

A Linkage Moment Approach to Modeling Condensation Polymerization with Multiple Monomers. I. Linear Polymers

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Received 23 February 2000; accepted 6 March 2000

ABSTRACT: In recent years, industrial interest in condensation copolymers with controlled microstructures has been increasing as these systems add an additional dimension to the design and manipulation of product properties without requiring completely new routes for monomer or polymer synthesis. The techniques used to control the compositional microstructure in condensation systems differ greatly from those in vinyl polymerization, as condensation polymers are continuously broken apart and reformed during the course of the polymerization. Blocky copolymers may be produced in a melt blending process only by limiting the contact time at reaction temperatures because the ultimate result of the polymerization and interchange reactions is complete randomization of the copolymer with a structure similar to that obtained in vinyl polymerization with all reactivity ratios equal to one. The design of processes yielding the desired product microstructure therefore requires a quantitative understanding of the effect of each reaction on the copolymer composition. As typical copolymer recipes include multiple monomers with different functionalities, in this paper a general copolycondensation model is presented that can accommodate an arbitrary number of monomers of differing reactivities. In this paper, only monofunctional and bifunctional monomers are considered; the extension to the case of gelating systems is left for a future paper. The use of this framework and the validity of the approach is demonstrated for an example situation in which a polyarylate is melt blended with PBT to produce a copolymer whose average sequence length may be controlled by limiting the extent of reaction. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 246–265, 2001

Key words: linkage moment approach; condensation polymerization; linear polymers

INTRODUCTION

Copolymerization has long been used to modify the properties of vinyl polymers; however, it has only been in the last decade that significant industrial interest has existed for the production of condensation copolymers comprised of multiple monomers or of blended polymer components. If the monomers for two different condensation

polymers are reacted in a one-pot synthesis, the result is a highly irregular microstructure reminiscent of that obtained in vinyl polymerization when all reactivity ratios are one. Condensation copolymers can also be produced by melt blending two homopolymers (which we can consider such polymers as PET and Nylon-6,6 to be as they possess complete structural regularity) at temperatures allowing interchange reactions to rearrange the monomer connectivity. At first, the product is a block copolymer, but as the interchange progresses, the block length shortens until finally the random microstructure characteristic of a one-pot synthesis is obtained (Fig. 1). Melt blending, therefore, allows both control over the

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Contract grant sponsors: Department of Energy; UWPREL; National Science Foundation.

Journal of Applied Polymer Science, Vol. 79, 246–265 (2001)
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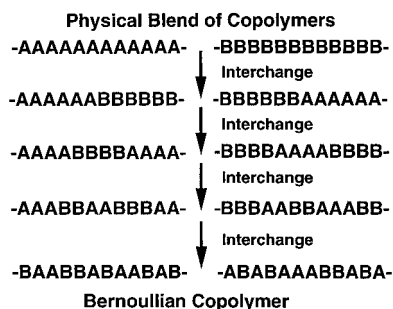


Figure 1 Control of compositional microstructure in copolymer blends through interchange reaction during mixing.

composition of the final product (by varying the feed ratio of each polymer component) and the average block length of each component. Such polymer blends have been found in many cases to possess superior mechanical properties than any single component; mixtures of a crystalline polymer (PBT or PET) with a high T_g amorphous polymer such as polycarbonate being common. Industrial interest in this technology is fueled by the fact that by reactively blending polymers with established synthesis routes and existing production facilities, little incremental investment is required to introduce new product grades.

The rational design of process conditions to yield a polymer with desired physical properties may be considered to consist of two stages. The first, and admittedly the most difficult, is deciding what microstructural properties (molecular weight, polydispersity, copolymer composition, etc.) are required to meet the property specifications. Once these microstructural parameters have been chosen, a process model with a quantitative description of the reaction kinetics is then required to determine the appropriate process operating conditions. This article focuses solely on the solution to this second question by developing a general kinetic framework for the effect of each of the major reactions in condensation polymerization upon copolymer composition. This model framework, constructed with an open architecture easily adapted to include system-specific thermodynamics, side reactions, and process operating characteristics, is well suited for use in computer-aided design.

The analysis of copolymer composition is well established for addition polymerization of vinyl monomers; however, the standard reactivity ratio approach cannot be extended to condensation reactions. In addition polymerization, the mean life-

time of a propagating chain is (except for living polymerizations) typically much shorter than the characteristic time of the reaction process, and once a growing chain is terminated, it does not usually react further. By contrast, in condensation polymerization no polymer is truly dead, because each chain continuously undergoes rearrangement through forward and reverse condensation and interchange reactions. No simple ratios of propagation rate constants can, therefore, describe the microstructure development in polycondensation processes, and an alternative approach is required.

As in the case of addition polymerization, a statistical method will be used to describe the microstructure, with the monomer connectivity encoded in the set of transition probabilities, $P(U_j|U_i)$, that in moving down a polymer chain a monomer of type i is followed by one of type j . In the familiar case of calculating the instantaneous copolymer composition in addition polymerization, these probabilities can be calculated from knowledge of the crosspropagation rate constants, $k_{p,ih}$, for addition of h -type monomer onto a growing chain with an i -type monomer at the propagation site and from the concentrations of each monomer, M_i .

$$P(U_j|U_i) = \frac{k_{p,ij}M_j}{\sum_h k_{p,ih}M_h} \quad (1)$$

This first-order Markovian model of chain growth assumes that the reactivity of a chain is dependent only upon the identity of the end group, and neglects penultimate effects. This condition is not always satisfied in vinyl polymerization; however, in condensation polymerization the sizes of the monomers are usually sufficiently large to insulate the reactive group on a chain end from the influence of the penultimate monomer unit. If all rate constants are equal, the transition probabilities are functions solely of the monomer concentrations, and the system is said to follow Bernoullian (zeroth-order Markov) statistics.

For modeling condensation polymerization, this statistical approach can be retained; however, the transition probabilities are no longer simply related as above to a set of rate constants, as the microstructure is affected by multiple parallel reactions. All chains in the system undergo continuous recombination through reverse condensation (linkage rupture by condensate) and interchange reaction (linkage rupture and recom-

bination by end groups or catalyst). Often the differences in monomer reactivities are slight; therefore, given sufficient time for rearrangement, a Bernoullian microstructure will result. Associated with this randomization of the microstructure is a relaxation of the chain length distribution to the Flory most probable distribution on a time scale $\approx DP_n$ times faster than the compositional randomization. This difference in time scales arises from the fact that only one breakage and reformation event is necessary per polymer chain for relaxation of the chain length distribution, whereas for complete randomization of the sequence length distribution all monomer units in each chain must undergo such an event. A general model for condensation copolymerization should therefore address the effect of each reaction upon both the sequence length and chain-length distributions.

In this work, such a model is developed by calculating the statistical properties of the sequence-length distribution in terms of the concentrations of linkages (e.g., amide or ester groups) labeled by the identities of the monomer units that they join. General rate expressions are then developed for the effect of each major condensation reaction upon these linkage concentrations. These governing equations can be augmented with equations describing the side reactions that are specific to each system (e.g., production of DEG in PET manufacture) or that describe the process operation (batch vs. continuous reactors). In this article, only linear polymers comprised of an arbitrary number of mono- and bifunctional monomers are considered; the extension to include multifunctional monomers and gelation phenomena is postponed for a later article. While statistical models of copolymer composition in condensation systems have been proposed previously,¹⁻¹² these have either been restricted to certain combinations of a limited number of monomers with specified functionality or have only used Bernoullian statistics with perhaps separate conversions for each end group type. The advantage of the current approach lies in the generality associated with an open framework for modeling systems with an arbitrary number of reactions and monomers.

The use of this general reaction framework is demonstrated in this article for an example case of a copolymer produced by holding two preformed polymers at reaction temperatures allowing interchange to partially randomize the sequence length distribution (Fig. 1). Such pro-

cesses have been successful in enhancing the properties of blends of polyesters, polycarbonates, and polyarylates.¹³⁻²¹ In most of these systems, the component polymers are initially immiscible, and mixing phenomena are also important in determining the rate of randomization. In this article, the general kinetic model presented is validated for a system of PBT and an amorphous polyarylate where no further description of the thermodynamic phase behavior of the multicomponent mixture is required.

STATISTICAL MODEL FOR THE CALCULATION OF THE SEQUENCE LENGTH DISTRIBUTION

The first step in constructing a general model is choosing a set of state variables that characterizes the compositional structure of the copolymer. As stated before, first-order Markov statistics provide an adequate description of the structure in condensation polymers; therefore, all one needs are expressions that relate the species concentrations to the necessary transition probabilities. In this section, these probabilities are defined for the simple case of linear polymerization where all monomers have two or fewer functional groups. In this situation, each polymer chain has only two ends so that one can envision a process of marching down the polymer chain in a consistent (though arbitrary) direction. During this process of marching down the chain, one encounters given sequences of monomer units, the likelihood of which can be expressed in terms of simple transition probabilities. These transition probabilities are, in turn, calculated from the values of the state variables that characterize the composition and connectivity in the copolymer system.

In the equations that follow, A_i denotes the concentration of unreacted acid end groups on the monomer of type i . B_j similarly designates the concentration of unreacted base groups on the j -type monomer. For simplicity of notation, all acid groups on a given monomer species are assumed to be equivalent; however, extension to the case of multiple acid groups with different reactivities on the same monomer involves merely the use of a greater number of subscripts. The same argument holds for the base groups. The terms "acid" and "base" are used to designate groups that take part in the condensation reaction; however, there is no strict chemical requirement that an acid group must be, for example, truly a car-

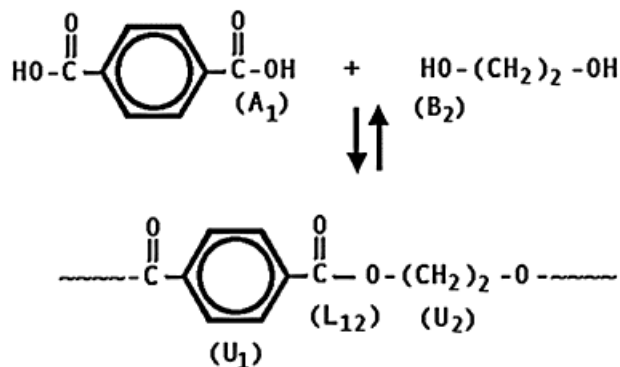


Figure 2 Nomenclature for PET example.

boxylic acid. Any pair of end groups that take part in reactions supporting stepwise chain growth are included within these definitions. The concentration of linkages in the system between A_i and B_j groups is designated as L_{ij} . As the first subscript denotes the source of the acid group and the second the source of the base group, $L_{ij} \neq L_{ji}$. In this article, linkages are assumed only to be possible between an acid and a base end group; however, linkages between two acid groups or between two base groups can easily be handled in a similar manner. The condensation reactions forming these linkages are described by rate equations analogous to those developed in this article. The functionality of each monomer is expressed in terms of the number of acid groups, α_i , and base groups, β_i , per monomer molecule. In the diagrams describing the mechanisms of each reaction, a L_{ij} linkage, e.g., $-\text{CONH}-$, is represented as consisting of an acid residue part a_i , e.g., $-\text{CO}-$, and a base residue part b_j , e.g., $-\text{NH}-$. The symbol U_i represents in these diagrams the part of the monomer unit of type i that is not part of an end group or linkage, e.g., $-(\text{CH}_2)_6-$ in the case of adipic acid. When used as a concentration, it denotes the total concentration of i -type monomer units including both free monomer, P_{1i} , and the reacted monomer units that have been incorporated into the polymer. The use of these symbols in the case of PET is shown in Figure 2.

From the set of the state variables $\{A_i\}$, $\{B_j\}$, and $\{L_{ij}\}$, all of the necessary probabilities for the calculation of the sequence length distribution can be derived. The probability that in marching down a polymer chain that a type- j monomer unit follows a type- i monomer unit is

$$P(U_j|U_i) = H(\alpha_i + \beta_i - 2) \frac{L_{ij} + L_{ji}}{A_i + B_i + \sum_k (L_{ik} + L_{ki})} \quad (2)$$

As monofunctional monomers always reside on the ends of chains, there is no chance of subsequently encountering another unit as one marches down a chain after a monofunctional unit has been encountered. The Heaviside step function, $H(x)$, in eq. (2) ensures that this behavior is included in the model.

As the copolymer chain has a finite molecular weight, a chain may also be terminated at any type- i monomer unit with the following probability.

$$P(T|U_i) = H(\alpha_i + \beta_i - 2) \times \frac{A_i + B_i}{A_i + B_i + \sum_k (L_{ik} + L_{ki})} + [1 - H(\alpha_i + \beta_i - 2)] \quad (3)$$

Again, the Heaviside step function ensures that monofunctional monomers automatically terminate a polymer chain. As after every type- i unit there must either be a bond to another unit or a chain end, all conditional probabilities sum to 1.

$$\sum_j P(U_j|U_i) + P(T|U_i) = 1 \quad (4)$$

When there are no differences in end-group reactivity, the final state of the compositional microstructure obtained in a single phase system is one following Bernoullian (zeroth-order Markov) statistics. In this case, the transition probabilities are dependent only upon the concentrations of each species, and the linkage concentrations can be written in terms of the end-group conversions

$$L_{ij,\text{Bern}} = (\alpha_i U_i p_{A_i}) \frac{\beta_j p_{B_j} U_j}{\sum_k \beta_k p_{B_k} U_k} \quad (5)$$

where p_{A_i} and p_{B_i} are the end-group conversions.

$$p_{A_i} = H(\alpha_i - 1) \frac{\sum_k L_{ik}}{A_i + \sum_k L_{ik}} \quad (6)$$

$$p_{B_i} = H(\beta_i - 1) \frac{\sum_k L_{ki}}{B_i + \sum_k L_{ki}} \quad (7)$$

The first factor on the left in eq. (5) represents the total number of reacted i -type acid groups in the system, and the second factor is the probability that one of these groups has reacted with a

j -type base group. The transition probabilities in the Bernoullian limit are

$$P(U_j|U_i)_{\text{Bern}} = H(\alpha_i + \beta_i - 2) \times \left\{ \left(\frac{\alpha_i}{\alpha_i + \beta_i} \right) p_{A_i} \frac{\beta_j p_{B_j} U_j}{\sum_k \beta_k p_{B_k} U_k} + \left(\frac{\beta_i}{\alpha_i + \beta_i} \right) p_{B_i} \frac{\alpha_j p_{A_j} U_j}{\sum_k \alpha_k p_{A_k} U_k} \right\} \quad (8)$$

$$P(T|U_i)_{\text{Bern}} = H(\alpha_i + \beta_i - 2) \times \frac{\alpha_i(1 - p_{A_i}) + \beta_i(1 - p_{B_i})}{\alpha_i + \beta_i} + [1 - H(\alpha_i + \beta_i - 2)] \quad (9)$$

In eq. (8), the factor within brackets on the left includes two terms, one each for the cases of reaction of an acid end group and of a base. The first term is the probability that an acid group on the i -type monomer is selected that has reacted with a j -type base group; the second is a similar probability for selecting a base.

Once the transition probabilities have been calculated, the probability of finding any sequence of monomer units can be determined by building a Markov chain as the product of the successive transition probabilities for the desired sequence of events. Using this approach, the fraction of sequences of i -type monomer units that are of length x , $(N_i)_x$, is given by the product of $x - 1$ transition probabilities for an i -type monomer following another i -type unit multiplied by the probability that after $x - 1$ such units have been added that either a different monomer type is encountered or the chain is terminated.

$$(N_i)_x = [P(U_i|U_i)]^{x-1} \left[\sum_{j \neq i} P(U_j|U_i) + P(T|U_i) \right] \quad (10)$$

Summing over the lengths of the sequences yields the number-average sequence length of U_i units.

$$\text{NASL}_i = \sum_{x=1}^{\infty} x(N_i)_x = [1 - P(U_i|U_i)]^{-1} \quad (11)$$

For a homopolymer, this distribution simply reduces to the Flory most probable distribution. With AA or BB monomer units, because the number-average sequence length is always 1, it is

more meaningful to consider the distribution of $U_i U_j$ dyads.

$$(N_{ij})_x = [P(U_i|U_j)P(U_j|U_i)]^{x-1} \times \left[\sum_{k \neq i} P(U_k|U_j) + P(U_i|U_j) \sum_{l \neq j} P(U_l|U_i) + P(T|U_j) + P(U_i|U_j)P(T|U_i) \right] \quad (12)$$

$$(\text{NASL})_{ij} = [1 - P(U_i|U_j)P(U_j|U_i)]^{-1} \quad (13)$$

For an AA/BB copolymer at a conversion p , the average dyad sequence length reduces as expected to approximately one-half of the number-average chain length (defined as the number of monomer units).

$$(\text{NASL})_{AA, BB} = \frac{1}{1 - p^2} \approx \frac{1}{2} DP_n \text{ when } p \approx 1 \quad (14)$$

From the construction of Markov chains, the relative frequency of dyad and triad sequences can also be calculated. The probability that a dyad chosen at random is of the exact order $U_i - U_j$ is

$$P(U_i U_j) = P(U_i)P(U_j|U_i) \quad (15)$$

where the probability that a randomly chosen monomer unit is of type i is

$$P(U_i) = \frac{U_i}{\sum_h U_h} \quad (16)$$

Because monofunctional units are always found at chain ends, this dyad probability expression will always be zero if the i -type monomer is monofunctional. It is only for the case where both i -type and j -type monomers are bifunctional that the following equality holds.

$$P(U_i U_j) = P(U_j U_i) \quad (17)$$

As expected, the summation of the probability over all possible outcomes is equal to 1.

$$\sum_{i,j} P(U_i U_j) + \sum_i P(U_i)P(T|U_i) = 1 \quad (18)$$

When the sequence length distribution is measured experimentally using NMR spectroscopy,

the concentrations of higher order sequences, most often of triads, are directly determined. The probability that a randomly chosen triad is of the exact order $U_i - U_j - U_k$ is

$$P(U_i U_j U_k) = P(U_i)P(U_j|U_i)P(U_k|U_j) \quad (19)$$

where again the total probability of all outcomes is 1.

$$\sum_{i,j,k} P(U_i U_j U_k) + \sum_{i,j} P(U_i)P(U_j|U_i)P(T|U_j) + \sum_i P(U_i)P(T|U_i) = 1 \quad (20)$$

Experimentally, it is not these order-specific probabilities that are measured but rather the fraction of U_j -centered triads that are bonded on one side to an i -type monomer unit and on the other to a k -type unit. These fractions are calculated from the triad probabilities when one accounts for the insensitivity of the experimental observation to inversion in the order of units from $U_i - U_j - U_k$ to $U_k - U_j - U_i$.

$$F_j(U_i U_j U_k) = \frac{P(U_i U_j U_k) + (1 - \delta_{ik})P(U_k U_j U_i)}{\sum_{i,k} P(U_i U_j U_k)} \quad (21)$$

By using the first-order Markov statistical expressions in this section, the complete nature of the sequence length distribution may be ascertained from knowledge of the monomer unit concentrations, $\{U_i\}$, the end group concentrations, $\{A_i\}$ and $\{B_j\}$, and the linkage concentrations, $\{L_{ij}\}$. A general dynamic model of the sequence length distribution in condensation systems can be obtained by quantifying how each chemical reaction affects this set of state variables.

GENERAL KINETIC MODEL FOR LINEAR CONDENSATION SYSTEMS

To use this statistical model for dynamic simulation, the contributions of the polymerization reactions to the rates of change of the end group and linkage concentrations are required. In the absence of end-group degradation reactions, the monomer unit concentrations can be calculated from these variables using eq. (22); therefore, they need not be included in the list of independent state variables.

$$U_i = \frac{A_i + B_i + \sum_k (L_{ik} + L_{ki})}{\alpha_i + \beta_i} \quad (22)$$

The concentration of condensate, W , and the concentrations of unreacted monomer of type i , P_{1i} , are also added as state variables.

If end-group degradation reactions are present, eq. (22) no longer is valid and a separate balance equation must be introduced for each monomer unit. As many side reactions involve only the end groups, the identities of the monomer units are unaffected, and the balances in this case include only terms from the input and output reactor flows. As the details of the side reactions are unique to the choice of system, no attempt is made here to provide a general framework; the rates of change of each quantity from these reactions are simply appended to the set presented in this work.

If P_x is the concentration of polymer consisting of x monomer units of any type, the k th moment of the chain length distribution is defined as

$$\lambda_k = \sum_{x=1}^{\infty} x^k P_x \quad (23)$$

Throughout this work, chain length is defined as the number of monomer units. For a regular copolymer such as Nylon-6,6, an alternative definition of chain length as the number of repeat units (e.g., AA/HMD dyads) is also possible; however, this definition cannot be extended to the case of irregular copolymers. Using only the zeroth, first, and second moments, the polymer number and weight-average degrees of polymerization are easily calculated.

$$DP_n = \frac{\lambda_1}{\lambda_0} \quad DP_w = \frac{\lambda_2}{\lambda_1} \quad (24)$$

The zeroth moment represents the total concentration of polymer chains, and the first moment is the total concentration of monomer units. The concentrations and moments are usually expressed in units of mole/unit mass (e.g., mol/kg) because of density changes during polymerization.

In the equations governing the evolution of the chain-length distribution, it is assumed that the copolymer composition is independent of the overall chain length. Because in polycondensation systems polymer chains are continuously breaking

$$r_{\lambda_1(fc)} = 0 \quad (30)$$

$$r_{\lambda_2(fc)} = 2 \left(\frac{\lambda_1}{\lambda_0} \right)^2 \sum_{i,j} k_{fc}^{(i,j)} A_i B_j \quad (31)$$

The rates of change of the other concentrations are

$$r_{W(fc)} = \sum_{i,j} k_{fc}^{(i,j)} A_i B_j \quad (32)$$

$$r_{A_i(fc)} = - \sum_j k_{fc}^{(i,j)} A_i B_j \quad (33)$$

$$r_{B_j(fc)} = - \sum_i k_{fc}^{(i,j)} A_i B_j \quad (34)$$

$$r_{L_{ij}(fc)} = k_{fc}^{(i,j)} A_i B_j \quad (35)$$

The rate of disappearance of monomer is proportional to the concentration of end groups attached to monomer, $\alpha_i P_{1i}$ and $\beta_i P_{1i}$.

$$r_{P_{1i}(fc)} = -P_{1i} \sum_j [k_{fc}^{(i,j)} \alpha_i B_j + k_{fc}^{(j,i)} \beta_i A_j] \quad (36)$$

REVERSE POLYCONDENSATION

The condensate molecule produced by the forward polycondensation reaction, if not removed, can attack a polymer linkage to cleave the chain and form new active ends. The reversibility of the condensation reaction is expressed in terms of the equilibrium constant $K_c^{(i,j)}$.

$$K_c^{(i,j)} = \frac{k_{fc}^{(i,j)}}{k_{rc}^{(i,j)}} = \left[\frac{L_{ij} W}{A_i B_j} \right]_{\text{equil}} \quad (37)$$

The rate of change of x -mer is the sum of the disappearance rate by condensate attack on its $(x - 1)$ linkages and the creation rate from the cleaving of larger molecules, each of which can yield an x -mer at two of its linkages. The first factor in eq. (38) on the left allows different rate constants for each linkage type.

$$r_{P_x(rc)} = \left[\sum_{i,j} k_{rc}^{(i,j)} W \frac{L_{ij}}{(\lambda_1 - \lambda_0)} \right] \times \left[-(x-1)P_x + 2 \sum_{y=x+1}^{\infty} P_y \right] \quad (38)$$

The rate of change of the k th moment of the CLD is

$$r_{\lambda_k(rc)} = \left[\sum_{i,j} k_{rc}^{(i,j)} W \frac{L_{ij}}{(\lambda_1 - \lambda_0)} \right] [-(\lambda_{k+1} - \lambda_k) + 2 \times \sum_{m=0}^k \binom{k}{m} B_m^* (k-m+1)^{-1} (\lambda_{k-m+1} - \lambda_0)] \quad (39)$$

where B_m^* is the m th element of the Bernoulli series²² (p. 1106).

$$(B_0^*, B_1^*, B_2^*, B_3^*, \dots) = (1, -1/2, 1/6, 0, \dots) \quad (40)$$

For the leading moments

$$r_{\lambda_0(rc)} = \sum_{i,j} k_{rc}^{(i,j)} W L_{ij} \quad (41)$$

$$r_{\lambda_1(rc)} = 0 \quad (42)$$

$$r_{\lambda_2(rc)} = \left[\sum_{i,j} k_{rc}^{(i,j)} W L_{ij} (\lambda_1 - \lambda_0)^{-1} \right] [(1/3)(\lambda_1 - \lambda_3)] \quad (43)$$

The appearance of the $(k + 1)$ st moment in the equation for the k th moment introduces the problem of closure. One common and successful method to close the set of moment equations is to approximate the third moment by its value for a Schultz-Flory distribution (an approximation that introduces little error even at implausibly high polydispersities):

$$\lambda_3 \approx \frac{\lambda_2(2\lambda_2\lambda_0 - \lambda_1^2)}{\lambda_1\lambda_0} \quad (44)$$

The rates of change of other state variables are

$$r_{W(rc)} = - \sum_{i,j} k_{rc}^{(i,j)} W L_{ij} \quad (45)$$

$$r_{A_i(rc)} = \sum_j k_{rc}^{(i,j)} W L_{ij} \quad (46)$$

$$r_{B_j(rc)} = \sum_i k_{rc}^{(i,j)} W L_{ij} \quad (47)$$

$$r_{L_{ij}(rc)} = -k_{rc}^{(i,j)} W L_{ij} \quad (48)$$

For the rate of generation of monomer of type i by reverse polycondensation, the probability $P(U_i, n_a, n_b)$ that a randomly chosen U_i unit will have exactly n_a acid groups and n_b base groups reacted is needed.

$$P(U_i, n_a, n_b) = H(\alpha_i - n_a)H(\beta_i - n_b) \times \left[\binom{\alpha_i}{n_a} p_{A_i}^{n_a} (1 - p_{A_i})^{\alpha_i - n_a} \right] \left[\binom{\beta_i}{n_b} p_{B_i}^{n_b} (1 - p_{B_i})^{\beta_i - n_b} \right] \quad (49)$$

The two Heaviside step functions ensure that the number of reacted groups cannot be greater than the total number of groups available. The other factors are the probabilities that of the $\alpha_i(\beta_i)$ groups exactly $n_a(n_b)$ are reacted and $\alpha_i - n_a(\beta_i - n_b)$ are unreacted. Because a free monomer is created only when the last remaining linkage connecting a U_i unit to a polymer chain is attacked, the rate of change of P_{1i} from reverse condensation is

$$r_{P_{1i}(rc)} = H(\alpha_i - 1) [U_i \alpha_i p_{A_i} (1 - p_{A_i})^{\alpha_i - 1} (1 - p_{B_i})^{\beta_i}] \times \left[\sum_j k_{rc}^{(i,j)} \frac{L_{ij} W}{\sum_k L_{ik}} \right] + H(\beta_i - 1) [U_i (1 - p_{A_i})^{\alpha_i} \times \beta_i p_{B_i} (1 - p_{B_i})^{\beta_i - 1}] \left[\sum_j k_{rc}^{(j,i)} \frac{L_{ji} W}{\sum_k L_{ki}} \right] \quad (50)$$

The rate of monomer generation when the last remaining linkage involves an acid group is calculated in the first part of this equation. The Heaviside function ensures that type- i monomer has at least one acid group. The factor in the first set of brackets is equal to the number of i -type monomer units in the system that are connected to polymer by only one linkage involving an acid group, $U_i \times P(U_i, 1, 0)$. The factor in the second set of brackets is the average rate that one of these units is attacked by condensate.

The randomizing nature of the reverse polycondensation reaction is demonstrated in Figure 4, in which equal weights of two AB oligomers, one of $DP_n = 10$ and one of $DP_n = 20$, are mixed together and react by forward and reverse polycondensation. The sequence lengths initially increase because of chain building through forward condensation; however, equilibrium of the chain-length distribution is soon attained. Although the overall chain length is constant from this point onward, the reorganization of polymer induced by

the reverse reaction continues to randomize the sequence length distribution. Eventually, a copolymer following Bernoullian statistics is obtained.

ALCOHOLYSIS

In the reverse polycondensation reaction, condensate breaks apart a chain linkage, usually at a carbonyl group that is vulnerable to nucleophilic attack. The end groups of other polymer chains can also attack the linkages through processes known as interchange reactions. When the attacking species is a base end group, the reaction is known as alcoholysis or aminolysis, depending upon the attacking group's identity (Fig. 5).²³ This reaction can be used to produce high molecular weight polymer, and is, in fact, the principal commercial process for the production of PET. End group attack at interior linkages merely results in the trading of chain sections between the two molecules; however, when a terminal linkage is attacked, a single monomer unit is released that, being volatile, may be removed by mass transfer. The removal of this monomer is used to drive upwards the average molecular weight and acts, in effect, as a pseudocondensation reaction between two base end groups.

The rate of change of x -mer from alcoholysis is calculated by cataloging its loss or gain through each of the four possible events diagrammed in Figure 5. X -mer is destroyed either when its base end attacks any other linkage in the system or when one of its $(x - 1)$ linkages is attacked by another base end. X -mer is created either when attack on a larger molecule splits off an x -mer or when a smaller polymer joins with a section of another molecule such that the combination has a total of x units. In the following population balance for the x -mer concentration, the rates of change from these four processes are listed in order inside the second brackets. The factor in the first set of brackets accounts for the fact that different end group and linkage types may have unequal reactivities.

$$r_{P_x(rb)} = \left[\sum_{h,i,j} k_{rb}^{(h,i,j)} \frac{B_h}{\lambda_0} \frac{L_{ij}}{(\lambda_1 - \lambda_0)} \right] \times \left[-(\lambda_1 - \lambda_0) P_x - \lambda_0 (x - 1) P_x + \lambda_0 \times \sum_{y=x+1}^{\infty} P_y + \sum_{y=1}^{x-1} P_y \sum_{z=x-y+1}^{\infty} P_z \right] \quad (51)$$

where $k_{rb}^{(h,i,j)}$ is the rate constant for a B_h attack of a L_{ij} linkage. The rate of change of the k th moment of the chain length distribution is

$$\begin{aligned}
 r_{\lambda_k(rb)} = & \left\{ \sum_{h,i,j} k_{rb}^{(h,i,j)} \frac{B_h}{\lambda_0} \frac{L_{ij}}{(\lambda_1 - \lambda_0)} \right\} \\
 & \times \{ -\lambda_k(\lambda_1 - \lambda_0) - \lambda_0(\lambda_{k+1} - \lambda_k) + \lambda_0 \\
 & \times \sum_{m=0}^k \binom{k}{m} B_m^* (k - m + 1)^{-1} (\lambda_{k-m+1} - \lambda_0) \\
 & + \sum_{m=0}^k \binom{k}{m} \lambda_{k-m} \left[(m + 1)^{-1} \sum_{n=0}^m \binom{m+1}{n} B_n^* (-1)^n \right. \\
 & \left. \times \left(\lambda_{m+1-n} - \sum_l P_{1l} \right) - \left(\lambda_m - \sum_l P_{1l} \right) \right] \quad (52)
 \end{aligned}$$

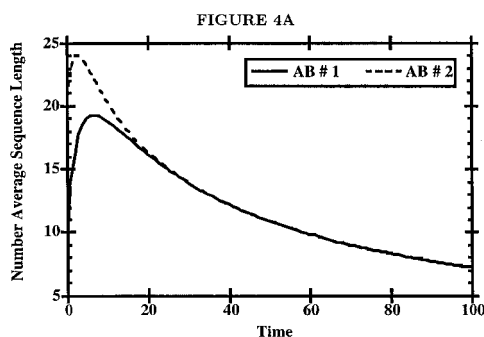
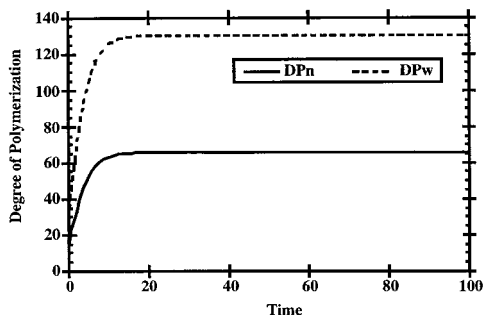


Figure 4 Microstructure randomization by reverse condensation. A mixture of two AB homopolymers, one with $DP_n = 10$ and the other with $DP_n = 20$, undergo reversible reaction with initially no condensate present and with $K_{eq} = 500$. The chain length distribution reaches equilibrium quickly; however, the copolymer microstructure continues to randomize. (a) DP_n , DP_w vs. time. (b) Number-average sequence lengths of each monomer.

Because the number and total length of the molecules is preserved during interchange, of the leading moments only the second is affected by this reaction.

$$r_{\lambda_0(rb)} = r_{\lambda_1(rb)} = 0 \quad (53)$$

$$\begin{aligned}
 r_{\lambda_2(rb)} = & \left[\sum_{h,i,j} k_{rb}^{(h,i,j)} \frac{B_h}{\lambda_0} \frac{L_{ij}}{(\lambda_1 - \lambda_0)} \right] \\
 & \times \left[\frac{1}{3} \lambda_0(\lambda_1 - \lambda_3) + \lambda_1 \lambda_2 - \lambda_1^2 \right] \quad (54)
 \end{aligned}$$

The rates of change of the end group, linkage, and monomer concentrations are

$$r_{W(rb)} = r_{A_i(rb)} = 0 \quad (55)$$

$$r_{B_h(rb)} = \sum_{i,j} [-k_{rb}^{(h,i,j)} B_h L_{ij} + k_{rb}^{(j,i,h)} B_j L_{ih}] \quad (56)$$

$$r_{L_{ij}(rb)} = \sum_h [-k_{rb}^{(h,i,j)} B_h L_{ij} + k_{rb}^{(j,i,h)} B_j L_{ih}] \quad (57)$$

$$\begin{aligned}
 r_{P_{1i}(rb)} = & -\beta_i P_{1i} \sum_{h,j} k_{rb}^{(i,h,j)} L_{hj} + H(\beta_i - 1) \\
 & \times [U_i(1 - p_{A_i})^\alpha \beta_i p_{B_i}(1 - p_{B_i})^{\beta_i - 1}] \\
 & \times \left[\sum_{h,j} k_{rb}^{(h,j,i)} B_h \frac{L_{ji}}{\sum_k L_{ki}} \right] \quad (58)
 \end{aligned}$$

In the expression for P_{1i} , the first term is the rate at which monomer attacks a linkage and is thereby added to a polymer chain. The second is the rate at which monomer that is attached to a polymer chain by only one base group is broken off by an interchange event. It is through this term that free ethylene glycol is produced in the alcoholysis interchange synthesis of PET.

ACIDOLYSIS

Acidic end groups can also attack linkages in a reaction that, at least in terms of the mathematical model, is equivalent to alcoholysis but with a change in the identity of the attacking group (Fig. 6). This reaction, acidolysis, is used commercially in the production of thermotropic liquid crystal polyarylates.²⁴ In this process, the alcohol ends

are converted to acetoxy end groups that expel acetic acid upon acidolysis. It is necessary for a consistent description of the polymerization and interchange processes to model the acetoxy end group as a linkage between the alcohol terminated monomer and an acetic acid monofunctional monomer. Although a ring compound intermediate has been proposed,²⁵ ¹H-NMR analysis of the reaction in model compounds²⁶ and the kinetic behavior of acidolysis in polyamides²⁷ suggest a mixed anhydride intermediate for this reaction.

The rates of change of the state variables from acidolysis are identical to those developed in the previous section with merely a change in notation from base-group attack to acid-group attack in the balance equations.

$$r_{P_x(ra)} = \left[\sum_{h,i,j} k_{ra}^{(h,i,j)} \frac{A_h L_{ij}}{\lambda_0 (\lambda_1 - \lambda_0)} \right] \times \left[-(\lambda_1 - \lambda_0)P_x - \lambda_0(x-1)P_x + \lambda_0 \times \sum_{y=x+1}^{\infty} P_y + \sum_{y=1}^{x-1} P_y \sum_{z=x-y+1}^{\infty} P_z \right] \quad (59)$$

$$r_{\lambda_k(ra)} = \left\{ \sum_{h,i,j} k_{ra}^{(h,i,j)} \frac{A_h L_{ij}}{\lambda_0 (\lambda_1 - \lambda_0)} \right\} \times \{ -\lambda_k(\lambda_1 - \lambda_0) - \lambda_0(\lambda_{k+1} - \lambda_k) + \lambda_0 \} \times \sum_{m=0}^k \binom{k}{m} B_m^* (k-m+1)^{-1} (\lambda_{k-m+1} - \lambda_0)$$

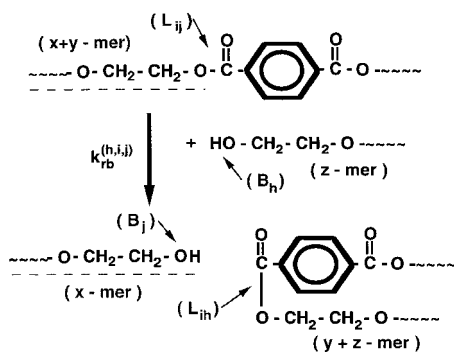


Figure 5 Reaction schema for alcoholysis interchange.

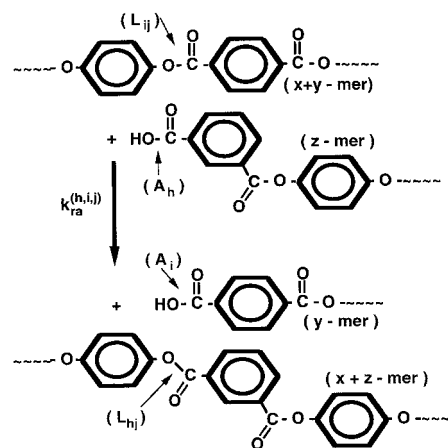


Figure 6 Reaction schema for acidolysis interchange.

$$+ \sum_{m=0}^k \binom{k}{m} \lambda_{k-m} \left[(m+1)^{-1} \sum_{n=0}^m \binom{m+1}{n} B_n^* (-1)^n \left(\lambda_{m+1-n} - \sum_l P_{1l} \right) - \left(\lambda_m - \sum_l P_{1l} \right) \right] \quad (60)$$

$$r_{\lambda_0(ra)} = r_{\lambda_1(ra)} = 0 \quad (61)$$

$$r_{\lambda_2(ra)} = \left[\sum_{h,i,j} k_{ra}^{(h,i,j)} \frac{A_h L_{ij}}{\lambda_0 (\lambda_1 - \lambda_0)} \right] \times \left[\frac{1}{3} \lambda_0(\lambda_1 - \lambda_3) + \lambda_1 \lambda_2 - \lambda_1^2 \right] \quad (62)$$

$$r_{W(ra)} = r_{B_j(ra)} = 0 \quad (63)$$

$$r_{A_h(ra)} = \sum_{i,j} [-k_{ra}^{(h,i,j)} A_h L_{ij} + k_{ra}^{(i,h,j)} A_i L_{hj}] \quad (64)$$

$$r_{L_{ij}(ra)} = \sum_h [-k_{ra}^{(h,i,j)} A_h L_{ij} + k_{ra}^{(i,h,j)} A_i L_{hj}] \quad (65)$$

$$r_{P_{1i}(ra)} = -\alpha_i P_{1i} \sum_{h,j} k_{ra}^{(i,h,j)} L_{hj} + H(\alpha_i - 1)$$

$$\times [U_i \alpha_i p_{A_i} (1 - p_{A_i})^{\alpha_i - 1} (1 - p_{B_i})^{\beta_i}]$$

$$\times \left[\sum_{h,j} k_{ra}^{(h,i,j)} A_h \frac{L_{ij}}{\sum_k L_{ik}} \right] \quad (66)$$

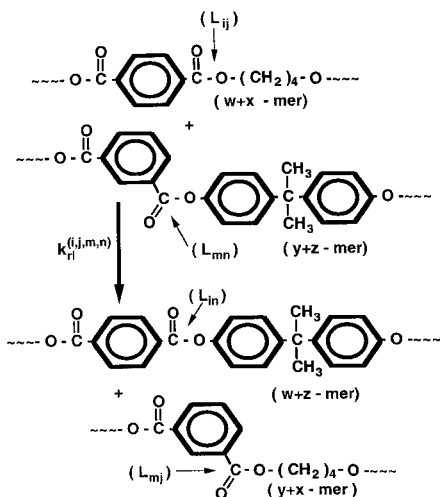


Figure 7 Reaction schema for direct linkage-linkage interchange.

DIRECT LINKAGE-LINKAGE EXCHANGE

In addition to interchange from end groups attack, other catalysts can induce reactions that appear to occur directly between linkages (Fig. 7). Titanium alkoxides such as $\text{Ti}(\text{O}-\text{Bu})_4$ accomplish this through ligand exchange of the $-\text{O}-\text{Bu}$ with a section $(-\text{O}-U_m-)$ of the chain backbone. The rate of this reaction is largely independent of chain length, as the linkage concentration is essentially constant at high conversions. Direct linkage-linkage exchange is the dominant process for randomization in many reactive blending processes.¹³

Lertola has developed a model for the response of the chain length distribution to direct linkage-linkage exchange.²⁸ As the full derivation is described in ref. 28, only the final result of the form of the population balance equation is presented here.

$$r_{P_x(r)} = \left\{ \sum_{i,j,m,n} k_{rl}^{(i,j,m,n)} \frac{L_{ij}L_{mn}}{(\lambda_1 - \lambda_0)^2} \right\} \\ \times \{-2(\lambda_1 - \lambda_0)(x - 1)P_x + 2 \\ \times \sum_{y=2}^x \sum_{z=x+2-y}^x \times (y + z - x - 1)P_y P_z + 4 \\ \times \sum_{y=2}^x \sum_{z=x+1}^{\infty} (y - 1)P_y P_z + 2$$

$$\times \sum_{y=x+1}^{\infty} \sum_{z=x+1}^{\infty} (x - 1)P_y P_z \quad (67)$$

The complex double sums in this equation preclude the simple derivation of moment equations; however, approximate moment equations for direct linkage-linkage exchange may be obtained through a simple modification of the moment equations for alcoholysis exchange. The alcoholysis equation is altered by replacing the B_h/λ_0 factor that represents the fraction of base chain ends that are of type h with $L_{ij}/(\lambda_1 - \lambda_0)$, the fraction of linkages that are between A_i and B_j . Also, as the rate of direct interchange is not proportional to the base-end group concentration but rather the total linkage concentration, the alcoholysis moment equation should be multiplied by $(\lambda_1 - \lambda_0)/\lambda_0$. The resulting approximate moment equation for direct linkage-linkage exchange is

$$r_{\lambda_2(r)} \approx \left[\sum_{i,j,m,n} k_{rl}^{(i,j,m,n)} \frac{L_{ij}L_{mn}}{\lambda_0(\lambda_1 - \lambda_0)} \right] \\ \times \left[\frac{1}{3} \lambda_0(\lambda_1 - \lambda_3) + \lambda_1\lambda_2 - \lambda_1^2 \right] \quad (68)$$

The use of this approximate moment equation has been tested over a wide range of batch and continuous simulations, and has been found to be in excellent agreement with the full set of population balances. Both the approximate moment equation and the full set of population balances predict a relaxation of the CLD to the Flory distribution on the same time scale.

The rates of change of the linkage concentrations from direct linkage-linkage exchange are

$$r_{L_{ij}(r)} = \sum_{m,n} [-k_{rl}^{(i,j,m,n)}L_{ij}L_{mn} + k_{rl}^{(i,n,m,j)}L_{in}L_{mj}] \quad (69)$$

The rates of change of all other state variables are zero.

$$r_{W(r)} = r_{A_i(r)} = r_{B_i(r)} = r_{P_1(r)} = 0 \quad (70)$$

SIMULATION OF REACTIVE BLENDING

The contents of the previous section allow one to simulate the time evolution of the chain-length

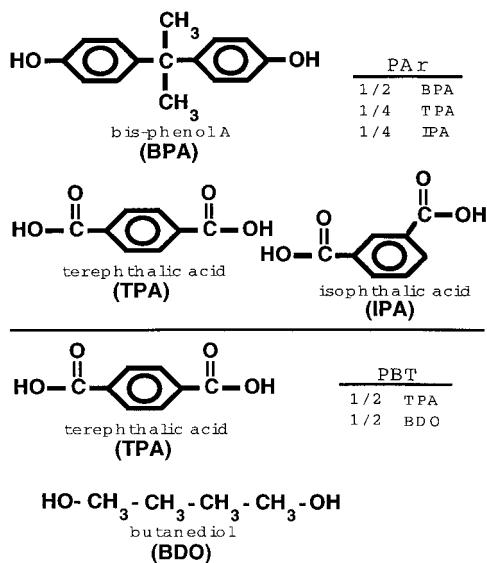


Figure 8 Composition of the copolymers polyarylate (PAr) and poly(butylene terephthalate) (PBT).

and sequence-length distributions in linear systems of an arbitrary number of monomers. The use of this general model is demonstrated in this section for a specific example in which a polyarylate (PAr) is melt blended with poly(butylene terephthalate) (PBT) to produce a block copolymer (Fig. 8). Although reactive blending has been studied in several systems,^{13–21} the PAr/PBT system is especially well suited to model validation, as the two polymers are miscible in the amorphous phase.¹³ In most other systems, the two polymer fractions do not become miscible until a certain amount of interchange has occurred. Fernandez-Berridi et al. have studied the kinetics of the sequence length randomization using ¹H-NMR to follow the concentration of triad structures during the course of the reaction.^{29,30} A Ti(O—Bu)₄ catalyst was used for the reaction, suggesting that in this system direct linkage-linkage interchange occurring through ligand exchange with the catalyst is the dominant reaction.

As can be seen from Figure 8, terephthalic acid monomer is found in both the polyarylate and the PBT fractions. As a TPA monomer that originates in the PAr has a different history than the TPA from the PBT, these two sources of monomer must be considered different species when calculating the sequence-length distribution. This must be done so that in determining the frequency of finding a given monomer sequence, one does not jump from a PAr chain to a PBT chain in the middle of the calculation. If the two sources of

TPA are not handled separately, the model would incorrectly predict the presence of BDO-TPA-BPA sequences in the initial physical blend before any interchange had occurred. Because the TPA monomer from either source is chemically equivalent, experimental observations are blind as to the origin of the TPA, and the contributions must be lumped together when calculating the distribution of triad sequences. This lumping process is accomplished through the following procedure.

First the integer Ω_{ij} is defined such that it is 1 if i -type and j -type monomers are chemically equivalent and is zero if they are not.

$$\Omega_{ij} = \begin{cases} 1 & \text{if } U_i \text{ and } U_j \text{ are chemically equivalent,} \\ 0 & \text{if } U_i \text{ and } U_j \text{ are different species} \end{cases} \quad (71)$$

Using these integers, a parameter Ω'_i is defined for each monomer that is nonzero for only one of a group of chemically equivalent monomers.

$$\Omega'_i = \delta_{1, \sum_h \Omega_{ih}} + H\left(-\sum_{h < i} \Omega_{ih}\right) \quad (72)$$

The first term counts monomer species i if it is chemically unique, and the second counts the species if it has the lowest index among the set of monomers that are identical to it. Once these two integer parameters have been defined, lumped transition probabilities are defined that do not discriminate between the monomer sources that can, therefore, be used to calculate the triad fractions measured experimentally.

The lumped probability that a randomly chosen monomer unit is equivalent to monomer of type i is

$$\tilde{P}(U_i) = \Omega'_i \left[\sum_h \Omega_{ih} P(U_h) \right] \quad (73)$$

The lumped transition probability that a monomer unit equivalent to type j follows a monomer unit identical to type i is

$$\tilde{P}(U_j|U_i) = \Omega'_i \Omega'_j \left[\frac{\sum_{h,k} \Omega_{ih} \Omega_{jk} P(U_h) P(U_k|U_h)}{\sum_h \Omega_{ih} P(U_h)} \right] \quad (74)$$

The lumped probability that a species equivalent to type i monomer terminates a polymer chain is

$$\tilde{P}(T|U_i) = \Omega_i \left[\frac{\sum_h \Omega_{ih} P(U_h) P(T|U_h)}{\sum_h \Omega_{ih} P(U_h)} \right] \quad (75)$$

The sequence-length expressions developed previously can then be used with these lumped transition probabilities to calculate triad sequence concentrations that do not discriminate between chemically identical species.

Figure 9 compares the prediction from the general model proposed here with the data of Fernandez-Berridi et al.¹⁴ for the rate of change of triad fractions centered on the terephthalic acid monomer for the base case with reaction at 270°C. The only simulation parameter used to fit the data is a single direct interchange rate constant, k_{rl} , common to all monomers. The agreement with experiment demonstrates that in condensation reactions among similar (e.g., aromatic) monomers with the same end group species (—COOH and —OH) the differences in reactivity between monomers are slight. The initial number average degrees of polymerization of the PAr and PBT were estimated to be 110 and 150, respectively, using the reported viscosity average molecular weights. All other parameters are directly calculable from the reported experimental conditions and the molecular weights of each species (Table I).

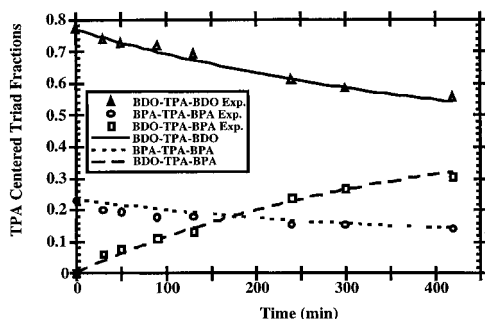


Figure 9 Comparison of model predictions with experimental data for TPA-centered triad fractions in the randomization of a PAr/PBT blend by direct linkage-linkage exchange. Data from Table I of Fernandez-Berridi et al.¹⁴

Table I PBT-PAr Simulation Parameters

Parameter	Value
DP_n of PBT	150
DP_n of PAr	110
Temperature	270°C
Catalyst conc.	1.16×10^{-6} mol/g
k_{rl}	2.039×10^{-4} kg/mol/min
Monomer 1	PBT-TPA
α_1	2
U_1	2.2603 mol/kg
L_{12}	4.5206 mol/kg
Monomer 2	PBT-BDO
β_2	2
B_2	0.06068 mol/kg
U_2	2.2907 mol/kg
P_{12}	2.0227×10^{-4} mol/kg
Monomer 3	PAr-TPA
α_3	2
U_3	0.69025 mol/kg
L_{35}	1.3805 mol/kg
Monomer 4	PAr-IPA
α_4	2
U_4	0.69025 mol/kg
L_{45}	1.3805 mol/kg
Monomer 5	PAr-BPA
β_5	2
B_5	0.050661 mol/kg
U_5	1.4058 mol/kg
P_{15}	2.3028×10^{-4} mol/kg

CHAIN-LENGTH DISTRIBUTIONS IN CONTINUOUS PROCESSES

The previous discussion of the role of each reaction in determining the polymer microstructure was presented within the context of batch polymerizations. In a continuous process, one generally expects a broader molecular weight distribution than the Flory distribution. The probabilistic approach used to derive the Flory distribution does not account for the effect of past history (i.e., the residence time distribution) and is, therefore, only valid for batch processes. As industrial processes for copolymer production are often continuous; in this section the effects of each reaction upon the chain length distribution in Continuous Stirred Tank Reactors (CSTRs) are investigated.

If forward condensation is the only reaction present, higher polydispersities than those obtained from batch processes are expected; however, the presence of reverse condensation and interchange reactions obviates this effect. Specif-

ically, whenever the characteristic time for chain breakage by these reactions is much less than the mean residence time of the reactor, each chain is broken apart and reformed several times during its stay within the reactor, and the influence of the residence time distribution (RTD) is erased.

The shape of the molecular weight distribution in a continuous process can be obtained by solving the set of population balances for each polymer species. This direct approach leads in practice to lengthy simulations; therefore, the concentrations of only a limited subset of chain lengths are calculated, with interpolation used to approximate the rest. When the chain length axis is broken into elements, and the chain lengths chosen for the calculation are those lying near the zeroes on these elements of orthogonal polynomials, the accuracy of the interpolation is highest. Because the discrete nature of the summations in the population balance equations is preserved, as the interpolation becomes exact, the calculated chain length distribution approaches the solution of the complete set of population balances.

For our calculations, we consider only the effect of the forward condensation, reverse condensation, and alcoholysis interchange reactions for a single AB -type monomer in a process with three CSTRs in series. The mass balance for polymer with a degree of polymerization x is

$$M \frac{dP_x}{dt} = FP_x^{\text{in}} - FP_x + M[r_{P_x}^{(fc)} + r_{P_x}^{(rc)} + r_{P_x}^{(rb)}] \quad (76)$$

where M is the total mass in the reactor (assumed constant) and F is the mass flowrate through the reactor. The mean residence time of the reactor is $\theta = M/F$. Using θ and the zeroth moment of the input stream, λ_0^{in} , the following dimensionless time, τ , and concentration, c_x , are defined.

$$\tau = t/\theta \quad c_x = P_x/\lambda_0^{\text{in}} \quad (77)$$

The moments of the dimensionless chain length distribution are $\mu_k = \sum_{x=1}^{\infty} x^k c_x$. The residence time of the reactor is determined by the value of the Damköhler number, $D_a = k_f \theta \lambda_0^{\text{in}}$, where k_f is the rate constant for the forward condensation reaction. The relative rate of the alcoholysis reaction is given by the ratio $\gamma_b = k_{rb}/k_f$. If K_{eq} is the equilibrium constant of the condensation reaction and $w = W/\lambda_0^{\text{in}}$ is the dimension-

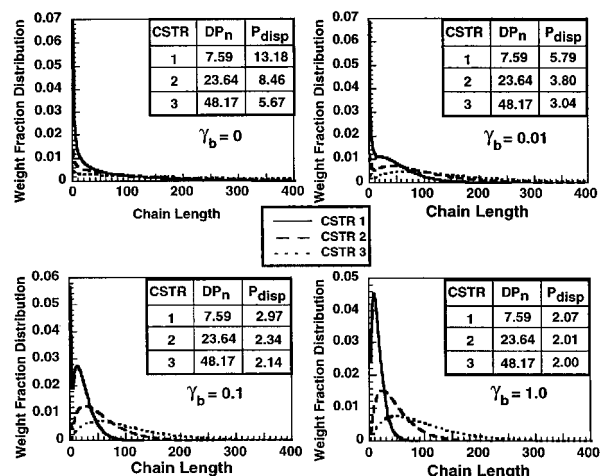


Figure 10 Weight fraction distributions in a system of three CSTR's in series, each with $D_a = 50$. No reverse condensation reaction. γ_b represents the rate of alcoholysis interchange relative to forward condensation.

less condensate concentration, the population balance for c_x is written in the following dimensionless form.

$$\begin{aligned} \frac{dc_x}{d\tau} = & c_x^{\text{in}} - c_x + D_a \left[-2\mu_0 c_x + \sum_{y=1}^{x-1} c_y c_{x-y} \right] \\ & + D_a K_{\text{eq}}^{-1} w \left[-(x-1)c_x + 2 \sum_{y=x+1}^{\infty} c_y \right] \\ & + \gamma_b D_a \left[-(\mu_1 - \mu_0)c_x - \mu_0(x-1)c_x \right. \\ & \left. + \mu_0 \sum_{y=x+1}^{\infty} c_y + \sum_{y=1}^{x-1} c_y \sum_{z=x-y+1}^{\infty} c_z \right] \quad (78) \end{aligned}$$

The weight fraction distributions, $WtFr_x = xP_x/\lambda_1$, for three CSTRs in series, each with $D_a = 50$ and with a monomer feed stream to the first reactor, are presented in Figure 10 with different values of γ_b . The condensation reaction is assumed to be irreversible. In the absence of interchange, $\gamma_b = 0$, much higher polydispersities are observed than are expected from the Flory distribution. As the rate of interchange increases, the continuous chain recombination erases the influence of the different past histories of the molecules in the reactor outlet. The polydispersity,

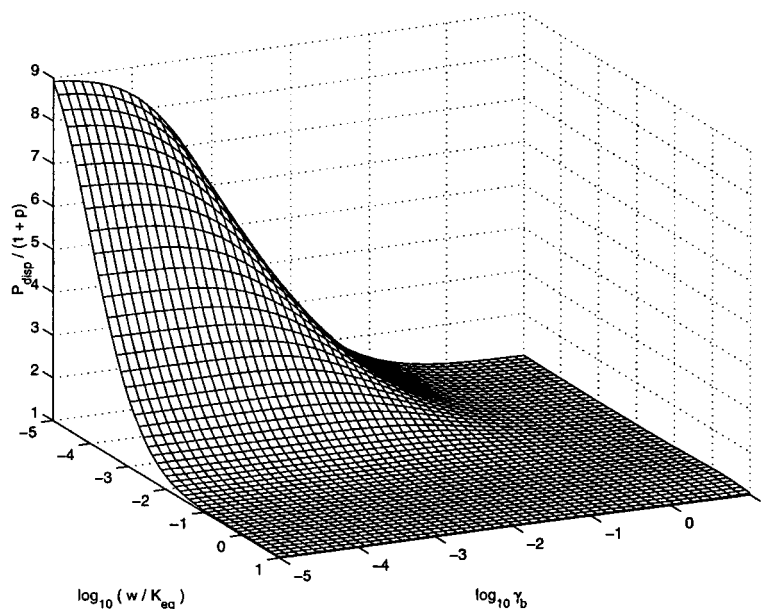


FIGURE 11A

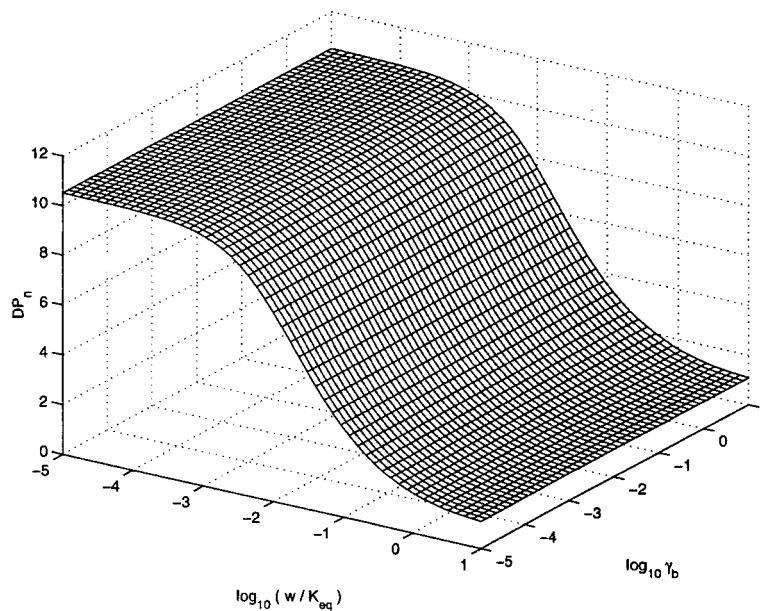


Figure 11 Effect of reverse condensation (w/K_{eq}) and interchange (γ_b) on P_{disp} and DP_n in a monomer-fed CSTR with $D_a = 100$. (a) actual P_{disp} divided by $1 + p$, the value expected from the Flory distribution. (b) DP_n .

therefore, is reduced to the value expected for a batch process. Close observation of Figure 10 reveals that the polydispersity is reduced primarily through the removal of chains with high molecular weights, as is expected considering that these molecules contain a large number of linkages and are, therefore, tempting targets for the base end groups involved in the interchange reaction.

As reverse condensation involves recombination of polymer chains, this reaction also removes the sensitivity of the polydispersity to the residence time distribution. In Figure 11, the polydispersity in a monomer-fed reactor divided by the expected value for the Flory distribution is plotted as a function of w/K_{eq} and γ_b . As w/K_{eq} increases, the reverse condensation reaction be-

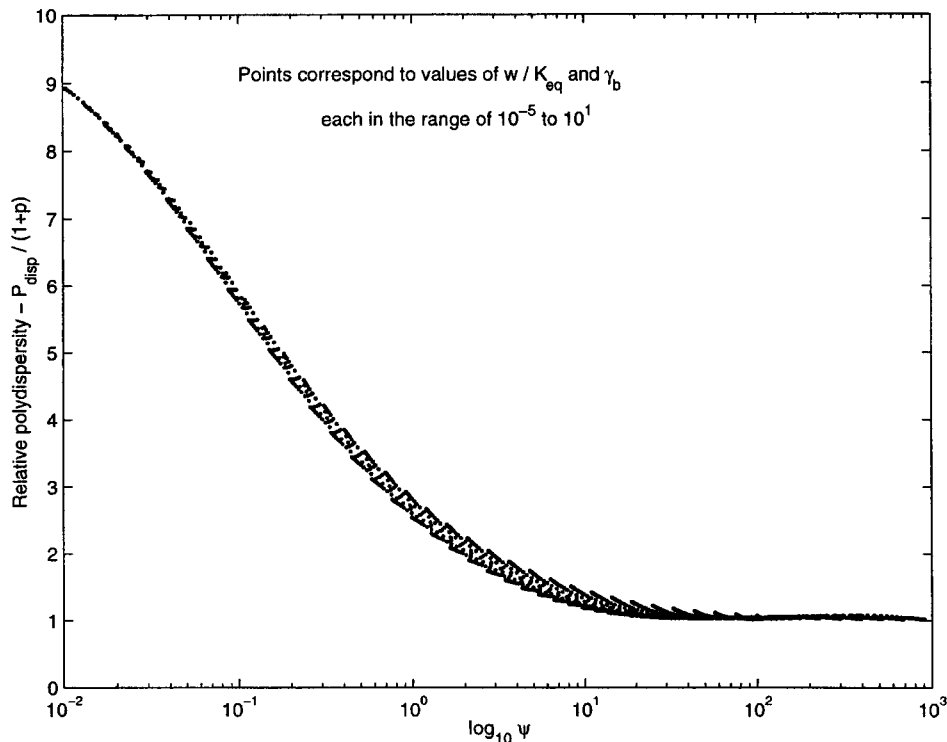


Figure 12 Plot of the polydispersity relative to that of a batch system vs. the RTD criterion parameter ψ of eq. (80). When this parameter is much greater than 1, the residence time distribution has no effect on polydispersity. The points correspond to the values of w/K_{eq} and γ_b in Figure 11.

comes more important, and the polydispersity approaches the Flory value even in the absence of interchange reactions. As the plot of DP_n shows, this occurs at the price of lower functional group conversions. Interchange reactions, by contrast, only alter the polydispersity and do not affect the number average chain length.

From these rate expressions, a simple criterion can be developed to determine whether the residence time distribution will have an effect upon the polydispersity. First, the rate (in units of inverse time) at which a polymer chain undergoes cleavage by reverse condensation or interchange is calculated.

$$R_{\text{cleave}} = [k_f K_{eq}^{-1} W + k_{rb} B + k_{ra} A + k_{rl}(\lambda_1 - \lambda_0)](DP_n - 1) \quad (79)$$

Here $A(B)$ is the total acid (base) end group concentration. k_{ra} and k_{rl} are the rate constants for acidolysis and direct linkage-linkage exchange. The residence time distribution will have no effect upon the polydispersity if this rate of chain cleav-

age is much greater than the rate at which a given molecule escapes from the reactor; that is, $R_{\text{cleave}} \gg \theta^{-1}$. Assuming that $\lambda_0^{\text{in}} = (1 - p^{\text{in}})\lambda_1$, where p^{in} is the conversion of the inlet stream, and that $A/\lambda_1 = B/\lambda_1 = 1/DP_n$, this yields the following dimensionless criterion that, when satisfied, ensures that the RTD will not affect the polydispersity.

$$\psi = D_a \left\{ K_{eq}^{-1} w + (1 - p^{\text{in}})^{-1} \times \left[\frac{\gamma_a + \gamma_b}{DP_n} + \gamma_l (1 - 1/DP_n) \right] \right\} (DP_n - 1) \gg 1 \quad (80)$$

The parameters γ_a and γ_l are ratios of rate constants defined in the same manner as γ_b , but for acidolysis and direct linkage-linkage exchange, respectively. In Figure 12, the polydispersity in the continuous system relative to that expected for a batch polymerization is plotted as a function of ψ for the CSTR of Figure 11, demon-

strating that for $\psi \gg 1$, the RTD has no effect on the polydispersity.

The question remains as to whether in real polycondensation processes the rate of reverse condensation and interchange is sufficient to remove the dependence of polydispersity upon the residence time distribution. In multistage processes such as that considered above, the cumulative residence time distribution becomes more narrow as the number of CSTRs is increased. This results in less sensitivity of the final product polydispersity to the RTD in any single reactor. Moreover, if the characteristic time for chain breakage by reverse condensation and interchange is less than the mean residence time, the RTD does not affect the breadth of the chain length distribution within a single reactor. The values of $K_{\text{eq}}^{-1}w$ and γ_b are required to ascertain whether this is the case; therefore, the results will be dependent upon the monomers, the catalyst, and the operating conditions.

In processes such as the transesterification route to polyester synthesis, the molecular weight is increased by removing the monomer (ethylene glycol) evolved whenever alcoholysis occurs at a terminal linkage. It is expected that γ_b should be near 1, as the same reaction is responsible for both chain growth and interchange. Indeed, from the data of Challa³¹ for PET, the value of γ_b is estimated to be 1.46 at 254°C and 2.1 at 280°C. The presence of direct linkage-linkage exchange is very sensitive to the choice of catalyst. In the absence of catalyst, Ramjit and Sedgwick³² obtained a value of γ_l of 0.0057 at 280°C; however, in systems other than PET where a titanium alkoxide catalyst is used, direct interchange is the dominant redistribution reaction. In a direct condensation synthesis of polyester, the equilibrium constant is on the order of 1; therefore, in this case as well, chain breakage occurs frequently during the course of a polymerization, and little dependence of polydispersity upon the RTD is to be expected.

In polyamide systems such as Nylon, the equilibrium constant is on the order of 100, and thus more favorable towards chain growth; therefore, the reverse reaction is not as effective in removing the RTD dependence as for polyesters. Chain growth occurs through direct condensation and not interchange; therefore, values of γ less than 1 are possible. Using the direct condensation rate data of Tai³³ and literature values for the interchange rate constants, values of γ in polyamide systems may be estimated. Han's data³⁴ on ami-

nolysis at 200°C yield $\gamma_b = 0.0045$. Beste and Houtz's data³⁵ at 245°C give $\gamma_b = 0.0048$. Miller²⁷ reports rate constants for interchange that yield for acidolysis at 255°C, $\gamma_a = 0.0969$, aminolysis at 231°C, $\gamma_b = 0.052$, and no evidence of a direct amide-amide reaction. This data suggests that polyamide systems are not as insensitive to residence time effects, especially when mass transfer is rapid and little reverse condensation occurs. The polydispersity of the product can be brought back to near 2; however, by holding the polymer near reaction temperatures until at least one linkage per polymer has been involved in a chain-breakage event. The approximate time required for this to occur is R_{cleave}^{-1} .

CONCLUSIONS

The compositional microstructure in condensation copolymers depends upon the interplay between the randomizing nature of the chemical reactions and the time of contact at reaction temperatures between samples of different polymers. The continuous breaking and reforming of polymer chains during condensation polymerization requires a different technique to calculate the copolymer composition than is used in addition polymerization. In this article, a general model framework has been developed and validated against literature experimental data for the dynamic simulation of the sequence length distribution in condensations systems that have multiple monomer species and multiple parallel reactions. The first-order Markov statistical model for the sequence length distribution is based upon transition probabilities defined in terms of the concentrations of linkages between each unique monomer species. In linear condensation systems, equally general equations for the chain-length distribution have also been developed. The general nature of this model makes it suitable for use in the computer-aided design of batch and continuous processes.

The authors are grateful to the Department of Energy, to the industrial sponsors of the University of Wisconsin Polymerization Reaction Engineering Laboratory (UWPREL), and to the National Science Foundation for financial support.

NOTATION

A_i Concentration of active acid groups from i -type monomer

B_m^*	m th element of Bernoulli series	$\tilde{P}(U_j U_i)$	$P(U_j U_i)$ lumped over identical monomers
B_j	Concentration of active base groups from j -type monomer	$\tilde{P}(T U_i)$	$P(T U_i)$ lumped over identical monomers
c_x	dimensionless x -mer concentration in CSTR	R_{cleave}	Rate at which a single chain undergoes cleavage
D_a	Damköhler number for CSTR	U_i	Concentration of type i repeat unit
DP_n	Number average degree of polymerization	W	Concentration of condensate
DP_w	Weight average degree of polymerization	w	Dimensionless condensate concentration in CSTR (W/λ_0^{in})
F	Mass flowrate through CSTR	WtFr_x	Weight fraction of x -mer
$F_j(U_i U_j U_k)$	Fraction of U_j centered trimers with U_i and U_k		
$H(x)$	Heaviside step function (1 if $x \geq 0$ else 0)		
$k_{fc}^{(i,j)}$	Forward condensation rate constant for A_i and B_j		
$K_c^{(i,j)}$	Equilibrium constant for A_i and B_j		
$k_{rc}^{(i,j)}$	Reverse condensation rate constant for A_i and B_j		
$k_{ra}^{(h,i,j)}$	Acidolysis rate constant for A_h and L_{ij}		
$k_{rb}^{(h,i,j)}$	Alcoholysis rate constant for B_h and L_{ij}		
$k_{rl}^{(i,j,m,n)}$	Direct exchange rate constant for L_{ij} and L_{mn}		
L_{ij}	Concentration of linkages between A_i and B_j		
M	Total reactant mass in CSTR		
$(N_i)_x$	Fraction of U_i sequences of length x		
$(N_{ij})_x$	Fraction of $U_i U_j$ dyad sequences of length x		
NASL_i	Number average U_i sequence length		
NASL_{ij}	Number average $U_i U_j$ dyad sequence length		
p_{A_i}	Conversion of A_i		
p_{B_j}	Conversion of B_j		
P_{1_i}	Concentration of i -type monomer		
P_x	Concentration of x -mer		
$P(T U_i)$	Probability of chain termination at U_i		
$P(U_i)$	Probability that randomly chosen repeat unit is U_i		
$P(U_j U_i)$	Probability of encountering U_j after U_i		
$P(U_i U_j)$	Probability that randomly chosen dyad is $U_i U_j$		
$P(U_i U_j U_k)$	Probability that randomly chosen triad is $U_i U_j U_k$		
P_{disp}	Polydispersity (DP_w/DP_n)		
$\tilde{P}(U_i)$	$P(U_i)$ lumped over identical monomers		

GREEK LETTERS

α_i	Number of acid groups on i -type monomer
β_i	Number of base groups on i -type monomer
γ_a	Rate constant ratio of acidolysis to polycondensation
γ_b	Rate constant ratio of alcoholysis to polycondensation
γ_l	Rate constant ratio of direct linkage exchange to polycondensation
δ_{ij}	Kronecker delta (1 if $i = j$ else 0)
λ_k	k th moment of the chain length distribution
μ_k	Dimensionless k th moment of CLD in CSTR
ω_i	Weight fraction of i -type monomer units
Ω_{ij}	1 for i -type and j -type monomers identical, else 0
Ω'_i	Selects one copy of each unique monomer type
ψ	value of criterion for RTD effect
θ	CSTR mean residence time
τ	dimensionless time for CSTR = t/θ

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