Application of the Monte Carlo Simulation Method to the Investigation of Peculiar Free-Radical Copolymerization Reactions: Systems with Both Reactivity Ratios Greater than Unity ($r_A > 1$ and $r_B > 1$)

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ABSTRACT: With a Monte Carlo simulation method, copolymer properties have been thoroughly studied, and the influence of the reactivity ratios and feed composition has been taken into consideration. Instantaneous alterations of the copolymer composition and copolymer heterogeneity, which is also called a randomness parameter, have been examined with data obtained from the simulation at each stage of the copolymerization reaction. The results prove the azeotropic behavior of copolymerization reactions in which both reactivity ratios are greater than unity, although some special reactivity ratio combinations ignore the azeotropic behavior. The copolymer composition reaches an azeotrope point at the end of the copolymerization reaction when the copolymerization is an azeotropic reaction. In addition, the randomness parameter takes its maximum value at the azeotrope point when reactivity ratio r_A is equal to reactivity ratio r_B. Finally, increasing the reactivity ratios causes no change in the trend of copolymer composition/feed composition curves when r_A is equal to r_B. However, the curves produced with larger r_A and r_B values show more fluctuations. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 4138–4147, 2007

Key words: Monte Carlo simulation; radical polymerization; copolymerization

INTRODUCTION

The application of stochastic methods to first-order Markovian processes such as (co)polymerizations is not an innovative technique in the case of polymer behavior modeling during the course of a reaction. A review of the related literature reveals the importance of probability theories, particularly Monte Carlo methods, in the investigation of polymer properties, regardless of the limitations of other methods.[1–4] Monte Carlo methods have been proved to be powerful tools for modeling the compositional heterogeneities, molecular weight distribution, effects of depropagation reactions, crystallization, and rationalization of processes such as adsorption and premature phase separation.[5–9] However, they can simply be used in the case of very complex reactions, such as multicomponent copolymerization reactions, for which conventional methods require a high level of sophistication and include many simplifying assumptions.[10–12]

The copolymerization of two or more monomers is considered a helpful means of changing the balance of properties of commercial polymers. Unlike the polymerization of a single monomer, which results in a limited number of various products, copolymerization facilitates the production of tailor-made polymers with particularly desired properties. Therefore, an almost unlimited number of products with different properties can be synthesized by the alteration of the nature and relative amounts of the monomers. The arrangement of the monomers along the copolymer chains is the cause of the different distributions of the properties in the final product; the optimal application of the final product makes it necessary to have good knowledge of these distributions. Although experimental methods are suitable tools sometimes, they are useless for very complicated systems and lack profitable results in many cases. On the other hand, because of the stochastic nature of (co)polymerization reactions, Monte Carlo methods can easily take advantage of the aforementioned distributions, leading to detailed analyses of polymer properties without being restricted to oversimplifying assumptions.[13–15]

Different authors have applied Monte Carlo methods to copolymerization reactions during the last decades. Here we deal with systems of copolymerization reactions in which both reactivity ratios are greater than unity. Although practically this peculiar case is not widespread in free-radical copolymerizations, it could be an effective approach to better understanding copolymerization systems.
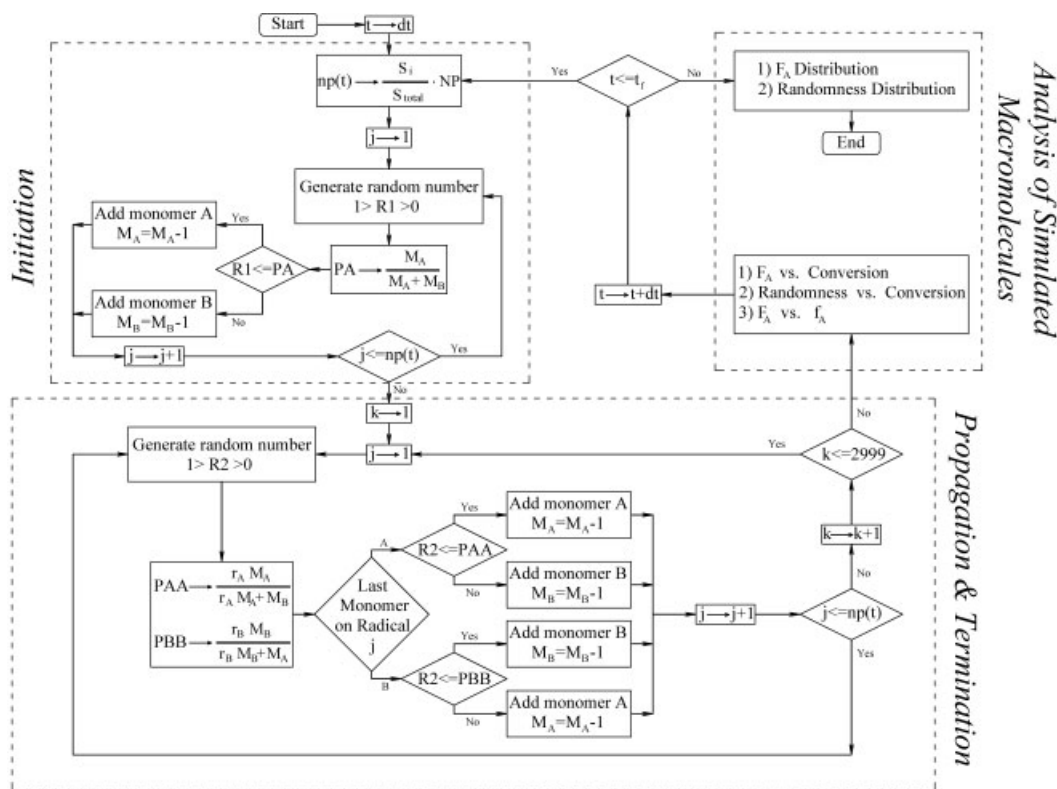
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Figure 1 Monte Carlo simulation algorithm for the free-radical copolymerization reaction.

MODEL AND SIMULATION

Theory of the simulation of free-radical copolymerization

In this work, a comprehensive study has been carried out to consider the simulation of peculiar copolymerization reactions in which both reactivity ratios are greater than unity. Simultaneously, the same simulation procedure has been applied to systems with both reactivity ratios less than unity for comparison. The results show similar azeotropic behaviors in the two systems. However, to avoid lengthening this work, only the results are illustrated in appendix A, and no discussion is presented.

Some assumptions have been applied to reduce the complexity of the proposed model and focus on the parameters by which the microstructure of copolymers is mostly determined. These assumptions can be summarized as follows:

1. The initiation of each copolymer chain is dependent only on the initial feed fraction of the monomers, and the effect of the monomer–initiator reactivity ratios is not considered:

$$P_A = \frac{M_A}{M_A + M_B} \tag{1}$$

where P_A is the initial feed fraction of the monomer A, M_A and M_B are the numbers of monomers A and B, respectively.

2. The propagation of macroradicals follows the concept of the first-order Markovian chain.
3. The quasi-steady-state assumption is applied in the simulation procedure.
4. The generated macromolecules are limited to 3000 monomers to neglect the termination reactions.
5. Elementary reactions are not diffusion-controlled, so the reaction rate constants of the propagation are assumed to remain unchanged in the course of the simulation.

The simulation procedure has been designed to take account of the initiation and propagation reactions simultaneously; in this way, it can mimic the real copolymerization events. Figure 1 shows the simulation flow chart.

As for the initiation reaction, one may discover different initiating procedures proposed by authors for the simulation of copolymerization reactions.[11,14,15] However, according to the principles of radically initiated reactions in macromolecular syntheses, it seems that none of these methods is practical. Hence, the method presented here is designed to consider more actual events in the initiation phase. The initiating procedure in this study follows the concepts that guarantee the occurrence of exponential behavior for initiation dissociation.

The number of primary radicals that are born in each moment is correlated with the number of initiator molecules that decompose in that moment. On the

other hand, according to the Quasi steady-state approximation (QSSA) theory, there is no accumulation of radicals in the polymerization course. Hence, it seems that the number of generated radicals in each polymerization time interval is nearly proportional to the area under the initiator dissociation curve in that interval.

Therefore, as shown in Figure 2, the number of copolymer chains that must be simulated in a time interval between t_{i-1} and t_i [$np(t_i)$] is given by

$$np(t_i) = \frac{S_i}{S_{\text{total}}} N_P \qquad (2)$$

where N_P is the total number of copolymer chains that must be simulated, S_i is the area under the initiator decomposition curve between t_{i-1} and t_i, and S_{total} is the total area under the initiator decomposition curve from zero to the final copolymerization reaction time. It is well known that the following equation is normally used to describe the trend of the thermal decomposition of initiators in radically initiated polymerization systems:

$$[I] = [I]_0 \exp(-k_d t) \qquad (3)$$

where $[I]_0$ and $[I]$ are the initiator concentrations at time zero and time t, respectively, and k_d is the rate of the initiator dissociation reaction. Applying numerical integration, we can calculate the aforementioned parameter, $np(t_i)$, as follows:

$$np(t_i) = \frac{\int_0^{t_i} \exp(-k_d t)dt - \int_0^{t_{i-1}} \exp(k_d t)dt}{\int_0^{t_f} \exp(-k_d t)dt} \qquad (4)$$

Because the growth of macroradicals intrinsically happens at the same time, the simulation procedure also manages to perform the propagation of macroradicals simultaneously. Four elementary reactions are considered to describe the copolymerization propagation
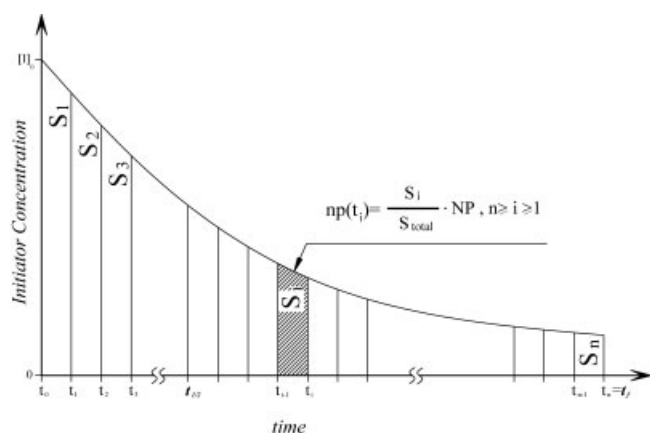
Figure 2 Simplified scheme of the selection criteria for the copolymer chains that must be generated in any time interval.
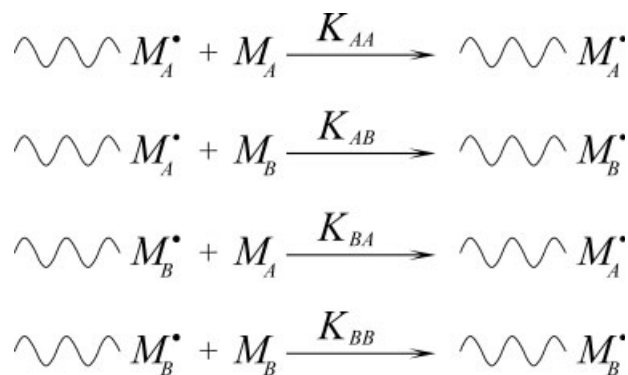
Figure 3 Schematic representation of the copolymerization propagation reaction associated with the reaction rate constants (K_{ij}).

reactions (see Fig. 3). To propagate a growing macroradical, a random number is generated and used to decide which monomer type will react. We define P_{AA} and P_{BB} as the probabilities of monomers of types A and B being incorporated into the growing macroradicals, respectively. These probabilities are related to the reactivity ratios and concentration of the monomers as follows:

$$P_{AA} = \frac{r_A M_A}{r_A M_A + M_B} \qquad (5)$$

$$P_{AB} = 1 - P_{AA} \qquad (6)$$

$$P_{BB} = \frac{r_B M_B}{r_B M_B + M_A} \qquad (7)$$

$$P_{BA} = 1 - P_{BB} \qquad (8)$$

In these equations, P_{ii} and P_{ij} are the conditional probabilities by which a chain ending in radical i adds monomers of types i and j, respectively. In this simulation, these probabilities are calculated before each event and compared with the magnitude of the generated random number. If the generated random number is less than or equal to P_{ii}, then a monomer of type i is added to the growing macroradical ending in i; otherwise, monomer j is selected to react with this growing macroradical. As already mentioned in the assumption section, a growing macroradical terminates as soon as its degree of polymerization reaches 3000.

One of the most significant features of any simulation procedure is perhaps its ability to analyze generated macromolecules. In other words, to analyze the microstructure of binary copolymer chains and especially to quantify the heterogeneity of copolymers, the simulation needs to be implemented with the appropriate procedures. According to Figure 1, the simulation program is implemented with procedures for the calculation of the instantaneous copolymer

composition (F_A) and randomness variations with the conversion as well as the variations of F_A with the instantaneous feed composition (f_A).

The following expression can theoretically be used to calculate F_A [eq. (9)].[16] This equation, also known as the copolymer composition equation, has been employed for a long time in the literature to determine the copolymer compositions in radical copolymerization systems. *A* is the monomer whose concentration or rather percentage in the copolymer chains is to be determined; this equation correlates the percentage of monomer *A* in the feed to its counterpart in the copolymer chains as follows:

$$F_A = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2f_A f_B + r_B f_B^2} \tag{9}$$

where f_A and f_B are the instantaneous molar fractions of monomers *A* and *B* in the copolymerization reactor, respectively.

Because the dyads, the smallest structural blocks, control the heterogeneity of chains in binary copolymers, counting the number of homodyads and heterodyads is another key task of the procedure.

To characterize the arrangement of monomers in a copolymer chain, various expressions have been reported.[14] It seems that the following equation is able to precisely describe the randomness of generated copolymer chains in this simulation:

$$f_{AB} = \frac{N_{AB}}{N_{AB} + N_{AA} + N_{BB}} \tag{10}$$

where N_{ii} and N_{ij} are the number of homodyads and heterodyads in the copolymer chain structure, respectively, and f_{AB} represents the randomness of copolymer chains. In fact, this expression yields the fraction of *AB* or *BA* dyads in copolymer chains. Particular values of f_{AB} can be interpreted as follows:

$f_{AB} = 0$: completely block copolymer.
$f_{AB} = 0.5$: completely random copolymer.
$f_{AB} = 1$: completely alternating copolymer.

Therefore, a copolymer chain with a randomness value between 0.5 and 1 defines an alternating random copolymer, whereas randomness values between 0 and 0.5 identify a block random copolymer.

It is notable that a copolymer consisting of *A* and *B* monomer units can be characterized by the fractions f_{AA}, f_{AB}, and f_{BB} of *AA*, *AB* and *BA*, and *BB* bonds. A ternary plot is particularly useful here because the dependence of the three dyad-type contents, for example, on the reaction condition can be shown. In such a case, a curve is obtained rather than a point. A schematic representation on a triangular graph is shown in Figure 4, in which point *M* represents a chain or chains with a molecular architecture described by $f_{AA} = 0.30, f_{AB} = 0.25$, and $f_{BB} = 0.45$.
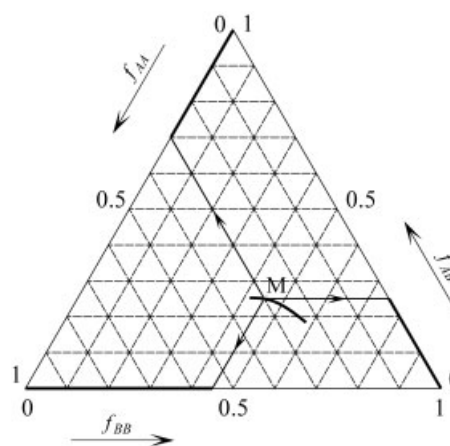

Figure 4 Description of the triad composition of a copolymer with a ternary graph.

Because of the complexity and partial overlapping of the results of disparate initial feed compositions (f_A^0), simple arrows are used to distinguish the results as clearly as possible. The direction and magnitude of these arrows indicate the direction and magnitude of the composition drift, respectively, where letters *A, B, C, D*, and *E* show the results for f_A^0, which is equal to 0.05, 0.3, 0.5, 0.7, and 0.95, respectively.

A suitable and optimized program according to the flow chart presented in Figure 1 was written in the language C++ and compiled under the SuSE Linux operating system (GCC 3.3.4). The runtime of the simulation on a 3.0-GHz (dual-core Intel processor) personal computer was approximately 170 min.

RESULTS AND DISCUSSION

Initiation

As 2,2'-azoisobutyronitrile (AIBN) and benzoyl peroxide are common thermal initiators in polymerization reactions, AIBN has been chosen to evaluate the efficiency of the proposed initiation model. The half-life and dissociation constant (k_d) are equal to 4.8 h and $4.01 \times 10^{-5} \, \text{s}^{-1}$, respectively, at 70°C.[17] Figure 5 shows the trend of this initiator dissociation for the proposed model. According to this figure, the total simulation time, that is, the polymerization reaction time, is assumed to be twice as long as the initiator half-life and is divided into 3.5×10^5 identical time intervals. When the number of copolymer chains is increased to more than 35 million, no significant change in our results is observed. Therefore, all simulations have been performed with 35 million copolymer chains.

Variation of the copolymer composition with the conversion

F_A, one of the important parameters for controlling copolymer properties, can be measured as a function of

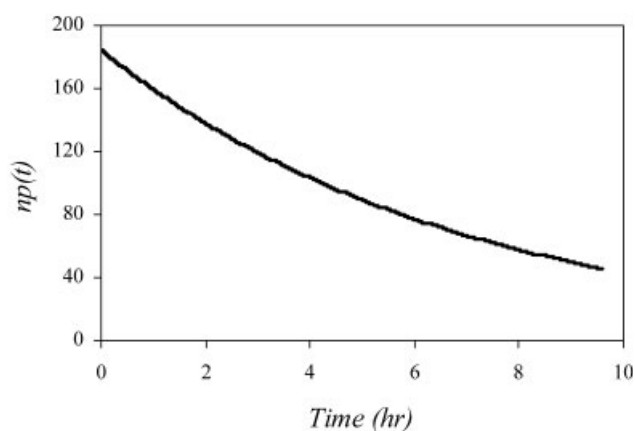

Figure 5 Number of generated primary radicals [$np(t)$] as a function of the simulation time.

the overall conversion percentage as the copolymerization reaction proceeds. With different values of f_A^0, the variation of F_A as a function of the reaction conversion is illustrated in Figure 6(a–l). To simplify the explanation of the graphs, they have been studied in groups of graphs with similar trends for the variation of F_A.

Figure 6(d,j–l) shows the variation of F_A for systems in which reactivity ratio r_A is equal to reactivity ratio r_B. As can be inferred from these figures, F_A shows the same behavior for different pairs of equal reactivity ratios, although the fluctuation of F_A curves increases as the reactivity ratios rise. Another interesting feature of these systems concerns the value of F_A at the end of the copolymerization reaction at which F_A approaches 0.5.

In Figure 6(l), F_A greatly fluctuates when the fractions of the monomer and comonomer are comparable in the initial feed, that is, when f_A^0 is equal to 0.3, 0.5, or 0.7. In fact, the predominant effect of large values of r_A and r_B can be traded off by the high fractions of monomers B and A in the initial feed, respectively. In other words, large r_A values compensate for small f_A^0 values, and large f_A^0 values balance large r_B values. However, when f_A^0 is equal to 0.3, 0.5, or 0.7, any slight change in the feed composition, caused by monomer consumption during the copolymerization reaction, results in a sudden alteration in the copolymer composition.

Figure 6(a–c) depicts the variation of F_A with the reaction conversion when r_A is constant and equal to unity. As r_B increases, F_A decreases at the beginning of the copolymerization reaction, especially when monomer A is in excess in the reaction vessel. An increase in r_B also causes a steeper slope of the increase in F_A. This trend has been seen for other systems that have disparate reactivity ratios [see Fig. 6(g,h)]. However, in such cases, the ratio of r_B to r_A is the key factor controlling the slope of F_A–conversion curves. For

instance, the equal ratios of r_A to r_B in Figure 6(f,h) lead to almost identical F_A–conversion curves.

In accordance with Figure 6(a–l), in some copolymerization systems, the copolymer composition, regardless of f_A^0, increases continuously as the reaction proceeds, and it somewhat tends to reach unity at the later stages of the copolymerization reaction. On the other hand, there are other copolymerization systems [Fig. 6(e,g,i)] in which F_A, depending on f_A^0, can either increase or decrease during the copolymerization reaction. In other words, these systems show azeotropic behavior, and the value of F_A at the end of the copolymerization reaction matches the azeotrope point. Moreover, in such copolymerization reactions, the azeotrope point always stands at the value of 0.5 when r_A is equal to r_B. However, the value of the azeotrope point varies on the basis of the reactivity ratio combinations when the copolymerization system lacks equal reactivity ratios.

Variation of F_A with f_A

To investigate the azeotropic behavior of copolymerization systems and compute the magnitude and direction of drift in the copolymer composition, one can make use of F_A–f_A graphs showing the variation of F_A as a function of f_A. Although the analytical relation between F_A and f_A can be used to simply draw F_A–f_A curves, this equation [eq. (9)] is not normally able to show the magnitude and especially the direction of drift in F_A. Figure 7(a–l), created with Monte Carlo simulation results, depicts the variation of F_A with f_A along with the magnitude and direction of drift in F_A.

From Figure 7(a–l), it is obvious that the drift in F_A exists for all copolymerization systems, regardless of f_A^0 and the reactivity ratio pairs. Another remarkable characteristic is related to the azeotropic behavior of these copolymer systems. Depending on the r_B/r_A values, the azeotrope point can move toward either higher or lower f_A values. When r_B is equal to r_A ($r_B/r_A = 1$), the azeotrope point always stands at 0.5, and there is no drift in F_A at this point when f_A^0 is equal to 0.5. It is clear that in these azeotropic systems, the direction of drift in F_A is always toward the azeotrope point.

By focusing on Figure 7(a–c), we can infer that no azeotropic behavior is found for copolymerization systems in which r_A is equal to unity and r_B is greater than unity. In such systems, an increase in r_B causes F_A–f_A curves to diverge from the $F_A = f_A$ curve (main diagonal); in other words, increasing r_B raises the tendency for B monomers to react with the same type, and therefore the amount of monomer B in the copolymer chains increases; this results in smaller F_A values in a wider range of f_A and the conversion. This divergence of F_A–f_A curves can also be seen for other
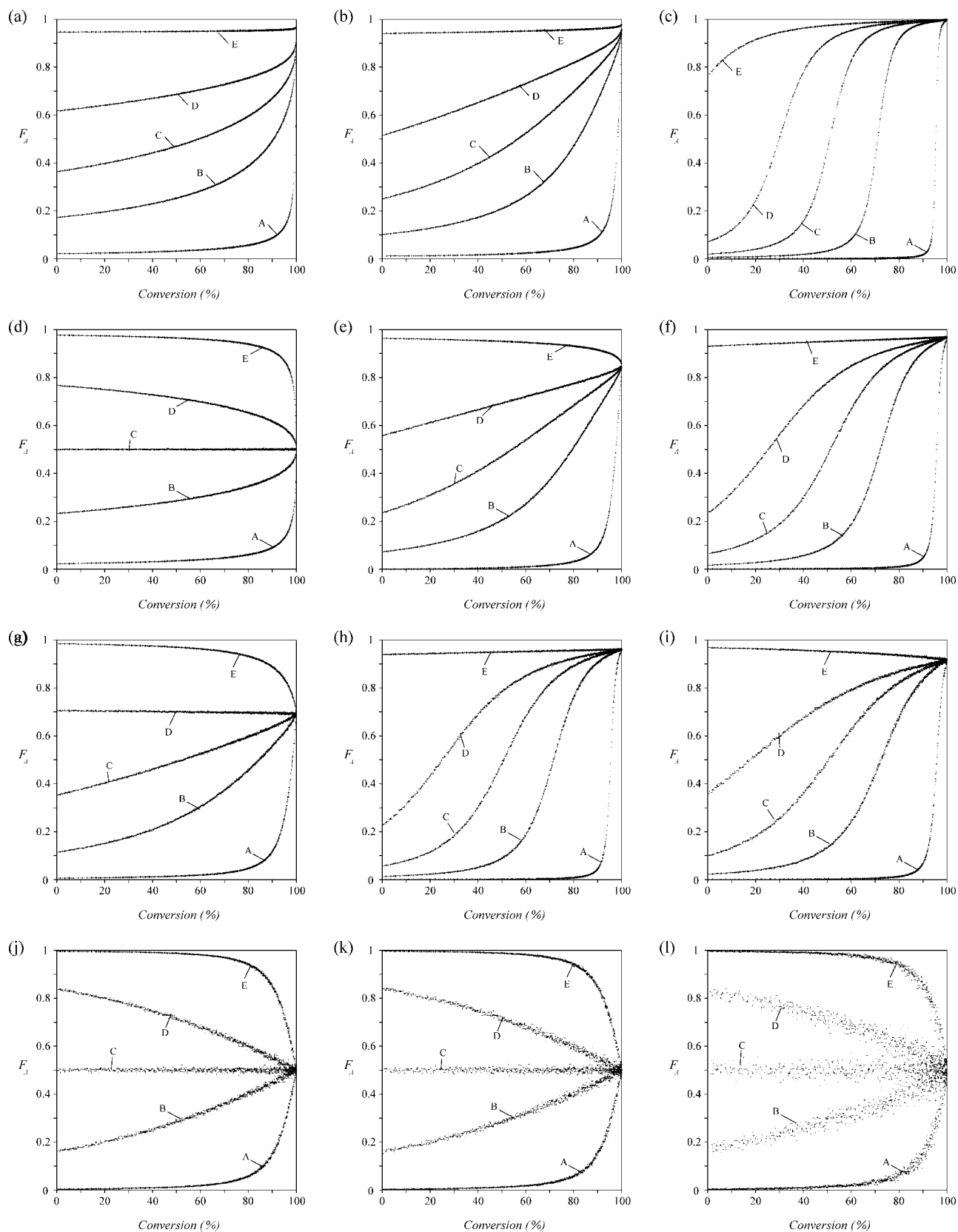
Figure 6 Changes in F_A for the simulated copolymer chains with the conversion for various values of f_A^0: (a) $r_A = 1$ and $r_B = 2.5$, (b) $r_A = 1$ and $r_B = 5$, (c) $r_A = 1$ and $r_B = 100$, (d) $r_A = 2.5$ and $r_B = 2.5$, (e) $r_A = 2.5$ and $r_B = 10$, (f) $r_A = 2.5$ and $r_B = 50$, (g) $r_A = 5$ and $r_B = 10$, (h) $r_A = 5$ and $r_B = 100$, (i) $r_A = 10$ and $r_B = 100$, (j) $r_A = 50$ and $r_B = 50$, (k) $r_A = 100$ and $r_B = 100$, and (l) $r_A = 1000$ and $r_B = 1000$.
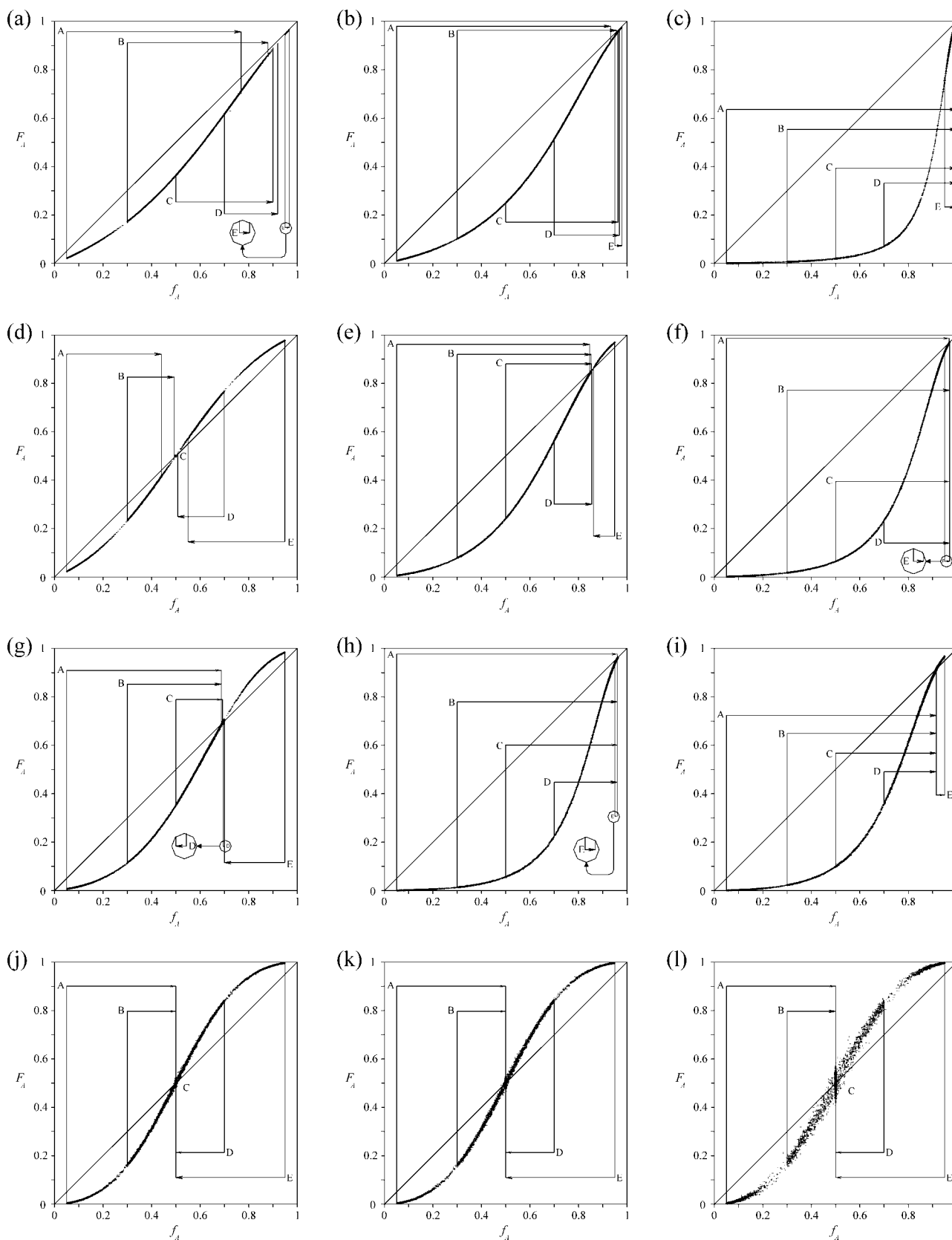
Figure 7 Changes in F_A for the simulated copolymer chains with f_A for different values of f_A^0: (a) $r_A = 1$ and $r_B = 2.5$, (b) $r_A = 1$ and $r_B = 5$, (c) $r_A = 1$ and $r_B = 100$, (d) $r_A = 2.5$ and $r_B = 2.5$, (e) $r_A = 2.5$ and $r_B = 10$, (f) $r_A = 2.5$ and $r_B = 50$, (g) $r_A = 5$ and $r_B = 10$, (h) $r_A = 5$ and $r_B = 100$, (i) $r_A = 10$ and $r_B = 100$, (j) $r_A = 50$ and $r_B = 50$, (k) $r_A = 100$ and $r_B = 100$, and (l) $r_A = 1000$ and $r_B = 1000$.

reactivity ratio combinations consisting of different r_A and r_B values.

From Figure 7(e–h), it can be inferred that (1) an increase in r_B/r_A causes the azeotrope point to shift to higher f_A values and finally vanish and (2) an increment in the ratio of r_B to r_A causes F_A–f_A curves to diverge from the $F_A = f_A$ curve, and therefore F_A is smaller. The production of copolymer chains consisting of a higher amount of monomer B is the origin of this behavior.

Variation of the randomness parameter on ternary graphs

The randomness parameter, or the fraction of hetero-dyads (AB or BA dyads) among all possible dyads (AA, BB, and AB or BA dyads), may be used to examine the heterogeneity of copolymer chains. The randomness parameter obtained here, f_{AB}, is drawn as a function of f_{AA} and f_{BB} on a ternary graph. The use of the ternary graphs makes it possible to consider the variations of all three parameters, f_{AA}, f_{BB}, and f_{AB}, as well as their drift simultaneously.

According to Figure 8(a–l), similarly to F_A, parameters f_{AA}, f_{BB}, and f_{AB} drift for all initial compositions, regardless of the reactivity ratio combinations; they also drift toward the azeotrope point. However, there is no drift in the randomness parameter when f_A^0 is equal to 0.5 and r_A is equal to r_B. In systems in which r_A is equal to r_B, increasing the reactivity ratios leads to smaller f_{AB} values and finally causes f_{AB} to approach zero. In other words, the macromolecules produced here are mainly separate A and B homopolymers. This can be found in other cases in a slighter way [see Fig. 8(g,h)].

With respect to the systems in which r_A is equal to unity [Fig. 8(a–c)], an increase in r_B results in smaller f_{AB} values. Indeed, increasing r_B, while r_A is constant and equal to unity, causes B monomers to have more chance to react with each other. Therefore, the macromolecular chains produced here mostly consist of B blocks (high f_{BB} values), and this makes f_{AB} and f_{AA} decrease.

Finally, Figure 8(c,h,i,k) shows that small values of f_A^0, large values of f_A^0, or large values of r_A make f_{AB} decrease. Small values of f_A^0 result in large f_{BB} values, whereas large values of f_A^0 and r_A lead to large f_{AA} values. Therefore, increasing either f_{BB} or f_{AA} brings about smaller f_{AB} values.

Taking the heterogeneity of copolymer chains and its effect on the final properties of copolymers, we find that the monitoring of the variation of the critical conversion, at which the produced macromolecules inherit their maximum alterations, is of great importance.

It seems that in addition to the Monte Carlo approach, an analytical expression can be derived to calculate the critical conversion. We have assigned a system consisting of A and B monomers in which r_A and r_B and M_A and

M_B are the reactivity ratios and numbers of monomers A and B, respectively. It is well known that the microstructure of copolymer chains is controlled and determined by reaction probabilities P_{AA} and P_{BB}. According to the definition of reaction probabilities, increasing P_{AB} or P_{BA} causes an increase in the alternative nature of the copolymer chains. Therefore, the maximum allowable alternation will be obtained when both P_{AB} and P_{BA} increase simultaneously, that is, when the product of P_{AB} and P_{BA} becomes maximum. As the sum of P_{AB} and P_{BA} is constant, varying from 0 to 2, the maximum of their multiplications is gained when the following condition is established:

$$P_{BA} = P_{AB} \tag{11}$$

By substituting the proper expressions for P_{AB} and P_{BA}, we can obtain the following expression to predict the critical conversion:

$$1 - \frac{r_B M_B}{r_B M_B + M_A} = 1 - \frac{r_A M_A}{r_A M_A + M_B} \tag{12}$$

$$\frac{M_B}{M_A} = \sqrt{\frac{r_A}{r_B}} \tag{13}$$

By rearranging this equation, we can obtain the following:

$$f_A^{\text{Critical}} = \frac{1}{1 + \sqrt{\frac{r_A}{r_B}}} \tag{14}$$

where f_A^{Critical} is the critical feed fraction at which the produced copolymer chains inherit their maximum alterations. Substituting f_A^{Critical} into Skeist's equation, we can obtain the critical conversion at which f_{AB} takes its maximum value as follows:[17]

$$p_{\text{Critical}} = 1 - \left(\frac{f_A^{\text{Critical}}}{f_A^0}\right)^\alpha \left(\frac{1 - f_A^{\text{Critical}}}{1 - f_A^0}\right)^\beta$$
$$\times \left(\frac{f_A^0 - \delta}{f_A^{\text{Critical}} - \delta}\right)^\gamma \tag{15}$$

where

$$\alpha = \frac{r_B}{1 - r_B}$$

$$\beta = \frac{r_A}{1 - r_A}$$

$$\gamma = \frac{(1 - r_A r_B)}{(1 - r_A)(1 - r_B)}$$

$$\delta = \frac{1 - r_B}{2 - r_A - r_B}$$

Figure 9 depicts the variation of the critical conversion with f_A^0 for different r_B values when r_A is equal to 2.5. According to this figure, an increase in f_A^0 leads to a continuous decrease in the value of the critical
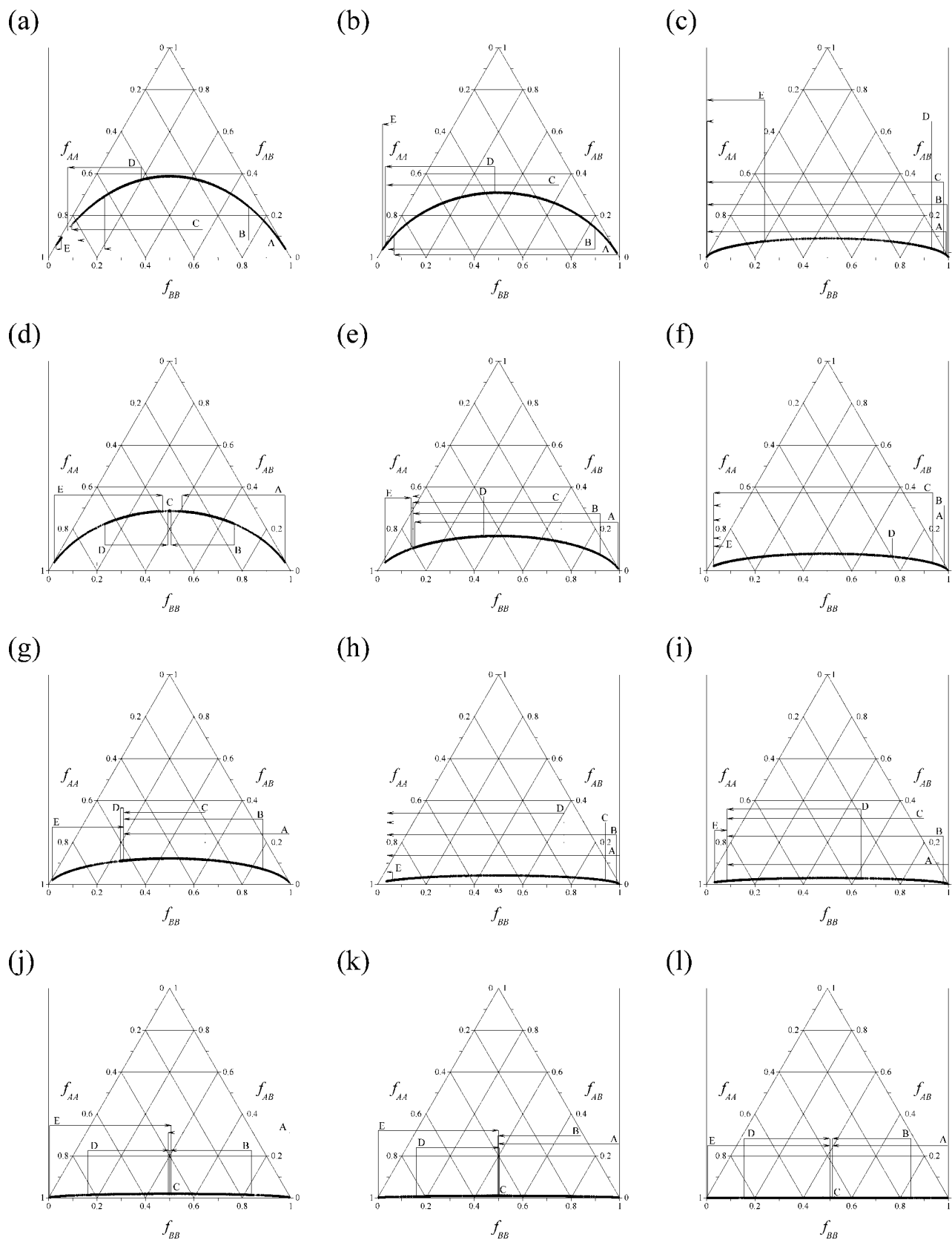
Figure 8   Changes in the sequence distribution for the simulated copolymer chains with the conversion for various values of f_A^0 on a ternary graph: (a) $r_A = 1$ and $r_B = 2.5$, (b) $r_A = 1$ and $r_B = 5$, (c) $r_A = 1$ and $r_B = 100$, (d) $r_A = 2.5$ and $r_B = 2.5$, (e) $r_A = 2.5$ and $r_B = 10$, (f) $r_A = 2.5$ and $r_B = 50$, (g) $r_A = 5$ and $r_B = 10$, (h) $r_A = 5$ and $r_B = 100$, (i) $r_A = 10$ and $r_B = 100$, (j) $r_A = 50$ and $r_B = 50$, (k) $r_A = 100$ and $r_B = 100$, and (l) $r_A = 1000$ and $r_B = 1000$.
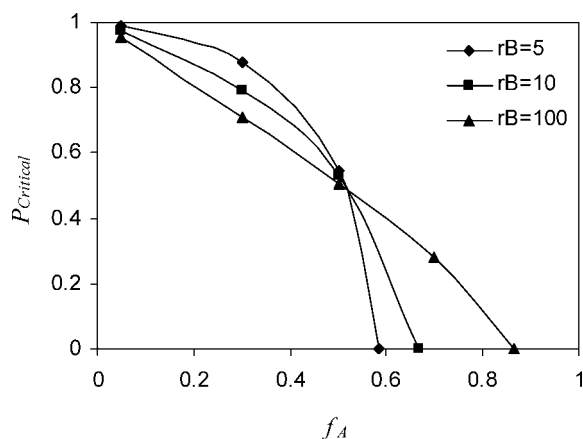
Figure 9 Variation of the critical conversion (P_{critical}) with f_A^0 for different r_B values with $r_A = 2.5$.

conversion. Furthermore, f_A^0 at which the critical conversion becomes zero is the critical feed composition for the corresponding reactivity ratio pair. In addition, increasing r_B causes the critical feed composition to rise to higher values. Indeed, increasing r_B leads copolymer chains to be made of more *B* blocks. Therefore, there is a necessity for more *A* monomers to limit the formation of *B* blocks.

CONCLUSIONS

With a Monte Carlo method, a comprehensive study has been carried out to cover different aspects of an uncommon copolymerization case thoroughly. In this study, the effects of the reactivity ratios ($r_A > 1$ and $r_B > 1$) and f_A^0 on the copolymer composition and heterogeneity have been investigated. According to the data obtained from the simulation, similarly to systems in which both reactivity ratios are less than unity, here the azeotropic behavior is the most outstanding observation. For equal

reactivity ratios, however, there is no drift in the copolymer composition or randomness parameter when f_A^0 is equal to 0.5, and the azeotrope point stands at 0.5. Moreover, F_A tends to approach the value of the azeotrope point at the end of the copolymerization reaction. Finally, mutually increasing the reactivity ratios to very large values (ca. 1000) brings about some oscillations in F_A–conversion and F_A–f_A curves.

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