Monte Carlo Simulation of Ethylene Copolymers: A Look into the Monomer Sequence Distribution

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Summary: A comprehensive mathematical model was developed using Monte Carlo simulation to describe the mechanism of ethylene and α-olefin copolymerization. The model studies the polymerization mechanism using coordination catalysts and is able to predict molecular weight and detailed chemical composition distributions. This work is considered to be a useful tool that enables us to understand and described the monomer sequence distribution as a function of chain length in semi-batch polymerization reactors.

Keywords: copolymerization; kinetics (polym.); Monte Carlo simulation; polyolefin molecular modeling

Introduction

In recent years there have been many efforts to develop and expand the ability of mathematical models capable of describing polymerization systems. Models can provide a key competitive advantage for the industry and research in terms of production and technology development. As new resins are continuously produced to meet the requirement of final applications and processability, it is imperative to pursue strong polymer characterization with special attention to detailed analyze of polymer microstructure. The microstructure of polyolefin is defined by its distribution of molecular weight, chemical composition, branching topology, and stereoregularity.

The chemical and physical properties of copolymers are influenced not only by their average composition, but also by the monomer sequence distribution along the polymer chains.[1] Predicting the molecular weight and comonomer distributions can lead to a better understanding of the possible morphology in solid state because they are considered to be the main structural parameters that affect the crystallinity of polymeric materials.[2] As a consequence, final physical properties such as the tensile properties of a copolymer could be controlled by the ratio of crystalline species in the polymer.[3]

Polyolefins include large volume materials such as polyethylene (PE), polypropylene (PP) and specialty materials. The major reasons behind the successful growth of the polyolefin industry are: their versatility with respect to physical and mechanical properties and application, the energy savings during their production and use in comparison with other materials and their low cost and the easily available raw materials.[4,5] Catalysis is the key to many chemical transformations. For successful industrial implementation of a catalyst certain prerequisites have to be fulfilled. The ideal catalyst has to combine high efficiency (i.e. effective use of starting materials, and minimal waste emission), high selectivity (i.e. optimal conversion to the desired product), and high total turnover (i.e. amount of product formed per given amount of catalyst) with durability (e.g. low toxicity) and low overhead expenditure (i.e. cheap catalyst, and little maintenance). Understanding how catalyst structure and properties can affect these parameters, combined with chemical curi-

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osity, is and will be the driving force for the future improvement and development of catalysis.

Single-site catalysts such as metallocenes are able to make polyolefins at very high yields and with a degree of microstructural control not possible to achieve using conventional Ziegler-Natta catalysts. Work on zirconium metallocene-methylalumoxane catalysts was brought by Kaminsky.[6] The largest tonnage plastic material produced worldwide is polyethylene which is produced commercially using free-radical initiators, or coordination catalyst systems like Phillips-type catalysts, Ziegler-Natta catalysts, and more recently, metallocene catalysts. Phillips and Ziegle-r-Natta system are known to have multiple active sites, while metallocene systems are well defined single-site catalysts. This is of fundamental relevance because each type of active site may have its own polymerization mechanism and kinetics of polymerization. By combining several metallocene catalysts products tailored end-use properties can be manufactured. This explains why metallocenes are playing a more and more important role in the polyethylene industry.[7]

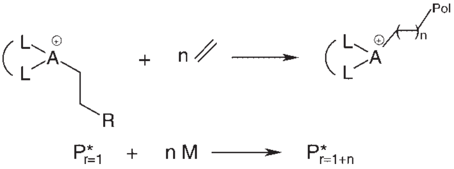
In this work, a Monte Carlo simulation model was developed to describe the polymerization mechanisms of olefin copolymerization using single-site coordination catalyst. The mathematical model is meant to describe molecular weigh and chemical composition distribution in copolymerization systems. More specifically, this research work will give a detailed study of the molecular structure for ethylene-α-olefin copolymer. The work can be useful in understanding and predicting the comonomer incorporation in olefin copolymers from a simple theoretical point of view. The average monomer sequence distribution can be easily obtained by using analytical methods for single site-catalysts. However, the detailed monomer sequence distribution includes the length of each segment sequence and the nature of that segment in terms of what type of monomers are present. To the best of the authors' knowledge, such detailed distribution is not available for the complete molecular weight distribution. The results discussed here will show the sequence length distribution, with the triad sequence distribution the topic of a future contribution.

Model Description

Copolymerization Kinetic Equations

Polymerization with coordination catalysts proceeds via two main steps: monomer coordination to the active site and monomer insertion into the growing polymer chain. Prior to insertion, the double bond in the olefin monomer coordinates to the vacancy site of the transition metal. After the olefin is inserted into the growing polymer chain, another olefin monomer can coordinate to the vacant site and the process of insertion is repeated to increase the size of the polymer chain by one monomer unit at a time until chain transfer takes place. In the case of copolymerization, there is a competition between the comonomers to coordinate to the active sites and to be inserted into the growing polymer chains. Different rates of coordination and insertion of comonomers determine the final chemical composition of the copolymer chain. Several chain transfer mechanisms are operative in coordination polymerization. The type of termination reaction determines the chemical group bound to the active site and the terminal chemical group in the polymer chain.[8]

Rate of Propagation for the model is described by the following equation:



$$P^*_{r=1} + n\,M \longrightarrow P^*_{r=1+n}$$

$$R_{pA} = k_{pA}[P_r^*][A]$$

$$R_{pB} = k_{pB}[P_r^*][B]$$

where

A = transition metal center (Ti, Zr, Ni,...)

L = ligands
R = alkyl group (methyl, ethyl)
R_{pA} = Rate of propagation of monomer A
R_{pB} = Rate of propagation of comonomer B
k_{pA} = Propagation reaction constant for monomer A
k_{pB} = Propagation reaction constant for monomer B
$[A]$ = Concentration of monomer A
$[B]$ = Concentration of comonomer B
$[P_r^*]$ = Concentration of the active species

The rate of termination is simplified by using one transfer mechanism.

$$R_{tA} = k_{tA}[P_r^*]$$

$$R_{tB} = k_{tB}[P_r^*]$$

where,
R_{tA} = Rate of termination for monomer A
R_{tB} = Rate of termination for monomer B
k_{tA} = Termination reaction constant for monomer A
k_{tB} = Termination reaction constant for monomer B

The number average chain length is related to the propagation rate (R_p) and termination rate (R_t) of each active site using the following equation:

$$r_n = \frac{R_p}{R_t}$$

The chain length is related to the molecular weight by the molar mass of the monomer unit and the probability of chain propagation ($\boldsymbol{P_p}$) is related to the number-average chain length, (r_n) by:

$$p_p = \frac{(R_{pA} + R_{pB})}{(R_{pA} + R_{pB}) + (R_{tA} + R_{tB})} = \frac{(k_{pA}[P_r^*][A] + k_{pB}[P_r^*][B])}{(k_{pA}[P_r^*][A] + k_{pB}[P_r^*][B]) + (k_{tA}[P_r^*] + k_{tB}[P_r^*])}$$

$$p_p = \frac{R_p}{R_p + R_t} = \frac{1}{1 + \frac{R_t}{R_p}} = \frac{1}{1 + \frac{1}{r_n}} \approx 1 - \frac{1}{r_n}$$

Therefore the probability of propagation is expressed through the polymerization reaction kinetics and is related to the number average chain length (r_n) by using the rates of propagation and termination for monomer A and monomer B.

The probability of propagation determines which direction the model would proceed and hence whether to add more monomer units to the growing polymer chain or terminate the chain and store the chain length and sequence length distribution of the terminated reaction for the specific active site. Here we are assuming a Bernoulli process rather than a first order Markov chain; i.e. end units do not affect whether monomer A or comonomer B is being added.

Copolymerization Model Flow Chart

Monte Carlo Model was developed to simulate steady state copolymerization reaction. The model is based on random number generation between 0 and 1. The propagation probability for adding monomer A and monomer B is compared with the random number. Monomer insertion continues until the condition for termination probability with the random number is broken and the polymer chain growth stops. For modeling simplicity, the termination mechanisms are simplified to chain transfer to hydrogen. Kinetic data on the literature with discrimination among β-hydride elimination, transfer to monomer, transfer to hydrogen, transfer to aluminum or other chain transfer agents is scarce. Other termination rates can be easily added to the model if kinetic constants are available.

The model operates in a condition of steady-state batch polymerization reactor. It assumes a constant catalyst and monomers concentrations. As polymer chains are formed, they accumulate in the reactor. All kinetic parameters were kept constant during the simulation. The total number of polymer chains to be simulated, the number average chain length and the ave-

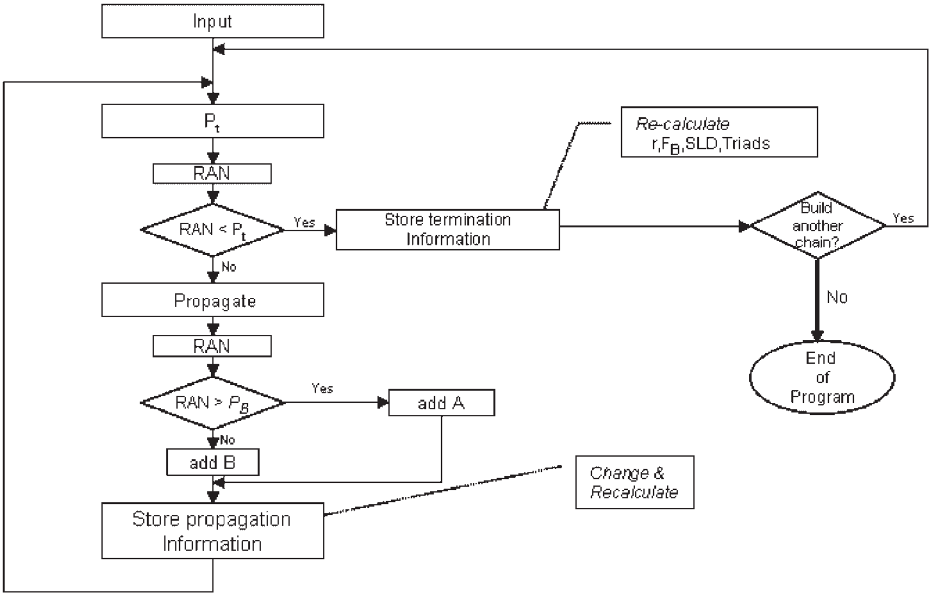


Figure 1.
Copolymerization Schematic Flow Chart.

rage comonomer composition are the parameters needed to run the model. The average chain length and the average comonomer composition can be calculated from the polymerization reaction kinetics or by analyzing polymer sample. The total number of chain simulated is determined by the degree of noise present on the final results. The model was developed with C++ programming language and run in a personal computer with Pentium 4^{TM} processor. The simulation result is stored as .txt file and the data is processed using Excel^{TM}. The copolymerization schematic flow chart is shown in (Figure 1).

Model Capability

Not only the average comonomer composition influences the physical properties of the copolymer but also the microcomposition and monomer sequence distribution along the polymer chain.[1] The proposed model is capable of calculating: a) the complete chain length distribution; b) polydispersity; c) average comonomer (B) composition; d) comonomer composition distribution as function of chain length; e) monomer (A) and comonomer (B) segment length distribution as function of chain length; f) average triads distribution; g) triad distribution as a function of chain length; and h) the distribution of monomer and comonomer as a function of segment length.

Results

Parameter Sensitivity

The kinetic parameters which were used for the simulation run are shown in (Table 1). The polymerization kinetic equations were used to obtain probability of termination, number average chain length and the probability of adding monomer B based on the final product. The reaction kinetic constants were calculated by satisfying the relationship between the reaction kinetic equations and the calculated values from probability of termination and the probability of adding monomer B. Such kinetic parameters are only for this simulation work and do not to represent a specific catalyst, although they are within the range of parameters determined experimentally. The fraction of comonomer incorporated in

Table 1.
Kinetic Parameters Used in the Model (for changing number average chain length and constant number fraction of comonomer).

k_{pA} (L/mole · s)	k_{pB} (L/mole · s)	k_{tA} (L/mole · s)	k_{tB} (L/mole · s)	Pp	r_n	P_B
1210	1910	2.70	1.10	0.99901	1007	0.05
2150	3395	1.35	0.91	0.99967	3005	0.05
3220	5080	1.23	0.80	0.99980	5010	0.05
3420	5340	0.98	0.56	0.99986	7010	0.05

$[Pr^*] = 10 \times 10^{-6}$ (mole/L), $[A] = 3$ (mole/L), $[B] = 0.1$ (mole/L), P_B = probability of adding comonomer B.

the polymer chain was not dependant on the chain length. The noise in the comonomer incorporation curves is due to small population of chains the high chain length range. This does not change the interpretation of results and can be minimized by increasing the number of chains (longer simulation times) or by lumping the points within a wider range (Figure 2).

The length of the crystallizable monomer sequence is parameter that determines the degree of crystallinity in polyethylene. Addition of comonomer decreases the length of the segment that can be crystallized, thereby decreasing the degree of crystallinity in these semi-crystalline polymers. Experimental work in the literature has shown segments from 4 up to 18 ethylene units in length do not contribute to crystalline phase in ethylene copolymers.[9] Haag and co-workers have previous chosen the value of 20 monomeric as the minimum segment length to be accounted for when simulating the effect of comonomer composition on the degree of crystallinity.[10] The model developed here keeps track of the fraction of monomer and comonomer sequence length An and Bn (Figure 3).

Figure 4 shows fraction of segments with different length, for monomer A and comonomer B. In this case the model simulated for number average chain length $r_n = 5004$ with average fraction of

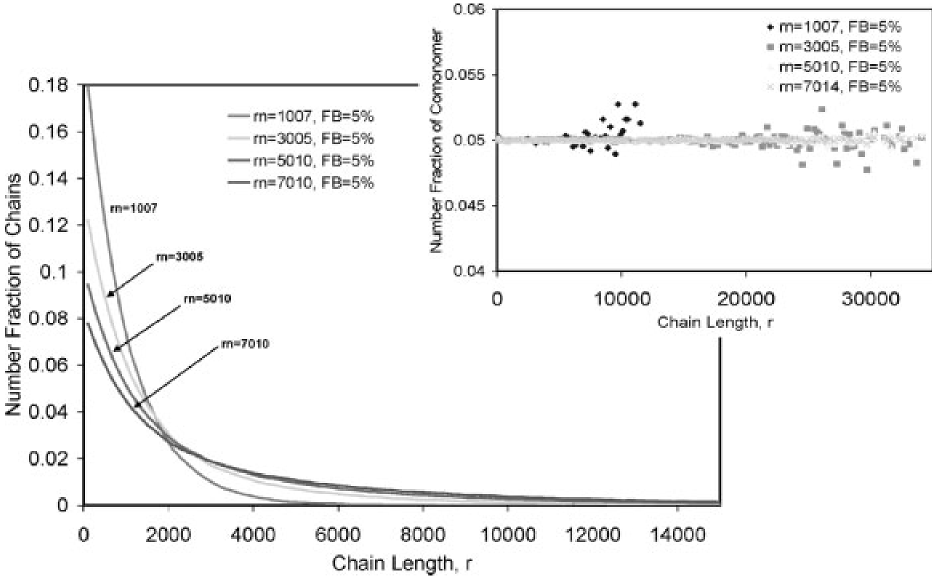


Figure 2.
Number fraction of chains as a function chain length (*r*) and comonomer distribution.

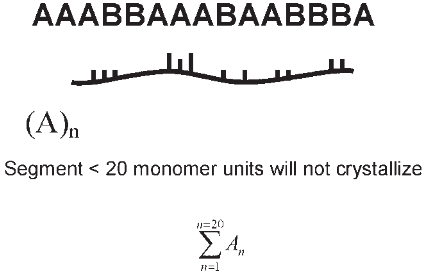


Figure 3.
Segment length.

comonomer $F_B = 3\%$. Most of the segments of comonomer B are isolated is sequences like ABA, that is $B_n = 1$, with a fraction equal to 0.9636. There is a monotonic decrease in the fraction of segments B_n when the segment length increases. The longest comonomer segment B_n was six monomers units. Most of the segments A_n have lengths between 1 and 100. Surprisingly, segment $A_n = 1$ representing sequences like BAB where the segment A is isolated by two adjacent segment Bs has the highest fraction. The fraction of segment length of monomer A_n decreases continuously as the segment length increases with an inflection point at around segment length $A_n = 80$.

As indicated before, the number of segments with length equal or smaller than 20 will be used to indicate the part of a polymer chain that cannot contribute to crystallization. The model is capable of calculating the fraction of all segments with length between 1 and 19, for monomer A and comonomer B, as a function of chain length. All segments with or larger that 20 are lumped as A_{20}. For simplicity, the summation of segments with length from 1 to 19 (A_{1-19} and B_{1-6}) is used to illustrate how this distribution changes as a function of chain length. Although in the case of copolymerization of ethylene (monomer A) with α-olefin (comonomer B) the comonomer sequence is unlikely to crystallize, it is interesting to see how the fraction of segments is distributed as a function of chain length (Figure 5).

Case Study

The model was used to explore the case where four semi-batch reactors with different condition (kinetic parameters) in each reactor. The purpose of this study is simply

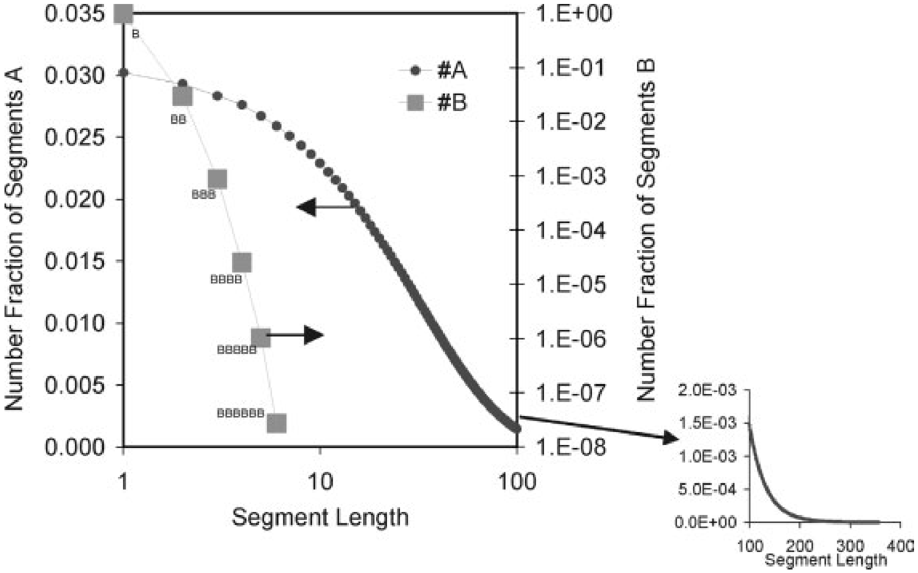


Figure 4.
Fraction of monomer and comonomer segment length, A_n and B_n respectively. ($r_n = 5004$, $F_B = 3\%$).

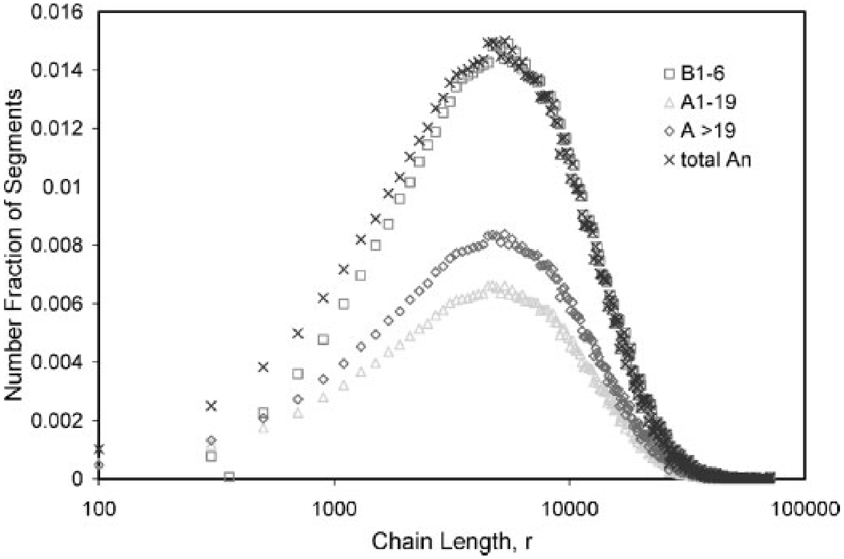


Figure 5.
Distribution of segments B_{1-6}, A_{1-19}, $A_{>19}$ and total A_n as a function of chain length ($r_n = 5004$, $F_B = 3\%$).

to illustrate the model capabilities and potential to understand the distribution of branching as a function of chain length. Running four different semibatch reactors with single site catalyst and mixing the final polymer has a similar effect as running one semibatch reactor with a multiple site catalyst. Note that the active (or yield) for each active site is proportional to the number of chains that are generated. In this case study, each reactor produces 250,000 copolymer chains with different number average chain lengths and number fraction of comonomer. The product from reactor 1 is mixed with reactor 2 to give 500,000 copolymer chains. Then mixed product from reactor 1 and 2 is mixed with the product from reactor 3 to give 750,000 copolymer chains. Finally the mixed product from reactor 1, 2 and 3 is mixed with reactor 4 to give a total of 1,000,000 copolymer chains (Figure 6). For each reactor the kinetics parameters did not change during each the simulation. The number average chain increased from $r_n = 1007$ to $r_n = 7024$. The average comonomer composition decreased from $F_B = 5\%$ to $F_B = 2\%$.

The number fraction of chains and the number fraction of comonomer are plotted as a function of chain length. The compositional drift is illustrated in the results. Figure 7 shows the impact of mixing the products of reactor 1 to 4 on the number fraction of chains produced. The increase in number average chain length r_n could be explained by knowing that the probability of propagation in reactor 4 is greater than the probability of propagation in reactor 1 (Table 2): Pp reactor $1 < Pp$ reactor $2 < Pp$ reactor $3 < Pp$ reactor 4.

With larger number average chain length produced in reactor 4 and lower fraction of comonomer we would be able to produce more crystalline product in reactor 4.

Figure 8 shows that the number fraction of comonomer F_B is clearly drifting by increasing the number of chains produced by mixing the products of reactor 1 to 4. Comparing the lines Figure 8 it is noticed that the comonomer fraction F_B decreases from reactor 1 to reactor 4 as the populations of the different reactors are mixed. It is clear that after mixing the products of reactor 1 to 4 the fraction of comonomer drifts to a certain point then it flattens and

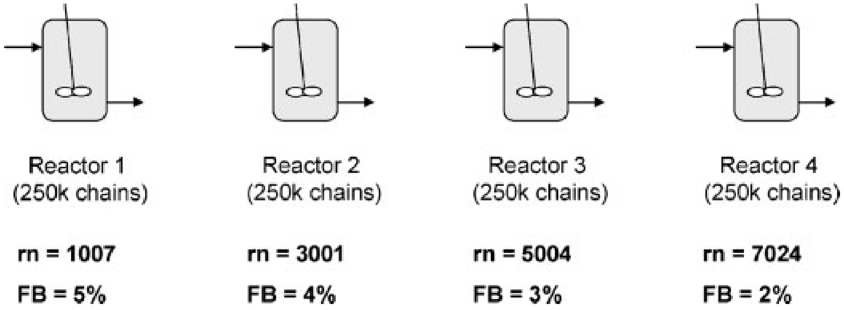


Figure 6.
Case studies considering 4 semi-batch reactors.

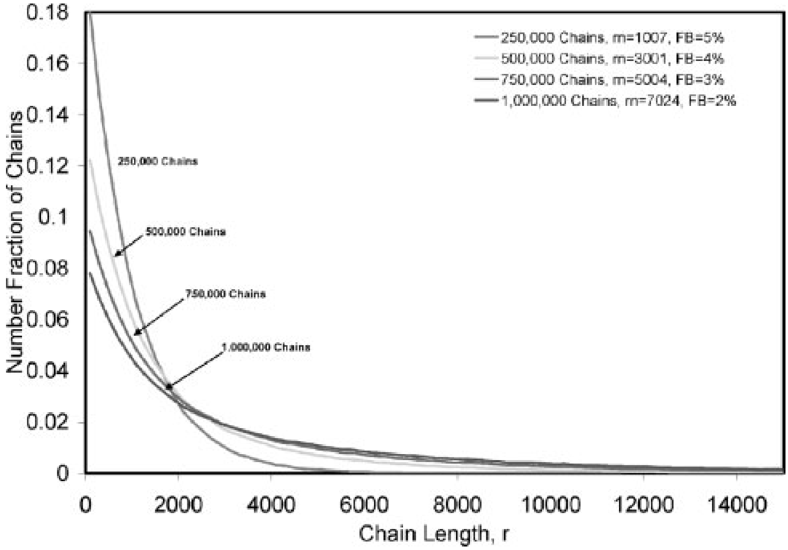


Figure 7.
Number fraction of chains from reactor 1 with 250,000 chain to reactor 4 with 1,000,000 chains as a function of chain length (varying r_n and F_B).

Table 2.
Kinetic Parameters Used in the Case Study (representing the products with $r_n = 1007$ to 7024 for reactor 1 to 4 respectively).

k_{pA} (L/mole · s)	k_{pB} (L/mole · s)	k_{tA} (L/mole · s)	k_{tB} (L/mole · s)	Pp	r_n	P_B
1210	1910	2.70	1.10	0.99901	1007	0.05
2160	2700	1.25	1.00	0.99967	3001	0.04
2200	2040	0.79	0.57	0.99980	5004	0.03
3900	2390	0.92	0.78	0.99986	7024	0.02

$[Pr^*] = 10 \times 10^{-6}$ (mole/L), $[A] = 3$ (mole/L), $[B] = 0.1$ (mole/L).

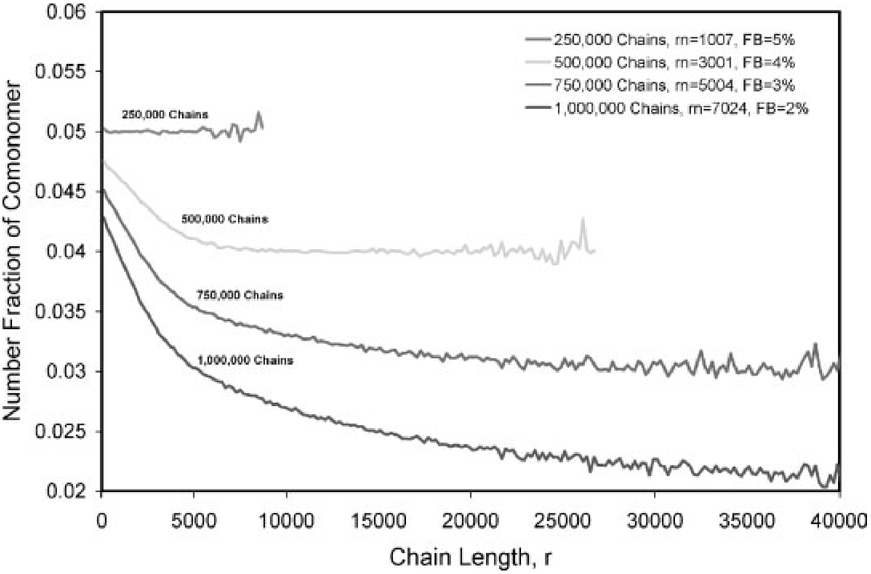


Figure 8.
Number fraction of comonomer from reactor 1 with 250,000 chains to reactor 4 with 1,000,000 chains as function of chain length (varying r_n, F_B).

becomes steady as a function of chain length.

Conclusions

The model was able to predict the number fraction of chains produced for a certain chain length. In case of copolymerization the fraction of monomer B incorporated in the polymer chain was not dependant on the size of the chain, in agreement with the polymerization mechanism. The information for model inputs can be obtained by polymer analysis or through the reaction kinetics. The probability of propagation is calculated from the reaction kinetics. From the probability of propagation we can find the number average chain length. The compositional drift was shown by mixing the products from different reactors. This model can be useful to explain non-homogeneous behaviour in real systems, like compositional drifting or heterogeneous temperature or concentration distribution. The model is currently being extended to provide the detailed triad distribution as a function of chain length.

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