

## Multiple Steady States, Viscosity, and High Conversion in Continuous Free-Radical Polymerization

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### Synopsis

Using existing literature data on the rate of a bulk polymerization of styrene in a batch reaction carried to high conversion, it is mathematically demonstrated that there is a clear possibility of the existence of multiple steady states induced by viscosity effects in isothermal continuous stirred tank reactors. In solutions of high viscosity, the rate of free-radical polymerization increases with conversion, reaching a peak at very high viscosity, then falling off rapidly. Given this sort of behavior, it is demonstrated mathematically that steady-state mass balance solutions are possible at three levels of conversion. The lower and higher steady states are stable while the middle steady-state condition is shown to be necessarily unstable. This multiplicity of steady states with its particular problems of stability is analogous to the much studied phenomena of temperature stability. It is closely related to the problems of concentration stability characteristic of autocatalytic and heterogeneous catalytic reactions. This multiple steady-state problem is qualitatively discussed in relation to reactor stability, control, and optimization.

### INTRODUCTION

The use of a continuous stirred tank reactor (CSTR) for linear chain-growth polymerization reactions has much to offer with respect to control of product properties. Denbigh,<sup>1</sup> for example, has shown that in vinyl polymerizations a molecular weight distribution can be achieved with a CSTR which is much narrower than that with a comparable batch reactor (BR). In addition, it has been shown that molecular weight or copolymer composition can be controlled by appropriate changes in variables such as degree of mixing, feed rate, or composition.<sup>2-4</sup> However, the control of a polymerization at high conversion in a CSTR offers unique problems, some of which are discussed below.

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### Temperature Stability

Much has been written on the temperature stability of a CSTR.<sup>5</sup> The question of temperature stability arises when a finite control device is used to regulate reaction temperature. For a steady-state condition to prevail, it is necessary that the governing mass balance(s) and energy balance be satisfied or, in less abstract terms, that the heat generated by the reaction(s) equal the heat removed by the temperature control provisions of the system. Because of the nonlinear nature of these equations it is generally true that three or more solutions are possible. The problem of instability, in its most basic sense, arises when, for example, at a particular steady-state condition the rate of heat generation varies more with temperature than the rate of heat removal. Thus, for a slight rise in temperature above the steady state, the rate of heat generation might be greater than the rate of heat removal, and the temperature will continue to rise. Conversely, a slight drop in temperature results in a continued drop in temperature.

### Concentration Stability

Matsuura and Kato<sup>6</sup> have shown that, even under isothermal conditions, a similar stability problem arises in autocatalytic and heterogeneous catalytic reactions. Considering the autocatalytic reaction  $A \rightarrow B$  as an example, a mass balance for product B is

$$[B]/\theta = R_B \quad (1)$$

where  $R_B$ ,  $[B]$ , and  $\theta$  are rate of production of B, concentration of B, and CSTR holding time, respectively. The shape of the  $R_B$  curve is shown in Figure 1, plotted as a function of  $[B]$ . Apparent in this is the typical rate increase with product buildup and the subsequent decrease of  $R_B$  at an advanced degree of conversion. The curve  $[B]/\theta$  versus  $[B]$ , commonly referred to as an operating line, is plotted on the same axes as  $R_B$  in Figure 1. The result is a graphic solution of eq. (1).

Three solutions are apparent in this illustration, of which  $X$  and  $Z$  are stable and  $Y$  is unstable. To clarify this, consider the case where  $[B]$  is slightly below  $[B]_x$ . In this condition

$$R_B > [B]/\theta.$$

This means that B is produced ( $R_B$ ) faster than it is removed ( $[B]/\theta$ ). As a result,  $[B]$  increases to  $[B]_x$ . The reverse occurs when  $[B]$  is slightly above  $[B]_x$  because in that case

$$R_B < [B]/\theta.$$

This same behavior applies at  $[B]_z$ . At  $[B]_y$ , however, an unstable situation exists. When  $[B]$  is slightly above  $[B]_y$ ,

$$R_B > [B]/\theta$$

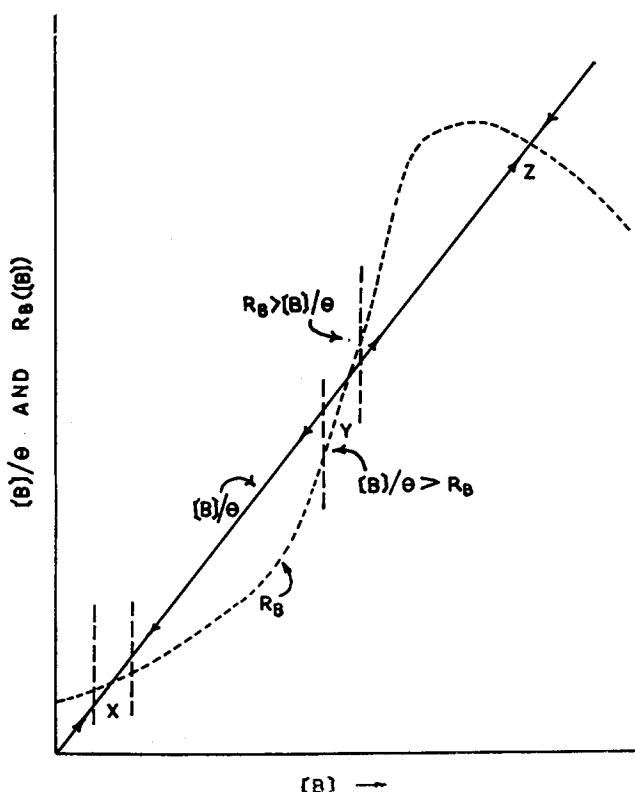


Fig. 1. Graphic solution of CSTR mass balance for autocatalytic reaction.

so that B is produced faster than it is removed. In this case  $[B]$  increases to stable point Z. Below  $[B]_y$ ,

$$R_B < [B]/\theta$$

product is removed faster than it is produced so that  $[B]$  decreases to point X.

### High-Conversion Free-Radical Polymerization

In this paper it is intended to show that a very similar set of phenomena apply to high-conversion free-radical polymerizations. This class of reactions is in a sense very similar to the autocatalytic case in that a reaction-accelerating effect, commonly referred to as the gel effect, is produced by the increase in viscosity accompanying the buildup of high polymer in the reaction mixture. The final stage of the polymerization is marked by a sudden decrease in rate to zero before 100% conversion is reached.

As a result of the work of Norrish and Smith,<sup>7</sup> it is well known today that the gel effect in polymer reactions is due to a decrease in the mobility of long-chain radicals with increasing viscosity and that as a result the termination reaction, being diffusion controlled at that stage, is greatly restricted.

The classical rate expression for catalyzed polymerization with first-order decay of initiator is

$$R_p = k_p[M][P_T] = k_p[M] \left( \frac{fk_d[I]_0 \exp(-k_d t)}{k_t} \right)^{1/2} \quad (2)$$

where  $[M]$ ,  $[P_T]$ ,  $[I]_0$  are concentrations of monomer, free radicals, and initial initiator, respectively, and  $k_p$ ,  $k_t$ , and  $k_d$  are rate constants for propagation, termination, and initiator decomposition, respectively, and  $f$  is the initiator efficiency.

Equation (2) shows that a decrease in  $k_t$ , accompanying an increasing viscosity, results in an increase in  $[P_T]$ , which in turn produces an accelerated rate of reaction. Unfortunately the situation at advanced levels of conversion is much more complex.<sup>8</sup> It is in fact the case that, even if variation of  $k_t$  is accounted for, eq. (2) does not apply with accuracy in a mechanistic sense in highly viscous media. The inconsistencies arise from the breakdown of the steady-state assumption in cases where  $[P_T]$  increases in an accelerating fashion; from the uncertainty of the usual second-order termination mechanism as an accurate descriptor; and, in general, from the increasing significance of side reactions (especially transfer reactions) involving small species as the mobility of macromolecular species becomes restricted. It has been observed, for example, that in viscous media there is an important increase in the yield of primary radical recombination products (cage effect), effecting a reduction in initiator efficiency with increasing viscosity.<sup>8</sup> Indeed, one chief recombination product is the initiator molecule itself. This means that, in addition to the decrease in  $f$ , there is a decrease in the net rate of initiator decomposition or, in parametric terms, a decrease in  $k_d$ . In general there is observed an increasing relative role of reactions of small species and a decreasing relative role of reactions of large species.

The final decrease in rate usually observed is not clearly understood. There is evidence<sup>8</sup> of a large decrease in  $k_p$ , suggesting inaccessibility of radical chain ends and diffusion control of propagation, yet the diffusion coefficients of monomers in polymeric networks are so high in relation to typical propagation rate constants that diffusion control of the propagation reaction might be untenable.<sup>9</sup> At the same time there is, at this stage of the reaction, evidence of nearly complete immobility of radical chain ends,<sup>8,10</sup> suggesting a form of "living polymer." One might speculate that termination at very high conversion may be a sort of residual reaction attributable mainly to primary radical termination and other transfer reactions.

## VISCOSITY STABILITY IN CSTR POLYMERIZATION

### CSTR Mass Balance

In order to apply the above considerations to CSTR operation, it is necessary to apply a steady-state mass balance to the monomer component, as follows:

$$0 = \frac{[M]_0 - [M]}{\theta} - k_p[M] \left( \frac{fk_a[I]_0}{k_t(1 + \theta k_a)} \right)^{1/2} \quad (3)$$

where  $[M]_0$  is the monomer concentration in the CSTR feed. Using the definition for fractional conversion,  $m$ ,

$$m = ([M]_0 - [M])/[M]_0,$$

eq. (3) may be written

$$m/\theta = R_p. \quad (4)$$

Since no experimental data on very high viscosity CSTR operation are presently available, the rate data required in eq. (4) have been derived from indirect sources. The  $R_p$  versus  $m$  data for Figures 2 and 3 were adapted from Nishimura's BR data on bulk polymerization of styrene at 60°C using 0.05 mole/l. AIBN.<sup>10</sup> This was done by making a correction for the inconsistencies in initiator concentration due to differences in reaction times for BR and CSTR operation. Since the rate of initiator (AIBN)

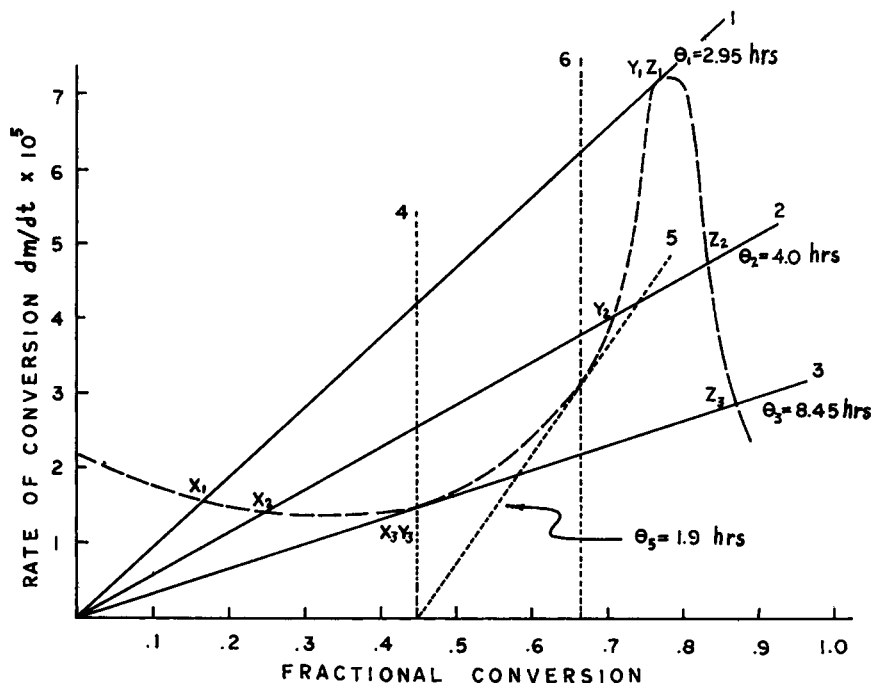


Fig. 2. Graphic solution of CSTR mass balance for high viscosity polymerization of bulk styrene at 60°C with 0.05 mol/l AIBN<sup>10</sup>. Solutions are shown for operating lines 1, 2, and 3, representing unrecycled CSTRs with holding times of 2.95, 4.0, and 8.45 hr. Recycled CSTRs are represented by operating lines 4, 5, and 6. Operating lines 4 and 5 represent the range of holding times possible ( $\theta = 0$  to 1.9 hr) with a recycle of  $m_0 = 0.45$ . Operating lines 5 and 6 represent the range of recycle possible ( $m_0 = 0.67$  to 0.45, with  $\theta = 0$  to 1.9 hr for operating lines 5 and 6, respectively) for CSTRs operated at  $m = 0.67$ .

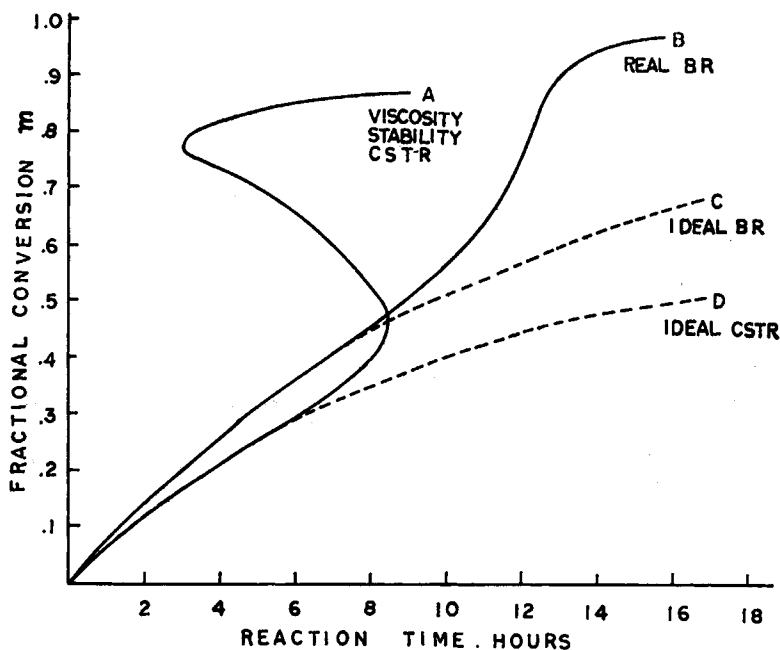


Fig. 3. Comparison of reaction paths ( $m$  vs.  $t$ ) for ideal and nonideal BRs and CSTRs.

decomposition is so small ( $k_d \sim 10^{-5}$ ), the correction is significant only where there are great differences in reaction times. It is conceded that this type of adaptation is not rigorous since it ignores the effect that rate of initiation has on chain length and, in turn, on viscosity and other reaction parameters such as  $k_t$ ,  $f$ ,  $k_d$ , and  $k_p$ . Furthermore, a concession must be made to the fact that fundamental differences in molecular weight distribution and average molecular weight, as described by Denbigh,<sup>7</sup> also affect important reaction parameters. These basic differences between CSTR and BR operation are ignored in the adaptation used here because of the lack of a suitable relation between chain length and reaction parameters. The procedure, however, is sufficient to illustrate the concepts of interest here.

The left and right sides of the steady-state mass balance eq. (4) are plotted as functions of conversion in Figure 2; and, as in the case of concentration stability in Figure 1, points of intersection represent steady-state conditions. Three steady states are apparent for all values of  $\theta$  over a range from 2.95 to 8.45 hr. As in the earlier result (Fig. 1), points  $X_t$  and  $Z_t$  are stable and points  $Y_t$  are unstable. The explanation is analogous to that given previously for autocatalytic reactions in general, except that the graphic representation has been done in terms of fractional conversion of monomer rather than product concentrations. Curves for holding times  $\theta_1$  and  $\theta_2$  represent upper and lower limits of steady-state multiplicity. In the former case (curve  $m/\theta_1$ ),  $X_1$  is a stable condition, but at point  $Y_1Z_1$

any perturbation of effective conversion results in a condition where the rate at which monomer is supplied is greater than its rate of consumption. The result is an instability where a decremental perturbation in  $m$  leads to a decrease in effective conversion to point  $X_1$ . Operation of a CSTR at a point  $Z$  near  $Y_1Z_1$  entails the risk of encountering this quenching phenomenon if  $\theta$  falls below  $\theta_1$ . Along curve  $m/\theta_3$ , the point  $X_3Y_3$  represents an unstable situation where any incremental perturbation in effective conversion results in monomer consumption exceeding monomer supply rate so that conversion advances to point  $Z_3$ . In practical application, such a response in this region near  $X_3Y_3$  could result, if unchecked, in viscosities increasing beyond the design limits of the reactor, even to the extent that flooding the reactor with monomer would not break up the resulting viscous mass.

As a supplement to the data of Figure 2, the viscosities measured by Nishimura<sup>10</sup> are listed in Table I. Viscosity increases rapidly from 24.3 poises at 51% conversion to about 14,500 poises at the peak of the rate curve where conversion is approximately 78%. Beyond this point,  $R_p$  drops sharply and viscosity increases dramatically to 67,000 poises at 82% conversion. We believe that CSTR operation in modified form is practiced for viscosities as high as  $10^4$  poises. It is conceivable, therefore, that in some cases, with specially designed reactors, it may be possible to operate a CSTR in stable region  $Z$ .

TABLE I  
Viscosity as a Function of Conversion in the Bulk Polymerization of Styrene at 60°C  
Using 0.05 mole/l. AIBN<sup>a</sup>

Fractional conversion	Viscosity, <sup>b</sup> centipoises	Fractional conversion	Viscosity, <sup>c</sup> poises
0.035	1.11	0.51	24.3
0.057	1.75	0.55	59.1
0.084	2.82	0.59	103.8
0.118	4.57	0.63	281.
0.168	8.57	0.67	1059.
0.202	13.9	0.74	3810.
0.258	27.0	0.76	14446.
0.294	42.2	0.82	67000.
0.343	80.9		
0.393	162.		
0.446	364.		
0.503	906.		

<sup>a</sup> From Nishimura.<sup>10</sup>

<sup>b</sup> Capillary method.

<sup>c</sup> Falling-ball method.

### CSTR and BR Conversion-Time Curves

Using eq. (4) and the CSTR rate data of Figure 2, the  $m$  versus  $\theta$  curve for a CSTR was calculated (curve B) as the locus of all possible intercepts

such as  $X$ ,  $Y$ , and  $Z$  in Figure 2. The results are shown in Figure 3 along with the batch reactor data (on curve A) from which it was derived. On the same axes, for comparison, are curves C and D, for batch and CSTR operation, which were calculated using ideal eqs. (2) and (3), respectively, and the apparent initial values of  $k_p$ ,  $k_d$ ,  $f$ ,  $k_t$ , and  $[I]_0$  of the real styrene system under study here.

Curves C and D, the idealized counterparts of curves A and B, illustrate the relative behavior of the batch and CSTR systems in the assumed absence of the gel effect. With first-order reactions,  $R_p$  (slope) decreases monotonically with time in both cases, and the batch operation is clearly superior with respect to reaction time. (The steady state assumption used in the ideal rate expressions lends pseudo-first-order character to the conversion-time curves. The decrease in  $[P_T]$  due to depletion of  $[I]$  is usually very slow.)

When the gel effect is considered (as it must be in actuality), the relation between batch and CSTR curves A and B is quite different. Most important is the reversal of the CSTR curve at 8.45 hr. As previously noted in Figure 2, for holding times between 2.95 and 8.45 hr, three steady states are possible of which the highest and lowest are stable and the middle is unstable. In the unstable region, conversion is greater at lower holding times, and the reaction time for a given level of conversion is much less than for the equivalent batch reactor. Although batch operation appears superior with respect to reaction time in the lower stable region, this is not the case with all systems. In general, systems with a more pronounced gel effect will often result in CSTR rates which are equal to or greater than equivalent batch rates in the lower stable region.

### Reaction Behavior and Reactor Configuration

In view of this behavior it is important to note that the usual methods of increasing CSTR capacity are not always effective for polymerization reactions. For example, the use of a series of CSTRs to increase overall reaction rate is effective only where  $R_p$  decreases with conversion. In polymerization reactions, however, the decrease in reaction rate, normally observed in most other types of reactions as reactants are depleted, is cancelled to varying degrees by the gel effect. As a result, the use of CSTRs in series is not always an effective means of increasing reactor capacity. In many cases, where polymerization rate increases with conversion, a single CSTR is superior to batch operation, and use of a series actually diminishes reactor capacity. In addition, it is often possible to utilize the increase in rate caused by the gel effect to a great extent by using a single CSTR and recycling a portion of its output. This possibility was recognized by Hui and Hamielec<sup>11</sup> in a computer study of the free-radical polymerization of styrene in a series of three CSTRs. This work was based on an experimentally well-verified correlation of kinetic behavior with viscosity.



Figures 4a, b, and c show typical polymerization rate curves with operating lines of the form

$$(m - m_0)/\theta = \text{monomer feed rate}$$

where intercepts  $m_0$  represent polymer introduced in the reactor feed. These operating lines may be interpreted as representing CSTRs in series or as individual CSTRs with recycle of polymer.

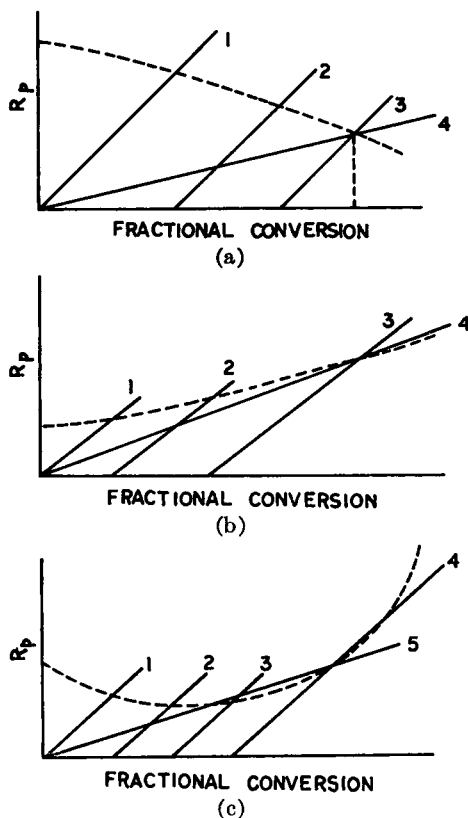


Fig. 4. The relationship between optimum reactor configuration and reaction behavior: (a) graphic solution for CSTR series and equivalent single CSTR where  $R_p$  decreases with  $m$ ; (b) graphic solution for equivalent series, recycled and single CSTRs where  $R_p$  increases with  $m$ ; (c) graphic solution for equivalent series, recycled and single CSTRs where  $R_p$  decreases initially then increases.

If the solvent concentration in solution polymerization is sufficiently high, the gel effect may be suppressed to the extent that no increase in polymerization rate occurs. This situation, typical of methyl methacrylate polymerization with greater than 40% or 50% solvent and styrene polymerization at greater than 20% or 30% solvent, is illustrated in Figure 4a.

Operating line 4 in Figure 4a represents a single CSTR operating at the same level of conversion as series 1-2-3, represented by operating lines 1, 2, and 3. Since the two reactor systems function over a region of decreasing rate of polymerization, it is necessarily true that, while CSTR 3 of series 1-2-3 and CSTR 4 operate at identical reaction rates, CSTRs 1 and 2 operate at higher rates. Consequently, the overall rate of polymerization of series 1-2-3 is greater than that of CSTR 4. In general, for a series of  $N$  (including  $N = 1$ ) CSTRs operating over a region of decreasing reaction rate up to a given level of conversion, the greater the number in series the greater the overall reaction rate. (The limiting case of an infinite series is equivalent to a BR.) The advantage to be gained by using a series of CSTRs for a given reaction system depends on the decrease in reaction rate with conversion. Clearly, if there were no decrease in rate and if the rate were nearly constant, then the single CSTR, the series, and the BR would all give nearly identical results. This is a very important consideration in polymerization reactions since frequently the gel effect offsets or reduces the normal tendency for the rate of polymerization to decrease with consumption of monomer.

At the other extreme, the gel effect may be so strong that the rate of polymerization increases from the start. This situation, typical of the bulk polymerization of methyl methacrylate, is illustrated in Figure 4b. Operating line 4 in Figure 4b represents a single CSTR operating at the same level of conversion as series 1-2-3, represented by operating lines 1, 2, and 3. Since CSTR 3 of series 1-2-3 and CSTR 4 operate at identical reaction rates and since CSTRs 1 and 2 of series 1-2-3 operate at lower rates, it is clear that the rate of CSTR 4 is greater than the overall rate of series 1-2-3. In general, by means of similar arguments, it may be shown that a single CSTR will outperform any series of  $N$  CSTRs when compared on the basis of operation over a region of increasing reaction rate up to a given level of conversion. It is, in fact, true that the larger the number  $N$  of reactors in series, the lower the overall rate. Thus, a single CSTR ( $N = 1$ ) is an upper limit on reactor capacity and, since  $N = \infty$  is equivalent to batch operation, the BR is a lower limit as  $N$  approaches infinity. The recycled CSTR, represented by operating line 3, operates at the same rate as CSTR 4; but since the holding time  $\theta$  (as shown by the slopes of the operating lines) of CSTR 3 is less than that of CSTR 4, the net conversion of CSTR 3 is lower than that of CSTR 4.

Figure 4c represents a commonly observed polymerization rate behavior. It is a combination of the cases illustrated in Figure 4a and 4b with the importance of each part dependent on the particular reaction system and conditions. The data used in Figure 2 for the bulk polymerization of styrene at 60°C with 0.05 mole/l. AIBN<sup>10</sup> are a good example of this behavior.

The principles set forth in the preceding discussion of the rate curves in Figures 4a and 4b also apply, within limits, to the rate curve in Figure 4c. A series of CSTRs is most effective in the region of decreasing rate prior to the rate increase (up to CSTR 3). Beyond this point the value of series

operation diminishes and single CSTR operation, with or without recycle becomes an effective means of increasing reactor capacity. It is clear, for example, that the recycled CSTR represented by operating line 4 is superior to CSTR series 1-2-3-4. Operating line 5 represents a single unrecycled CSTR equivalent in conversion to CSTR 4. Clearly, based on the earlier discussion of stability, CSTR 5 is unstable at the conversion level of interest. The recycled CSTR 4, on the other hand, is stable and is superior in rate to any other reactor configuration at that conversion. Furthermore, by using recycles with higher  $m_0$  and lower  $\theta$ , it is possible to operate with stability even higher on the rate curve. Operating line 6 represents an extreme example of this. The difficulty in following this procedure is that the lower  $\theta$ 's required result, in the limit, in a differential reactor with differential output. In order to increase reactor capacity further, one is faced with the remaining alternative of operation of unstable CSTRs.

### Recycled CSTR Operation

Operating lines 4 and 5 of Figure 2 show the holding times possible (0 to 1.9 hr) with a recycle such that the entering feed is a 45% solution of polymer in monomer ( $m_0 = 0.45$ ). (The discrepancies in initiator concentrations and viscosities arising from application of the  $R_p$  data of a single CSTR to a CSTR with recycle has been neglected throughout this section. This simplifies the presentation but does not seriously affect the results.) As with operating line 3, for unrecycled CSTR operation, the maximum holding time for stability is determined by the point of tangency of the operating line and the rate curve. An increase in holding time beyond  $\theta_s$  or  $\theta_c$  eliminates the multiplicity of steady states leaving only the possibility of steady states along the decreasing  $R_p$  region of the rate curve where viscosity is extremely high ( $>67,000$  poises). Operating line 5 shows that rates as high as 1.5 times the initial rate ( $R_p^0 = 2.1 \times 10^{-5} \text{ sec}^{-1}$ ) are possible by operating at  $m = 0.67$  with a 45% polymer recycle.

For CSTR operation at a particular conversion (e.g.,  $m = 0.67$ ), rather than at a particular recycle, the net conversion ( $m - m_0$ ) is determined by the amount of recycle ( $m_0$ ) and the holding time used. Curves 5 and 6 represent the range of net conversion possible for operation at  $m = 0.67$ . Curve 6 represents zero net conversion for recycled operation at  $m = 0.67$  where  $\theta = 0$  and  $m_0 = m$ . The maximum net conversion is represented by operating line 5, the tangent to the rate curve at  $m = 0.67$ . This operating line is the line of maximum holding time and minimum recycle for operation at  $m = 0.67$ . In this case the maximum net conversion is 0.22 ( $m - m_0 = 0.67 - 0.45$ ).

### Unsteady-State CSTR Operation

In view of the extremely high reaction rates in the unstable CSTR region, it is tempting to consider the possibility of reactor operation under those conditions. One possibility is the use of an oscillating monomer feed

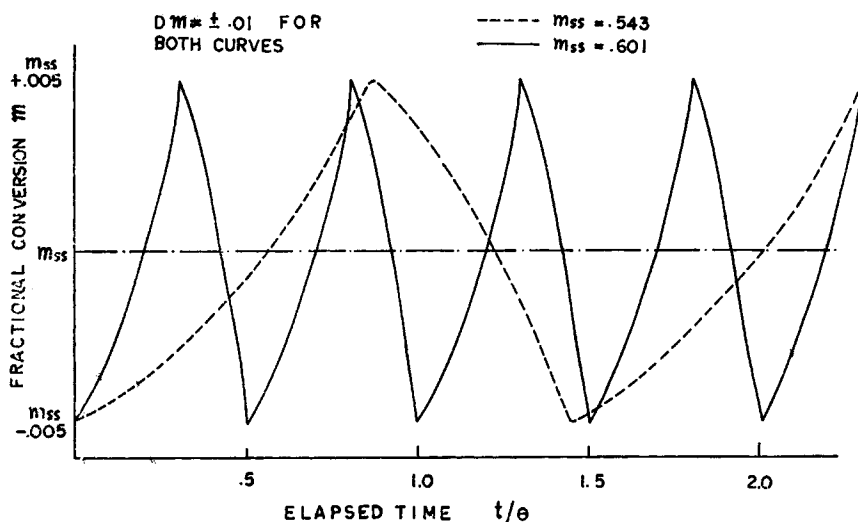


Fig. 5. Variation of conversion in an unstable CSTR operated with programmed oscillating feed. The result for  $m_{ss} = 0.601$  illustrates the higher degree of instability at higher conversions and the effect of this on the period of feed oscillation. Calculations are based on the polymerization of styrene at  $60^\circ\text{C}$  with 0.05 mole/l. AIBN.<sup>10</sup>

with amplitude and period calculated to control conversion within predetermined limits  $m_{ss} \pm Dm$ . With feed rate adjusted for a steady state of  $m_1$ , at  $\theta$  (where  $m_{ss} > m > m_1$ ) conversion is allowed to drift upward away from  $m_1$  until  $m_{ss} + Dm$  is reached. At that point, the monomer feed is increased so that an effective steady state of  $m_2$  ( $m_{ss} < m < m_2$ ) at  $\theta_2$  is achieved. Due to the instability at  $m_2$ ,  $m$  will decrease to  $m_{ss} - Dm$ . At this point, the flow rate is again adjusted for a steady state of  $m_1$ , and the cycle is repeated.

Calculations based on this scheme (Fig. 5) show control periods varying within the very reasonable limits of  $1/2$  to 2 holding times depending on the driving force used to control the drift (i.e.,  $m_1$  and  $m_2$ ), the control limits ( $\pm Dm$ ), and the degree of instability at the point of control. Points in the nearly vertical segment of the  $R_p$  versus  $m$  curve may be very unstable. The rate of drift between  $m_{ss} \pm Dm$  is high for unstable steady-state conditions in this region. It is possible, however, to reduce a degree of instability by using a recycled CSTR whose  $(m - m_0)/\theta$  curve is more nearly parallel to the  $R_p$  curve at the point of control than a corresponding unrecycled  $m$  versus  $\theta$  curve.

### CONCLUDING REMARKS

The above is intended as an introduction to the concept of viscosity stability in free-radical polymerization. Thorough application of this concept requires consideration of additional problems.

For example, it should be noted that increasing reactor capacity in the manner described above not only makes existing reaction processes seem more attractive but also makes possible some reactions which normally are so slow as to seem impractical. An example of this is the copolymerization of monomer pairs which are kinetically incompatible, such as methyl methacrylate and vinyl acetate ( $r_1/r_2 = 20./0.015$ ). The copolymerization of this pair becomes extremely slow at low mole fractions of methyl methacrylate.<sup>2,12</sup> By operating a CSTR in the unstable high-rate portion of the rate curve, reasonable levels of conversion are possible.

Further work in the laboratory is aimed at clarifying the implications of viscosity stability with respect to such aspects as the influence of important kinetic parameters, temperature stability, mixing, and reactor configuration.

### Notation

[B]	concentration of product B
[B] <sub>x</sub> , [B] <sub>y</sub> , [B] <sub>z</sub>	concentrations of product B at specific CSTR steady states X, Y, and Z
<i>Dm</i>	CSTR control parameter for steady state maintained within the conversion limits of $m \pm Dm$
<i>f</i>	initiator efficiency
[I]	concentration of initiator, moles/l.
[I] <sub>0</sub>	concentration of initiator at start of reaction, moles/l.
<i>k<sub>d</sub></i>	rate constant for first-order initiator decomposition, sec <sup>-1</sup>
<i>k<sub>p</sub></i>	rate constant for propagation, l./mole-sec
<i>k<sub>t</sub></i>	rate constant for termination, l./mole-sec
<i>m</i>	fractional conversion based on monomer consumption
<i>m<sub>0</sub></i>	fractional conversion of monomer in CSTR feed material
<i>m<sub>ss</sub></i>	fractional conversion of monomer at a specific steady state
[M]	concentration of monomer, moles/l.
[M] <sub>0</sub>	concentration of monomer at start of reaction or in CSTR feed, moles/l.
[P <sub>T</sub> ]	concentration of free radicals, moles/l.
<i>R<sub>B</sub></i>	rate of production of product B, moles/l.·sec
<i>R<sub>p</sub></i>	rate of monomer consumption, moles/l.·sec
<i>t</i>	time, sec
$\theta$	CSTR holding time, sec or hr

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