MULTIPLICITY OF STATES IN CONTINUOUS STIRRED COPOLYMERIZATION REACTORS: ITS EXISTENCE AND CONSEQUENCES

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MULTIPLICITY OF STATES IN CONTINUOUS STIRRED COPOLYMERIZATION REACTORS: ITS EXISTENCE AND CONSEQUENCES*

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The dynamic behaviour of a continuous copolymerization stirred tank reactor is analyzed. The evolution of multiple steady states due to Trommsdorf or gel effect in free radical bulk copolymerization systems is illustrated for the first time taking into consideration the changes in the cross termination rate constant [or the ϕ factor] at high extent of reaction. The effect of concentration multiplicity on cumulative copolymer composition is illustrated. The consequences of the results of the present analysis in copolymerisation reactor operation and design have been discussed.

INTRODUCTION

The existence of multiple steady states under isothermal conditions has received considerable attention in reaction engineering literature. Both theoretical and experimental studies in this field have been reviewed recently [Schintuch and Schmitz 1977; Slinko and Slinko 1978]. Most of these analyses were confined to nonviscous systems and relatively little attention has been paid to analysis of viscous systems such as might be encountered in continuous polymerizations.

The early studies in this area include those of Amundson and coworkers [Aris and Amundson, 1968; Warden and Amundson, 1962; Goldstein and Amundson, 1965 a,b,c] who analysed several problems in the area of polymerization reactors. The case of free radical polymerization was specifically studied by Mimashi *et al* [1967] and Chiu and Heines [1971], and more recently, in presence of solvent, by Schmidt and Ray [1980]. The literature on emulsion polymerization has been reviewed by Gerrens [1975] and specifically for the methyl methacrylate system by Kirilloo and Ray [1978]. Bulk polymerization systems such as vinyl momomers etc. are characterized by Trommsdorf or gel effect. Knorr and O'Driscoll [1970] have analysed the viscosity effects for such systems.

Almost all the analyses in the literature have been restricted mostly to homopolymeric systems. The present paper attempts to provide a quantitative theory for bulk free radical copolymerization systems. The dependence of ϕ factor on the nature, composition of comonomer feed and its drift with changes in comonomer composition during the course of reaction has been accounted for along with the viscosity effects

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[see for example Bonsall *et al*, 1951; Arlman *et al*, 1950]. The nonlinearity introduced into the model formulation as a result of this can lead to multiplicity of states under certain sets of operating conditions. The question of stability of these states and product distribution corresponding to each of the steady states has also been examined. The computations are carried out for an industrially important copolymerization of styrene and acrylonitrile.

THEORY

Let us consider the free radical bulk copolymerization reaction carried out in a continuously stirred tank reactor [CSTR]. If we allow a fresh feed of monomer A to be mixed with monomer B, containing initiator I, then the material balance equations for CSTR can be written as

$$(A_o) - (A) = R_A\theta \tag{1}$$

$$(B_o) - (B) = RB\theta \tag{2}$$

$$(I_o) - (I) = R_I\theta \tag{3}$$

where $R_I = 2fk_d(I)$ and $\theta = V/F$ and the quantities in brackets denote the concentrations of respective species.

In highly viscous polymer solutions, the reaction rates of the monomers are accelerated due to Trommsdorf or gel effect. The changes in the cross termination rate constant or the ϕ factor are accounted for by introducing the enhancement factor, E in the rate expressions as follows:

$$R_A = Ek_A(A)(I)^{1/2} \tag{4}$$

$$R_B = Ek_B(B)(I)^{1/2} \tag{5}$$

The enhancement factor approach used here is similar to that used by Ludwico and Rosen [1976] and Mahabadi and O'Driscoll [1977]. In equations [4] and [5], k_A and k_B are apparent rate constants. These are given by

$$k_A = [(r_A - 1] x + 1]/Y_1^{1/2} \tag{6}$$

$$k_B = [(1 - r_B) x + r_B]/Y_1^{1/2} \tag{7}$$

where

$$Y_1 = (r_A\delta_A'x)^2 + 2\phi_x r_A r_B\delta_A'\delta_B'x(1 - x) + [r_B\delta_B'(1 - x)]^2$$

and

$$x = (A)/(A) + (B); \delta'_A = \delta_A/(2f_A k_d)^{1/2}$$

$$\delta'_B = \delta_B/(2f_B k_d)^{1/2}; \phi_x = \phi f_A^{1/2} f_B^{1/2}/f;$$

$$\delta_A = (k_{t_{AA}}/k_{p_{AA}}^2)^{1/2}; \delta_B = (k_{t_{BB}}/k_{p_{BB}}^2)^{1/2}$$

$$\phi = k_{t_{AB}}/(k_{t_{AA}} k_{t_{BB}})^{1/2}$$

$$r_A = (k_{p_{AA}}/k_{p_{AB}}); r_b = (k_{p_{BB}}/k_{p_{BA}}) \tag{8}$$

Substitution of equations [6] and [7] in equations [4] and [5] and subsequent addition leads to the expression for rate of copolymerization $[R_p]$ widely reported in the literature [see for example Odian (1970)].

Rearrangement of equation [1]–[3] taking into account the definitions of R_A and R_B leads to

$$\frac{m}{\theta} = \frac{R_p}{(A_o) + (B_o)} \tag{9}$$

Equation [9] represents the design equation of the CSTR and as such is non-linear. The equation under certain sets of operating conditions can possess more than one solution, and is likely to have multiplicity of steady states. It is possible, in principle, to determine the necessary and sufficient conditions for the existence of such multiplicity. However, in view of the complex nonlinear nature of this equation, the derivations of these criteria have not been attempted in this work. Instead, we have focussed our

TABLE 1

Experimental Conditions
[Miyata and Nakashio (1973)]

Run	(A_o) (g · mol/l)	(B_o) (g · mol/l)	x_o (−)	(I_o) (g · mol/l)
1	8.73	0	1.00	0.0326
4	8.73	0	1.00	0.0298
5	7.64	1.80	0.809	0.0302
3	7.04	2.94	0.704	0.0308
16	7.00	5.03	0.698	0.0301
6	6.54	3.87	0.627	0.0302
11	6.55	3.70	0.639	0.0137
12	6.56	3.79	0.634	0.0045
13	6.63	3.50	0.654	0.0579
7	5.46	5.69	0.489	0.0300
2	4.24	7.83	0.351	0.0292
15	4.33	7.66	0.361	0.0302
8	3.28	9.70	0.252	0.0300
14	3.19	9.58	0.250	0.0301
9	1.66	12.30	0.118	0.0304
10	0.875	13.90	0.0592	0.0301

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TABLE 2

Kinetic Parameters
[Miyata and Nakashio (1973)]

Temperature $= 343°K$
$k_d = 0.00255$ min^{-1}
$r_A = 0.42$
$r_B = 0.06$
$\delta'_A = 64.5$ [(g · mol ·/l)$^{1/2}$(min)]
$\delta'_B = 13.7$ [(g · mol/l)$^{1/2}$ (min)]0.8
$f_A - f_B = 0.8$
$\phi_x = 9.0$

attention on a specific industrially important system, the copolymerization of styrene and acrylonitrile.

Pertinent experimental data to enable model calculations were taken from the work of Miyata and Nakashio [1973]. The operating parameters and the values of kinetic parameters obtained by these authors in a batch reactor are given in Tables 1 and 2. In order to facilitate numerical computations, we thought it desirable to correlate the enhancement factor, E, with the data obtained by Miyata and Nakashio as shown in Figure 1. It can be easily seen that a relation between E and conversion can be expressed as:

$$E = \exp[(\alpha(m - m_g)] + c \tag{10}$$

where α is the slope and m_g is the conversion corresponding to the point of start of the gel effect. The modified plot corresponding to equation [10] is shown in Figure 2. We shall use equation [10] in our analysis.

Now R_p, (A_o) and (B_o) appearing in equation [9] are functions of E, which in turn is a function of conversion [see equation (10)]. Equation [9] can therefore be expressed explicitly in terms of conversion. It should be remembered, however, that the parameters α and m_g are functions of the particular system being analysed.

RESULTS AND DISCUSSION

Equation [9] is 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 Figure 3. It is clearly seen from this figure that for a set of fixed parameter values there exists a range of residence times [$20.83 < \theta < 50.31$] in the reactor where three steady-state solutions are possible. The dotted curve in the figure refers to the case when density variations with the extent of conversion are taken into account. The variation of density with the extent of conversion has been correlated by Miyata and Nakashio [1973] for the bulk copolymerisation of styrene and acrylonitrile and has been used in the present calculations. It is seen from the computed results that accounting for the density variations induces a shift in the multiplicity region which
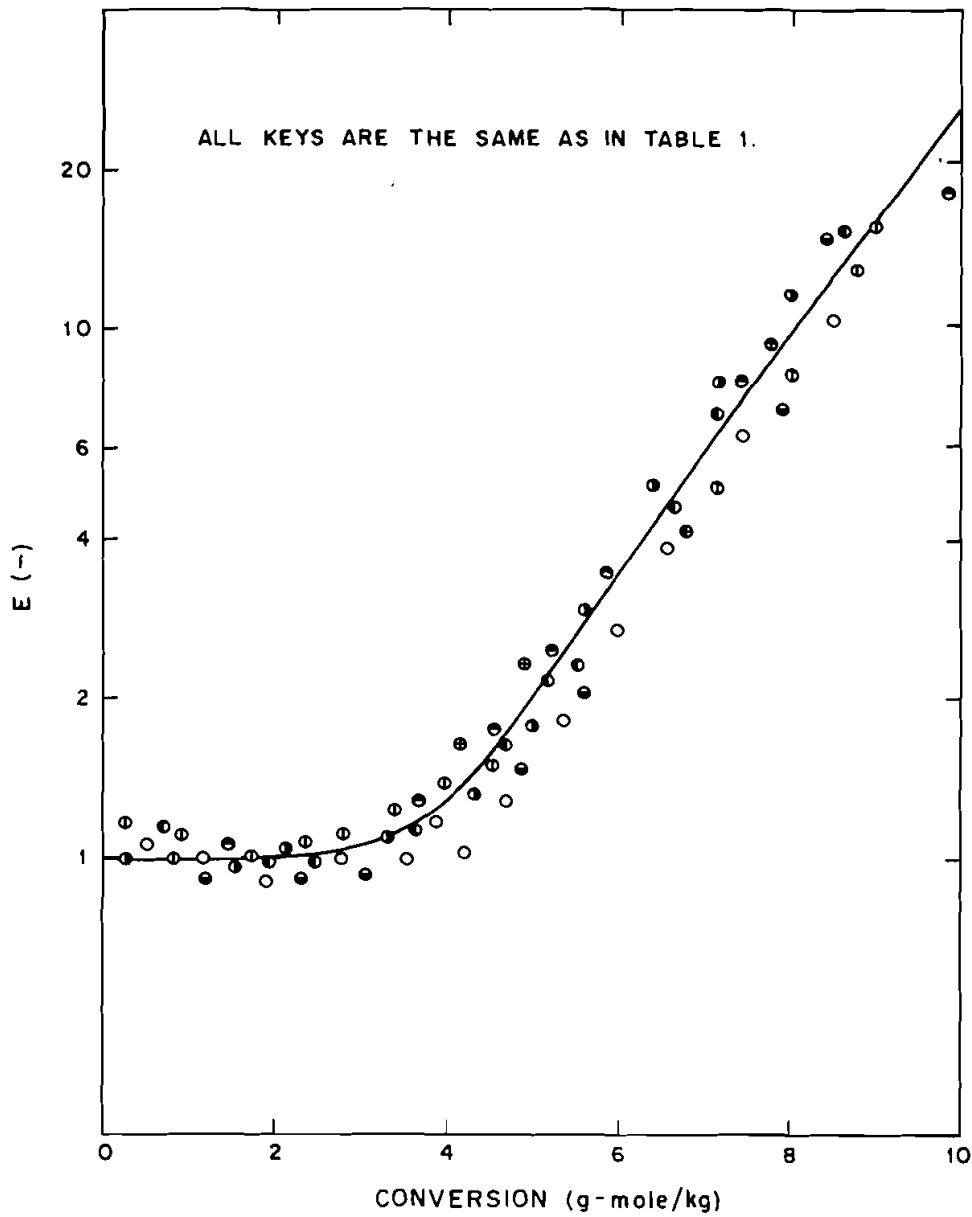
FIGURE 1   Enhancement Parameter vs Conversion. [Data from Miyata and Nakashio. (1973)]

now exists for lower values of the residence time [$18.45 < \theta < 48.19$]. The deviations caused by incorporating the density variations are, however, small and further computations are therefore carried out for the constant density case.

The local stability character of the steady states of the reactor has been determined by examining the performance of the corresponding transient equations [eq. (1-3)]
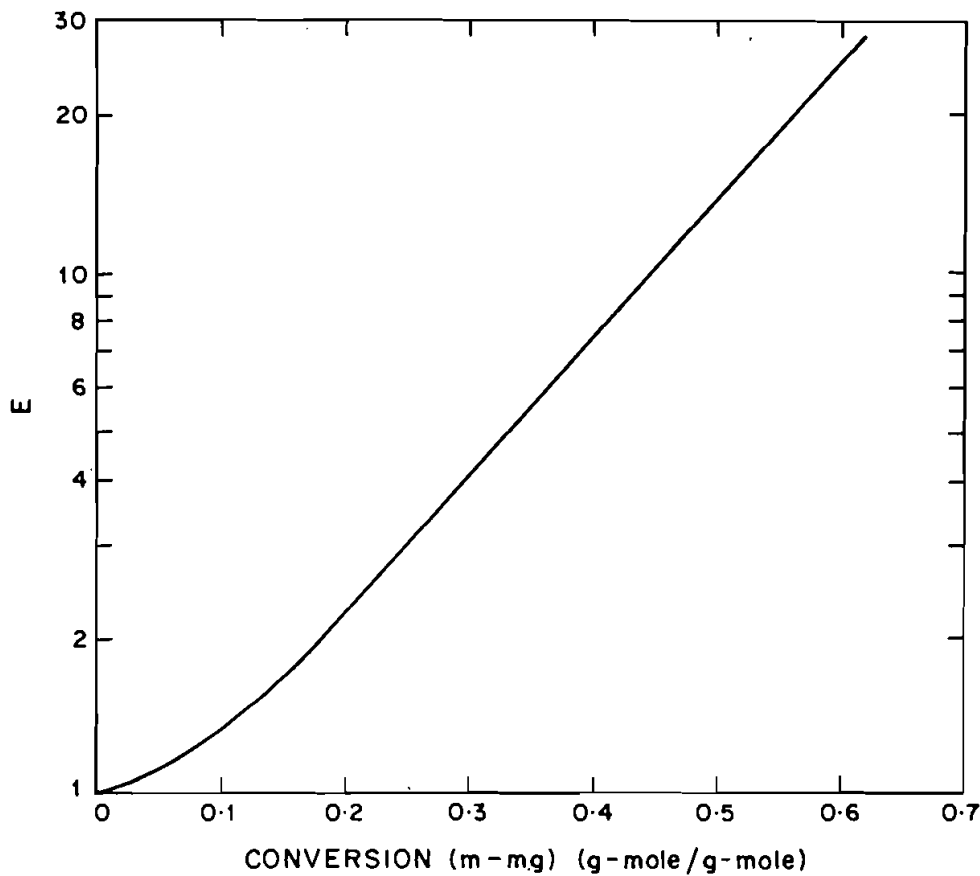
CONVERSION (m – m.g) (g – mole / g – mole)

FIGURE 2   Modified plot of enhancement parameter vs conversion.

linearized about the steady state. For this purpose the Jacobian matrix is formulated as

$$
\overline{A} = \begin{vmatrix} \left(\dfrac{\partial f_1}{\partial(A)}\right) & \left(\dfrac{\partial f_1}{\partial(B)}\right) \\[2mm] \left(\dfrac{\partial f_2}{\partial(A)}\right) & \left(\dfrac{\partial f_2}{\partial(B)}\right) \end{vmatrix}
\tag{11}
$$

and the condition for the steady state to be asymptotically stable is that det $\overline{A} > 0$ and trace $\overline{A} < 0$.

To examine the global stability of the steady states, the transient equations have been solved numerically using a fourth order RKG integration method. Figure 4 indicates the existence of only two stable states, the lower and the upper one, the middle state being unstable.
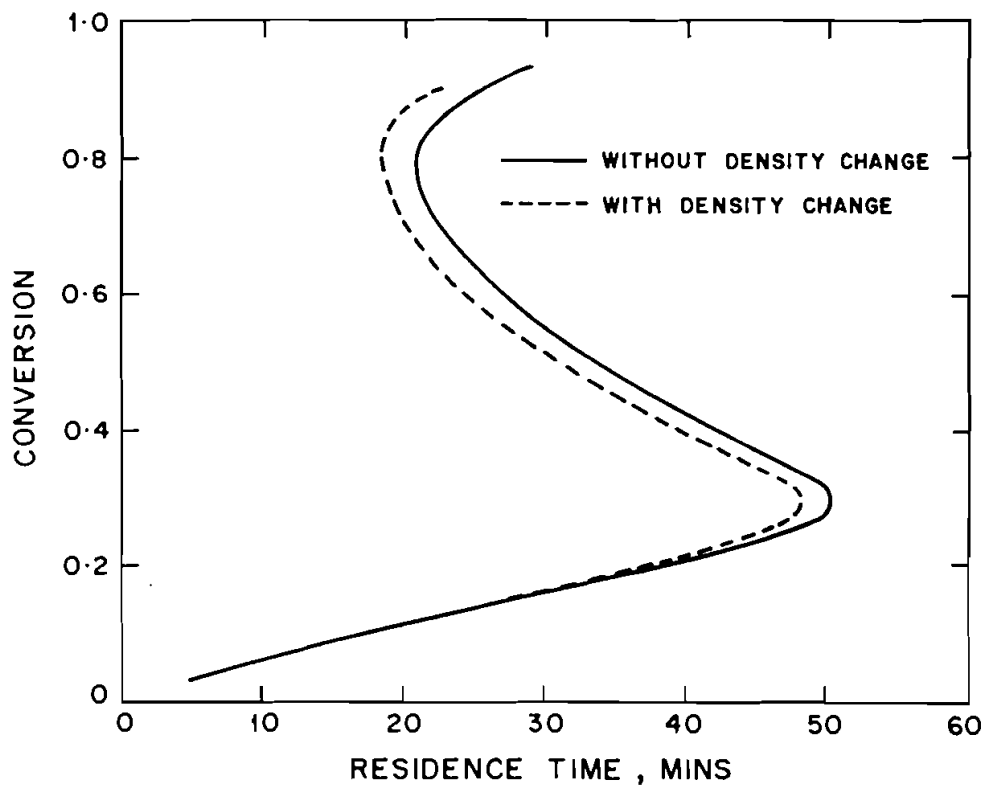
FIGURE 3   Conversion vs residence time for system with and without density change.
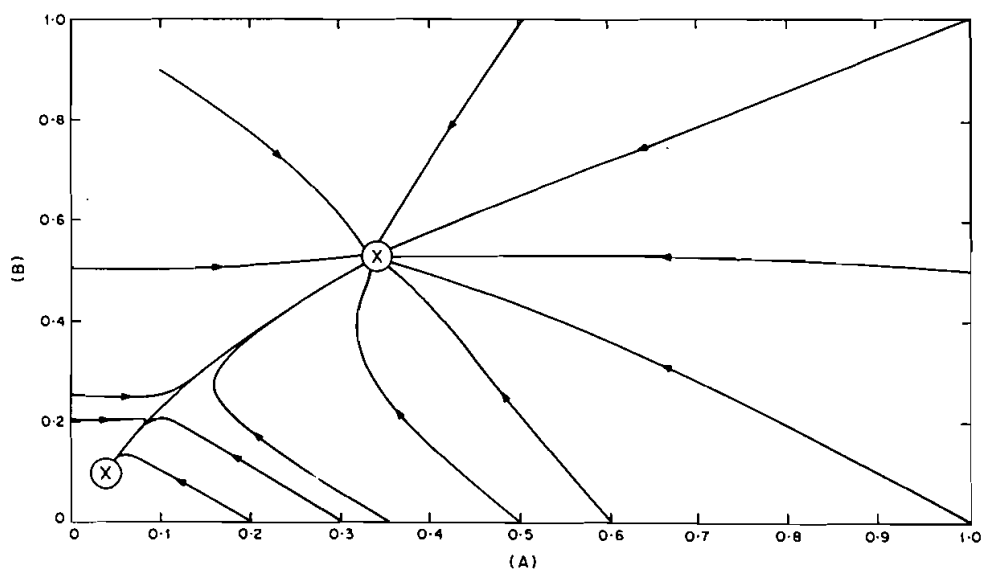

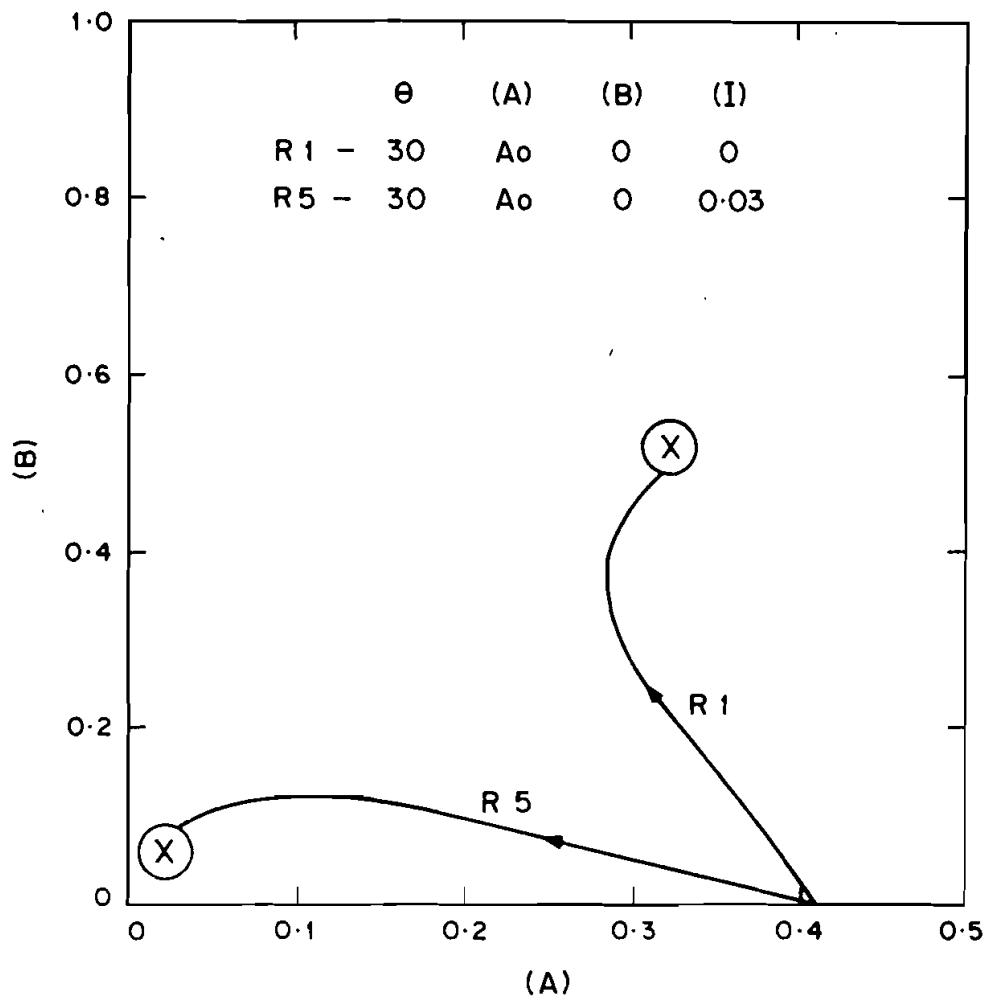FIGURE 4   Phase plane trajectories.

FIGURE 5   Effect of initiator concentration on phase plane trajectories.

The effect of initiator concentration on the multiplicity is illustrated in Figure 5. Reactor conditions at R1 and R5 have the same feed concentrations but different initiator concentrations as indicated in the figure. By increasing the initiator concentrations, the steady state is shifted from the lower to the upper one at a shorter duration of interval.

The question of cumulative average composition assumes great importance in copolymerization. In order to illustrate this, in Figure 6 we have shown the influence of cumulative copolymer composition on important mechanical properties such as impact, tensile and flexural strengths for SAN copolymers prepared from varying proportions of acrylonitrile monomer [Ziemba (1964)]. These data clearly indicate that optimum properties are obtained when the cumulative average composition of
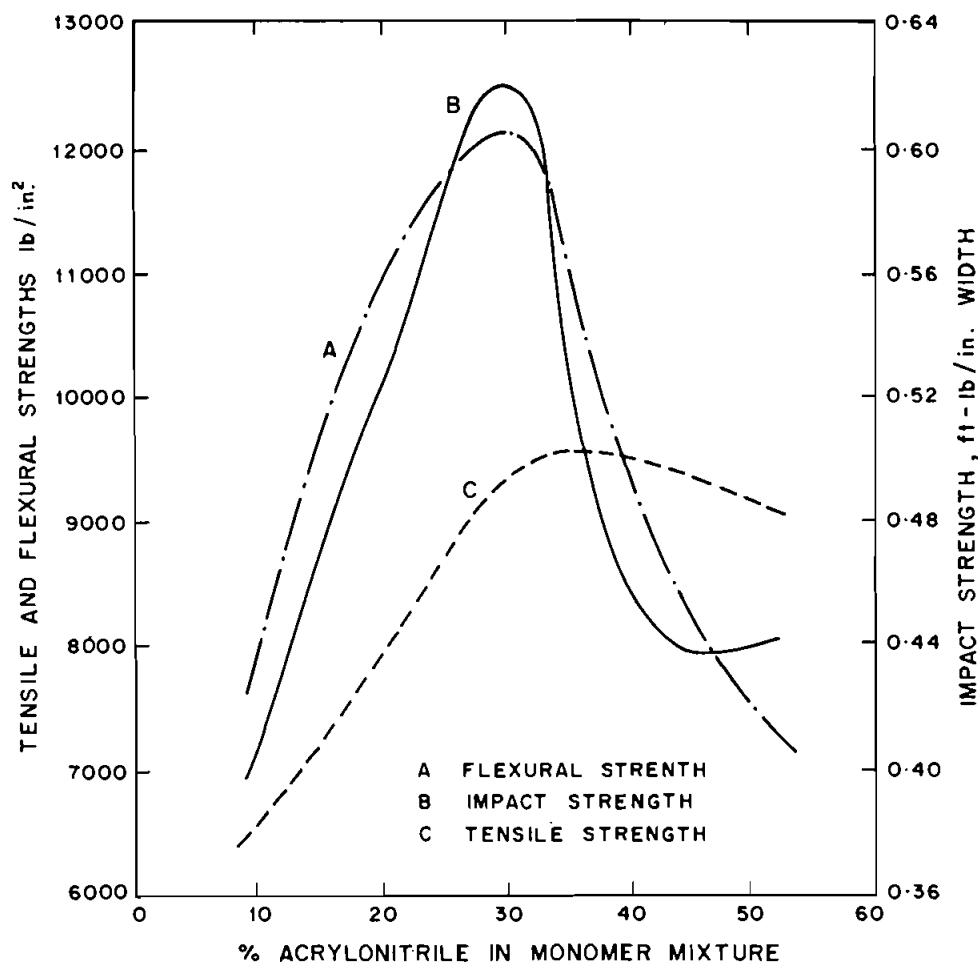
FIGURE 6   Influence of cumulative copolymer composition on important mechanical properties of SAN copolymers.

acrylonitrile in the copolymer is around 30 wt. percent. In view of this it is practically important to study the effect of conversion achievable at different steady states on the cumulative average composition of acrylonitrile in the copolymer. This is shown in Figure 7. The figure indicates that the drift in cumulative average composition of acrylonitrile in the copolymer is drastic when the conversion is more than 25.4%. Hence production of a uniform copolymer at a stable steady state restricts the conversion levels in a CSTR. An innovative way of accomplishing this can be considered in the light of the findings of this work. We can consider operating the reactor in the unstable region. We can then reduce the degree of instability and the drift in the copolymer composition by the use of an oscillating feed of the more reacting monomer or recycling a part of the product [polymer in monomer]. When product quality is a prime consideration it follows that in the case of copolymerization
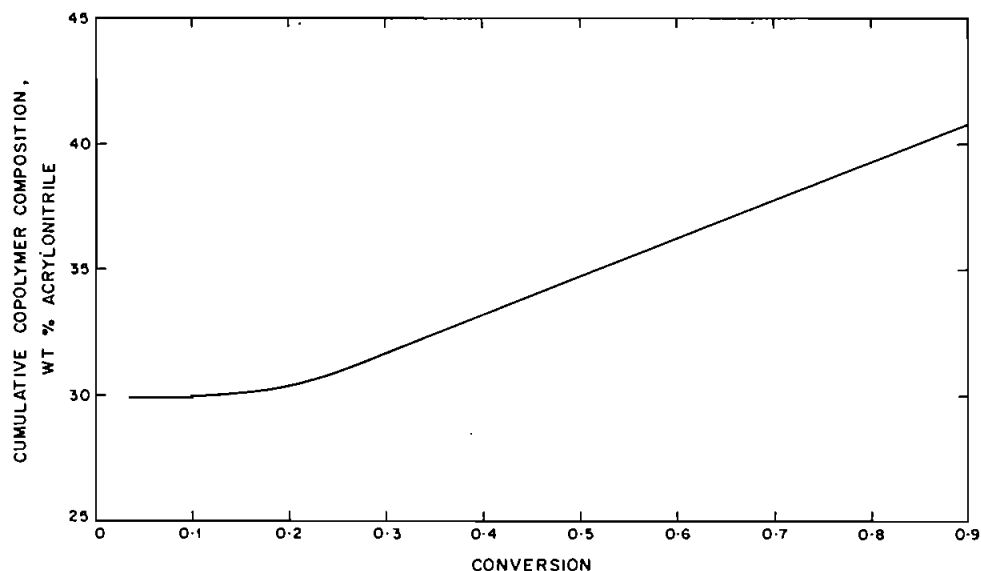
FIGURE 7   Variation of cumulative copolymer composition with conversion.

reactors, easy controllability of the reactor should be one of the major considerations in reactor design.

CONCLUSIONS

In this work we have shown the existence of multiple steady states in bulk copolymerization reactors. The theory is exemplified by considering an industrially important system of copolymerization of styrene and acrylonitrile. The existence of stable steady states and the influence of the system parameters on the reactor behaviour are illustrated by means of phase plane plots. Additionally the effect of concentration multiplicity on the cumulative average composition of monomer in the copolymer is examined.

NOTATION

(A)	concentration of monomer A
(B)	concentration of monomer B
E	enhancement factor defined by equations [4] and [5]
F	flow rate of monomers
f	initiator efficiency for copolymerization
f_A	initiator efficiency for homopolymerization of monomer A
f_B	initiator efficiency for homopolymerization of monomer B

(I)	concentration of initiator
k_A, k_B	apparent rate constant defined by equations [6] and [7]
k_d	rate constant for initiator decomposition
$k_{p_{AA}}$, $k_{p_{AB}}$, $k_{p_{BA}}$, $k_{p_{BB}}$	rate constants for propagation
$k_{t_{AA}}$, $k_{t_{AB}}$, $k_{t_{BB}}$	rate constants for termination
m	conversion of monomers defined by equation [9]
m_g	conversion of monomers corresponding to the point of start of gel effect defined by equation [10]
R_A	rate of polymerization of monomer A
R_B	rate of polymerization of monomer B
R_p	total rate of copolymerization
r_A, r_B	monomer reactivity ratios defined by equation [8]
V	reactor volume
x	defined by equation [8]
Y_1	defined by equation [8]

Greek

α	defined by equation [10]
δ_A, δ_B	defined by equation [8]
δ_A, δ_B	defined by equation [8]
θ	residence time
ϕ	defined by equation [8]
ϕ_x	defined by equation [8]

Subscripts

A	monomer A
B	monomer B
I	initiator
o	initial state

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