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Computer simulation of vinyl copolymerisation : I. Irreversible copolymerisation

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Abstract

A generalised scheme is given for obtaining copolymer composition and sequence distribution in irreversible copolymerisation by Monte Carlo simulation on digital computer. The scheme has no restriction on the number of monomers in the copolymerisation system and is thus applicable to binary, ternary or any higher multicomponent systems. Several models are used in the scheme, such as chain growth model based on conditional probability of monomer addition, diad and triad models based on unconditional probabilities, and modified diad and triad models involving both conditional and unconditional probabilities. It is concluded by comparison with analytical results that the chain growth model is the best among all the models considered.

Key words : Copolymerisation, chain growth model, diad, triad, binary, ternary, cumulative probability matrix, monomer matrix.

1. Introduction

The composition of vinyl polymers formed in simple two-component copolymerisation is described by the well-known Mayo-Lewis equation[1]. Similar equations have been derived for calculating terpolymer composition[2–5] and these have been further extended to multi-component copolymerisation of four or more monomers[6–8]. These equations afford calculation of copolymer composition, but do not yield any information about sequence distribution in the copolymer chain. Computer simulation of copolymerisation, on the other hand, enables one to see the simulated copolymer chain, thus providing both the composition and sequence distribution of the copolymer chain at a glance.

Price[9] was the first to demonstrate the value of computer simulation by the Monte Carlo approach for visualising the nature of a polymer chain. He, however, limited his chains to 101 units of length and as a consequence had considerable scatter in

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his results. Marconi *et al*[10] in simulating binary copolymerisation treated as many as 10^4 or more monomer units resulting in impressive precision of the Monte Carlo results. Saito and Matsumura[11] also used Monte Carlo simulation to determine sequence distributions. They simulated the chlorinated polyethylene chain by a single 'copolymerisation' type of process. O'Driscoll and coworkers[12-15] in a series of papers dealt with simulation of binary copolymerisation where the possibility of depropagation must be considered. A detailed account of the concepts of Markovian processes as applied to polymer simulation in the description of copolymer composition and the characterisation of polymer tacticity can be found in an excellent article by Price[16].

While the application of the probability concept in copolymer simulation is firmly established, the object of the present work is to present a generalised approach for computer simulation which could be applied to copolymerisation of two-, three- and any higher multi-component systems and to evaluate several stochastic models, namely, a direct chain growth model and diad, triad, or higher models involving probability sequences of two, three or more number of units in the chain. In the present work, all propagation steps of copolymerisation have been assumed to be irreversible. The approach will be extended in a subsequent paper to computer simulation of copolymerisation with reversibility.

2. Copolymerisation as a stochastic process

2.1. *Chain growth model*

The copolymer composition as also sequence distribution in irreversible binary copolymerisation is determined by four irreversible propagation reactions which can be represented by

$$\begin{aligned}
&\sim\!\sim A^* + A \xrightarrow{k_1} \sim\!\sim AA^* \\
&\sim\!\sim A^* + B \xrightarrow{k_2} \sim\!\sim AB^* \\
&\sim\!\sim B^* + A \xrightarrow{k_3} \sim\!\sim BA^* \\
&\sim\!\sim B^* + B \xrightarrow{k_4} \sim\!\sim BB^*.
\end{aligned} \tag{1}$$

where k_1, k_2, k_3 and k_4 are the rate constants of the propagation steps. The steady-state kinetic solution of this scheme leads to the well-known Mayo-Lewis equation for copolymer composition. The conditional probability, p_{ab}, of a chain ending in a monomer A adding on a monomer B can be expressed in the kinetic terms as

$$p_{ab} = \frac{k_2[B]}{k_2[B] + k_1[A]} = \frac{1}{1 + r_1[A]/[B]} \tag{2}$$

where $r_1 = k_1/k_2$

Similarly

$$p_{ba} = \frac{1}{1 + r_2[B]/[A]} \tag{3}$$

where

$$r_2 = k_4/k_3.$$

The other conditional probabilities are

$$p_{aa} = \frac{1}{1 + [B]/r_1[A]} \tag{4}$$

and

$$p_{bb} = \frac{1}{1 + [A]/r_2[B]} \tag{5}$$

Since a chain ending in monomer A can only add either monomer A or B,

$$p_{aa} + p_{ab} = 1 \tag{6}$$

and similarly,

$$p_{ba} + p_{bb} = 1 \tag{7}$$

Knowing the values of the four probabilities p_{aa}, p_{ab}, p_{bb} and p_{ba}, as defined above, one can then carry out random experiments to construct a polymer chain by stepwise addition of monomer units to chain end using Monte Carlo method. We term this model the 'chain growth' or 'singlet' model. The sequence of monomer addition, if stored in computer memory, affords both the sequence distribution and the composition of the copolymer chain.

For adapting to computer programming, the four probabilities defined above are arranged in a matrix form as

$$\begin{pmatrix} p_{aa} & p_{ba} \\ p_{ab} & p_{bb} \end{pmatrix} \tag{8}$$

For determining the chain end addition by the Monte Carlo technique it is more convenient to use a cumulative probability matrix. Thus the cumulative probability matrix corresponding to the probability matrix (8) is

$$\begin{pmatrix} p_{aa} & p_{ba} \\ p_{aa} + p_{ab}, & p_{ba} + p_{bb} \end{pmatrix} \text{ or } \begin{pmatrix} p_{aa} & p_{ba} \\ 1{\cdot}0 & 1{\cdot}0 \end{pmatrix} \tag{9}$$

For a ternary copolymerisation system involving monomers A, B and C, the cumulative probability matrix becomes

$$\begin{pmatrix} p_{aa} & p_{ba} & p_{ca} \\ p_{aa} + p_{ab} & p_{ba} + p_{bb} & p_{ca} + p_{cb} \\ 1\cdot 0 & 1\cdot 0 & 1\cdot 0 \end{pmatrix} \tag{10}$$

The cumulative probability matrix for any higher order copolymerisation system (involving more than three monomers) can be similarly written.

Depending on the chain end unit, such as either A or B in binary copolymersation, the unit to be added next is determined. Thus, in a binary copolymerisation of monomers A and B, each chain growth step consists of generating a random number between 0 and 1 and comparing it with the elements of the appropriate column of the cumulative probability matrix (9) in order to determine the unit to be added next. For example, if the chain end is A, the random number is compared with the matrix elements (i, j) in column 1 and if the random number is found to be equal to or less than, say, the (2, 1) element but greater than the (1, 1) element, the monomer unit to be added is evidently B. Consequently, in the next growth step the random number is compared with the matrix elements in column 2 to determine the monomer unit to be added next. Thus, if the random number is found to be equal to or less than, say, the (1, 2) element, the monomer unit to be added is A. The number of the row of the particular element, 1 or 2, thus corresponds to the monomer unit, A or B, respectively. On a computing machine the chain addition is therefore conveniently performed with the help of the monomer matrix $\begin{pmatrix} 1 \\ 2 \end{pmatrix}$, with 1 and 2 representing, respectively, A or B.

Similar arguments apply for ternary or any other higher multi-component copolymerisation systems. For example, for ternary copolymerisation the corresponding monomer matrix is $\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$, with 1, 2 and 3 representing, respectively, monomers A, B and C.

A general computer program was written based on the above simulation approach and run on a DEC-1090 computer assuming different values of monomer reactivity ratios (r_1, r_2) and copolymer chain lengths.

Some simulation results of copolymer composition obtained for high and low values of r_1 and r_2 are compared with the values calculated from the Mayo-Lewis equation[1] in table I. The agreement is good and is seen to improve as a higher chain length is considered for simulation. However, the improvement obtained with chain length greater than 2000 is only marginal. The sequence of monomers in a simulated copolymer

Table I

Comparison of simulated and analytical copolymer compositions

Monomer reactivity ratio r_1	r_2	Feed composition [A]	[B]	Chain length n	Copolymer composition, F_1 Simulated	Analytical
0·01	0·01	0·4	0·6	1000	0·500	0·498
20·0	20·0	0·4	0·6	1000	0·360	0·316
				1500	0·333	0·316
				2000	0·310	0·316

chain for $r_1 = 0{\cdot}01$, $r_2 = 0{\cdot}01$ is observed to be almost completely alternate as would be expected in view of the low values of both r_1 and r_2. When both r_1 and r_2 are considerably greater than unity a block copolymer would be expected to result. The simulated copolymer chain obtained directly as the computer output for a feed of 40 mole per cent A and 60 mole per cent B, $r_1 = 20$, $r_2 = 20$ and a chain length of 1000 units is shown in fig. 1, clearly revealing the expected block nature of the copolymer.

2.2. *Diad and triad models based on unconditional sequence probability*

In a copolymer chain of monomer units A and B, there can be four *diad sequences* namely $-A{\cdot}A-$, $-A{\cdot}B-$, $-B{\cdot}A-$ and $-B{\cdot}B-$. The unconditional probability of finding a particular sequence, say $-A{\cdot}B-$, is then given by[12]

$$f_{ab} = \frac{p_{ab} \cdot p_{ba}}{(p_{ab} + p_{ba})} \tag{11}$$

where p_{ab} is the conditional diad probability of unit A being followed by B and p_{ba} that of B being followed by A, given by equations (1) and (3), respectively. The other three unconditional probabilities f_{aa}, f_{ba} and f_{bb} can be similarly defined and it can be easily shown that

$$f_{aa} + f_{ab} + f_{ba} + f_{bb} = 1 \tag{12}$$

In a copolymer chain consisting of A and B units there can obviously be eight *triad sequences*. The unconditional probabilities of these sequences, namely, f_{aaa}, f_{aab}, f_{aba}, f_{abb}, f_{baa}, f_{bab}, f_{bba} and f_{bbb} can be readily obtained by multiplying the proper unconditional diad probabilities. Thus, f_{aba} is given by

$$f_{aba} = f_{ab} \cdot p_{ba} \tag{13}$$

and so on,

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AAAAABBBBBBBBBBBBBBBBBAAAAAAAAAAAAAAAAAABBBBBBBBBB
BAABBBAAAAAAAAAAAAABBBBBBBBBBBBBBBBBBBBAAAAAABBAAA
AAAAAAAAAAAAAABBBBBBBBBBBBAAAAABBBBBBBBBBBBBBBBBBB
BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAABBBAABBBAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAABBBBBBBBBBBBBBBBBBBBBBBAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAABBBBBBBBBA
AAAAAAAAAAAAAABAAAAAAAAAAAAAAAAAAAAAAAAAAAAAABBBBB
BBBBBBBBBBBBBBBAAAAAAABBBBAAAAAAAAAAAAAAAAAAAAABBA
ABBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBAAAAAAAAAAABBB
BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
BBBAAAAAAAAAAAAAAAAAAAABBBBBBBBBBBBAAAAAAAABBBBBBB
BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
BBBBAAAAAAABBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
BBBBBBBBBBBBBAAAAAAAAABBBBBBBBBBBBBBBBBBBBBBBBBBBA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAABBBBBBBBB
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FIG. 1 Simulated copolymer chain : Feed composition $[A] = 0 \cdot 4$, $[B] = 0 \cdot 6$; monomer reactivity ratios $r_1 = 20 \cdot 0$, $r_2 = 20 \cdot 0$ and chain length $n = 1000$.

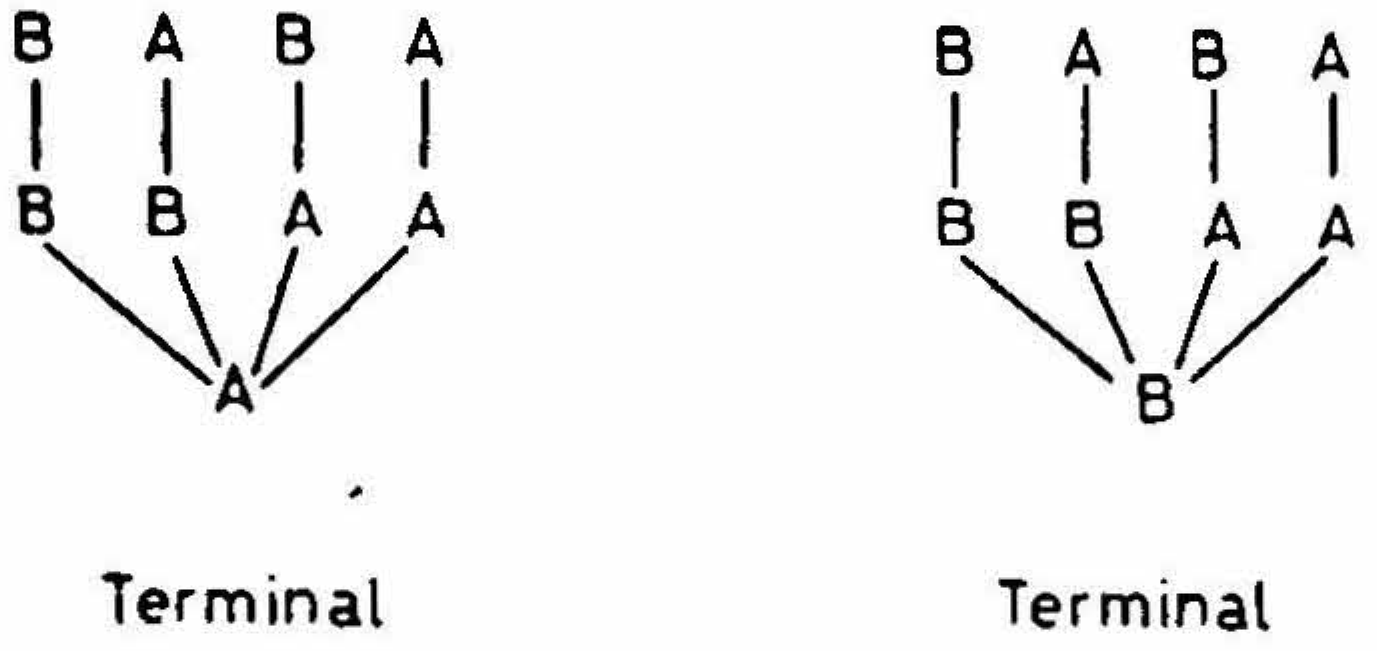
A copolymer chain is constructed by Monte Carlo technique using either diad unconditional probabilities or triad unconditional probabilities. Tetrad and higher models can similarly be developed.

A number of simulation experiments were conducted to obtain copolymer chain sequence distribution and copolymer compositions for different feed compositions and monomer reactivity ratios r_1 and r_2 using both diad and triad models. In all cases, while the copolymer composition was found to be in excellent agreement with the value calculated from the copolymer composition equation, the sequence distribution however, was at variance with what was predicted by the chain growth model and what would be expected from the theory of copolymerisation. Thus, a copolymer chain sequence obtained for $r_1 = 0 \cdot 01$ and $r_2 = 0 \cdot 01$ was considerably less alternate in character and that obtained for $r_1 = 20 \cdot 0$ and $r_2 = 20 \cdot 0$ showed much shorter blocks of each monomer than in the chain growth model.

The anomaly in sequence distribution produced in the above diad and triad models can be attributed to the fact that while the sequence in each diad or triad block is based on the probability principle described above, the linking of the consecutive diads or triads does not, however, obey any probability criterion. Thus, for example, if in applying the diad model, *AB* and *BA* are obtained as two consecutive diads by the Monte Carlo method, the *BB* pair in the resulting chain segment *ABBA* would exist without obeying any predetermined probability criterion. This results in anomalous sequence distribution as actually observed. Similar arguments also hold good for triad and any other higher modes.

2.3. *Modified diad and triad models*

Since the sequence anomaly in the aforesaid diad and triad models stems from the linking of diad or triad segments without obeying any predetermined probability criteron, the above models have been modified so that at any stage the chain end unit is taken into consideration in determining the subsequent diad or triad segment. Thus in the modified diad model for binary copolymerisation of *A* and *B* monomers, one has to consider the following two conditional tree structures depending on the terminal unit being either *A* or *B*



Thus for terminal *A* there are four conditional probabilities for diad addition namely. p_{aaa}, p_{aba}, p_{aab} and p_{abb}, each given by a product of conditional probabilities of appropriate diad sequences. Thus, $p_{aba} = p_{ab} \cdot p_{ba}$ and so on.

The corresponding cumulative probability matrix for Monte Carlo simulation of copolymer chain can then be written as

$$\begin{array}{c}\begin{pmatrix} p_{aaa} & p_{baa} \\ p_{aaa} + p_{aab} & p_{baa} + p_{bab} \\ p_{aaa} + p_{aab} + p_{aba} & p_{baa} + p_{bab} + p_{bba} \end{pmatrix} \\ 1 \qquad\qquad\qquad 1 \end{array} \tag{14}$$

and the corresponding monomer matrix as

$$\begin{pmatrix} 11 \\ 12 \\ 21 \\ 22 \end{pmatrix} \tag{15}$$

With 1 and 2 representing, respectively, *A* and *B* monomer units. The cumulative probability matrix and the corresponding monomer matrix can be similarly written for ternary or any other higher copolymerisation systems.

For the modified triad model, one can similarly write the conditional tree structures for terminal units (cf. 13), the cumulative probability matrix (cf. 14) and the corresponding monomer matrix (cf. 15).

Computer programs were written for the modified diad and triad models based on the above schemes and applicable in general to binary, ternary or any higher copolymerisation systems. The programs were run on a DEC 1090 computer using various combinations of monomer reactivity ratios and feed compositions. The modified models resulted in significant improvement in simulation performance over the original diad and triad models. Thus while the simulated copolymer compositions were in excellent agreement with the theoretical compositions (to within 99%), the simulated chain sequences were also in good accord with theoretical predictions.

3. Conclusions

Using Monte Carlo techniques and several probability models, namely, a singlet chain growth model, a diad model, a triad model, and modified diad and triad models, copolymerisation with irreversibility has been simulated on the computer in order to obtain both the copolymer composition and sequence distribution in the form of a symbolic representation of the copolymer chain. In each case, the procedure involves generating a random number between 0 and 1, and comparing it with the elements of a particular column (depending on the chain end unit) of an appropriate cumulative probability matrix to determine, with the help of the corresponding monomer matrix the monomer unit or sequence of monomer units to be added to the chain end. This procedure is repeated till the desired chain length is achieved. A generalised computer program has been developed which can be applied to any of the above models to simulate a copolymer chain. It is observed, however, that no additional saving in computer time is achieved by adopting more complex diad, triad or higher models instead of the simple chain growth (singlet) model, all of them requiring about 0·20 second. The chain growth model is also conceptually simpler as it represents a direct simulation of the growth of the copolymer chain.

Nomenclature

A : Monomer
B : Monomer
f : Unconditional probability
F : Mole fraction of monomer in copolymer
k : Rate constant of propagating step
p : Conditional probability
r : Reactivity ratio

Subscripts

a : Monomer A
b : Monomer B.

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