$$N_A(n) = \frac{P_{n+2}\{BA_n B\}}{P_2\{AB\}}$$

Number distribution function

$$\sum_{n=1}^{\infty} N_A(n) = 1$$



$$\bar{l}_A = \frac{\sum_{n=1}^{\infty} n P_{n+2}\{BA_n B\}}{P_2\{AB\}}$$

Number Average Length of A or B Runs

$$\bar{l}_A = \frac{\sum_{n=1}^{\infty} n P_{n+2} \{BA_n B\}}{P_2 \{AB\}}$$

$$\sum_{n=1}^{\infty} n P_{n+2} \{BA_n B\} = 1 \cdot P_3 \{B \underline{A} B\}$$

$$+ 2 \cdot P_4 \{B \underline{A} \underline{A} B\} + 3 \cdot P_5 \{B \underline{A} \underline{A} \underline{A} B\} + \dots$$

$$\sum_{n=1}^{\infty} n P_{n+2} \{BA_n B\} = P_1 \{A\}$$

All A units will be included in the sum.

$$\bar{l}_A = \frac{P_1 \{A\}}{P_2 \{AB\}}$$

$$\bar{l}_B = \frac{P_1 \{B\}}{P_2 \{BA\}}$$

Recall that

$$P_2 \{AB\} = P_2 \{BA\}$$