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Chemical Composition Distribution of Multicomponent Copolymer Chains

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Summary: Probability theory was used to model the microstructure of copolymer chains. Specifically, we derived analytical expressions to describe the chemical composition distribution of multicomponent random copolymers and the longest monomer sequence length distribution of binary copolymers. The results agree with Stockmayer's distribution for binary copolymers and with Monte Carlo simulations for multicomponent copolymers.

Keywords: chemical composition distribution (CCD); microstructure; Monte Carlo simulation; multicomponent copolymers

1. Introduction

Polymers differ from small molecules because of their large molar masses. Additionally, most synthetic polymers are composed of molecules having a distribution of molar masses, as opposed to a single value. As a consequence, the physical properties of polymers depend not only on their average molar masses but also on their distribution.

The physical properties of copolymers are also influenced by how comonomer units are distributed on the copolymer chains. Comonomer incorporation gives rise to two different distributions: the monomer sequence length distribution (SLD) and the chemical composition distribution (CCD). The SLD describes how the monomers are distributed within the copolymer chains and reflects intramolecular heterogeneity. On the other hand, the CCD describes the distribution of the average comonomer content of the copolymer chains, thus reflecting intermolecular heterogeneity.

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While the theory describing the SLD for various copolymerization models, for both binary and multicomponent copolymers, are well developed,[1] a general analytical equation for the CCD of multicomponent copolymers is not available. Stockmayer's distribution[2] is useful for understanding copolymer microstructure and modeling certain polymer characterization techniques, such as temperature rising elution fractionation (Tref) and crystallization analysis fractionation (Crystaf).[3-4] However, Stockmayer's distribution is only valid for linear binary copolymers, even though it has also been modified for special circumstances.[5-7] Xu[8] attempted to develop an equation describing the CCD of random terpolymers following the same strategy used by Stockmayer. Unfortunately, the equations are too complicated for convenient use. Furthermore, the possibility of extending their approach to copolymers with four of more comonomers is limited.

In this work, we developed an equation similar to Stockmayer's distribution using a statistical approach. The equation is generalized to the case of multicomponent random copolymers. We validated our results by comparison with Stockmayer's distribution and Monte Carlo simulations. In the case of binary copolymers, we also derived an analytical expression describing the distribution of the longest monomer sequence length, which can be useful in understanding crystallization processes from the melt and solution.

2. Monte Carlo Simulations

Monte Carlo simulation was used to investigate the distribution of chemical composition and longest monomer sequence length, and to validate the derivations. Each polymer molecule is simulated by comparing random numbers with a chain propagation probability and probabilities of incorporation for each monomer type.

Whether chain propagation takes place is decided using the probability of chain propagation, pp. Polymer chains propagate if a random number is less than pp and terminate otherwise. This parameter is related to the number average kinetic chain length, r_N, according to the relation: $pp = (r_N - 1)/r_N$. If the chain propagates, another random number is generated to decide which monomer type is incorporated onto the chain. This decision in made by comparing a random number with the probabilities of incorporation of each monomer type. The probability of incorporation of each monomer type is equal to the average mole fraction of that monomer type in the copolymer, for the case of random copolymers. Finally, when the chain is terminated, information of the whole molecule is saved for calculating the miscrostructural distributions. More details on the Monte Carlo algorithm used in these simulations have been given in our previous publications.[9-10]

3. CCD of Binary Copolymers

Simha and Branson first derived a general theory of copolymerization[11-12] that included the description of the CCD of binary copolymers. It became widely known later as Stockmayer's distribution, from Stockmayer's development of a simplified expression from this general theory.[2] Later, the effect of the molar masses of different monomer types was taken into account[13] and the resulting CCD expression became:

$$\begin{aligned} f_{w,s}(r,n_A) = {} & \frac{r}{\overline{r}_N^{\,2}} \cdot exp\left[-\frac{r}{\overline{r}_N}\right] \cdot \frac{1}{\sqrt{2\pi \cdot \overline{n}_A(1-\overline{n}_A)/r}} \cdot exp\left[-\frac{(n_A-\overline{n}_A)^2}{2\overline{n}_A(1-\overline{n}_A)/r}\right] \\ & \times \left[1+\frac{(n_A-\overline{n}_A)(1-M_B/M_A)}{M_B/M_A+\overline{n}_A(1-M_B/M_A)}\right] \end{aligned} \tag{1}$$

This function describes the weight fraction of molecules having a kinetic chain length of r and a mole fraction of monomer A of n_A. The parameter $\overline{r_N}$ is the number average kinetic chain length, $\overline{n_A}$ is the average mole fraction of monomer A, and M_A and M_B are the molar masses of monomers A and B, respectively. Although this function is useful, it is difficult to extend to a more general case.

Using a statistical approach we obtained a similar bivariate distribution:

$$\begin{aligned} f_{W,P}(r,n_A) = {} & \sqrt{\frac{1}{2\pi \cdot r \cdot n_A(1-n_A)}} \cdot \left(\frac{P[A]}{n_A}\right)^{r \cdot n_A} \cdot \left(\frac{1-P[A]}{1-n_A}\right)^{r\cdot(1-n_A)} \cdot r^2 \cdot (1-pp)^2 \cdot pp^{r-1} \\ & \times \left[\frac{M_A \cdot n_A + M_B \cdot (1-n_A)}{M_A \cdot P[A] + M_B \cdot (1-P[A])}\right] \end{aligned} \tag{2}$$

where $P[A]$ is a probability of incorporation of monomer A.

The details of the derivation are given in our previous publication.[9] Figure 1 shows that the results from the statistical approach agree with the ones from Stockmayer's distribution.

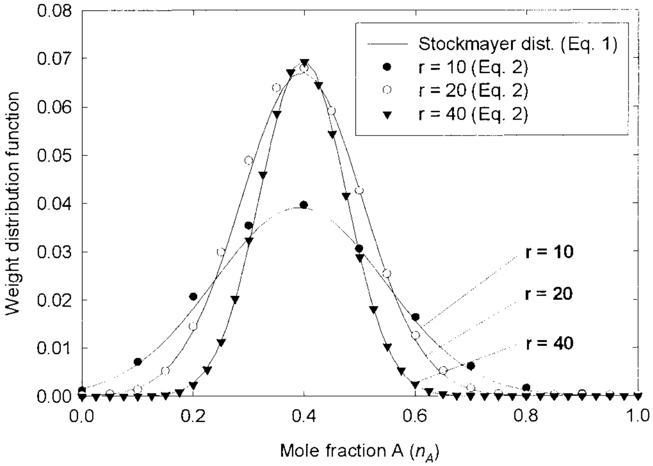

Figure 1 Comparison of CCD predictions with Stockmayer's distribution, Equation (1), and our statistical approach, Equation (2)

4. CCD of Multicomponent Copolymers

The more general case of random multicomponent copolymers formed by m monomer types can be described using the same strategy:

$$f_W(r,n_1,n_2,\dots,n_{m-1}) = f_W(n_1,n_2,\dots,n_{m-1} \mid r)\cdot f_W(r) \tag{3}$$

where $f_W(n_1,n_2,\dots,n_{m-1} \mid r)$ is the weigth distribution function of chains having mole fraction of n_1, n_2, n_3, ..., and n_{m-1} when only chains having kinetic chain length r are considered:

$$\begin{aligned} f_W(n_1,n_2,\dots,n_{m-1} \mid r) = & \sqrt{\frac{r^{m-1}}{(2\pi)^{m-1} n_1\cdot n_2\cdot\ldots\cdot n_{m-1}(1-n_1-n_2\ldots\ldots-n_{m-1})}} \\ & \times\left(\frac{P[1]}{n_1}\right)^{r\cdot n_1}\left(\frac{P[2]}{n_2}\right)^{r\cdot n_2}\cdots\left(\frac{P[m-1]}{n_{m-1}}\right)^{r\cdot n_{m-1}} \\ & \times\left(\frac{1-P[1]-P[2]\ldots-P[m-1]}{1-n_1-n_2\ldots-n_{m-1}}\right)^{r(1-n_1-n_2\ldots-n_{m-1})} \\ & \times\left[\sum_{i=1}^{m}(M_i\cdot n_i)\Big/\sum_{i=1}^{m}(M_i\cdot P[i])\right] \end{aligned} \tag{4}$$

and $f_W(r)$ is the weight distribution function of chains having kinetic chain length r, which follows the most probable distribution:

$$f_W(r) = r\cdot(1-pp)^2\cdot pp^{r-1} \tag{5}$$

The special case for terpolymers can be obtained by substituting m by 3 in Equation (3) and (4):

$$f_W(r,n_A,n_B) = f_W(n_A,n_B\,|\,r)\cdot f_W(r) \tag{6}$$

where,

$$\begin{aligned} f_W(n_A,n_B\,|\,r) = {} & \frac{r}{2\pi}\sqrt{\frac{1}{n_A n_B(1-n_A-n_B)}}\left(\frac{P[A]}{n_A}\right)^{r\cdot n_A}\left(\frac{P[B]}{n_B}\right)^{r\cdot n_B}\left(\frac{1-P[A]-P[B]}{1-n_A-n_B}\right)^{r(1-n_A-n_B)} \\ & \times\left[\frac{M_A\cdot n_A+M_B\cdot n_B+M_C(1-n_A-n_B)}{M_A\cdot P[A]+M_B\cdot P[B]+M_C(1-P[A]-P[B])}\right] \end{aligned} \tag{7}$$

The CCD of terpolymers was also calculated by Monte Carlo simulation to verify the results from our derivation. The parameter used for the simulations were: $P[A] = 0.3$, $P[B] = 0.4$, $P[C] = 0.3$, $M_A = 28$, $M_B = 42$, $M_C = 104$ and $pp = 0.95$. Figure 2 compares the results from Monte Carlo simulation with the ones from Equation (7).

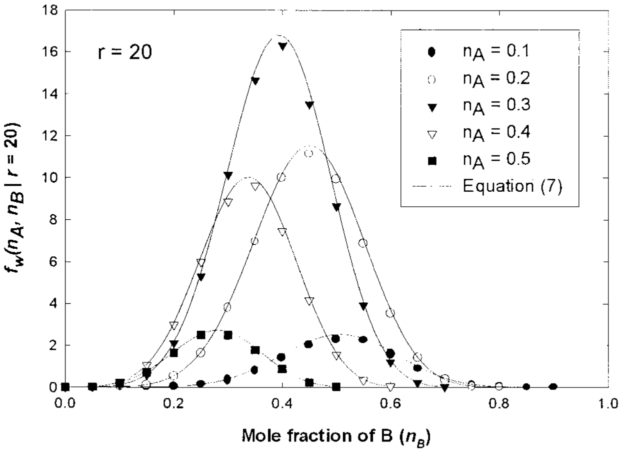

Figure 2 Comparison of the CCDs predicted with Equation (7) and with Monte Carlo simulation

To illustrate an interesting aspect of the CCD of terpolymers, we now use Equations (6) and (7) to calculate tri-dimensional and contour plots of the CCD of monomer A and B for different kinetic chain lengths (see Figure 3). The results indicate that the higher the kinetic chain length, the narrower the CCD. Unlike the breadth of CCD, the peak position is found to be independent of kinetic chain length. The Stockmayer distribution predicts a similar behaviour for binary copolymers.

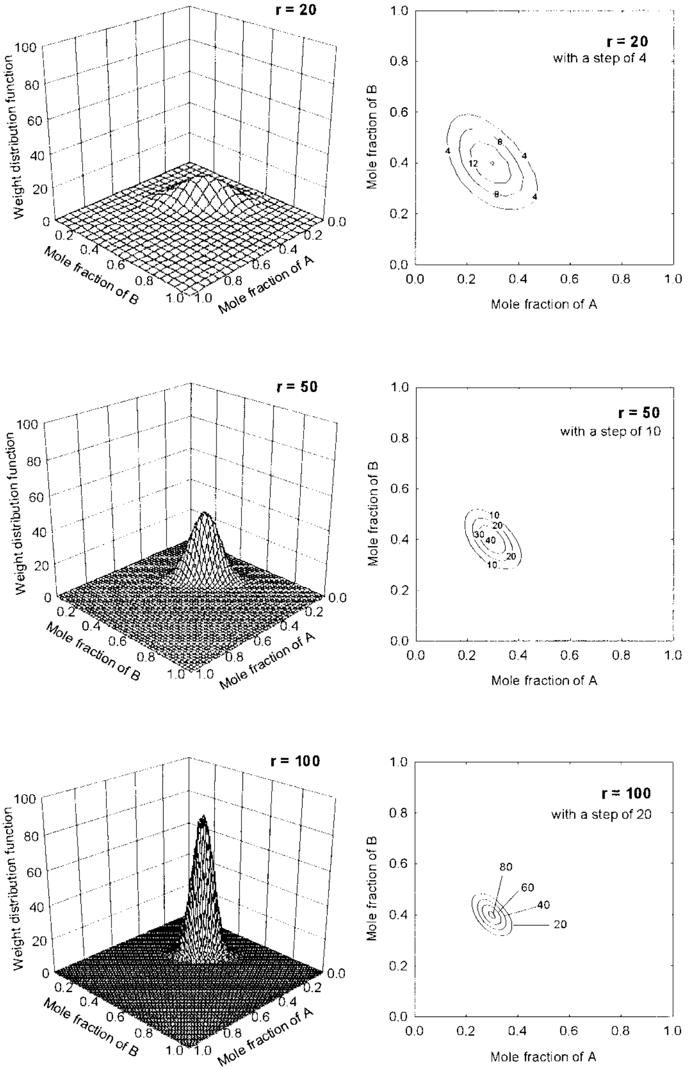

Figure 3 Chemical composition distributions of random terpolymers with various kinetic chain lengths

5. Longest Comonomer Sequence Length Distribution of Binary Copolymers

We now consider the distribution of the longest monomer sequence per chain for binary copolymers. Each copolymer chain contains sequences of monomer A and comonomer B. For example, consider the copolymer chain BB AAAAAA BB AAAAAA B AAA, which contain 20 monomeric units. This particular chain contains 6 sequences, 3 of which are A sequences. Consider that sequences of monomer A are crystallizable, while sequences of comonomer are not. This is the case, for example, for ethylene/1- olefin copolymers, where A stands for ethylene and B stands for the 1-olefin comonomer. We are interested in the longest sequence of monomer A per chain because this particular sequence is potentially the first one to crystallize upon cooling from the melt or solution.

Using a statistical argument with probability theory, we derived the equation expressing the weight distribution of longest sequence (*LS*):

$$f_w(LS) = \frac{(1-Pa)(1-pp)}{Pa}\left[F\left(1-(pp\cdot cp)^{LS}\right)-F\left(1-(pp\cdot cp)^{LS-1}\right)\right] \tag{8}$$

The function F(K) is defined as

$$F(K) = \frac{Pa.K}{(1-Pa.K)^2}\left[LS\left(1-\frac{Pa.K}{1-(pp\cdot cp)^{LS}}\right)+\frac{Pa.K}{1-(pp\cdot cp)}\right] \tag{9}$$

where *Pa* is the probability that the chain ends with a comonomer unit ($Pa = pp(1\text{-}cp)/(1\text{-}cp \times pp)$), *pp* is the chain propagation probability, and *cp* is probability of incorporation of monomer A. The process of deriving this equation is rather long and tedious and is described in a previous publication.[9]

Having derived this expression, it is now interesting to see the effect of the parameter *pp* and *cp* on the distribution of longest monomer sequences (see Figures 4 and 5). The results from our derivation were also compared with ones from Monte Carlo simulation for validation. This equation can be useful for modeling a polymer characterization technique called crystallization analysis fractionation (Crystaf).[14-16] More details on this modeling technique can be found in our recent publications.[9, 17-18]

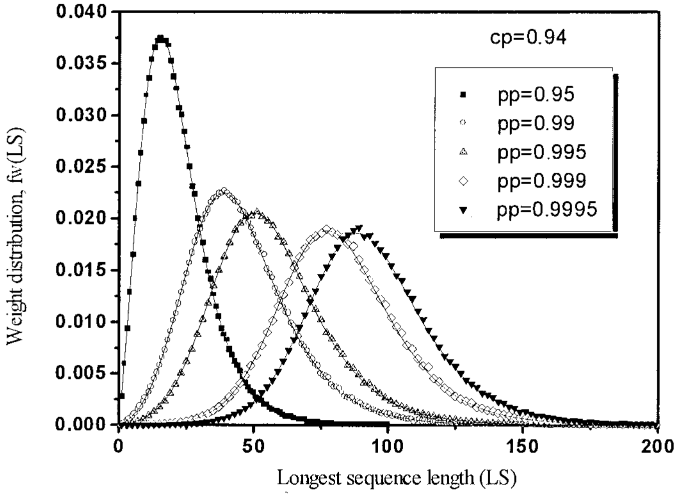

Figure 4 Effect of the propagation probability (*pp*) on distribution of longest monomer sequences

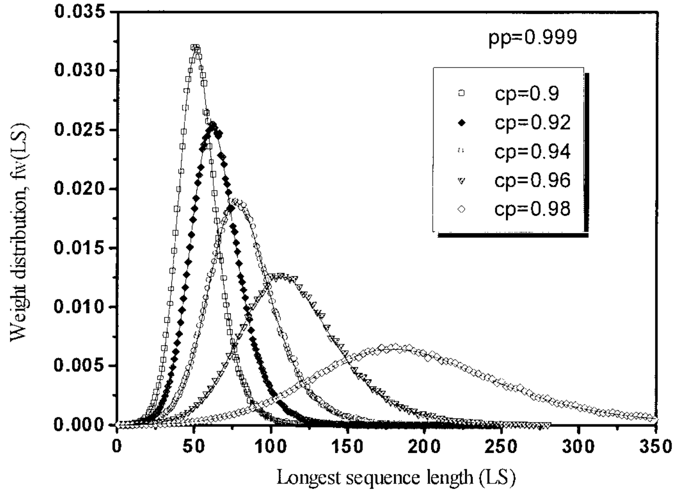

Figure 5 Effect of monomer incorporation (*cp*) on the distribution of longest monomer sequences

6. Conclusion

An analytical expression describing the chemical composition distribution of multicomponent random copolymers was derived in the form of a weight distribution function of copolymer chains having different kinetic chain lengths with a particular composition. The results from our derivation agree with Stockmayer's distribution for binary copolymers and with Monte Carlo simulations for terpolymers. An analytical expression for the distribution of the longest monomer sequences per chain for binary copolymers was also developed and the results agreed with Monte Carlo simulations.

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