

An Analysis of CSTRs in Series for Solution Copolymerization*

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Synopsis

Continuous copolymerization is used in order to achieve a product of uniform composition. However, it is difficult to attain high conversions without resorting to very high residence times in a single tank. The way to avoid this is to use a series of stirred reactors with addition of one comonomer and initiator to each one after the first. The allowable half-life of the initiator is a function of the residence time. When all the reactors are equal in volume so that the residence time is the same in each, it can be shown that the incremental conversion in each successive reactor must decrease in a well-ordered manner. As a specific example, a copolymerization is postulated with total polymer concentration restricted to the region where viscosity is manageable with conventional mixing equipment. Under these conditions the relative reactivity ratios are presumed to be constant and temperature can be held within narrow bounds.

INTRODUCTION

As pointed out recently by Hamer et al.¹ and Wittmer,² there is little mention of continuous solution polymerization in the open literature despite its industrial importance. Continuous homopolymerization has been dealt with, especially for emulsion systems.³⁻⁶ Some topics addressed in the last few years include the possibility of multiple steady states^{1,7} and composition control by temperature manipulation.⁸ Another feature to be expected in the continuously fed stirred tank reactor (CSTR) is the increased probability of branched structures depending on the residence time.^{9,10} Incomplete mixing also is known to present real problems in any polymerization, but even more so in a continuous process.¹¹

It is rare for the incremental copolymer formed from a mixture of monomers to have the same composition as the monomer feed. The result in a batch operation is that the compositions of monomer and polymer drift with conversion. On the other hand, by keeping the monomer composition in a reactor constant and feeding monomers at suitable rates while an equivalent volume stream is removed, a uniform copolymer can be formed. In a single CSTR the problems considered are typically those of stability, variations of rate constants with viscosity, and response to changes in conditions (flow rates and temperature).

It is shown later that if series of CSTRs is employed, the total volume of the series can be appreciably smaller than the volume of the single reactor

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for the same conversion with polymer composition and molecular size being the same. Various options are available in designing a series. One architecture would consist of a small CSTR operating at moderate conversion followed by a larger CSTR for a longer "soak." The second CSTR may be operated at a higher temperature than the first and may require additional monomer and initiator. Matching molecular weights and polymer composition in both CSTRs can be difficult.

The series case analyzed in the present work is a simplified one. Each reactor is of equal size (and, therefore, equal residence or space, times τ). The supplemental flows of monomer and initiator are considered to be small enough that they do not change τ appreciably. Moreover, rather dilute solutions (less than 15%) and modest molecular weights (less than 10^5) are contemplated so that rate constants can be assumed to vary only with temperature and to be independent of viscosity and composition.

We assume the usual conditions for simple, generalized copolymerization to apply:

(1) High molecular weights (greater than 10^3) are produced so only the propagation reactions are significant consumers of monomer.

(2) The relative reactivity ratios are constant.

(3) Initiator decomposes by ordinary first-order kinetics.

(4) Initiator efficiency is constant.

(5) There is no chain transfer, and the termination reaction, whether by coupling or disproportionation or some combination, does not vary with concentrations.

(6) All reaction rate constants are known or can be safely estimated and depend only on temperature. In the derivations which follow we will assume that conversion and properties in a single CSTR can be measured. In such a case all the rate constants do not have to be known in detail. It is possible to make useful generalizations about the efficiency obtained from using multiple CSTRs and the limitations that this operating architecture impose on the initiator stability.

We assume a series of reactors (CSTR) each denoted by the subscript n subject to the following constraints.

ASSUMED

(a) Each reactor has the same volume V , residence (space) time τ , and temperature T .

(b) Each reactor is to produce the same molecular weight polymer \bar{x} .

(c) Each reactor has inputs of monomers and initiators.

(d) Each reactor is to produce the same composition, that is, $(P_a/P_b)_n$ is a constant.

After the first reactor, the input also will include "dead" polymer. The streams are identified in Figure 1. The flows are in mol/s. The amount of polymer formed is given by $P_a + P_b$ which, in turn, are the differences in output and input:

$$(P_a)_n = A_n - (A_{n-1} + A'_{n-1}) \quad (1a)$$

$$(P_b)_n = B_n - B_{n-1} \quad (1b)$$

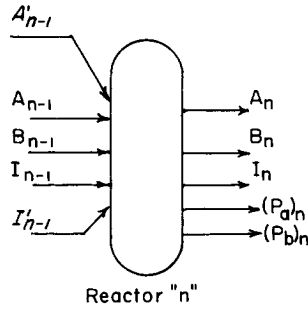


Fig. 1. Each reactor (CSTR) receives monomers A and B and initiator I from the previous reactor in the series together with some additional A and I (labeled as A'_{n-1} and I'_{n-1}).

The units of P_a and P_b are moles of monomers. The cumulative amount of each is

$$\sum_1^n (P_a)_n \text{ and } \sum_1^n (P_b)_n.$$

NECESSARY CONDITIONS

(a) In order to produce the same composition from each reactor, it usually is sufficient that the ratio of monomers be the same, that is,

$$([A]/[B])_n = \text{const} \tag{2}$$

The composition produced is independent of the absolute value of $[A]$ or $[B]$.

(b) In order to produce the same molecular size from each reactor, it usually is sufficient that the ratio of initiator to either monomer be kept constant according to

$$\{[I]^{1/2}/[A]\}_n = \text{const} \text{ or } \{[I]^{1/2}/[B]\}_n = \text{const} \tag{3}$$

(c) The relationship between conversion and initiator concentration and space time can be derived from Mayo and Walling's equations.^{12,13} These show that the rate at which monomer A_{n-1} is converted to polymer $(P_a)_n$ will be proportional to the concentration of A in the reactor, A_n , the square root of the initiator concentration I_n , and the space-time τ . Over a period of time τ we will get

$$(1/C_a)_n - 1 = K_a [I]_n^{-1/2} \tau^{-1} \tag{4a}$$

and

$$(1/C_b)_n - 1 = K_b [I]_n^{-1/2} \tau^{-1} \tag{4b}$$

where $(C_a)_n$ is the conversion of monomer A in reactor n and so on. The constants K_a and K_b are functions only of the ratio $(A/B)_n$ and independent of the total concentration of monomers.

Recurrence Formula for Conversion in Successive Reactors

When the unreacted monomer from one reactor effluent becomes the sole feed to the next reactor and so on, a simple recurrence formula can be derived for conversion in each reactor. This can be the case, for example, when monomer B is used up less rapidly than A, and when a series of reactors (CSTR) is used to push overall conversion of B to high values. If B is hard to recover and recycle from the final polymer-monomer mixture, or if B is particularly valuable or toxic, it may be worthwhile to operate in this fashion.

Consider reactors n and $n + 1$. Apply eqs. (4) to each, remembering that space-time τ and K_b are the same in each:

$$\frac{(1/C_b)_{n+1} - 1}{(1/C_b)_n - 1} = \left(\frac{[I]_n}{[I]_{n+1}} \right)^{-1/2} \quad (5)$$

Also, from eq. (3),

$$\left(\frac{[I]_n}{[I]_{n+1}} \right)^{-1/2} = \frac{[B]_n}{[B]_{n+1}} \quad (6)$$

Conversion of B in reactor $n + 1$ also is given by

$$(C_b)_{n+1} = 1 - ([B]_{n+1}/[B]_n) \quad (7)$$

Combining eqs. (5)–(7) yields

$$\frac{(1/C_b)_{n+1} - 1}{(1/C_b)_n - 1} = \frac{[B]_n}{[B]_{n+1}} = \frac{1}{1 - (C_b)_{n+1}} \quad (8)$$

Rearranging into a somewhat simpler form,

$$\left(\frac{1 - C_b}{C_b} \right)_n = \left(\frac{1 - C_b}{C_b} \right)_{n+1}^2 \quad (9)$$

Solving explicitly for $(C_b)_{n+1}$ gives the desired recurrence formula:

$$(C_b)_{n+1} = \{ Y - (Y^2 - 4)^{1/2} \} / 2 \quad (10)$$

where $Y = \{ C_b + 1 \} / C_b \}_n$.

The conversion in a series of reactors can be stepped off on a diagram that superficially resembles the classical McCabe-Thiele plot used in binary distillation calculations. For example, if the conversion of B in the first of a series of reactors is 66.7%, the conversion in the second will be 50.0%, in the third is 38.2%, and so on (Fig. 2).

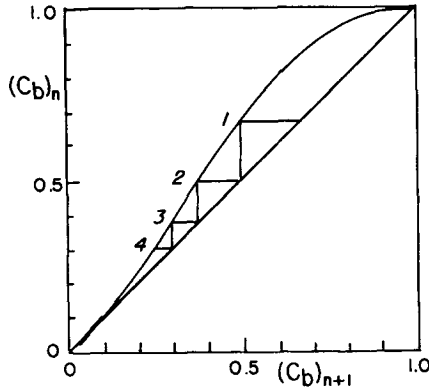


Fig. 2. Fractional conversion of component B (less rapidly used monomer) in a series of CSTRs as a recurrent relationship.

Recurrence Formula for Component A

If we assume that monomer A is used up faster than B, then it is necessary to add a quantity A'_{n-1} to each reactor in order to keep the ratio $(A/B)_n$ in each reactor constant. Because of this added quantity, eq. (10) will not apply for A. However, the conversion of A in each reactor can be calculated simply from the corresponding conversion of B. According to eqs. (4a) and (4b), the ratio of K_a/K_b determines the relationship between $(C_a)_n$ and $(C_b)_n$. If conversion of A and B are known in reactor 1, the ratio of K 's is fixed and

$$\left(\frac{1 - C_a}{C_a}\right)_n = \frac{K_a}{K_b} \left(\frac{1 - C_b}{C_b}\right)_{n+1} \quad (11)$$

or

$$(C_a)_n = \frac{1}{1 + (K_a/K_b)[(1/C_b)_n - 1]} \quad (12)$$

Thus, the conversion of A in any reactor can be calculated from the conversion of B which, in turn, is given by eq. (10).

Material Balances for Monomers

If the inputs A_0 and B_0 are known along with $(C_a)_1$ and $(C_b)_1$, then

$$A_1/A_0 = 1 - (C_a)_1 \quad (13)$$

and

$$B_1/B_0 = 1 - (C_b)_1 \quad (14)$$

For all subsequent reactors,

$$\frac{A_{n+1}}{A_n + A'_n} = \frac{A_{n+1}/A_n}{1 + (A'_n/A_n)} = [1 - (C_a)_{n+1}] \quad (15)$$

From eqs. (2) and (7),

$$(I_{n+1}/I_n)^{1/2} = A_{n+1}/A_n = B_{n+1}/B_n = [1 - (C_b)_{n+1}] \quad (16)$$

Eliminating the ratio A_{n+1}/A_n between eqs. (15) and (16) yields

$$\left(\frac{A'}{A}\right)_n = \left(\frac{1 - (C_b)}{1 - (C_a)}\right)_{n+1} - 1 \quad (17)$$

The amount of A to be added to each reactor A'_n is seen to be a function of the amount of A issuing from the previous reactor, A_n and the conversions in reactor $n + 1$.

As monomer is depleted from one reactor to the next, it is necessary to deplete the initiator concentration in such a way that the molecular size \bar{x} will remain constant according to eqs. (6) and (7). That is,

$$\left(\frac{I_{n+1}}{I_n}\right)^{-1/2} = \frac{B_n}{B_{n+1}} = \frac{1}{[1 - (C_b)_{n+1}]} \quad (18)$$

Also, we are assuming that some initiator I_n is added in each reactor. Within each reactor the initiator decomposes according to first order kinetics. For a space-time of τ , we have that

$$\frac{I_n + I'_n}{I_{n+1}} = 1 + k_d\tau \quad (19)$$

where k_d is the decomposition rate constant. But, eq. (18) can be rearranged to give

$$\frac{I_n}{I_{n+1}} = \left(\frac{1}{1 - (C_b)_{n+1}}\right)^2 \quad (20)$$

Because we assume I_n is a positive number, we can combine eqs. (19) and (20) as an *inequality* such that

$$k_d\tau \geq \frac{I_n}{I_{n+1}} - 1 = \left\{ \frac{(C_b)_{n+1}(2 - (C_b)_{n+1})}{(1 - (C_b)_{n+1})^2} \right\} \quad (21)$$

Another way of expressing the initiator's stability is in terms of its half-life, which is conventionally given as

$$t_{1/2} = (\ln 2)/k_d \quad (22)$$

and thus

$$t_{1/2} \leq \left(\frac{\tau(1 - (C_b)_{n+1})^2(\ln 2)}{(C_b)_{n+1}(2 - (C_b)_{n+1})} \right) \quad (23)$$

Since C_b decreases monotonically in a series of reactors, a necessary condition becomes that the half-life of the initiator has to be governed by the conversion of B in the *first* reactor ($n = 0$) and the space-time τ .

For example, if C_b in the first reactor is 0.667, then

$$k_d \geq 8.00/\tau \quad (24)$$

according to eq. (21), and the half-life is restricted correspondingly to

$$t_{1/2} \leq 0.0866\tau \quad (25)$$

If the half-life exceeds this value, it becomes impossible to maintain the same molecular size in each reactor unless there is some way of selectivity destroying some of the initiator that came from the previous reactor. It certainly would appear more convenient to arrange that the initiator be unstable enough to require addition at each stage rather than to try to reduce the concentration by addition of an inhibitor of some sort.

Example

Consider a series of reactors for which the following conditions apply:

Input to reactor 1. Monomer A, $A_0 = 5.00$ mol/s, monomer B, $B_0 = 3.00$ mol/s, initiator I, $I_0 = 2.25 \times 10^{-3}$ mol/s.

Reactor parameters. Space-time $\tau = 1.0 \times 10^4$ s, conversion of A, $(C_a)_1 = 0.800$, conversion of B, $(C_b)_1 = .667$. As calculated in the last section, the half-life for the initiator has to be less than 866 s [from eq. (23)]. An acceptable value is 770 s, in which case eqs. (19) and (22) indicate that there will be a tenfold decrease in concentration of initiator between input and output streams. It is necessary to add initiator I_n at each stage. Furthermore, we assume that the effluent conditions for reactor 1 specify the constant factors in eqs. (2)–(4).

The calculated results for reactor 1 are summarized in Table I. The factor K_a/K_b in eq. (11) is 0.500. The outputs from reactor 1 become the inputs to reactor 2. They are supplemented by monomer A_1 and initiator I_1 . The sequence of calculations is summarized in Table II. Conversions in reactor 2 are calculated. Then the supplemental monomer and initiator quantities can be calculated. The output parameters follow immediately. These become the inputs for the next stage, and so on. The flow sheet (Fig. 3) includes also the cumulative amount of monomer produced. The *overall* conversion increases with each stage, although the actual conversion in each reactor decreases.

The overall conversion (OC) is given by

TABLE I
Calculated Results for Reactor 1 Quantities (mol/s)

Input			
B_0	Given		3.00
A_0	Given		5.00
$I_0 \times 10^4$	Given		22.5
Output			
B_1	Eq. (14)		1.00
A_1	Eq. (13)		1.00
$I_1 \times 10^4$	Eq. (20)		2.25
$(P_a)_1$	Eq. (1a)		4.00
$(P_b)_1$	Eq. (1b)		2.00

TABLE II
Calculated Results for n Reactors^a

	Eqs. used	$n = 2$	$n = 3$	$n = 4$
Input parameters				
B_{n-1}	—	1.00	0.500	0.309
A_{n-1}	—	1.00	0.500	0.309
$I_{n-1} \times 10^4$	—	2.25	0.563	0.215
Conversion				
$(C_b)_n$	(10)	0.500	0.382	0.302
$(C_a)_n$	(12)	0.667	0.552	0.464
Added streams				
A'_{n-1}	(17)	0.500	0.191	0.093
I'_{n-1}	(19)	3.38	1.59	0.83
Output parameters				
B_n	(7)	0.500	0.309	0.216
A_n	(16)	0.500	0.309	0.215
$I_n \times 10^4$	(16)	0.563	0.215	0.105
$(P_a)_n$	(1a)	1.00	0.382	0.186
$(P_b)_n$	(1b)	0.500	0.191	0.093

^a Quantities in mol/s except conversions which are dimensionless.

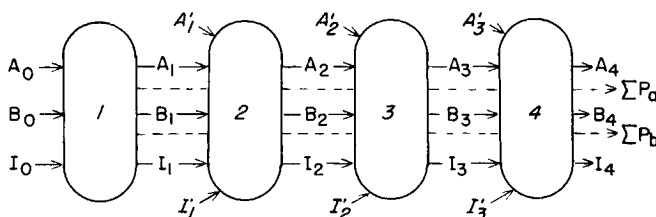


Fig. 3. The monomer, initiator, and polymer streams in a series of four CSTRs are summarized in Tables I-III.

$$(\text{OC}_a)_n = \left\{ \sum^n (\text{P}_a)_n \right\} / A_0 + \sum^n A_n \quad (26)$$

$$(\text{OC}_b)_n = \left\{ \sum^n (\text{P}_b)_n \right\} / B_0 \quad (27)$$

Through the use of four consecutive reactors, the overall conversion for monomer B is pushed to 93% and that for monomer A is 96% (Table III). A general plot of conversion vs. number of reactors (Fig. 4) indicates the importance of relatively high conversion in the first reactor. This plot is completely general for the component which is *not* supplemented. Under the assumptions made, the amount of monomer remaining unreacted is a function only of the conversion in the first reactor. Superficially, this resembles the case in which equalized CSTRs in series are used to approximate plug flow.¹⁴ However, the same equations do not apply because of the constraints placed on the copolymerizing system as opposed to a simple first-order system with decaying concentration.

Single CSTR vs. Series

In order to achieve high conversion and high molecular weight in a single CSTR, effluent conditions must be the same as those in a comparable series. If a single CSTR* (with all quantities denoted by an asterisk) is to equal the output of, say, the first three reactors in the example, then overall conversion of B* must be 90% [(C_b)* = 0.900] and so on. The output conditions for the single tank must be the same as those for reactor 3 of the series. Using the conversion of 90% and the initiator concentration of 0.215 × 10⁻⁴ in eq. (4) leads to a space-time for the single reactor of

$$\tau^* = \frac{K_b}{[(1/0.900) - 1][0.215 \times 10^{-4}]^{1/2}} = 1.94 \times 10^3 K_b$$

On the other hand, each stage of the series of reactors in the example requires the same space-time as the first in the series:

$$\tau = \frac{K_b}{[(1/0.667) - 1](2.25 \times 10^{-4})^{1/2}} = 0.134 \times 10^3 K_b$$

TABLE III
Fractional Conversion of Monomers

	Reactor (n)			
	1	2	3	4
Monomer A				
Incremental conversion (C _a) _n	0.800	0.667	0.552	0.464
Overall (cumulative) conversion (OC _a) _n	0.800	0.909	0.945	0.964
Monomer B				
Incremental conversion (C _b) _n	0.667	0.500	0.382	0.302
Overall (cumulative) conversion (OC _b) _n	0.667	0.833	0.897	0.927

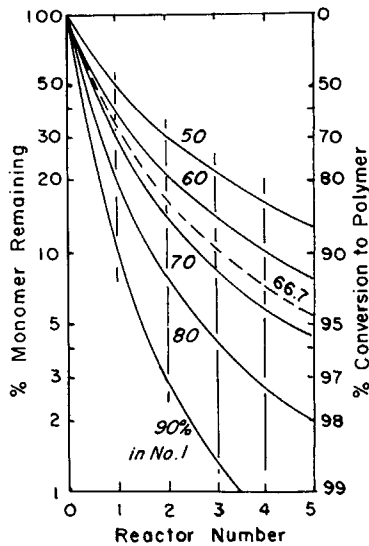


Fig. 4. Overall conversion of monomer B (less rapidly used monomer) in a series of CSTRs is a function of the conversion in the first reactor.

The single CSTR would have to be τ^*/τ , or 14.5 times as large as each of the series reactors. For example, instead of three 1000-L reactors in series, a single 14,500-L reactor would be required. The penalty paid for the smaller volume is the need for metering the supplemental monomer A and initiator I to two of the series reactors.

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