Bulk Copolymerization of Styrene-Acrylic Esters: Some Analysis and Design Considerations

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A common framework for the analysis of styrene-acrylic ester systems has been developed by analyzing the pertinent kinetic information. This is shown to lead to a well defined strategy for the design of copolymerization reactors especially in the industrially relevant high conversion region. The existence of stable steady states and its influence on the system parameters has been illustrated for the case of a continuous stirred tank reactor (CSTR). A novel strategy of a CSTR operated with a recycle is proposed. This is shown to lead to an operation in the unique steady state with the added advantage of a high conversion and uniform copolymer composition. This would seem to be the first such analysis in the high conversion region.

INTRODUCTION

The use of a continuous stirred tank reactor (CSTR) for free radical polymerization reactions has much to offer with respect to control of product properties (1-3). The design of such a reactor for copolymerization of monomers requires a thorough understanding of the rate processes for the basic steps of initiation, propagation, and termination. At low conversion, the propagation and termination processes are essentially independent of conversion. At high conversion, with the onset of the gel effect, the propagation and termination processes show considerable deviations with the extent of conversion. The ensuing non-linearities make the problem a very complex one to analyze and yet it is this very region that is of industrial significance.

A look at the existing literature on copolymerization in a CSTR (for instance, 4, 5) shows that the dependence of the rate processes on the extent of conversion in the reactor has been generally ignored and the analysis is simplified. Also the theoretical analysis is mostly restricted to specific systems and, therefore, the results cannot be generalized.

It is apparent that a more general and comprehensive methodology for the analysis of a copolymerization CSTR, operating at high levels of conversion, for a sufficiently wide class of reacting systems is lacking. This gap was the motivation behind the present work. More specifically, the copolymerization of styrene with acrylic esters is considered as an example to present the methodology of analysis and design.

In this paper we have developed a sufficiently general model, which presents an improvement over the prior art in two ways. Firstly, it can be applied over a much wider range of conversions and, secondly, it can be applied to copolymerization reactions of styrene with

any of the acrylic esters. We have explored the model further to point out some novel features that arise out of operating the CSTR with recycle. We show that significant improvements in conversion and in uniformity of the product composition can be obtained.

KINETIC MODELS FOR COPOLYMERIZATION

The three important kinetic models reported in the literature for the free radical copolymerization are (1) ϕ factor model, (2) diffusion model and, (3) penultimate effect model. The salient features of these three models will be discussed briefly to justify the final choice of the model made in this work.

ϕ Factor Model

The overall rate of copolymerization depends on the relative rates of initiation, propagation, and termination of the monomer radicals. Dostal (6) was the first to devise a copolymerization reaction scheme by assuming that the rate of addition of a monomer to growing free radicals depends only on the nature of the radical chain end. Subsequently, Mayo and Walling (7) added the quasi-steady state assumption to Dostal's reaction scheme and derived the overall polymerization rate as:

$$R_p = \frac{(r_A C_A^2 + 2C_A C_B + r_B^2)R_K^{1/2}}{[(r_A \delta_A C_A)^2 + 2\phi r_A r_B \delta_A \delta_B C_A C_B + (r_B \delta_B C_B)^2]^{1/2}} \quad 1/2$$

where

$$r_A = k_{PAA}/k_{PAB}$$

$$r_B = k_{PBB}/k_{PBA}$$

$$\delta_A = (2k_{tAA}/k_{PAA}^2)^{1/2}$$

$$\delta_B = (2k_{tBB}/k_{PBB}^2)^{1/2}$$

$$\phi = k_{tAB}/2(k_{tAA} \cdot k_{tBB})^{1/2}$$

$$R_K = 2fk_d C_k \text{ and } C_K = C_{Kf}\theta^{-k_d t}$$

(1)

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Thus, in the classical terminal model described by *Eq 1*, seven rate constants for chain growth and termination have been reduced to five relative rate groups. r_A and r_B are the reactivity ratios, and they define the rate constants for a given chain end adding to its own monomer relative to that of the same chain end adding to the other monomer. δ_A and δ_B contain the rate constants of individual monomers in homopolymerization and ϕ is a measure of the cross termination reaction, being the ratio of the rate constant for cross termination to the geometrical mean of the rate constants for symmetrical termination.

Equation 1 is expressed in terms of the individual rates of reacting monomers as:

$$R_A = \frac{-dC_A}{dt} = k_A C_A C_K^{1/2} \text{ for monomer A} \quad (2)$$

$$R_B = \frac{-dC_B}{dt} = k_B C_B C_K^{1/2} \text{ for monomer B} \quad (3)$$

In *Eqs 2* and *3*, k_A and k_B are the apparent rate constants. These are given by

$$k_A = [(r_A - 1)x + 1]/T_1^{1/2} \quad (4)$$

and

$$k_B = [(1 - r_B)x + r_B]/T_1^{1/2} \quad (5)$$

where

$$x = \frac{C_A}{(C_A + C_B)} \quad (6)$$

$$T_1 = T_c/(2fk_d) \quad (7)$$

and

$$T_c = (r_A \delta_A x)^2 + 2\phi r_A r_B \delta_A \delta_B x(1 - x) + [r_B \delta_B(1 - x)]^2 \quad (8)$$

The parameter T_1 in *Eqs 4* and *5* involves the constants corresponding to the termination rate processes.

Diffusion Model

Benson and North (8) suggested that the termination reaction in many free radical polymerizations does not depend on chemical reactivities but on physical processes. They assumed a three stage consecutive process, in which the first two steps (translational diffusion and segmental rearrangement) are diffusion controlled and are followed by the chemical reaction. They have proposed an empirical equation describing the overall polymerization rate for diffusion controlled systems.

Penultimate Effect Model

Russo and Munari (9) proposed the penultimate effect model for copolymerization. The model postulates that the polar and steric characteristics of a chemically controlled termination process depends upon the nature of the last four carbon-carbon bonds in each chain involved. Thus, for vinyl comonomers with two carbon atoms per repeat unit, ten termination steps are distinguishable.

The penultimate effect model alone accounts for the influence of temperature variations on cross termination reactions and, hence, has a considerable merit.

However, the requisite data for individual model parameters are scanty. Further, this model is more complex and its validity at high conversion levels is yet to be experimentally confirmed. Likewise, the chain propagation and termination constants for the diffusion model have not yet been accurately determined for many monomers. As against this, the relative rate groups for the ϕ factor model are well reported in the literature and, therefore, the model can be used with greater reliability. It has been shown by Sebastian and Biesenberger (10) that with appropriate assumptions, the diffusion model and the penultimate effect model reduce to those for the geometric mean or the ϕ factor model. There appears to be a considerable merit in using the ϕ factor model and this model will be used throughout this work.

COPOLYMERIZATION OF STYRENE AND ACRYLIC ESTERS—DEVELOPMENT OF SOME GENERALIZED CORRELATIONS

Variation of ϕ Factor with the Composition of Monomer Feed

The contrast in polarity and resonance stabilization between styrene and acrylic esters has made this combination a particularly interesting one for studies of copolymerization mechanism and kinetics. The copolymerization rates lie in between these of the homopolymerization of individual monomers, although the rate is reduced to a much greater extent by the addition of a small amount of styrene to the acrylic ester than it is increased by the addition of a small amount of acrylic ester to styrene.

The rate of termination of unlike radicals is considerably greater than the termination of like radicals, as expressed by the ϕ factor in *Eq 1*. The ϕ factor increases with increasing styrene in the monomer mixture. The increase is relatively minor with methyl acrylate and methacrylate but is quite pronounced with butyl acrylate as shown in *Fig. 1*. The experimentally reported variations of ϕ [as calculated from the reported values of
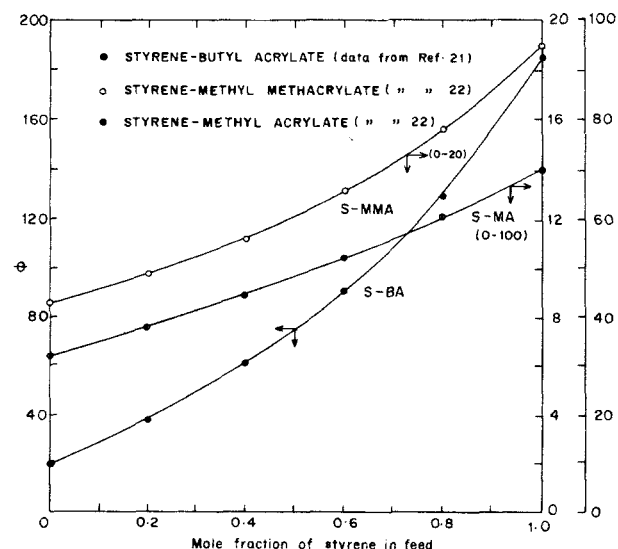

Fig. 1. Variation of ϕ with the composition of the monomer feed for styrene acrylate esters.

rate (11, 12)] with composition of styrene has been correlated by us and represented by the following equation:

$$[(1 - x)\beta + r_A x]/[(1 - x) + r_A x] = \frac{\phi}{\phi_{max}} \quad (9)$$

where ϕ_{max} is the maximum value of ϕ and r_A is the reactivity ratio of monomer A.

Note that in the asymptotic range for $x = 0$ and $x = 1$ we obtain

$$\phi/\phi_{max} = \beta, \ x = 0 \quad (10)$$

and

$$\phi/\phi_{max} = 1, \ x = 1 \quad (11)$$

The values of β and ϕ_{max} deduced by us for various systems are reported in *Table 1*. According to Bonsall, *et al.* (13), the entropy factors also contribute largely to the enhanced rate of interaction of unlike radicals. The values of $[\Delta S_{12} - (\Delta S_1 - \Delta S_2)/2]$ calculated by them for styrene-acrylic ester combinations are also given in *Table 1*. It is interesting to note that the magnitude of the entropy term is approximately the same in each case. This is perhaps to be expected since all the systems are of the same general type with a styrene-acrylate interaction.

Variation of the Relative Rate Groups with Conversion Trommsdorff or Gel Effect

Many vinyl monomers display a linear decrease of the overall reaction rate, (R_p) with conversion according to a first order process with respect to monomer concentration. However, at higher conversion, R_p rises again, reaches a maximum and then decreases. As Trommsdorf (14) and many others (15, 16) have shown, the effect is likely to be caused by the diffusion control of the termination reaction. Apparently, this is determined by the diffusion of the macromolecules, but the diffusion of the chain segments controls the numerical value of the termination processes. Decreasing rate of termination causes an increase in the concentration of radicals and induces a change in the relative rate groups with conversion.

Variation of r_A and r_B with Conversion

The viscosity is believed not to be high enough to prevent much smaller monomer molecules from moving relatively freely through the reaction mixture so that they are still able to continue to add to the active ends of the growing macroradicals in a manner which does not

Table 1. Estimated ϕ_{max} and β Values (for Eq 9) and the Reported Entropy Values for Styrene-Acrylic Esters

Monomer Pair	ϕ_{max}	β	$[\Delta S_1 - (\Delta S_1 + \Delta S_2)/2]$ Cal/mole °K [Ref. 13]
Styrene-Methylmethacrylate	19	0.4421	3.78
Styrene-Methyl acrylate	70	0.45	3.83
Styrene-Butyl acrylate	185	0.1	3.92

affect the rate of elementary propagation reaction, (k_p) since its values are smaller than the values of k_t by a factor of 10^4 to 10^5. However, in the copolymerization of styrene with acrylic esters, the steric effect restricts the mobility of styrene, especially in the highly viscous medium and leads to a decrease in r_A with an increase in r_B.

From the available kinetic data for the systems styrene-methylmethacrylate (17, 18) and styrene-acrylonitrile (19), and using *Eqs 4* and *5*, we calculated the reactivity ratios. The computer program of Montgomery and Fry (20) was utilized. We propose to correlate these data by a polynomial form of the following kind:

$$r_A = r_{Ao} + \sum_{i=1}^{i=n} a_i(m - m_g)^i \quad (12)$$

and

$$r_B = r_{Bo} + \sum_{i=1}^{i=n} b_i(m - m_g)^i \quad (13)$$

where m_g and m are the extents of conversion at the gel point and in the post gel point region. For simplicity we terminate the series at $i = 3$. Further by definition $a^+ m \le m_g$. The values of r_A and r_B equal those before the onset of gel effect, viz. r_{Ao} and r_{Bo} respectively. The values of r_{Ao}, r_{Bo}, and m_g are specific for each system. We deduced the individual values of coefficients by linear regression as:

$$a_1 = -0.2603, \ a_2 = 0.1505, \ a_3 = -0.1825$$
$$(14)$$
$$b_1 = 1.376, \ b_2 = -2.85, \ b_3 = 1.957$$

In *Fig. 2* we show a comparison of this curve with the experimental data for styrene methylmethacrylate system (17). We have also shown the data on the system styrene-acrylonitrile (19) on the same curve. The superposition is seen to be excellent implying that a unique set of a_i and b_i values can be assumed to be applicable for a class of reacting systems typified as styrene-acrylic esters. In the subsequent analysis, we shall use these
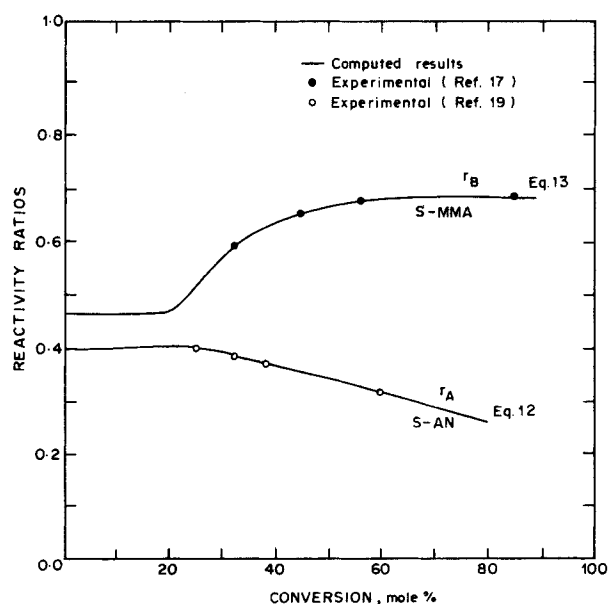

Fig. 2. Variation of reactivity ratios with conversion.

values of a_i and b_i universally. Of course, it would have been desirable to test the universality of this relationship by comparison with other styrene-acrylic ester copolymerization systems. Such data are unfortunately not available at the present time. We will, therefore, use these values of a_i and b_i in the subsequent analysis.

Variations of δ_A, δ_B, ϕ and f Conversion

With the onset of the gel effect, the relative rate groups corresponding to the termination rate processes, δ_A, δ_B, and ϕ also start changing with the extent of reaction at high levels of conversion. The use of variations of δ with conversion, as obtained from the homopolymerization data for use in the copolymerization analysis may be objectionable, since the transfer and gel effect processes may start affecting the δ values at different levels of conversion in the homo and copolymerization systems. It has also been observed that in viscous media there is an increase in the yield of primary radical recombination product (cage effect) causing a reduction in the initiator efficiency with increasing viscosity (21). Hence, in the absence of a feasible process to determine individually the variations of the rate parameters δ_A, δ_B, ϕ, and f with conversion, we propose that variation of T_1 (Eq 7) which embodies the termination process be considered. Here again we correlate the reported data for the systems styrene methylmethacrylate (17, 18) and styrene-acrylonitrile (19) and the gel effect parameter is presented in the following polynomial form:

$$\gamma = 1 \Big/ \Big(1 + \sum_{i=1}^{i=n} a_i(m - m_g)^i\Big) \qquad (15)$$

and

$$T_1^{1/2} = (T_1^{1/2}) \ at \ m = m_g/\gamma \qquad (16)$$

The individual coefficients were deduced by linear regression as:

$$a_1 = -1.4741, \ a_2 = 10.94, \ a_3 = -15.64, \ a_4 = 10.19 \qquad (17)$$

The various coefficients in Eq 17 could be assumed to be approximately the same for the copolymerization of various styrene and acrylic esters.

In summary, we have analysed the data on the copolymerization of styrene and acrylic esters to obtain generalized correlations for ϕ with the feed composition. In addition, the reactivity ratios for the individual monomers and the termination process have been correlated with the extent of conversion. This generalized analytical framework developed by us forms the basis of the ensuing design considerations which will be explained with an elaborate illustrative example.

ILLUSTRATIVE EXAMPLE

In order to elucidate the procedure employing the proposed correlations for the copolymerization of styrene and acrylic esters, we have considered the free radical bulk copolymerization of styrene-methyl methacrylate in (1) batch reactor, (2) CSTR and (3) CSTR with recycle under isothermal conditions at 60°C. The feed concentrations of monomers and initiator fed to the reactor are: $C_{Af} = 5.354$ mole/cm³, $C_{Bf} = 3.575$ mole/cm³,

and $C_{Kf} = 0.00826$ mole/cm³. The kinetic constants and physical data used in this work are summarized in Table 2. The conversion corresponding to the gel point (m_g) is 20 mole percent.

Batch Reactor

Dionisio and O'Driscoll (18) studied the high conversion copolymerization of styrene and methylmethacrylate in a batch reactor at 60°C and 60 mole percent styrene in the feed. Their experimental results are compared with the computed results obtained by solving Eqs 2 and 3 simultaneously by numerical integration using the proposed correlations. The results are shown in Fig. 3. There is a close agreement between the computed results and the experimental values, showing the validity of the correlations proposed by us.

While computing the above results, it has been assumed that the volume change during the copolymerization is marginal and has very little influence on the total conversion of the copolymer. Our assumptions are supported by the recent observations of Kartavykh et al. (22) who studied the effect of the change in volume on the degree of conversion of monomer and its possible reflection on the calculated kinetic parameters in free radical polymerization. They concluded that the change in volume during polymerization affects conversion to a very small extent. Their conclusion was that in the analysis of kinetic experiments in free radical polymerization, it is possible to use the kinetic expression derived without taking into account the volume change. However, the volume change can be easily incorporated into the general analysis strategy, if required.

CSTR

If we allow a fresh feed of monomer A to be mixed with monomer B, containing the initiator K, then the material balance equations can be written as:

$$C_{Af} - C_A = R_A \tau \qquad (18)$$

$$C_{Bf} - C_B = R_B \tau \qquad (19)$$

$$C_{Kf} - C_K = R_K \tau \qquad (20)$$

The corresponding transient governing equations are:

$$\frac{dC_A}{dt} = \frac{C_{Af} - C_A}{\tau} - R_A \qquad (21)$$

Table 2. Pertinent Physico-Chemical Data Used in this Study (Ref. 23)

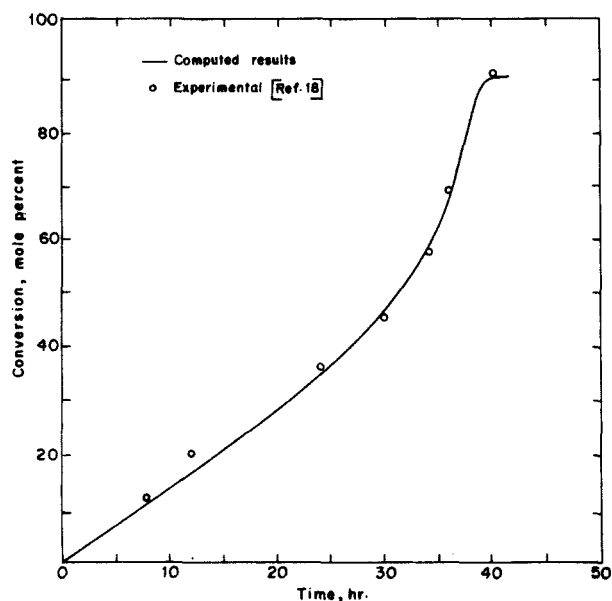|	Styrene	Methylmethacrylate
Reactivity ratios	1.83 exp(−450/T)	1.27 exp(−340/T)
k_p(cm³/mole sec)	1.057 × 10⁷ exp (−3557/T)	9 × 105 exp (−2365/T)
k_t(cm³/mole sec)	1.255 × 10⁹ exp (−843/T)	1.1 × 10⁸ exp (−604/T)
ρ(g/cm³)	0.9010	0.9380
Molecular weight	104.14	100.00
k_d (sec⁻¹) (initiator = Benzoyl peroxide)	2.8 × 10⁻⁶	
Efficiency, f	0.75	

Fig. 3. *Conversion vs. time for the bulk copolymerization of styrene-methylmethacrylate in the batch reactor.*

$$\frac{dC_B}{dt} = \frac{C_{Bf} - C_B}{\tau} - R_B \qquad (22)$$

$$C_K = \frac{C_{Kf}}{(1 + k_d)}\left[1 - \exp - \left(\frac{1}{\tau} + k_d\right)t\right]$$

$$+ C_{K_o} \exp - \left(\frac{1}{\tau} + k_d\right)t \qquad (23)$$

where

$$\tau = \frac{V}{F}$$

Taking into account the definitions of R_A and R_B *(Eqs 2 and 3)* and the rearrangement of *Eqs 18* to *20* leads to

$$m = \frac{R_p}{C_{Af} + C_{Bf}} \qquad (24)$$

Equation 24 represents the design equation of the CSTR. It was solved for a set of parameter values to obtain the steady state conversion for varying values of residence time in the reactor. The results are shown in *Fig. 4.* It is clearly seen from this figure that for a set of fixed parameter values there exists a range of residence times $(7.7 < \tau < 19.4 \text{ hr})$ in the reactor, where the solutions of the governing equations show three steady states. The total rates of copolymerization evaluated at steady state conversions are shown in *Fig. 5.*

Effect of Feed Composition

The effect of feed composition on the multiplicity region is shown in *Fig. 4.* The increase in styrene concentration from $x = 0.2$ to 0.8 induces a shift and enlarges the region of multiplicity (from $3.5 < \tau < 11.75$ to $10.5 < \tau < 24$ hr).

Stability Analysis

The local stability character of the steady states of the reactor has been determined by examining the transient equations *(Eqs 21* to *24)* linearized about the steady state. For this purpose, the Jacobian matrix is formulated as:
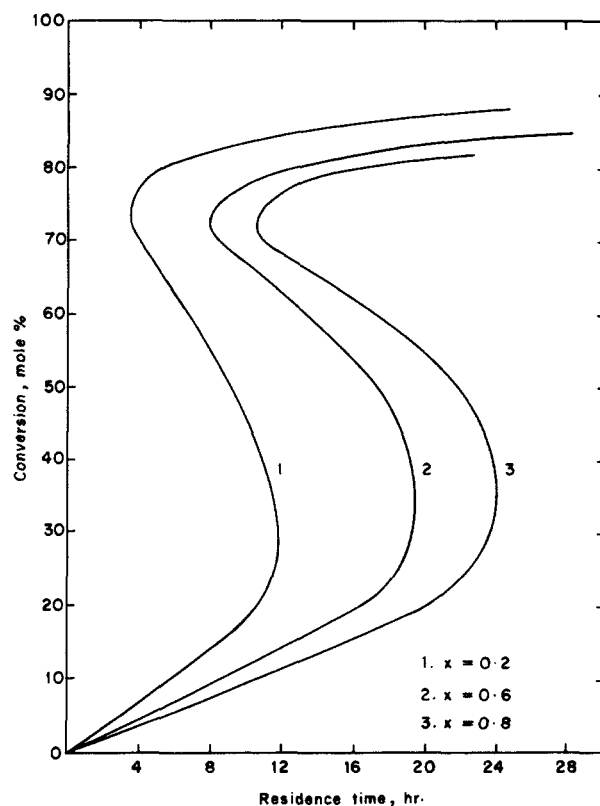

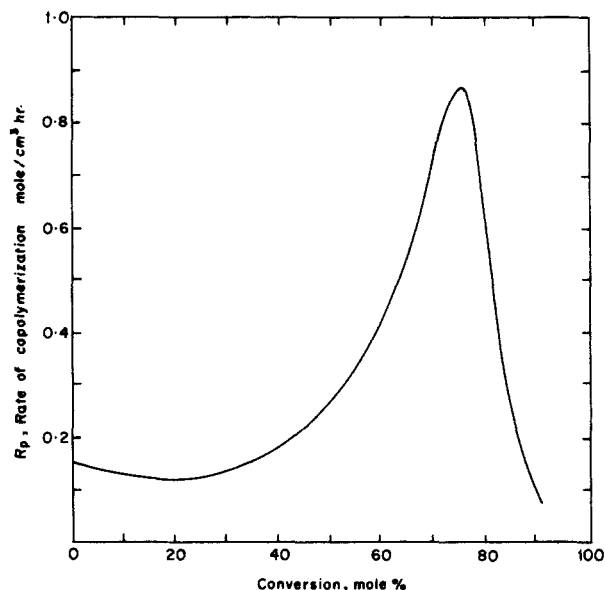Fig. 4. *Effect of feed composition on the region of multiplicity.*

Fig. 5. *Variation of the total rate of copolymerization with conversion.*

$$\bar{A} = \begin{vmatrix} \dfrac{\partial f_1}{\partial C_A} & \dfrac{\partial f_1}{\partial C_B} \\ \dfrac{\partial f_2}{\partial C_A} & \dfrac{\partial f_2}{\partial C_B} \end{vmatrix} \qquad (25)$$

The condition for the steady state to be asymptotically stable is det. $\bar{A} > O$ and trace $\bar{A} < O$. The lower and the upper steady states have been found to be always asymptotically stable while the middle one is unstable. To examine the global stability of the steady states, the transient equations were solved numerically using a fourth order RKG integration method. *Figure 6* indi-
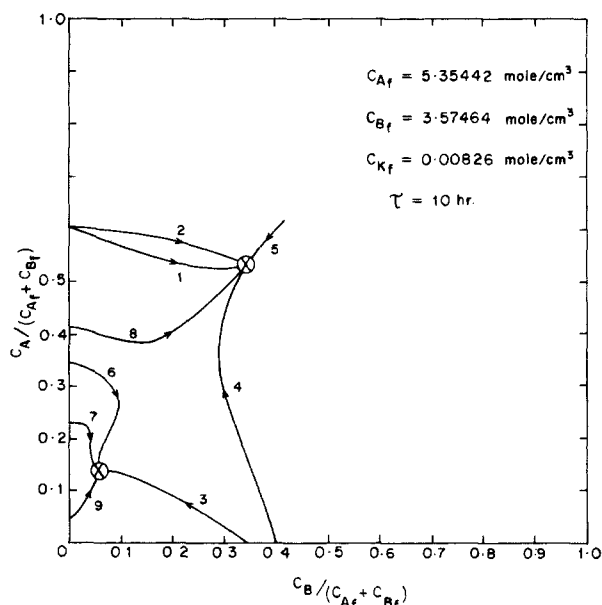
Fig. 6. Phase plane trajectories.

cates the existence of only two stable states, the lower and the upper one, the middle state being unstable. *Figure 4* indicates that production of a copolymer at a stable steady state restricts the conversion levels in a CSTR.

An innovative way of improving the conversion and producing a copolymer at uniform composition is by recycling a part of the product (24). Apparently, this mode of reactor operation has not been considered hitherto in the high conversion range, and we shall elaborate on some of the novel features of this mode.

CSTR with Recycle

The copolymerization carried out in a recycled CSTR is illustrated along with that carried out in the normal CSTR mode in *Figs. 7* and *8*. A normal CSTR, operating at $\tau = 16.32$ hr in the multiple steady state region gives a steady state conversion of 19.5 mole percent as shown in *Fig. 7*. To operate the reactor in the unique steady state region and to achieve higher conversion, a part of the product stream is recycled as shown in *Fig. 8*. The balance equations at point A now become

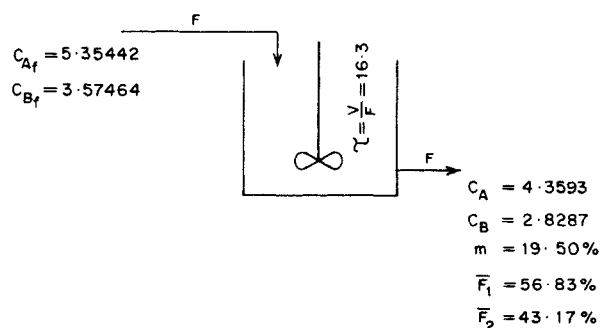$$V \frac{dC_A}{dt} = \lambda FC_{AF} + F(1 - \lambda)C_A - FC_A - Vk_AC_AC_K^{1/2}$$
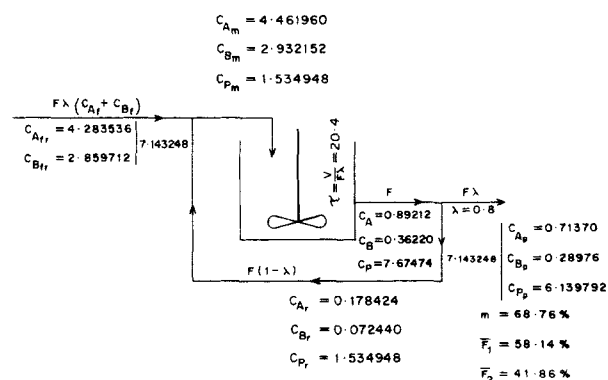
$$(26)$$

Fig. 7. CSTR.

Fig. 8. CSTR with recycle.

$$V \frac{dC_B}{dt} = \lambda FC_{Bf} + F(1 - \lambda)C_B - FC_B - Vk_BC_BC_K^{1/2}$$

$$(27)$$

Note that $\lambda = 0$ corresponds to total recycle, and $\lambda = 1$ corresponds to zero recycle.

Equations 26 and *27* are simplified and rewritten as

$$\frac{dC_A}{dt} = \frac{C_{Af} + (1 - \lambda)C_A - C_A}{\tau} - R_A \qquad (28)$$

$$\frac{dC_B}{dt} = \frac{C_{Bf} + (1 - \lambda)C_B - C_B}{\tau} - R_B \qquad (29)$$

The above equations are solved by numerical integration to get C_A and C_B. At steady state,

$$FC_{Am} = F\lambda C_{AF} + F(1 - \lambda)C_A \qquad (30)$$

and

$$FC_{Bm} = F\lambda C_{Bf} + F(1 - \lambda)C_B \qquad (31)$$

The complete material balance of the recycled CSTR is shown in *Fig. 8*. The total conversion achieved in the CSTR at 20 percent recycle is 68.76 mole percent. The copolymer produced is also uniform in composition. Hence, operating the CSTR with recycle gives higher conversion and improved product properties. An additional advantage is that the reactor is also operated in the unique steady state region.

CONCLUSIONS

The analysis for the design of a copolymerization reactor until now has been restricted to a specific system. In the present work an attempt has been made for the first time to generalize the strategy for the design of copolymerization reactors for a class of reacting systems. The typical example analyzed considers the copolymerization of styrene with acrylic esters. The data on these systems are analyzed to obtain generalized correlations for the variation of ϕ with the feed composition. In addition, the reactivity ratios for the individual monomers and the termination process have been correlated with the extent of conversion.

The procedure employing the proposed correlations is illustrated by considering the industrially important system of copolymerization of styrene and methylmethacrylate in a batch reactor, a CSTR, and a CSTR with a recycle. The results computed for the batch reactor are compared with the experimental results of Dionisio and

O'Driscoll (18) showing the validity of the proposed correlations. The existence of stable steady states and the influence of system parameters on the reactor behavior are illustrated for the CSTR by means of phase plane plots. An innovative way of operating the CSTR in the unique steady state region to produce copolymers at higher conversions and uniform composition is also illustrated.

ACKNOWLEDGMENT

NOMENCLATURE

a_i = Individual values of coefficients in *Eqs 12* and *15*.

A = Facobian matrix defined by *Eq 25*.

b_i = Individual values of coefficients in *Eq 13*.

C_A = Concentration of monomer A, mole/cm^3.

C_B = Concentration of monomer B, mole/cm^3.

C_K = Concentration of initiator K, mole/cm^3.

f = Initiator efficiency for copolymerization.

f_1, f_2 = Functions in facobian matrix defined by *Eqs 21* and *22*.

F = Flow rate of reactants, cm^3/hr.

k_A, k_B = Apparent rate constants (cm^3/mole)$^{1/2}$ (hr)$^{-1}$.

k_d = Rate constant for initiator decomposition (hr)$^{-1}$.

k_{pAA}, k_{pAB}, k_{pBB}, k_{pBB} = Rate constants for propagation, cm^3/mole hr.

k_{tAA}, k_{tAB}, k_{tBB} = Rate constants for termination, cm$_2$/mole hr.

m = Conversion of monomers.

r_A, r_B = Reactivity ratios.

R_A = Rate of polymerization of monomer A, mole/cm^3 hr.

R_B = Rate of polymerization of monomer B, mole/cm^3 hr.

R_K = Rate of initiation, mole/cm^3 hr.

R_p = Total rate of copolymerization, mole/cm^3 hr.

t = Reaction time, hr.

T = Temperature, °K.

T_c = Termination rate parameter defined by *Eq 8*, (mole/cm^3)$^{1/2}$ (hr)$^{1/2}$.

T_1 = Termination rate parameter defined by *Eq 15* (mole/cm^3)$^{1/2}$ hr.

V = Volume of reaction mixture, cm^3.

x = Mole fraction of monomer A.

β = Defined by *Eq 10*.

ΔS_1, ΔS_2, ΔS_{12} = Entropies of polymerization, cal/mole °K.

γ = Gel effect parameters defined by *Eq 15*.

δ_A, δ_B = Defined by *Eq 1*.

ϕ = Defined by *Eq 1*.

ϕ_{max} = Defined by *Eq 9*.

τ = Residence time, hr.

λ = Recycle ratio, defined by *Eq 27*.

A = Monomer A.

B = Monomer B.

K = Initiator K.

f = Feed.

p = Product.

r = Recycle.

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