

Chain Copolymerization Reactions: An Algorithm To Predict the Reaction Evolution with Conversion

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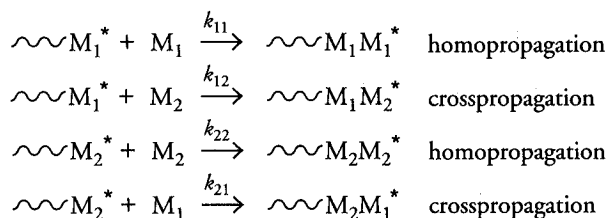
Macromolecular chemistry is a common topic in undergraduate and postgraduate studies that deals with materials (or polymer) science. One of the basic subjects is chain copolymerization, which is relevant from both theoretical and technological points of view. Theoretically, it is interesting to focus on the effect of the chemical structure on the reactivity of monomers and active species. Technologically, chain copolymerization can be used to produce an unlimited number of different products by varying the nature and relative quantities of reactants.

The chain copolymerization of two or more monomers forms a copolymer chain that is not an alloy of homopolymers. The monomers enter into the copolymer in overall quantities and sequence distribution determined by their relative concentrations and reactivities. This fact allows the synthesis of an almost unlimited number of different products by variations in the nature, relative quantities, and microstructure of the monomer units in the copolymer product. In this way, several types of important copolymers for technological applications can be synthesized. Student understanding of a chain copolymerization (the role and determination of the reactivity ratios, the evolution of the composition, and sequence microstructure with conversion, etc.) should be one of the main goals for a polymer science instructor.

Terminal Model

For statistical copolymers formed by simultaneous chain polymerization of two or more monomers, the comonomer incorporation into the growing chains (or the probability of finding a given comonomer along the macromolecular chain), follows some statistical laws that are related to the influence of the nature of the different reactants. The terminal model is historically the most relevant and corresponds to first-order Markov statistics, where the probability of finding a comonomer depends on the nature of the neighbor unit. Thus in the terminal model, the addition of a comonomer in the propagation step depends on the nature of both the monomer and the terminal unit of the active growing chain. This model has been successfully used during the last decades to correctly predict copolymer composition and sequence distribution.

Using this model we have four kinetically different propagation reactions for binary copolymerization,



where k_{ij} ($i, j = 1, 2$) is the rate constant for the addition of a monomer M_j to a propagating chain end $\sim M_i$. The asterisk

represents a generic active center, such as a radical, anion, and so forth. A homopropagation or self-propagation reaction occurs when $i = j$, and a crosspropagation or crossover reaction proceeds when $i \neq j$.

Assuming several approaches as the stationary state (the concentration of active species stays constant), Mayo and Lewis in 1944 derived, from the rates of disappearance of the two monomers, an equation that governs the addition of the reactive units to the growing chains in chain copolymerizations following the terminal model (1):

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1 [M_1]^2 + [M_1][M_2]}{r_2 [M_2]^2 + [M_1][M_2]} \quad (1)$$

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the homopropagation/crosspropagation kinetic constant ratios referred to as the monomer reactivity ratios and $[M_1]$ and $[M_2]$ are the monomer feed concentrations. A reactivity ratio value for monomer 1, r_1 , greater or less than 1, indicates that a growing chain end $\sim M_1$ is more reactive towards a monomer 1 or 2, respectively.

Equation 1 is known as the copolymerization composition equation and can be expressed in molar fractions instead of concentrations because the infinitesimal decrease of monomer concentration (left part of the equation) corresponds to the infinitesimal incorporation to the growing chains:

$$\frac{f_1}{f_2} = \frac{r_1 F_1^2 + F_1 F_2}{r_2 F_2^2 + F_1 F_2} \quad (2)$$

$$F_1 + F_2 = 1 \quad \text{and} \quad f_1 + f_2 = 1$$

where F_i and f_i ($i = 1, 2$) are the instantaneous feed molar fraction and the instantaneous copolymer molar fractions, respectively, of the monomer i . For a given feed monomer ratio and known reactivity ratios, eq 2 gives the composition of the instantaneous copolymer chains formed in the reaction. The representation of f_1 versus F_1 is the well-known composition diagram.

In addition to this instantaneous compositional information, the reactivity ratios can also predict the instantaneous sequence distribution that is intimately related to the microstructure of the macromolecular chains. The conditional probabilities, p_{ii} and p_{ij} for the i or j monomer addition to a growing chain end $\sim M_i$ ($i, j = 1, 2$), are given by the propagation rates ratio (where $r_i = k_{ii}/k_{ij}$),

$$p_{ii} = \frac{k_{ii}[M_i]}{k_{ii}[M_i] + k_{ij}[M_j]} = \frac{r_i}{r_i + \frac{[M_j]}{[M_i]}} \quad (3)$$

$$p_{ij} = 1 - p_{ii}$$

The instantaneous molar fraction of any sequence is equal to the probability of existence of the first unit (f , the copolymer molar fraction) multiplied by the corresponding conditional probabilities. For instance, the i centered triad molar fractions will be

$$f_{iii} = f_i p_{ii} p_{ii}; \quad f_{ij+ji} = 2f_i p_{ii} p_{ij}; \quad f_{jji} = f_j p_{ji} p_{ij} \quad (4)$$

The sequence molar fraction is related to the sequence population and therefore to the microstructure (sequence distribution). Another valuable parameter is the number-average sequence length of i -sequences:

$$\bar{N}_{i\text{-seq}} = 1 + r_i \frac{[M_i]}{[M_j]}$$

The information given by this sequence analysis is very valuable and complementary to that obtained by the composition equation.

Instantaneous and Cumulative Copolymer Chains

Equation 1 (or 2) is a differential equation and provides instantaneous information. As one of the comonomers is usually more reactive than the other, there is a preferential consumption of it. Thus there is a continuous change in the feed composition and in the composition and sequence distribution of the forming macromolecular chains. There is a substantial difference between the instantaneous and the cumulative copolymer chains. The latter is the final product of the reaction but its characteristics and properties depend on the chain distribution formed during the entire reaction,

that is, on the successive instantaneous copolymer chains. This heterogeneous character is specially relevant for those copolymerizations with high comonomer differential reactivity.

It is not easy to show in a classroom the drift of the composition and sequence distribution with the conversion for a given copolymer reaction and the relevance of the reactivity ratio values. A computer program was developed to facilitate this teaching. To describe the reaction evolution with conversion under the first-order model an integrated equation, such as the *exact solution* (2, 3) or the Skeist approximation (4), must be used. An algorithm was developed where the well-known exact solution (eq 5) of the differential equation was incorporated,

$$\frac{[M_2]}{[M_2]_0} = \left(\frac{[M_2]_0 [M_1]}{[M_1]_0 [M_2]} \right)^{\frac{r_2}{1-r_2}} \times \left[\frac{(r_1 - 1) \frac{[M_1]}{[M_2]} - r_2 + 1}{(r_1 - 1) \frac{[M_1]_0}{[M_2]_0} - r_2 + 1} \right]^{\frac{r_1 r_2 - 1}{(1-r_1)(1-r_2)}} \quad (5)$$

where $[M_i]_0$ and $[M_i]$ represent the initial and the remaining concentration of the monomer i ($i = 1, 2$), respectively. This equation relates, by means of reactivity ratios, the residual monomer at any reaction time with the initial monomer feed concentration. Simple material balances can put this information in terms of conversion or cumulative copolymer composition:

$$f_{1,\text{cum}} = \frac{[M_1]_0 - [M_1]}{[M_1]_0 + [M_2]_0 - [M_1] - [M_2]}$$

$$\text{conversion} = \frac{[M_1]_0 + [M_2]_0 - [M_1] - [M_2]}{[M_1]_0 + [M_2]_0}$$

The algorithm, named Conversion, was programmed in QuickBasic (4.5), a useful language for doing rapid routines that can easily compute many data sets. The results are output in a data file ready to read or plot in any program.

Conversion is able to theoretically predict, without any approximation (except those considered by the terminal model), the course of any binary reaction with the conversion. Moreover, it gives information on a series of parameters such as the instantaneous and cumulative copolymer molar fraction, the microstructural arrangements in terms of triad molar fractions, or the number-average sequence length of 1-sequences as a function of the initial feed molar fraction and the conversion.

Conversion has a universal character; that is, it is able to predict the progress of the reaction for any comonomer couple (independent of r_1 and r_2 values, except for the unity). In terms of differential reactivity between the monomers 1 and 2, there are four possible reactions that are shown as composition diagrams in Figure 1. If the compositional curve remains below the diagonal for the range of molar fractions (Figure 1C when $r_1 < 1$ and $r_2 > 1$), the feed is enriched dur-

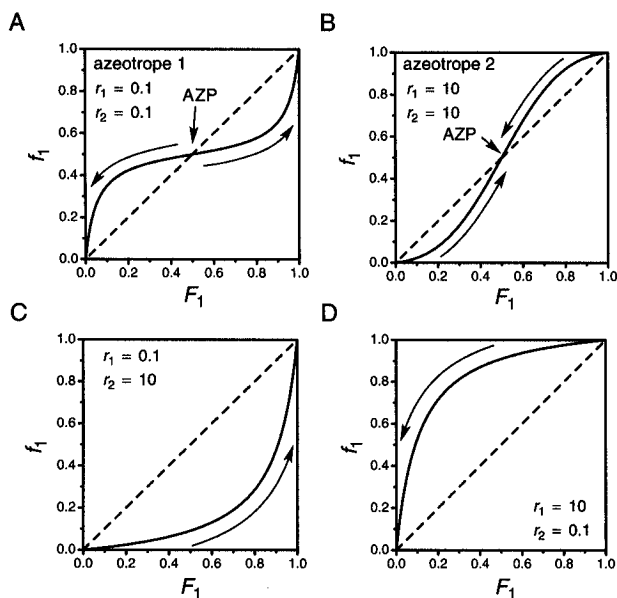


Figure 1. Composition diagrams of the four copolymerization types considered in this article: examples A and B are azeotropic systems with both values of the monomer reactivity ratios below or above 1 ($r_1, r_2 < 1$ and $r_1, r_2 > 1$, respectively) and examples C and D have the values of the monomer reactivity ratios value below and above the unity ($r_1 < 1, r_2 > 1$ and $r_1 > 1, r_2 < 1$, respectively). AZP is the azeotropic point.

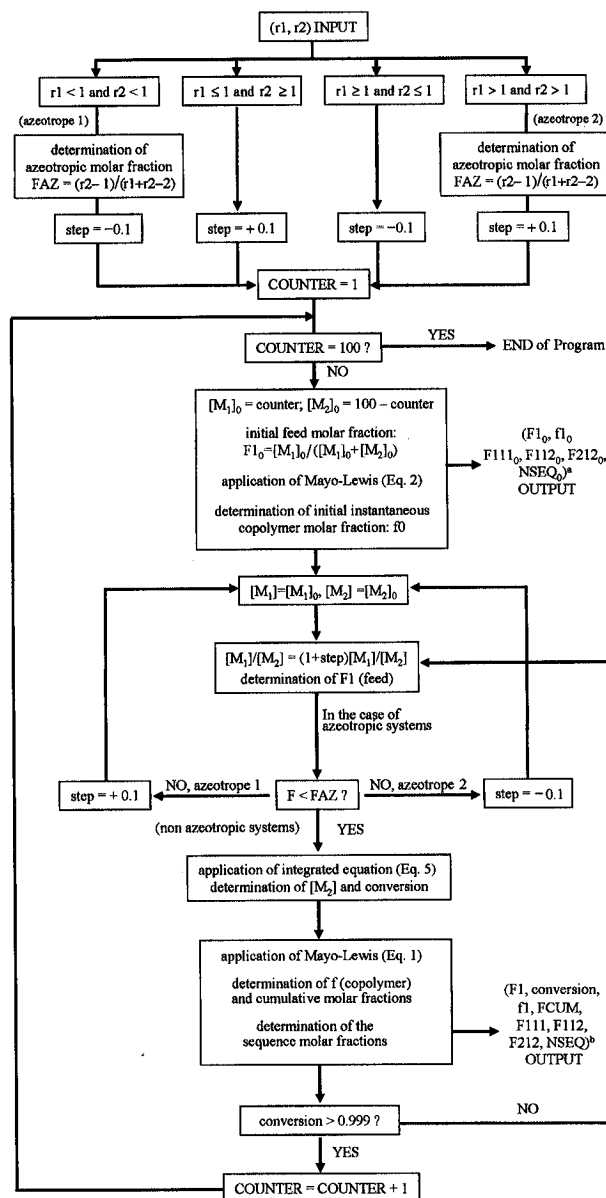


Figure 2. Schematic representation of the developed algorithm. F_1 and f_1 are the feed and copolymer molar fractions of the monomer 1. F_{111} , F_{112} , and F_{212} are the molar fractions of the triads 111, 112+211, and 212 as defined in the text. NSEQ is the average length of sequences of the monomer 1. The program uses an upper limit defined by the user. Conversion and FCUM (cumulative copolymer molar fraction) are obtained by material balances as indicated in the text. (Note that the abbreviations used in the figure are slightly different from those used in the text).

ing the copolymerization with the less reactive monomer 1, giving rise to macromolecules progressively richer in species 1. This trend is represented in the figure by the arrow. The opposite case, $r_1 > 1$ and $r_2 < 1$ (Figure 1D), is represented by curves situated above the diagonal. In this case, the reaction evolves with conversion towards the formation of copolymer chains progressively richer in the less reactive monomer 2. In addition to those cases (which are the same depending on the assignments of 1 and 2), we have to consider the two possible azeotropic systems (AZS). For these azeotropic situations, there are two clearly differentiated regions in the composition diagram, separated by the azeotropic point (AZP), which is the crossover point between the diagonal and the f_1 versus F_1 curve. This occurs when the copolymer and feed molar fraction are the same and copolymerization occurs without a change in the feed composition at any conversion. In the first type of AZS ($r_1 < 1$ and $r_2 < 1$), the course of the copolymerization tends towards the ho-

mopolymers. That is, reactions with feed molar fractions lower than AZP consume preferentially monomer 1, so that the forming macromolecular chains become progressively richer in the component 2, while the reactions in the upper region present the opposite trend. The second type of AZS ($r_1 > 1$ and $r_2 > 1$, which is unusual behavior) (5), exhibits a very different behavior. In this case, the reactions evolve towards the AZP and not towards the homopolymers. The molar fraction region below AZP consumes preferentially monomer 2, leading to macromolecules progressively richer in the monomer 1. On the other hand, the molar fractions over the AZP consume preferentially monomer 1 and the reaction tends to copolymers rich in the monomer 2.

How Conversion Works

A simplified scheme of the proposed algorithms is shown in Figure 2, while the complete program is available in the

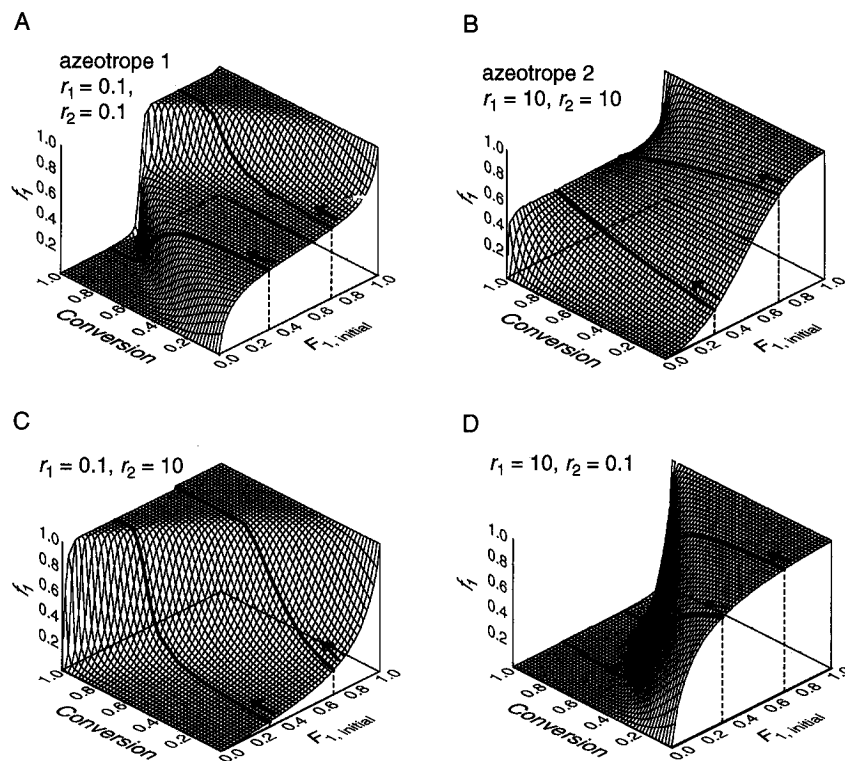


Figure 3. Instantaneous copolymer molar fraction as a function of the conversion and the initial molar fraction in the feed. The figure represents the four examples using the results obtained from the computer program. The thick lines represent the course of the reactions starting at 0.3 and 0.7 molar fractions in the feed, taken as model copolymerizations.

Supplemental Material.^W Conversion recognizes the type of copolymerization (from among the four examples represented in Figure 1) and defines a positive or negative step that is a function of the consumption preferences in the reaction media. Then the program is directed to a common routine where theoretical reaction points are generated (line 10000 and following in the program). In these lines, reactions in all the feed molar range are theoretically predicted with the help of a counter. The routine initially generates the points at zero conversion (creating the composition diagram) and after that, the evolution with conversion is predicted for each reaction by using eqs 2 and 3. The program finishes each particular reaction when the conversion degree reaches a 0.999 value, going to predict the next one. In the case of the azeotropic reactions, there is a redefinition in the step sign in the AZP (as explained in the Supplemental Material^W).

How To Use Conversion in a Classroom Setting

Knowing the reactivity ratios, the program is able to generate a wide array of data for a binary copolymerization that follows the terminal model. Users simply run the executable program, Conversion.exe, in a Windows environment. The program asks for a name for the output data file (filename.dat) that must be less than eight characters. The program then asks for the reactivity ratio values and for the upper limit of the number-average sequence length (of 1-sequences). The

program begins to run, generates the filename.dat file, and finishes. The data file is in ASCII format and provides eight columns with values for:

1. Initial feed molar fraction of monomer 1, $F_{1,initial}$
2. Conversion
3. Instantaneous copolymer molar fraction of monomer 1, f_1
4. Cumulative copolymer molar fraction of monomer 1, f_{cum1}
5. 111 Triad molar fraction, f_{111}
6. 112+211 Triad molar fraction, $f_{112+211}$
7. 212 Triad molar fraction, f_{212}
8. Number-average sequence length of 1-sequences (until the limit), \bar{N}_{1-seq}

These data can be read and plotted by graphing programs such as Surfer (6). The most valuable information can be obtained from plotting the data in the first and second columns (initial feed molar fraction and conversion) as x, y data and one of the remaining columns as the z data.

The program has been evaluated with the four examples showed in Figure 1. The points, instantaneous copolymer molar fraction versus conversion versus initial molar fraction in the feed, were depicted using the Surfer software, giving rise to the four surfaces represented in Figure 3. The

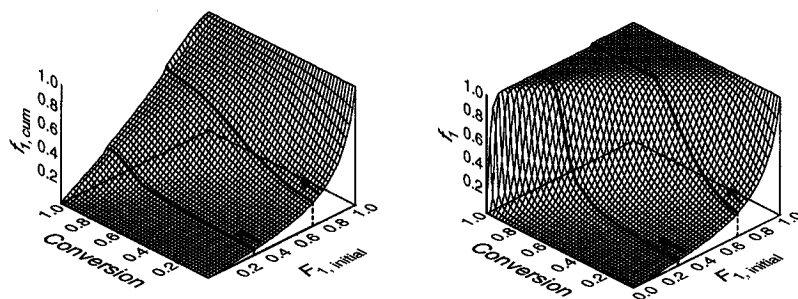


Figure 4. Cumulative (left side) and instantaneous (right side) copolymer molar fraction as a function of the conversion and the initial molar fraction in the feed, for the example C. Values were obtained from the computer program. The thick lines represent the course of the reactions starting at 0.3 and 0.7 molar fraction in the feed, taken as model copolymerizations.

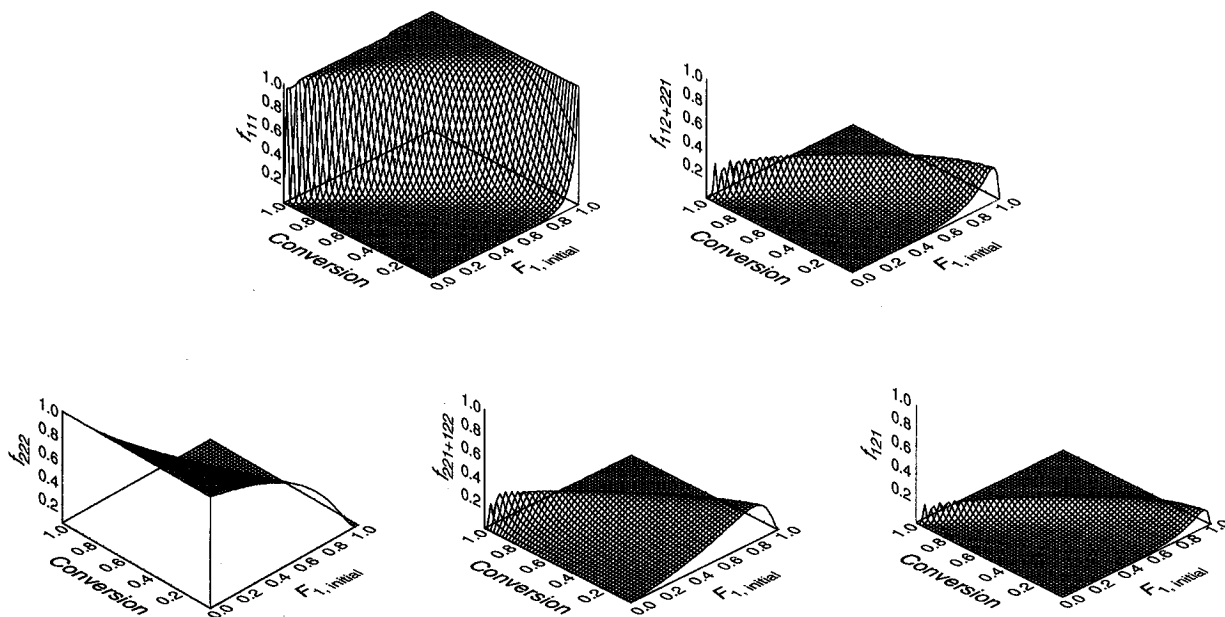


Figure 5. Molar fractions of triads as a function of the conversion and the initial molar fraction in the feed for example 3. Values were obtained from the computer program Conversion.

surfaces are similar to the classical ones obtained by using the Skeist approximation (7). One characteristic of these three-dimensional surfaces is that the crossing curve at conversion zero, leads to the composition diagram of Figure 1. For the sake of clarity in discussion, two courses of model reactions (at 0.3 and 0.7 initial molar fractions in the feed) are depicted. The large heterogeneous character of most of the reactions is clearly observed, which is related to the choice of reactivity ratios far from unity (0.1 and 10). For monomer couples with r_1 and r_2 values close to 1, the copolymerization reactions take place in a much more homogeneous way. This theoretical prediction is of great importance for systems with a high differential reactivity (as the examples in Figures 1 and 3).

While the reactions of the azeotrope 2 tend to the AZP as conversion advances and the reaction takes place more or less homogeneously (Figure 3B), the reactions of the azeotrope 1, which tend towards the homopolymers (Figure 3A), exhibit a very interesting behavior. In this case, both reactions initially form copolymers with a composition close to the AZP, but at conversions higher than 50% they take divergent ways, so that below AZP the final chain compositions are very rich in monomer 2, while above AZP compositions are rich in monomer 1. It has to be noted that there is no known real copolymerization (to our knowledge) that fits the example B (azeotropic system with $r_1 > 1$ and $r_2 > 1$). Examples C and D are in fact the same copolymerization where monomers 1 and 2 have been interchanged. In both cases, two species are formed along the course of the reaction.

Macromolecules rich in the most reactive component are initially formed and after the consumption of a great quantity of this monomer, chains rich in the less reactive monomer are formed. A global analysis of the reaction, however, does not give this valuable information. In this sense, Figure 4 shows the cumulative and instantaneous copolymer molar fractions for example C ($r_1 = 0.1$ and $r_2 = 10$). The average composition increases gradually till the system reaches the initial feed composition. This trend does not reveal information about the real distribution of the macromolecular chains, which is highly heterogeneous and can have a large influence on the material properties.

In addition, the program is able to predict the evolution with conversion of other valuable parameters that provide information on the copolymer microstructure, such as sequence molar fractions or average sequence length. Figure 5 shows, as an example, the triad molar fractions of one of the model systems ($r_1 = 0.1$ and $r_2 = 10$). The molar fractions are in good agreement with the previous discussion and

with the highly heterogeneous character of the reaction that leads to the formation of two main species rich in each one of the two components. In this case, as the monomer 2 is much more reactive than 1, at low conversions and high initial composition of that monomer, 222 triads are predominantly formed. At high conversions and high initial composition of monomer 1, 111 triads mainly populate the chains. Low percentages of heterotriads (112+211, 212, 221+122 or 121) are formed along the diagonal that separates the formation of the two main species. The molar fractions of the triads centered in the monomer 2 have been obtained by running the program with opposite monomer identification.

The number-average sequence length data are given in the last column of the data file. To facilitate the graphing of these data, an upper limit has to be defined and the program asks for it before computing. Without an upper limit, this average sequence length would tend to infinity in the homopolymer.

Conclusion

This algorithm is a very useful tool to study and understand the behavior of chain copolymerization reactions. Given a binary copolymerization reaction that follows the terminal model, Conversion is able to predict the evolution of different parameters, such as instantaneous and cumulative copolymer molar fractions, or molar fractions of any sequence with the conversion.

Supplemental Material

The source code for the program and an executable file of the program are available in this issue of *JCE Online*.

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