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

$$P_1\{A\} + P_2\{B\} = 1$$

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

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

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

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

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

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

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

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:

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

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

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

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

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

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

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

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

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:

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

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 kth 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)

$k = 0$ ⇒ $P_n\{A^n\} = (P_1\{A\})^n$

First-order Markovian statistics: (Terminal model)

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

Second-order Markovian statistics: (Penultimate model)

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

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):

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

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

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.

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

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

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

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

For example,

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

Number Average Length of A or B Runs

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

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

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

Number distribution function

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

$$\Rightarrow \quad \overline{l_A} = \frac{\sum_{1}^{\infty} n P_{n+2}\{BA_nB\}}{P_2\{AB\}}$$

Number Average Length of A or B Runs

$$\bar{l}_A = \frac{\sum_{1}^{\infty} nP_{n+2}\{BA_nB\}}{P_2\{AB\}}$$

$$\sum_{1}^{\infty} nP_{n+2}\{BA_nB\} = 1 \bullet P_3\{B\underline{A}B\}$$

$$+2 \bullet P_4\{B\underline{AA}B\} + 3 \bullet P_5\{B\underline{AAA}B\} + \ldots$$

$$\sum_{1}^{\infty} nP_{n+2}\{BA_nB\} = P_1\{A\}$$

All A units will be included in the sum.

$$\bar{l}_A = \frac{P_1\{A\}}{P_2\{AB\}} \qquad \bar{l}_B = \frac{P_1\{B\}}{P_2\{BA\}}$$

Recall that

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