Superscripts

L = to be evaluated at the bulk conditions of the liquid phase
V = to be evaluated at the bulk conditions of the vapor phase

Subscripts

f = packing boundaries adjacent to the feed mixing section
i = component number ($1 \leqq i \leqq c$)
j = integer for numbering the increments of the column; the first increment at the top of the column is assigned the number 1 and the last increment at the bottom, the number $N + 1$. At the top of the column where the packing begins $z = z_1$, and at the bottom where the packing ends, $z = z_{N+1}$. The condenser is assigned the number zero, and the reboiler the number $N + 1$
N = total number of elements of packing plus the feed-distributor plate where it is treated as a mass transfer section

Mathematical Symbols

$\sum_{i=1}^{c} x_i$ = sum over all values x_i ($1 \leqq i \leqq c$)
$\{x_j\}$ = set of all values x_j belonging to the particular set under consideration

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Manuscript received February 1, 1968; revision received April 9, 1968; paper accepted April 11, 1968. Paper presented at AIChE St. Louis meeting.

Copolymerization and Terpolymerization in Continuous Nonideal Reactors

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A simple means for predicting composition distributions in copolymers is used to illustrate the strong influence of segregation effects in the reactor. A recycle loop reactor can be used to produce uniform copolymers by narrowing the macroscopic composition distribution, but there is a limiting microscopic distribution which results from probabilistic effects.

This paper is aimed at the development of industrially feasible techniques for the production of homogeneous copolymers and terpolymers. Such multicomponent polymers are often required to meet specific physical and chemical properties which are unobtainable with simple homopolymers. However, production of good quality co- and terpolymers is generally more difficult and requires more careful polymerization techniques than are needed for homopolymers.

The properties of homopolymers are primarily determined by two factors:

1. The average molecular weight and the distribution of molecular weights about this average.
2. The extent of branching and cross linking.

These factors are of course important for multicomponent polymers, but a third major factor must also be considered:

3. The average chemical composition of the polymer and the distribution of compositions about this average.

The importance of this third factor may be illustrated by considering styrene-acrylonitrile copolymers. The pure homopolymers (polystyrene and polyacrylonitrile) are incompatible and a gross physical mixture of these materials gives a very brittle product which is hazy or even opaque. In a styrene-acrylonitrile copolymer the two constituents are combined within individual polymer molecules, giving a new chemical species rather than a physical mixture. Provided that the compositions of the individual molecules are fairly similar, the copolymer will be self-compatible, giving a reasonably tough, transparent, colorless product. If, however, there is a broad range of molecular compositions, a poor product will again result due to internal incompatibility (*5, 6*).

Two copolymer molecules formed from the same monomer mixture will generally have slightly different compositions due to random (probabilistic) variations on the molecular level. However, these differences are usually very small and such microscopic composition distributions can often be ignored. A far more serious cause for composition distributions is due to actual changes in monomer compositions. In a mixture of two monomers, one will usually polymerize at a faster rate than the other. Thus the monomer and polymer phases will have different compositions, the polymer being enriched with the more reactive component. The instantaneous monomer and polymer compositions can be related by the well-known copolymer composition equation:

$$\frac{dA}{dB} = \frac{A(r_A A + B)}{B(A + r_B B)} \tag{1}$$

where A and B denote the mole fractions of the two monomers and r_A and r_B are constants known as copolymer reactivity ratios. Values for r_A and r_B are now available in the literature for nearly all industrially important monomers. The book by Ham (*1*) gives a particularly comprehensive collection. In some cases where direct experimental results are missing, it may be possible to estimate r_A and r_B using the semitheoretical $Q - e$ scheme developed by Alfrey (*1*).

Table 1 gives the reactivity ratios, selected from Ham (3), which were used for the calculations in this paper. The values are believed to be good estimates for free radical polymerization with either thermal or catalytic initiation. Assuming that polymerization proceeds by a free radical mechanism, it has been found that r_A and r_B are insensitive to both the method of initiation and to the reaction temperature (*2*).

TABLE 1. COPOLYMERIZATION REACTIVITY RATIOS

Monomer *A*	Monomer *B*	r_A	r_B
styrene	acrylonitrile	0.41	0.04
styrene	α-methyl styrene	1.25	0.10
α-methyl styrene	acrylonitrile	0.10	0.06

CONTINUOUS NONIDEAL REACTORS

For nonideal reactors, equilibrium relationships such as Equation (1) provide insufficient information to predict reactor performance, and the polymerization kinetics must also be considered. The need for introducing kinetic relationships is due to two characteristics common to all nonideal flow systems: There is a distribution of residence times in the reactor, and individual portions of the reacting mass maintain their identity for a finite period of time.

In perfect mixers, there is a distribution of residence times but the second characteristic does not apply. In piston flow reactors, individual fluid portions maintain their identity throughout the reactor, but all portions have the same residence time. Thus these ideal reactors represent special degenerate cases of general mixing phenomena.

Polymerization Kinetics

Rigorous theoretical expressions for co- and terpolymerization reaction rates are widely available in the literature (*2, 4*). Unfortunately, these expressions are rarely useful due to a lack of the necessary constants. However, useful results may be obtained by assuming a pseudo first-order, isothermal, reaction scheme:

$$\frac{-dA}{dt} = K'_A A \tag{2a}$$

(batch reaction)

$$\frac{-dB}{dt} = K'_B B \tag{2b}$$

where K'_A and K'_B are constrained by the equilibrium relationship:

$$\frac{dA}{dB} = \frac{-dA/dt}{-dB/dt} = \frac{K'_A A}{K'_B B} = \frac{A[r_A\ A + B]}{B[A + r_B\ B]} \tag{3}$$

Assuming the velocity constant K'_A really is constant, the constrained value for K'_B is given by

$$K'_B = K'_A \left[\frac{A + r_B\ B}{r_A\ A + B} \right] \tag{4}$$

The above assumption will be used throughout the remainder of this report. It is justified if conversions are small, and provides very valuable semi-quantitative results even for high conversions. However, it should be pointed out that the mathematical techniques which follow do not inherently require any specific form for the rate equations. They, and even the computer programs used to obtain numerical results, can easily be modified should better rate expressions become available.

Complete Segregation

The first characteristic of nonideal flow systems can be specified by means of the residence time decay function, $R(t)$. For any value of time, $t \geqq 0$, $R(t)$ gives the fraction of entering material which remains in the reactor for a time greater than t. Means for measuring and evaluating residence time data are well known. Knowledge of the residence time distribution, by itself, does not allow specification of the second characteristic of nonideal systems, since there are any number of mixing substates which differ with respect to the identity of individual fluid portions.

If individual fluid portions maintain their identity throughout the reactor, the system is said to be "completely segregated," and complete segregation represents one important limit on the state of mixing in any real system (*8*). This limit may be closely approached in single phase bulk polymerization reactors. Indeed, any laminar flow process will be completely segregated if molecular diffusion can be ignored.

In a completely segregated system, each fluid portion acts as a batch reactor. The over-all performance is governed by:

$$\overline{A} = -\int_0^\infty A(\theta)dR(\theta) \quad \text{where} \quad -\frac{dA}{d\theta} = K_A A \tag{5a}$$

$$\overline{B} = -\int_0^\infty B(\theta)dR(\theta) \quad \text{where} \quad -\frac{dB}{d\theta} = K_A \left[\frac{A + r_B B}{r_A A + B}\right] B \tag{5b}$$

$$\overline{S} = -\int_0^\infty S(\theta)dR(\theta) \quad \text{where} \quad \frac{dS}{d\theta} = -\frac{dA}{d\theta} - \frac{dB}{d\theta} \tag{5c}$$

where $\overline{A}$, $\overline{B}$, and $\overline{S}$ are exit mole fractions and θ is the dimensionless residence time, $\theta = t/\overline{t}$. The rate constant K_A also has a dimensionless form in these equations. It is related to the rate constant appearing in Equation (2*a*) by

$$K_A = \overline{t}K'A$$

Integration of Equation (5) will give the composition of the exit stream from the reactor. Normally, K_A will be unknown and must be found by iterating until the desired final solids is obtained. During the integration process, the composition distribution of the copolymer may also be found. The three curves marked (CS) in Figure 1 give composition distributions for a styrene/acrylonitrile copolymer reacted to 60% solids by weight. The residence time distributions chosen for these calculations correspond to piston flow and perfect mixing elements in series. The curves are characterized by the percent tubularity which corresponds to the volume fraction of the piston flow element. For 0% tubularity, the decay function is exponential. A completely segregated system with this residence time distribution is termed a *well stirred* reactor to distinguish it from a perfect mixer which has the same resi-

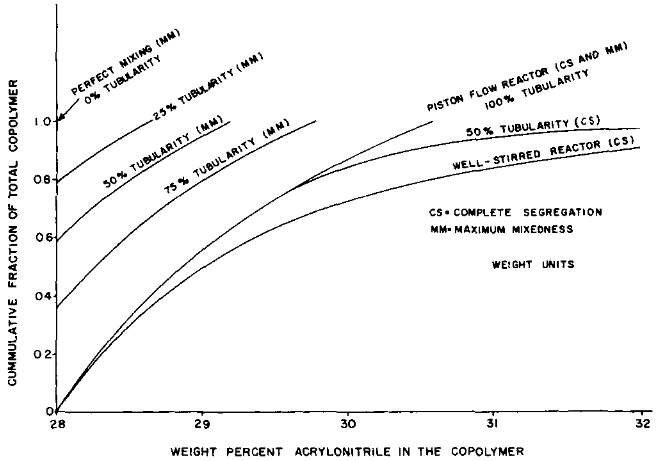


Fig. 1. *Predicted effect of nonideal mixing on styrene/acrylonitrile copolymer (60% final solids).*

dence time distribution. For 50% tubularity with complete segregation, the system corresponds to well stirred and piston flow elements in series, both elements having equal volumes. For 100% tubularity, the system is equivalent to a simple piston flow reactor.

For the results shown in Figure 1, the initial monomer compositions were chosen so that the first differential amount of copolymer would contain exactly 28% acrylonitrile by weight. As polymerization continues, the instantaneous composition shifts toward higher acrylonitrile contents. For the lower two curves shown in Figure 1, some of the individual fluid portions react to essentially 100% solids; and for these portions the instantaneous copolymer approaches pure polyacrylonitrile. For any point on the curves in Figure 1, the value of the Y coordinate gives the weight fraction of the total copolymer which has an acrylonitrile content less than the value of the X coordinate. Thus, for the well stirred reactor, about half of the total copolymer contains less than 29% acrylonitrile while 90% of the copolymer contains less than 32% acrylonitrile.

Maximum Mixedness

In complete segregation, fluid portions maintain their identity throughout the reactor. The opposite extreme to this is for individual fluid portions to have no identity whatsoever, but this situation is, by definition, perfect mixing. We now consider the case in which there is a maximum amount of mixing between individual portions (8). This maximum amount of mixing is, however, subject to the restriction of a fixed residence time distribution, and this state of maximum mixedness does not degenerate to a perfect mixer unless the distribution of residence times is exponential.

The performance of a maximum mixedness reactor can be described by a set of simultaneous differential equations conceptionally similar to Equation (5). These equations are fairly complex, particularly with regard to boundary conditions. However, if the residence time distribution corresponds to piston flow and perfect mixing elements in series, a simple physical interpretation of maximum mixedness is possible. A perfect mixing element is followed in series by a piston flow element; the percent tubularity of the system merely represents the fraction of the total volume contributed by the piston flow element.

The curves marked (MM) in Figure 1 show the composition distributions which result from maximum mixedness reactors. At 100% tubularity, completely segregated and maximum mixedness reactors give the same composition distribution which uniquely corresponds to piston flow. At lower percent tubularities, the composition distributions become narrower; and at 0% tubularity, a completely uniform copolymer is obtained. At 0% tubularity, the maximum mixedness reactor is of course identical to a perfect mixer.

Implications for Real Reactors

The most significant fact to be gained from the results shown in Figure 1 is that improved agitation does not necessarily give a more uniform copolymer. Indeed, a wider variation in compositions may actually result. As the turnover rate in the vessel is increased relative to the throughput rate, the residence times will approach an exponential distribution. However, viscosities are normally high in polymerization vessels and the fluid will be in the laminar flow regime. Unless special provisions are made, the vessel will exhibit a high degree of segregation and will thus behave as a well stirred reactor. This gives the worst copolymer composition distribution of those shown in Figure 1.

In the final analysis, high turnover rates are needed to give a uniform copolymer. However, they must be combined with a regular, systematic means for destroying the identity of individual fluid portions. This can be done by localized intensive mixing to increase the interfacial area between fluid portions which have different monomer concentrations. If this area is made sufficiently large, diffusion will give the necessary microscopic mixing.

To achieve the necessary small-scale dispersion of the reacting mass, very high power inputs per unit volume of fluid would be needed. However, these high inputs need not be applied throughout the entire reactor. Instead, they can be localized to quite small regions; and thus over-all power requirements can be kept within reasonable bounds.

RECIRCULATING LOOP REACTOR

Figure 2*a* illustrates a recirculating loop reactor for the production of chemically uniform co- and terpolymers. This reactor should be feasible from an industrial viewpoint. However, and perhaps more importantly, it serves as a model for more complex reactors.

To analyze the performance of the loop reactor, refer to the schematic representation given in Figure 2*b*. The entering flow rate is Q (lb./hr.). The quantities A_0 and B_0 are the weight fractions of the two monomers in this feed stream, and for convenience we assume $A_0 + B_0 = 1$. The flow rate through the reactor is R and that through the recycle line is $R - Q$. The composition of the streams which enter and leave the reactor are specified by the weight fractions A_I, B_I, and S_I at the entrance and A_F, B_F, and S_F at the exit ($A_I + B_I + S_I = A_F + B_F + S_F = 1$). The quantity X_A represents the weight fraction of component A which has been incorporated into the polymer. This composition is, of course, expressed on a monomer-free basis so that $1 - X_A$ is the weight of B in the polymer.

The flow through the loop reactor will correspond to laminar flow through a circular pipe. However, the fluid will be non-Newtonian; and to predict the effects of such behavior, the power law will be assumed. This gives the

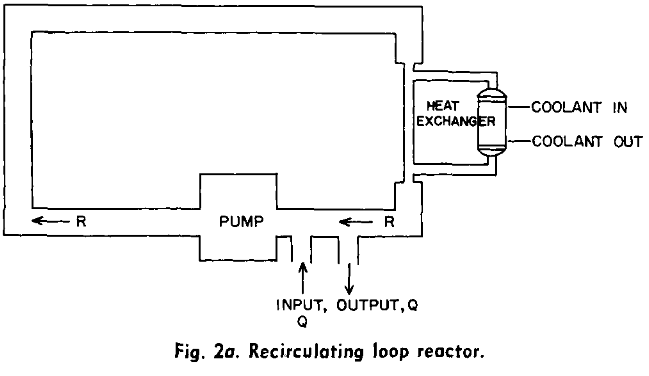


Fig. 2a. Recirculating loop reactor.

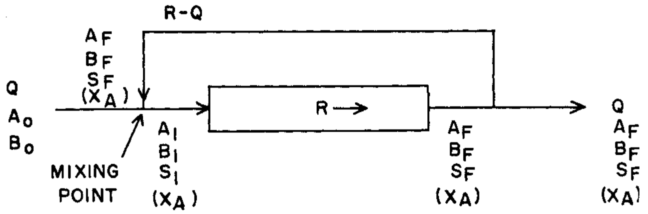


Fig. 2*b*. Schematic representation of loop reactor.

following residence time decay function:

$$R(\theta) = 1, \ \ \theta \leqq n + 1/3n + 1$$

$$R(\theta) = 1 - \left[1 + \frac{2n}{(3n+1)\ \theta} \right] \frac{1-n+1}{(3n+1)\ \theta}\ \frac{2n}{n+1},$$

$$\theta > \frac{n+1}{3n+1} \tag{6}$$

where n is the power law constant (flow behavior index). If $n = 1$, Equation (6) reduces to

$$R(\theta) = 1, \ \ \theta \leqq 1/2$$

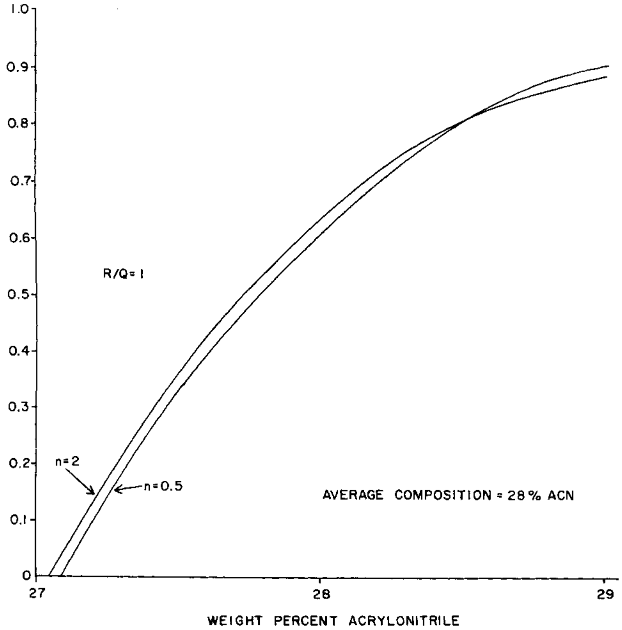
$$R(\theta) = \frac{1}{4\theta^2}, \ \ \theta > 1/2 \tag{7}$$

which corresponds to the ordinary parabolic velocity distribution for Newtonian fluids in circular pipes. For pseudoplastic fluids, $n < 1$; and the velocity profile is flattened, approaching piston flow as a limiting case. For dilatant fluids, $n > 1$; and the velocity profile becomes sharper, eventually approaching a conical distribution.

Within the loop, the fluid will have a high degree of segregation so that Equation (5) governs the polymerization reaction. The pump shown in Figure 2*a* corresponds to the mixing point in Figure 2*b*. This pump acts as a redistributor for the reacting fluid and completely destroys the identity of individual fluid portions. Note that this destruction is done only once per pass and not continuously through the reactor.

A few material balances will now complete the mathematical definition of the loop reactor. Referring to Figure 2*b*, a solids balance around the mixing point gives

$$S_I = S_F\ (1 - Q/R) \tag{8}$$



ig. 3. Effect of non-Newtonian behavior on styrene-acrylonitrile copolymer (60% final solids).

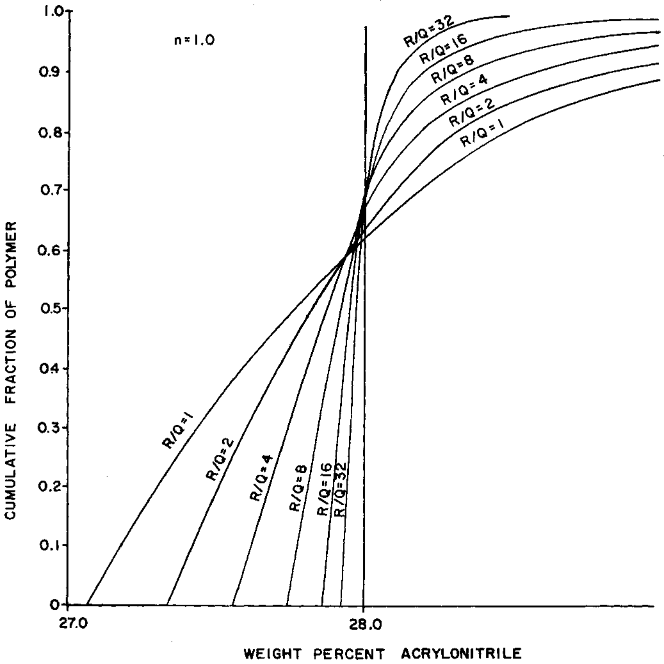


Fig. 4. Effect of recirculation ratio on styrene/acrylonitrile copolymer (60% final solids).

A balance on component A across the reactor gives

$$X_A = \frac{A_I - A_F}{S_F - S_I} \tag{9}$$

and an overall balance on A gives

$$A_o = A_F + X_A S_F \tag{10}$$

The performance of the system is now defined by the simultaneous set of equations: (5*a*), (5*b*), (5*c*), (6), (8), (9), and (10) and by the relations $A_o + B_o = A_I + B_I + S_I = A_F + B_F + S_F = 1$. Assume that the power law constant, n, is known, and that the final solids content, S_F, will be specified together with the average copolymer composition, X_A. Then for a fixed recirculation ratio, R/Q, it is desired to complete the material balances and to calculate the composition distribution for the copolymer. This entails a double trial-and-error process. Values for A_I and K_A are assumed and adjusted until the desired S_F and X_A are obtained.

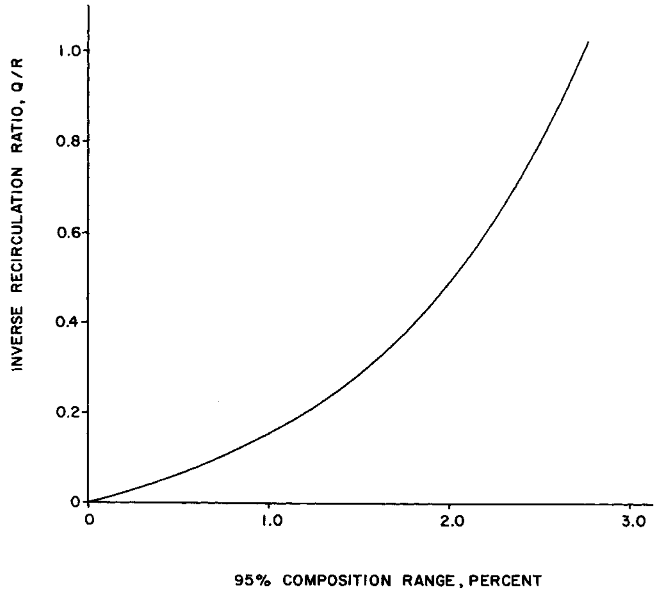


Fig. 5. Spread in copolymer compositions (styrene/acrylonitrile copolymer, 60% final solids).

Effect of Non-Newtonian Behavior

Figure 3 indicates the effect of the power law constant, n, on the composition distribution of a styrene/acrylonitrile copolymer. The curves correspond to a single pass through the reactor ($R/Q = 1$) to give 60% solids by weight. The average composition in each case is 28.00% acrylonitrile by weight.

The curves for $n = 2$ (a dilatant fluid) and for $n = 0.5$ (a pseudoplastic) are seen to be very similar. The dilatant behavior gives a somewhat wider composition distribution, but the differences are exaggerated by the unrealistically low recirculation rate. Although not shown in Figure 3, the curve for $n = 1$ (a Newtonian fluid) lies approximately midway between the curves for $n = 2$ and $n = 0.5$.

For most purposes, it would be completely adequate to assume $n = 1$. Polymer solutions are pseudoplastics so that this assumption will be slightly conservative.

Effect of Recirculation Ratio

Figure 4 shows the composition distribution of the copolymer for various recirculation ratios, R/Q. Again, the final solids content is 60% by weight, and the average copolymer composition is 28.00% acrylonitrile. Newtonian flow was assumed in all cases.

The graph shown in Figure 5 represents a useful method for characterizing the composition distributions given in Figure 4. The X coordinate of this graph gives the range for the copolymer composition, expressed in weight percent, which includes 95% of the total amount of copolymer. Thus, for $R/Q = 16$ ($Q/R = 0.0625$), Figure 4 shows that 95% of the polymer has a composition between approximately 27.9% acrylonitrile and about 28.4% acrylonitrile, giving a 95% composition range of 0.5%. It is this value which is plotted in Figure 5. If an allowable value for the composition range is known, the necessary recirculation ratio may be read directly from Figure 5.

Effect of Average Composition

The spread in copolymer compositions for any given system depends strongly on the desired average composition. This is illustrated in Figure 6 which shows the composition distributions for a 23.5% acrylonitrile/76.5% styrene copolymer together with the 28% acrylonitrile copolymer. With $r_A = 0.41$ and $r_B = 0.04$, the styrene/acrylonitrile system has a so-called "azeotrope" at 23.85% acrylonitrile. At the azeotrope, the reaction rates of the monomers becomes equal so that there is no (macroscopic) composition distribution. Since the 23.5% copolymer is nearer the azeotrope than the 28% material, it shows a narrower composition distribution. Also, this 23.5% copolymer is on the other side of the azeotrope so that the composition distribution tails off toward polystyrene rather than polyacrylonitrile.

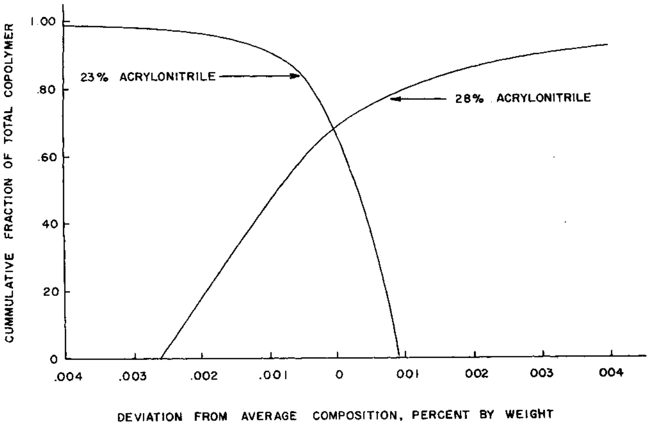


Fig. 6. Effect of average composition. $R/Q = 1.0$, 60% final solids.

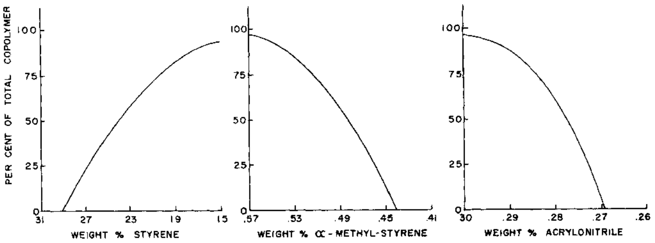


Fig. 7. Loop terpolymerization of styrene/α-methyl styrene/acrylonitrile. $R/Q = 1.0$, 60% final solids.

Loop Terpolymerization

The analysis of the loop reactor can easily be extended to terpolymers. The calculations are much more lengthy, and solution normally involves a triple trial-and-error process. However, the calculations are still feasible for a small digital computer.

Figure 7*a*, 7*b*, and 7*c* show sample composition distributions for a styrene/α-methyl styrene/acrylonitrile terpolymer. The average compositions are 23% styrene, 49% α-methyl styrene, and 28% acrylonitrile (all by weight).

MICROSCOPIC COMPOSITION DISTRIBUTIONS

In this section we are concerned with differences in overall composition between molecules formed from the same monomer mixture. This microscopic composition distribution represents a limit on the uniformity of a copolymer. Even if the copolymerization were carried out in a perfect mixer (thus giving an absolutely sharp macroscopic distribution) the residual microscopic distribution would still exist.

Knowledge of the microscopic distribution is useful since it allows an estimate of the goodness of mixing which is worth seeking in a real reactor. Taking the loop reactor as an example, there is no advantage in increasing the R/Q ratio much beyond that point where the macroscopic and microscopic composition distributions have the same spread.

Stockmayer (7) has derived an expression for the microscopic distribution of copolymer composition. Let X_A denote the mole fraction of component A in the polymer, and define a parameter K as

$$K = [1 - 4X_A\,(1 - X_A)(1 - r_A r_B)]^{1/2} \qquad (11)$$

Let N denote the average number of monomer units which together form a growing polymer radical. Then

$$F(X) = 3/4\left[\frac{N}{2X_A(1-X_A)K}\right]^{1/2}\left[1+\frac{(X_A-X)^2\,N}{2X_A(1-X_A)K}\right]^{-5/2} \qquad (12)$$

is the frequency function of the radical composition distribution. This function is defined such that $F(X)\,dX$ gives the fraction of the total number of polymer radicals which have a composition between X and $X + dX$.

The only major assumption in Equation (12) is that the chain length is sufficiently long so that the radical composition is independent of the exact nature of the initiation process. However, note that Equation (12) gives the composition distribution of radicals rather than finished polymer molecules, and this does not reflect the termination step. If termination were spontaneous, these distributions would be identical. For termination by combination, the average length of a finished molecule will be twice the average radical length. From this viewpoint, the proper value for N should be half the value calculated from the number-average molecular weight; but this neglects the narrowing of the composition distribution which also results from the combination process. A radical with a large deviation from the average composition will usually combine with a radical which is much nearer to the average in composition. This, of course, tends to reduce the spread in compositions for the finished molecules.

The two effects described above tend to cancel, and as a working approximation it will be assumed that Equation (12) applies to the finished molecules when N is calculated from the number-average molecular weight.

As defined by Equation (12), the quantity $F(X)\ dX$ represents a mole fraction. To convert to weight fractions, define $g(X)$ as

$$g(X) = \left[\frac{X\ W_A + (1-X)\ W_B}{X_A\ W_A + (1-X_A)\ W_B}\right] F(X) \qquad (13)$$

where W_A and W_B are the molecular weights of the two monomers. Then $g(X) d_X$ gives the weight fraction of the polymer which has a composition between X and $X + d_X$. (X and X_A still denote mole fractions of the monomers, however.)

The microscopic distribution was calculated for the 28% acrylonitrile styrene copolymer using Equations (11), (12), and (13), and the results are shown in Figure 8. The weight average molecular weight was assumed to be 180,000 which is fairly typical for such products. The number-average molecular weight should be about half this or 90,000. For a copolymer containing 28% acrylonitrile by weight, this gives $N = 1100$. The microscopic distribution is symmetrical about the average composition with tails tending toward both polystyrene and polyacrylonitrile (a negligible skewness is caused by expressing the distribution in weight units).

To compare the microscopic distribution with the macroscopic distributions due to drifting monomer compositions, it is convenient to use a cumulative distribution function. Expressed in this form, the microscopic composition distribution can be compared directly to the results given for the loop reactor in Figure 4. It was found that the microscopic distribution gives the same fraction of high acrylonitrile containing polymer as the distribution for the loop reactor with $R/Q = 8$ (60% solids). The two distributions are shown in Figure 9. It was logical to compare the distributions in the high acrylonitrile region since this region has the strongest influence on product quality.

In actual fact, the copolymer made in a continuous reactor will have some overall composition distribution which is due to the combined microscopic (molecular statistics) and macroscopic (monomer drift) effects. To some extent this overall distribution can always be improved by increasing the recirculation rate. However, the microscopic distribution shown in Figures 8 and 9 represents a definite limit on the overall distribution, and it is obvious that improvements in the macroscopic distribution can soon reach a point of diminishing returns. From the comparison shown in Figure 9, it is seen that for copolymer at 60% solids, there is little to be gained beyond a recirculation ratio of 8. However, some improvement is still possible; and a number of simplifying assumptions were necessary in calculating the composition distributions. Thus it seems better to take $R/Q = 16$ as a rough a priori limit on the break-even point between product quality and pumping costs.

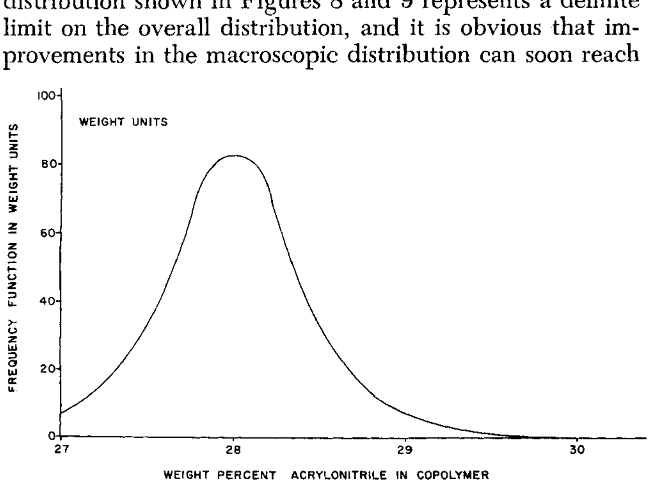


Fig. 8. Microscopic distribution for styrene/acrylonitrile copolymer.

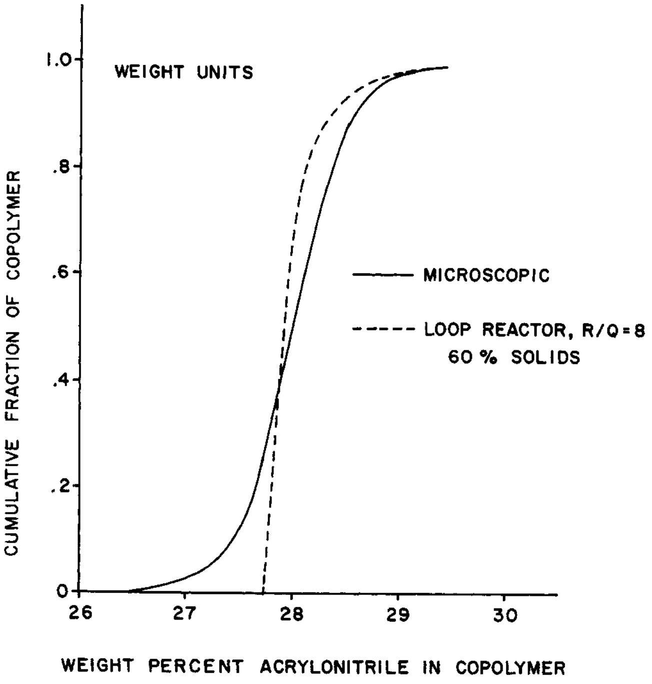


Fig. 9. Comparison of macro- and microscopic composition distributions. Styrene/acrylonitrile copolymer.

CONCLUSIONS

This paper has attempted to demonstrate the importance of flow and mixing effects on the production of copolymers and has predicted copolymer composition distributions for several model reactors. To produce a chemically uniform material, the reaction vessel must approximate a perfect mixer. However, an ill conceived approach to this can give the worst possible results. One must achieve a system residence time distribution close to that of a perfect mixer; but more importantly, it is necessary to periodically destroy the identity of individual portions of the reacting mass. Of the two mixing extremes known as complete segregation and maximum mixedness, it is maximum mixedness that is needed for good copolymers. One way to approach this is via the loop reactor which we have discussed in detail. Also, the loop reactor can serve as a design model for other types of reaction vessels.

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Manuscript received February 1, 1968; revision received April 24, 1968; paper accepted April 25, 1968. Paper presented at AIChE St. Louis meeting.