

Monte Carlo Modeling of Exchange Reactions in Polyesters. Dependence of Copolymer Composition on the Exchange Mechanism

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ABSTRACT: Two models were developed which describe the synthesis of an A/B copolyester via reactive blending of a mixture of homopolymer A and homopolymer B. The models take into account two different exchange mechanisms: the first one describes inner-group ester-ester exchange, and the second describes the process in which an active terminal group attacks an ester group. The two models were incorporated in a computer program, MOSES, which simulates the exchange reaction using the Monte Carlo approach. The models yield different values for the composition of the copolymer formed: the first one predicts that the copolymer composition is always identical to the sample composition, whereas the second one predicts that deviations can occur in the initial stages of the process. This result can be used to discriminate between the two exchange mechanisms. The predictions of the two models are compared with recent experimental mass spectral data concerning a poly(ethylene adipate-co-ethylene terephthalate) copolyester. Comparison with experiment favors the active end group mechanism. The dependence of copolymer composition on reaction conditions was investigated using the MOSES program. From the overall set of concentration values calculated, a simple analytical formula was found (eq 9) which allows computation of the copolymer composition from the knowledge of the reaction conditions.

Introduction

A general question when dealing with interchange reactions in polyesters is the mechanism by which the exchange takes place. There are two mechanisms by which the reaction may proceed:¹ by direct exchange between inner ester groups (Figure 1A,B) or by attack of active chain ends on ester groups (Figure 1C,D).

In 1942, Flory² presented his thermodynamic approach for the study of interchange reactions in polyesters. The theory predicts that the distribution of molecular weights changes with reaction time until it reaches the most probable distribution. Flory's result was derived under the assumption that exchange takes place by direct interaction of two inner ester groups.² Notwithstanding this, the result is valid also when the driving mechanism is the attack of active chain ends on ester groups. This implies that most polymer properties display a very weak dependence on the exchange mechanism. For instance, the curve which displays the evolution of the weight-average polymerization degree at different reaction times has the same shape, independently of the exchange mechanism, and therefore a qualitative inspection of a series of experimental data on ester-ester exchange is not sufficient to discriminate between the two reaction mechanisms. To overcome this shortcoming, it is necessary to search a quantity whose time behavior displays a sensible dependence on the reaction mechanism. This objective can be pursued by developing two distinct models of the exchange process (the first model describes the direct interaction of two inner ester groups, and the second one describes the attack of active chain ends on ester groups), together with a simulation method which allows monitoring of the time behavior of all the measurable quantities. By performing a series of simulations under different conditions, one can find the "diagnostic" quantity and give indications on how to design an experiment which yields unambiguous results about the reaction mechanism.

If one simulates exclusively exchange processes in homopolymers, it is very difficult to find a quantity³ which depends strongly on the exchange mechanism. Therefore,

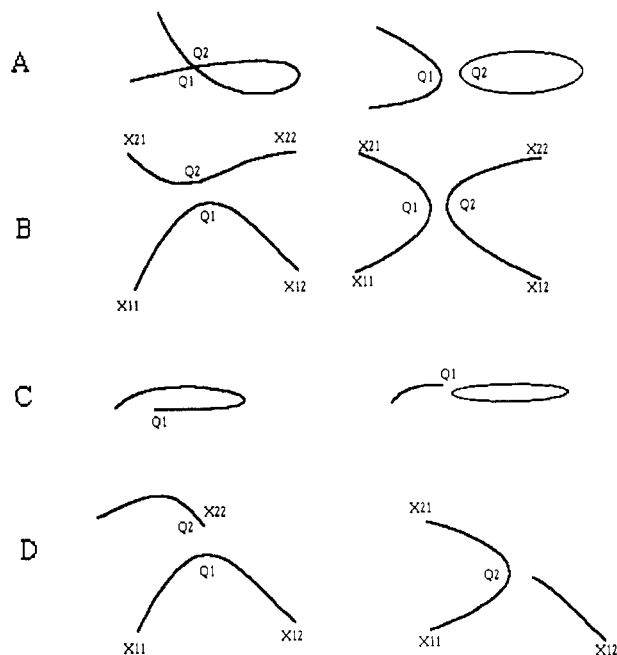


Figure 1. Schematic mechanism of the exchange process when the exchange involves inner groups and only one macromolecule (case A) or two macromolecules (case B) and when the exchange involves attack of ester groups by terminal groups and only one macromolecule (case C) or two macromolecules (case D).

it is necessary to broaden the range of the investigation to include more complex interchange reactions such as those occurring in mixtures of different homopolymers or in copolymers. These phenomena are better suited for searching a "diagnostic" quantity. In fact, these reactions give rise to a wide variety of phenomena which are absent in homopolymers. Among these, a most interesting one, in view of its practical applications, is the process in which homopolymer A and homopolymer B are heated together and react to yield an A/B copolymer.⁴⁻⁶ Since this reaction takes place in the molten state, this synthetic route is often referred to a melt mixing or as reactive blending. In this paper, it is shown that the composition of the

copolymer formed during melt mixing displays a strong dependence on the exchange mechanisms. In fact, when the driving mechanism is the attack of active chain ends on ester groups (Figure 1C,D), the copolymer composition (c_A) deviates from the composition of the sample (s_A), whereas when the exchange proceeds by direct exchange between inner ester groups (Figure 1A,B), no deviation occurs. Thus, the curve which reports the evolution of the copolymer composition at different reaction times can be used to discriminate between the two exchange mechanisms. This result was obtained by developing a computer program (MOSES: Monte Carlo simulation of ester exchange)⁷ which simulates the reactive blending process and monitors the changes in the sample properties as the reaction goes on. In the following section, the features of the Monte Carlo approach are discussed in some detail.

Monte Carlo Simulation Procedure

The numerical procedure used in this paper to simulate ester interchange reactions consists in generating an "artificial" sample containing 10^4 – 10^5 molecules and using a random-number generator to pick up at random from the artificial sample⁸ the macromolecules which will undergo exchange. In this way, the interchange process is reduced to a series of exchange events. The variable which controls the process is the number of exchange events per initial molecule^{1,8,9} (S). To simulate the initial stages of the reaction, S is set to a low value (for instance $S = 0.2$ or $S = 0.5$), whereas the final stages of the reaction correspond to higher S values (for instance $S = 3$ or $S = 4$). As the number of exchange events per initial molecule increases, the abundance of macromolecular species in the artificial sample varies. This variation reproduces only approximately the corresponding variation in the actual sample, due to statistical fluctuations. The underlying assumption of the Monte Carlo approach is that the size of the fluctuations decreases and that the approximation becomes better and better as the size of the artificial sample increases.

The MOSES computer program is structured in three sections: the vector-filling, the vector-updating, and the vector-screening sections. The vector-filling section has three subsections. The first subsection accepts the input data, namely, the molar fraction of A in the sample (s_A), the number of exchanges per initial molecule (S), the total number of units in the sample (L), $Y^0(A)$ and $Y^0(B)$ (the initial number-average degrees of polymerization), the polydispersity index (D), and the exchange mechanism option (INNER or TERMINAL). The second subsection fills the contents of the V_k vector to simulate the molecular sizes distribution at time $t = 0$. The third subsection fills the contents of the W_k vector to simulate the initial sequence distribution. The W_k vector is filled with two strings of the type AAAAAA and BBBB. The length of the two strings is equal to s_AL and $s_B L$. The vector-updating section performs different tasks, depending on the type of exchange reaction to be simulated. When the exchange mechanism option is INNER and the exchange process involves two molecules (see Figure 1B), the program chooses randomly two oligomers from the artificial sample and selects the points Q_1 and Q_2 at which the exchange takes place (Q_1 belongs to the first oligomer whereas Q_2 belongs to the second one). In a first step, the program computes the distances x_{11} , x_{12} , x_{21} , and x_{22} of Q_1 and Q_2 from the chain ends (see Figure 1B). In a second step, the program generates two new oligomers in which the monomeric units alternate in a different manner along the chain with respect to the old oligomers. The new

oligomers differ from the old ones also in length: the old lengths are $x_{11} + x_{21}$ and $x_{12} + x_{22}$ whereas the new lengths are $x_{11} + x_{12}$ and $x_{21} + x_{22}$. In a third step, the program replaces the old oligomers with the new ones. When the exchange involves a single molecule (see Figure 1A), the program chooses randomly an oligomer and selects the point Q_1 at which the exchange takes place. Then it selects another point, Q_2 , belonging to the same oligomer and it forms a cycle consisting of n_{cyc} monomeric units, where $n_{cyc} = (Q_2 - Q_1)$. The program chooses Q_2 so that the probability of forming an oligomer having n_{cyc} units, $G(n_{cyc})$, follows the simple power law predicted by the Jacobson–Stockmayer theory:¹⁰

$$G(n_{cyc}) = 4.242641(n_{cyc})^{-5/2} \quad (1)$$

When the exchange mechanism option is TERMINAL and the exchange process involves a single molecule (see Figure 1C), the program simulates exchange reactions involving end-group attack. The computer code differs from the previously described one in the way the point Q_1 (at which the exchange takes place) is selected. This point is no longer chosen randomly along the oligomer's backbone. Instead, it is set at the oligomer's head. When the exchange involves a single molecule, the dimensions (n_{cyc}) of the cyclic molecule formed depend exclusively on the point Q_2 . In this case, the process is kinetically controlled¹⁰ and $G(n_{cyc})$ (the probability of forming an oligomer having n_{cyc} units) is given by

$$G(n_{cyc}) = 2.828423(n_{cyc})^{-3/2} \quad (2)$$

The vector-screening section uses the contents of the vectors V_k and W_k to compute the number of times, $N_{A_mB_n}$, an oligomer identified by the formula A_mB_n appears in the simulated sample. The knowledge of $N_{A_mB_n}$ allows computation of the molar fraction of A in the copolymer (c_A), the molar fraction of homooligomers (e_{HOM}), the weight fraction of homopolymer A in the sample¹² (w_{HA}), the weight fraction of homopolymer B in the sample (w_{HB}), and the weight fraction of cooligomers (w_{CO}):

$$c_A = \left[\sum_m \sum_n m(1 - d_{n,0})(1 - d_{m,0})N_{A_mB_n} \right] / \left[\sum_m \sum_n (m + n)(1 - d_{n,0})(1 - d_{m,0})N_{A_mB_n} \right] \quad (3)$$

$$e_{HOM} = 1 - \left[\sum_m \sum_n (1 - d_{n,0})(1 - d_{m,0})N_{A_mB_n} \right] / \left[\sum_m \sum_n N_{A_mB_n} \right] \quad (4)$$

$$w_{HA} = \left[\sum_m mN_{A_mB_n} \right] / \left[\sum_m \sum_n (m + n)N_{A_mB_n} \right] \quad (5)$$

$$w_{HB} = \left[\sum_n nN_{A_mB_n} \right] / \left[\sum_m \sum_n (m + n)N_{A_mB_n} \right] \quad (6)$$

$$w_{CO} = \left[\sum_m \sum_n (m + n)(1 - d_{n,0})(1 - d_{m,0})N_{A_mB_n} \right] / \left[\sum_m \sum_n (m + n)N_{A_mB_n} \right] \quad (7)$$

where $d_{n,0} = 1$ when $n = 0$ and $d_{n,0} = 0$ otherwise.

In the following section it will be shown that, using the Monte Carlo simulation to investigate the reactive blending reaction, it is possible to determine how the exchange mechanism affects the rates at which A and B units are incorporated in the copolymer and how the reaction conditions influence the above rates.

Results and Discussion

The MOSES computer code was used to simulate the reactive blending process and to monitor the composition

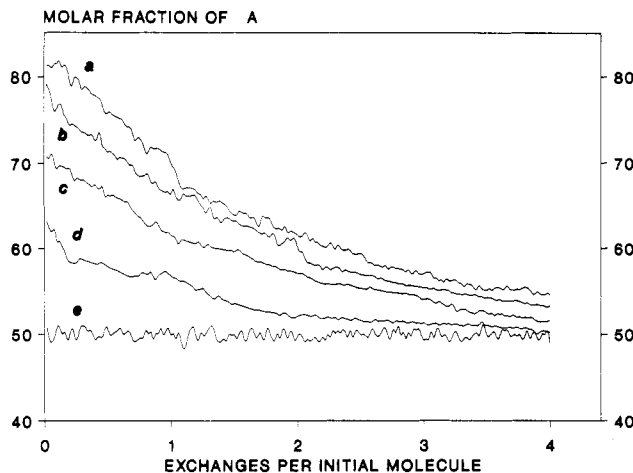


Figure 2. Computed copolymer composition versus number of exchanges per initial molecule. The calculation was performed using program MOSES with the following input: exchange mechanism option = TERMINAL, $s_A = 0.50$ and $Y^0(B) = 100$. The other input values were $Y^0(A) = 4$ (curve a), $Y^0(A) = 10$ (curve b), $Y^0(A) = 35$ (curve c), $Y^0(A) = 70$ (curve d), and $Y^0(A) = 100$ (curve e).

of the copolymer formed (c_A) under different reaction conditions. Among these conditions, the most important one is the molar fraction of A in the sample (s_A). However, c_A depends on the exchange mechanism and on other variables. The general expression for c_A is

$$c_A = f(\text{MEC}, s_A, Y^0(A), Y^0(B), S) \quad (8)$$

where f denotes generic dependence and where MEC denotes the exchange mechanism (INNER or TERMINAL). For the sake of simplicity, c_A in eq 8 was assumed to be independent of the polydispersity index (D). To proceed further, the general expression must be put in an explicit form. A number of Monte Carlo simulations have been performed to determine in an explicit manner the way c_A depends on the four reaction conditions and on the exchange mechanism. The approach used consists in using the MOSES program to create a tabulation of c_A values and then searching an empirical law which can describe the tabulated values.

In a first session, the program was launched with the following input values: exchange mechanism option = TERMINAL, $L = 10^7$, $D = 2.0$, $Y^0(A) = 4$, $Y^0(B) = 100$, and $s_A = 0.50$. Figure 2 (curve a) reports the variations in copolymer composition (c_A) as the number of exchanges per initial molecule (S) increases from 0 to 4. The copolymer composition deviates very markedly from the sample composition (s_A). At the initial stages of the process, c_A takes the value = 0.82 and then it decreases steadily. At later stages of the process, the difference between c_A and s_A becomes smaller and smaller and eventually vanishes. The other traces in Figure 2 (curves b–d) were obtained by running the program with all input values identical to those above (exchange mechanism option = TERMINAL, $L = 10^7$, $D = 2.0$, $Y^0(B) = 100$, and $s_A = 0.50$) except for the value of $Y^0(A)$ (the initial degree of polymerization of A). The latter quantity was progressively increased as follows: $Y^0(A) = 10$ in curve b, $Y^0(A) = 35$ in curve c, and $Y^0(A) = 70$ in curve d. The copolymer composition displays the same qualitative behavior as in Figure 2a. However, the initial difference between c_A and s_A becomes less marked as $Y^0(A)$ increases. Figure 2 (curve e) reports the computed copolymer composition when the initial degrees of polymerization of A and B coincide. In this case the copolymer composition is a constant, independent of the number of exchanges.

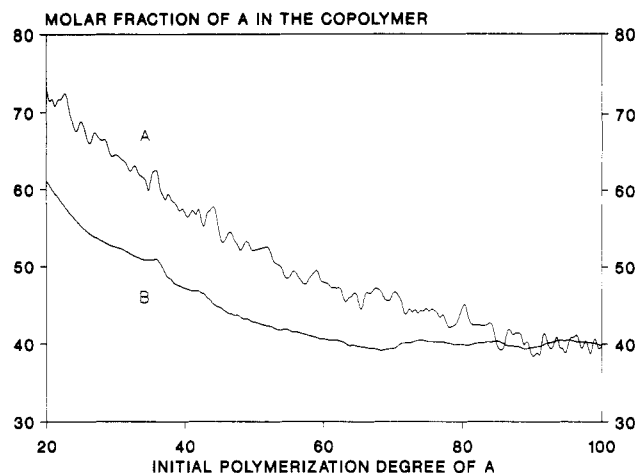


Figure 3. Computed copolymer composition versus $Y^0(A)$ (the initial polymerization degree of homopolymer A). The calculation was performed using program MOSES with the following input: exchange mechanism option = TERMINAL, $s_A = 0.40$ and $Y^0(B) = 100$. The other input values were $S = 0.1$ (curve A) and $S = 1.0$ (curve B).

In a second session, the program was launched with the following input values: exchange mechanism option = TERMINAL, $L = 10^7$, $D = 2.0$, $S = 0.1$, $Y^0(B) = 100$, and $s_A = 0.40$. The value $S = 0.1$ was selected to explore the behavior at the beginning of the reactive blending reaction. Figure 3 (curve A) reports the variations in copolymer composition (c_A) as the initial degree of polymerization of A increases from $Y^0(A) = 20$ to $Y^0(A) = 100$. When $Y^0(A)$ is significantly different from $Y^0(B)$, the concentration of A in the copolymer differs from the concentration of A in the sample. As $Y^0(A)$ approaches $Y^0(B)$, difference between c_A and s_A becomes vanishingly small. The value of S was then changed to $S = 1.3$ to simulate intermediate stages of the exchange reaction. The other input values were left unchanged. Curve B in Figure 3 reports computed c_A values versus $Y^0(A)$. Again, the largest deviations between c_A and sample composition are seen in the first part of the curve, when the difference between $Y^0(A)$ and $Y^0(B)$ is large.

Other Monte Carlo simulations were performed to investigate the variation of the copolymer composition with $Y^0(B)$ and with s_A (the exchange mechanism option was set to TERMINAL). Successively, the c_A values obtained in the various computer sessions were used to obtain an empirical formula for the c_A dependencies implicitly indicated in eq 8. Various formulas were tried. The formula which gave the best results was

$$c_A = s_A + a_1 \exp(-20a_2a_3S) \quad (9)$$

where a_1 , a_2 , and a_3 are given by

$$a_1 = 1 - s_A^2 a_2 / (1 + s_A) \quad (9a)$$

$$a_2 = \{[Y^0(A) - Y^0(B)]/[Y^0(A) + Y^0(B)]\}^2 \quad (9b)$$

$$a_3 = [(1 + s_A)/(2 - s_A)]^{1/2} \quad (9c)$$

The above equations describe how the composition (c_A) of the copolymer formed via the reactive blending process depends on the reaction conditions when the mechanism of exchange is the one depicted in Figure 1C,D (when terminal groups play a relevant role). As the number of scissions increases, the exponential term in eq 9 decreases (the exponent argument is always negative). Moreover, the difference between copolymer composition and sample composition becomes smaller and smaller as the difference between the initial polymerization degrees decreases.

A series of simulations were performed setting the exchange mechanism option to INNER. The Monte Carlo program was launched a number of times varying the four input values s_A , $Y^0(A)$, $Y^0(B)$, and S , and the resulting copolymer composition was recorded. The finding was that

$$c_A = s_A \quad (10)$$

The above formula states that the copolymer composition equals the sample composition, independent of the reaction conditions. Therefore, if one chooses the initial degrees of polymerization in such a way that $Y^0(A) \ll Y^0(B)$, the two models in eqs 9 and 10 give widely different predictions for the value of c_A . In fact, eq 9 implies that c_A is significantly different from s_A (when the average number of scissions per initial macromolecule is low), whereas eq 10 states that no difference exists between the two values.

This result allows the design of an experiment which can discriminate between the two reaction mechanisms. This diagnostic experiment must include an experimental setup which allows one to measure separately sample composition and copolymer composition. The latter measurement turns out to be difficult by NMR spectroscopy (which is the experimental technique most used to follow reactive blending kinetics^{1,5,11}), since the number of data points which measures exclusively copolymer properties is so small that the copolymer composition cannot be determined.^{1,5,11} In practice, only mass spectrometry (MS) has the required sensitivity.^{4,6,11} Recently, the reactive blending kinetics of a polyester sample containing poly(ethylene adipate) and poly(ethylene terephthalate) was followed by mass spectrometry¹¹ and the analysis of these data showed that the composition of the copolymer formed deviates significantly from the sample composition.¹¹ The model which is based on the exchange mechanism in Figure 1A,B (inner-group exchange) cannot explain this experimental result and it must be therefore discarded. On the contrary, the active terminal group model (Figure 1C,D) is in agreement with the experimental data.

Conclusions

In the foregoing sections it has been shown how Monte Carlo calculation can be used to simulate the exchange processes that occur in the reactive blending of two polymers. Although the application given here refers to ester exchange processes, the Monte Carlo formalism developed can be used to simulate numerous other type of exchange reactions (ester-amide, amide-amide, ester-carbonate, amide-carbonate, etc.).

A remarkable result of the Monte Carlo modeling is the finding of a strong dependence of the copolymer composition on the exchange mechanism and on the molecular weight of the two polymers participating in the exchange reaction. A family of copolymer composition curves was originated (Figures 2 and 3) from the Monte Carlo calculations, and it was therefore possible to derive from them eq 9, which predicts how the composition of the copolymer in the reactive blending process varies with the number of exchanges.

Equation 9 is a simple analytical expression that allows one to calculate immediately the concentration curve of

the copolymer formed in the exchange reaction occurring through the active chain end mechanism, without the need to perform any Monte Carlo simulation. It provides a facile, diagnostic test for the reaction mechanism and it has a considerable practical value, since it predicts also the values of molecular weights of the reactant polymers necessary to obtain a given molar ratio of the two components in the copolymer formed. Ester-ester is the only process where experimental data already exist.¹¹ It would be desirable that other type of exchange reactions be investigated in the future to check how eq 9 applies to these processes.

References and Notes

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- (12) Kotliar reported an analytical treatment for the exchange process.⁹ However, this author did not develop his approach to the stage of finding an expression relating c_A to the number of exchanges per initial molecule (S), which is crucial to the purpose of predicting sensible deviations of c_A from s_A . Therefore his treatment does not yield the desired information. Kotliar⁹ derived instead an expression for the weight fraction of homopolymer A in the sample, namely, $W_{HA} = 1/[(1 + S)^2]$. We computed values for W_{HA} (referred to as W_{HA}^{theo}) using his formula and compared them with values for W_{HA} (referred to as W_{HA}^{num}) computed using the MOSES program. The two sets of figures compare favorably, and the percent difference between W_{HA}^{theo} and W_{HA}^{num} was better than 8% for all S values.