JOURNAL OF APPLIED POLYMER SCIENCE VOL. 17, PP. 1339-1360 (1973)

# Analysis of Tanks-in-Series Model with Backflow for Free-Radical Polymerization

J. S. SHASTRY, L. T. FAN, and L. E. ERICKSON, *Department of Chemical Engineering, Kansas State University, Manhattan, Kansas 66506*

## Synopsis

Free-radical polymerization in a flow reactor represented by the tanks-in-series model with backflow was considered. Conversions and molecular weight distributions were computed as functions of the backflow parameter, and the results were compared with the conversion and molecular weight distribution from a CSTR and those from a plug-flow reactor. Backflow was found to be undesirable for the polymerization mechanism under investigation. Values of the degree of segregation for the tanks-in-series model were calculated by using Zwietering's approach as a function of backflow.

## INTRODUCTION

The use of continuous-flow reactors for commercial production of polymers and for kinetic study of polymerization reactions has increased considerably in the last decade. Two types of basic reactors, the tubular reactor and the stirred-tank reactor (or any combination thereof), have been employed for this purpose. The properties of the polymers produced from these reactor systems are greatly influenced by the type of reactors used and the reactor configuration. For example, the molecular weight distributions in these systems vary considerably and are also strongly dependent on the mechanism of polymerization reaction (lifetime of free radicals).[1] In modeling and simulating flow polymerization reactors,[2-10] the tubular reactor has been considered almost always as a plug-flow reactor and the stirred-tank reactor, as a completely mixed reactor. In reality, however, the flow behavior in a polymerization reactor usually does not follow either of these two ideal flow patterns. The flow behavior can often be approximated by using a tanks-in-series model with backflow. This model includes the two extreme cases of plug flow and complete mixing as well as a number of cases with intermediate amounts of mixing. It should be pointed out that the tanks-in-series with backflow model does not restrict the design of the polymerization reactor. For example, a tubular reactor with axial mixing can be modeled by a tanks-in-series with backflow model.

The purpose of this paper is to present the model of a flow polymerization reactor which was derived based on the assumption that the flow pattern could be represented by stirred tanks-in-series with backflow model. The simulated performance data under various conditions including residence time distributions, conversions, and molecular weight distributions are also presented and analyzed. Extreme conditions, which result in limiting conditions of the model, namely, the CSTR and the plug-flow model are also examined.

## FLOW MODEL

Modeling of a flow chemical reactor consists of three different aspects: (i) modeling the kinetics of the chemical reactions to obtain a batch-kinetics expression, (ii) modeling the flow behavior or the macromixing condition, and (iii) modeling the micromixing condition. The flow model investigated in this work is shown in Figure 1. In this figure, $q_0$ is the overall forward flow rate and $q'$ is the backflow rate (flow from tank $i$ to tank $i - 1$: $2 < i < N$). This model assumes that all the tanks have the same volume; extension to cases with unequal volumes is straightforward. The backflow parameter $B$ is defined as

$$B = \frac{q'}{q_0}. \tag{1}$$

The macromixing effect is accounted for by the number of tanks in the model and the extent of backflow.

Macromixing in reactor systems can be described by the residence time distribution (RTD) of the fluid elements in the reactor. Shinnar and Noar[11] developed a general method for calculating residence time distributions for systems with internal reflux. They examined the $N$ tanks-in-series model with backflow and computed RTDs for some special cases. In the present work, expressions for RTDs for the system in Figure 1 were derived by considering an impulse input of a tracer into the first reactor (Appendix I).

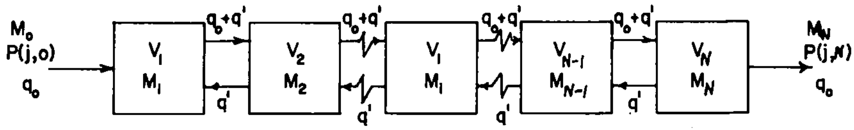


Fig. 1. Schematic representation of the $N$-tank model with backflow.

When there are three tanks of equal volume in the model, the age distributions are

$$E_3(\theta) = 27(1 + B)^2\bar{t}\left\{\frac{e^{-a\theta}}{(b - a)(c - a)} + \frac{e^{-b\theta}}{(a - b)(c - b)} + \frac{e^{-c\theta}}{(a - c)(b - c)}\right\}. \tag{2}$$

$$E_2(\theta) = 9(1 + B)\bar{t}\left\{\frac{1}{c - b}\left(e^{-b\theta} - e^{-c\theta}\right)\right\} \tag{3}$$

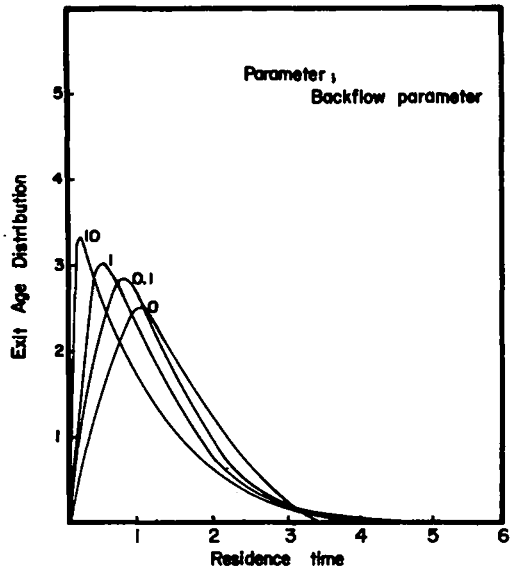


Fig. 2. Effect of backflow on the exit age distribution, $E_3(t)$.

and

$$E_1(\theta) = 3\bar{t}\left\{\frac{b^2 - a_1b + a_0}{(c-b)(a-b)}\,e^{-b\theta} + \frac{c^2 - a_1c + a_0}{(b-c)(a-c)}\,e^{-c\theta} + \frac{a^2 - a_1a + a_0}{(b-a)(c-a)}\,e^{-a\theta}\right\} \quad (4)$$

in which $E_i(\theta)$ = exit age distribution in tank $i$; $\theta$ = dimensionless time, $t/\bar{t}$; $\bar{t}$ = mean residence time in the reactor system; $a = 3(1 + B)$; $b = [3(2 + 3B) + \sqrt{9(2 + 3B)^2 - 36(1 + B)}]/2$; $c = [3(2 + 3B) - \sqrt{9(2 + 3B)^2 - 36(1 + B)}]/2$; $a_1 = b + c$; and $a_0 = bc + 9B + 9B^2$. These RTD values are shown in Figure 2 and are compared with RTD when $B = 0$. It can be seen that all three roots of the cubic $a$, $b$, and $c$ coincide when $B = 0$, and this represents the case when there is no backflow in the system. Another extreme case arises when $B$ is infinitely large, i.e., $B = \infty$. In this case, the model reduces to one CSTR, as there is an infinite exchange of matter between the tanks in the model.

For nonlinear reactions, macromixing alone is not enough to determine the conversion and MWD in a flow reactor. Under these situations, the micromixing component, which specifies the concentration history experienced by the molecules during their passage through the system, must be considered. Often the concept of degree of segregation ($J$) is used to quantify the micromixing in a reactor system. This concept was first introduced be Zwietering[12] and involves calculation of $J$ by using the relationship

$$J = \frac{\text{var } \alpha_p}{\text{var } \alpha} \quad (5)$$

TABLE I
Effect of Backflow and Number of Tanks-in-Series on Degree of Segregation Under the State of Sequential Mixedness

| No. of tanks in model | Backflow parameter | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | ∞ |
| 1 | 0.0 | — | — | — | — | |
| 2 | 0.1429 | 0.1129 | 0.0912 | 0.0591 | 0.0251 | 0.0 |
| 3 | 0.250 | 0.1941 | 0.1412 | 0.1131 | 0.0781 | 0.0 |
| 5 | 0.400 | 0.3018 | 0.2165 | 0.1510 | 0.1104 | 0.0 |
| 10 | 0.600 | 0.5100 | 0.4210 | 0.3000 | 0.2510 | 0.0 |
| ∞ | 1.000 | 1.00 | 1.00 | 1.00 | 1.00 | — |

in which $J$ = the degree of segregation; $\alpha$ = age of a fluid element; and $\alpha_p$ = mean age of a molecule within a point.

It was shown by Zwietering[12] that for a maximum mixedness stirred-tank reactor, the value of $J$ is zero, and for a completely segregated reactor, $J$ is unity. (It is interesting to note that $J$ is equal to unity for a completely segregated CSTR and also for a completely segregated plug-flow reactor.) Various cases of the model considered in this investigation lie between these two extreme cases, and therefore the values of $J$ calculated for these cases must be between zero and 1. The calculated $J$ values for all cases of the model are presented in Table I (see Appendix II). The results given in this paper were obtained on the assumption that the whole system is in the state of sequential mixedness, that is, each tank is sep-

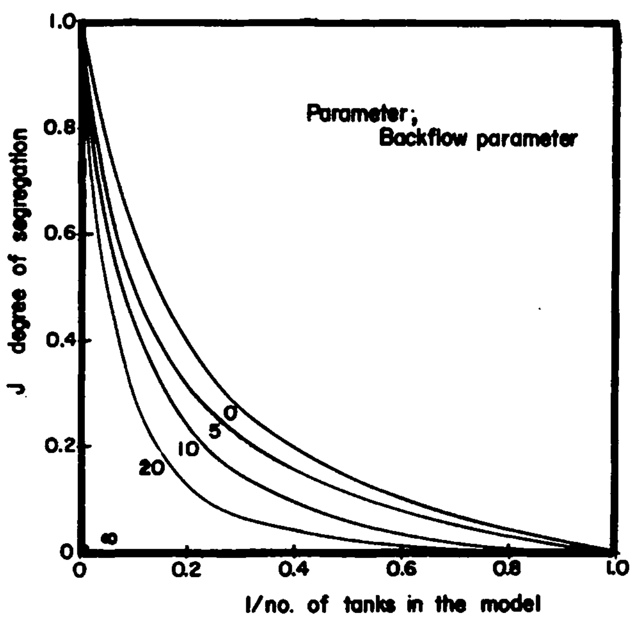


Fig. 3. Effect of backflow on the degree of segregation for $N$ tanks-in-series model.

arately in the state of maximum mixedness, and the material from tank $i$ is fed to tank $i + 1$. Extension to other cases where some or all the tanks are in the state of segregation is not straightforward and remains unsolved. It can be seen from Table I that if the $N$ CSTRs-in-series model is used to generate an RTD between the RTD of the CSTR and that of the plug-flow reactor, the farther the RTD of the model deviates from the RTD of the CSTR, the farther the $J$ under the state of sequential mixedness deviates positively from zero. It increases up to 1 as the RTD of the model approaches the RTD of the plug-flow reactor. For a fixed number of tanks, an increase in backflow makes the RTD of the model approach the RTD of the CSTR, and hence $J$ decreases as backflow is increased and reaches a value of zero for infinite backflow. For the same backflow parameter ($B$), an increase in the number of tanks in the model increases the degree of segregation. The effect of backflow on the degree of segregation is presented in Figure 3.

## POLYMERIZATION MODEL

The polymerization mechanism considered in this investigation consists of three steps—initiation, propagation, and termination:

$$M_1 \xrightarrow{k_{in}} P_1 \qquad \text{initiation}$$

$$P_j + M_1 \xrightarrow{k_p} P_{j+1} \qquad \text{propagation}$$

$$P_j + M_1 \xrightarrow{k_t} M_{j+1} \qquad \text{termination}$$

here $M_1$ represents the monomer, $P_j$ the active polymer of chain length $j$, and $M_j$ the dead polymer of chain length $j$.

Isothermal conditions were assumed for the flow reactor under consideration; this means that the rate constants in all the tanks in series were identical. Material balance equations were derived for monomer concentration, active polymer concentration, dead polymer concentration, and total active polymer concentration.

In what follows, the first index within the parenthesis refers to chain length while the second index refers to the number of the tanks: The monomer material balances for the flow reactor are

$$M(1,0)\alpha_{f_1} + \{M(1,2) - M(1,1)\}\alpha_{b_1} - \alpha_{f_1}M(1,1) - M(1,1)\left\{k_{tn} + \sum_{j=1}^{\infty}[(k_p + k_t)P(j,1)]\right\} = 0 \qquad \text{tank 1} \quad (6)$$

$$\alpha_{T_i}\{M(1,i-1) - M(1,i)\} - M(1,i)\left\{k_{tn} + \sum_{j=1}^{\infty}[(k_p + k_t)P(j,i)]\right\} + \alpha_{b_i}\{M(1,i+1) - M(1,i)\} = 0 \qquad \text{tank } i(1 < i < N) \quad (7)$$

$$\alpha_{T_N}M(1,N-1) - \alpha_{b_N}M(1,N) - \alpha_{f_N}M(1,N) - M(1,N)\left\{k_{tn} + \sum_{j=1}^{\infty}[(k_p + k_t)P(j,N)]\right\} = 0 \qquad \text{tank } N \quad (8)$$

For an active polymer of chain length $1 (j = 1)$, the material balances are

$$-\alpha_{f_1}P(1,1) + M(1,1)\{k_{in} - (k_p + k_t)P(1,1)\} + \alpha_{b_1}\{P(1,2) - P(1,1)\} = 0 \quad \text{tank 1} \quad (9)$$

$$\alpha_{T_i}\{P(1,i-1) - P(1,i)\} + M(1,i)\{k_{in} - (k_p + k_t)P(1,i)\} + \alpha_{b_i}\{P(1,i+1) - P(1,i)\} = 0 \quad \text{tank } i(1 < i < N) \quad (10)$$

$$\alpha_{T_N}P(1,N-1) - \alpha_{b_N}P(1,N) - \alpha_{f_N}P(1,N) + M(1,N)\{k_{in} - (k_p + k_t)P(1,N)\} = 0 \quad \text{tank } N \quad (11)$$

For an active polymer of chain length $j$ $(j \geq 2)$, the material balances are

$$-\alpha_{T_1}P(j,1) + \alpha_{b_1}P(j,2) + M(1,1)\{k_pP(j-1,1) - (k_p + k_t)P(j,1)\} = 0 \quad \text{tank 1} \quad (12)$$

$$\alpha_{T_i}\{P(j,i-1) - P(j,i)\} + \alpha_{b_i}\{P(j,i+1) - P(j,i)\} + M(1,i)\{k_pP(j-1,i) - (k_p + k_t)P(j,i)\} = 0, \quad \text{tank } i(1 < i < N) \quad (13)$$

$$\alpha_{T_N}P(j,N-1) - \alpha_{b_N}P(j,N) - \alpha_{f_N}P(j,N) + M(1,N)\{k_pP(j-1,N) - (k_p + k_t)P(j,N)\} = 0 \quad \text{tank } N \quad (14)$$

The material balances for dead polymer of chain length $j (j \geq 2)$ are

$$-M(j,1)\alpha_{T_1} + M(j,2)\alpha_{b_1} + k_tP(j-1,1)M(1,1) = 0 \quad \text{tank 1} \quad (15)$$

$$\alpha_{T_i}\{M(j,i-1) - M(j,i)\} + \alpha_{b_i}\{M(j,i+1) - M(j,i)\} + k_tP(j-1,i)M(1,i) = 0 \quad \text{tank } i(1 < i < N) \quad (16)$$

$$\alpha_{T_N}M(j,N-1) - \alpha_{b_N}M(j,N) - \alpha_{f_N}M(j,N) + k_tP(j-1,N)M(1,N) = 0 \quad \text{tank } N \quad (17)$$

in which $M(j,i)$ = concentration of dead polymer of chain length $j$ in reactor, $i, j \geq 2$; $M(1,i)$ = concentration of monomer in reactor; $P(j,i)$ = concentration of active polymer of chain length $j$ in reactor; $k_{in}, k_p$, and $k_t$ = rate constants; $\alpha_{f_i} = q_0/V_i$; $\alpha_{b_i} = q'/V_i$; $\alpha_{T_i} = (q_0 + q')/V_i$; and $V_i$ = volume of the $i$th reactor.

The relation between the total active polymer concentration and the concentration of individual polymers

$$P_T(i) = \sum_{j=1}^{\infty} P(j,i) \quad (18)$$

is necessary to solve the system of eqs. (6) through (17). The material balances for the total polymer are

$$-\alpha_{f_1}P_T(1) + M(1,1)\{k_{in} - k_tP_T(1)\} + \alpha_{b_1}\{P_T(2) - P_T(1)\} = 0 \quad \text{tank 1} \quad (19)$$

$$\alpha_{T_i}\{P_T(i-1) - P_T(i)\} + M(1,i)\{k_{in} - k_t P_T(i)\} + \alpha_{b_i}\{P_T(i+1) - P_T(i)\} = 0 \qquad \text{tank } i(1 < i < N) \tag{20}$$

$$\alpha_{T_N} P_T(N-1) - \alpha_{b_N} P_T(N) - \alpha_{f_N} P_T(N) + M(1,N)\{k_{in} - k_t P_T(N)\} = 0 \qquad \text{tank } N \tag{21}$$

Equations (6) through (21) completely describe the polymerization process in the flow reactor represented by the $N$ tanks-in-series with backflow model.

## SIMULATION

Steady-state simulation of the given reactor system was carried out by simultaneously solving eqs. (6) through (21). The following rate constants and flow parameters employed by Liu and Amundson[15] were used:

| | |
|---|---|
| $k_{in} = 0.025$ hr$^{-1}$ | $M_0 = 1.0$ g mole/l. |
| $k_p = 60.0$ l./g mole hr | total volume = 3.6 liters |
| $k_t = 1.0$ l./g mole hr | $q = 1.0$ l./hr |

Simulation results were obtained for different backflow rates and different numbers of tanks in the series. An iterative solution procedure was employed to solve the set of nonlinear simultaneous algebraic equations. A solution was assumed in the solution space (Fig. 4) for $P(j,i)$ and $M(j,i)$; $j = 1, 2, \ldots, 150$, and $i = 2, \ldots, N$. This assumed solution was improved upon by iteration using eqs. (6) through (21) till a desired accuracy was obtained. The following stopping criteria were used for terminating the iterative procedure:

$$|M(1,i)^{k+1} - M(1,i)^k| \leq \epsilon_1 \tag{22}$$

$$|P_T^{k+1}(i) - P_T^k(i)| \leq \epsilon_2 \tag{23}$$

$$M(1,0) - M(1,N) = \sum_{j=1}^{150} jP(j,N) + \sum_{j=2}^{150} jM(j,N). \tag{24}$$

Equations (22) and (23) were used to determine the stopping criteria, whereas eq. (24) was used for checking the accuracy of the solution by examining the amount of polymer formed and the amount of monomer consumed. The molecular weight distributions and corresponding moments were calculated using the relationships

$$W(j,i) = \frac{j[P(j,i) + M(j,i)]}{M(1,0) - M(1,i)} \tag{25}$$

$$\mu(i) = \frac{\sum_{j=1}^{\infty} jW(j,i)}{\sum_{j=1}^{\infty} W(j,i)} \tag{26}$$

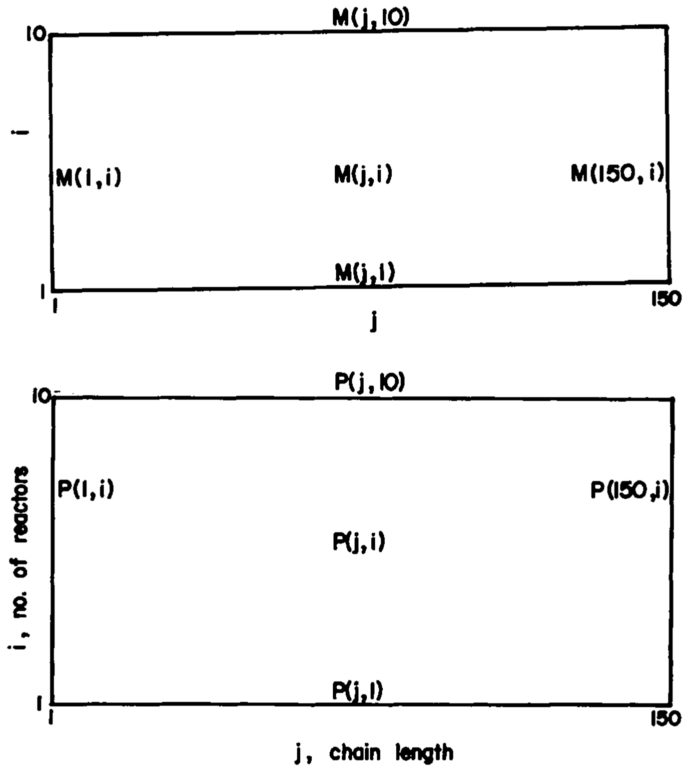


Fig. 4. Solution spaces for $M(j,i)$ and $P(j,i)$.

$$\sigma^2(i) = \frac{\sum_{j=1}^{\infty} j^2 W(j,i)}{\sum_{j=1}^{\infty} W(j,i)} - \mu^2(i) \qquad (27)$$

in which $W(j,i)$ = weight fraction of a polymer chain length $j$ in reactor $i$; $M(1,0)$ = feed monomer to tank 1; $\mu(i)$ = mean of molecular weight distribution in reactor $i$; and $\sigma^2(i)$ = variance of molecular weight distribution in reactor $i$.

## RESULTS AND DISCUSSION

### Computational

Results computed on an IBM 360/50 model computer are presented in this section. About 3–5 min of computer time were required for one set of calculations for the model without backflow, but the time required for computation increased with the introduction of backflow. In addition, a a larger number of iterations were required to obtain the desired accuracy for the cases with backflow than for the case without backflow.

## No Backflow

Four cases of the tanks-in-series model consisting of 1, 2, 3, and 5 tanks in series were considered, and the results obtained were compared with those of the ideal plug-flow reactor model (infinite number of tanks with no backflow).

Results for the case without backflow are presented in Table II. It is well known that as the number of tanks increases, the flow pattern of the

TABLE II
Results of Computations for Zero Backflow

| No. of tanks in model | Exit monomer concn. | Exit mol wt distribution | | |
|---|---|---|---|---|
| | | Mean | Variance | Peak at |
| 1 | 0.2399 | 44.89 | 610.84 | 28 |
| 2 | 0.1438 | 44.19 | 589.97 | 26 |
| 3 | 0.0633 | 38.73 | 549.98 | 20 |
| 5 | 0.0174 | 34.60 | 541.66 | 13 |
| ∞ | 0.0151 | 30.32 | 513.91 | 11 |

tanks-in-series model approaches that of the plug-flow reactor. It is evident from the table that as the number of tanks ($N$) in the model increases, the conversion increases and the monomer concentration falls. The molecular weight distribution (MWD) becomes narrower as $N$ is increased, and this reduces the variance of MWD. The mean of the MWD and the mode both decrease as $N$ increases as shown in Table II and Figure 5. It can be seen that the results for the tanks-in-series model approach those of the plug-flow model as $N$ approaches infinity. It should be noted here that the conversion in the first tank is reduced as the number of tanks are increased because the holding time in the first tank is reduced.

Molecular weight distributions of the product polymer obtained from models with 2, 3, and 5 tanks are presented in Figures 6 through 8. Comparison of these figures shows that inclusion of additional tanks in the model narrows the MWD and reduces the variance, and a lower variance makes the product more desirable. Exit molecular weight distributions from the three cases are compared with each other and with the extreme cases (plug flow and CSTR) in Figure 5. It can be concluded that for the polymerization mechanism under consideration, the plugflow reactor (infinite number of tanks in the model) gives the maximum conversion and the narrowest MWD.

## Backflow

If backflow is introduced, the model tends to become more homogeneous, and at a very high backflow, the system behavior approaches that of the CSTR (for a finite number of tanks). Conversions obtained fort he three cases (2, 3, and 5 tanks) of the tanks-in-series model and im-

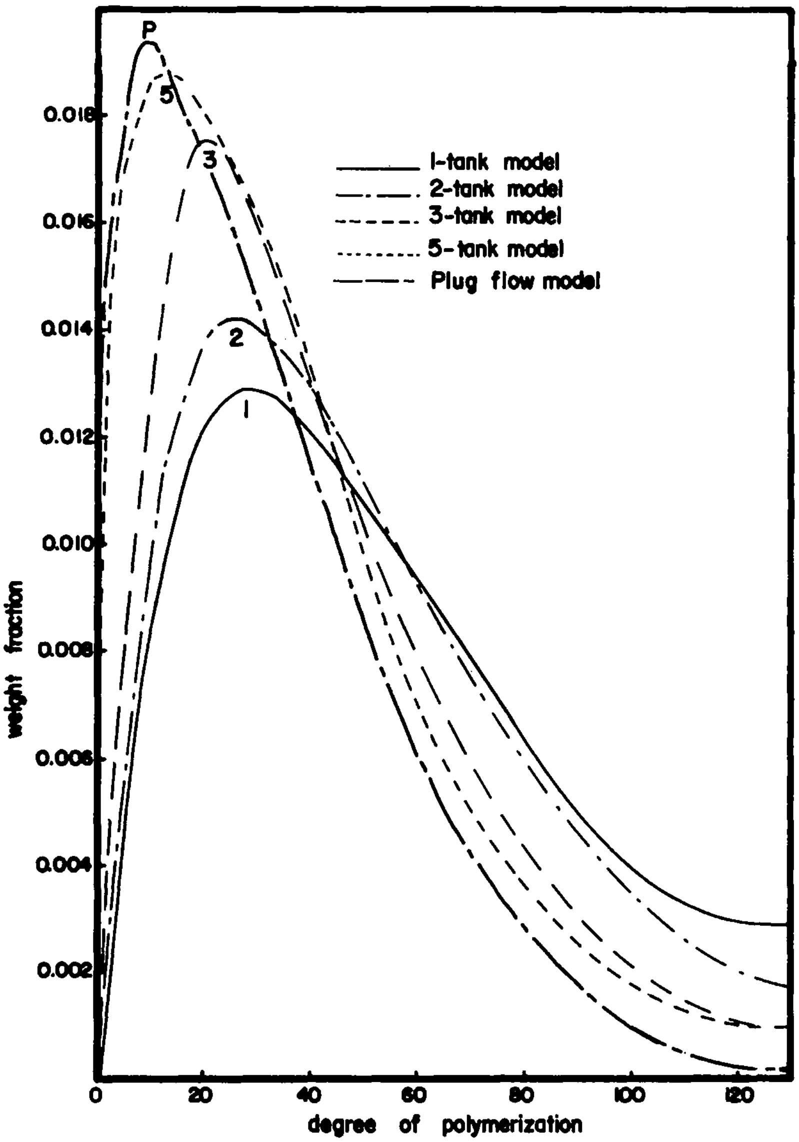


Fig. 5. Comparison of exit molecular weight distribution for the four models.

portant MWD parameters are presented in Tables III through V. An increase in backflow reduces the overall conversion in all three cases, and if the backflow is increased infinitely, conversion for each of the three cases approaches the conversion obtained from the one-tank model, which is the lower limit for conversion for the mechanism under consideration. Exit molecular weight distributions of the product polymer from the three cases are shown in Figures 9 through 11. It is evident that as backflow is increased, the variance of the MWD increases making the polymer less

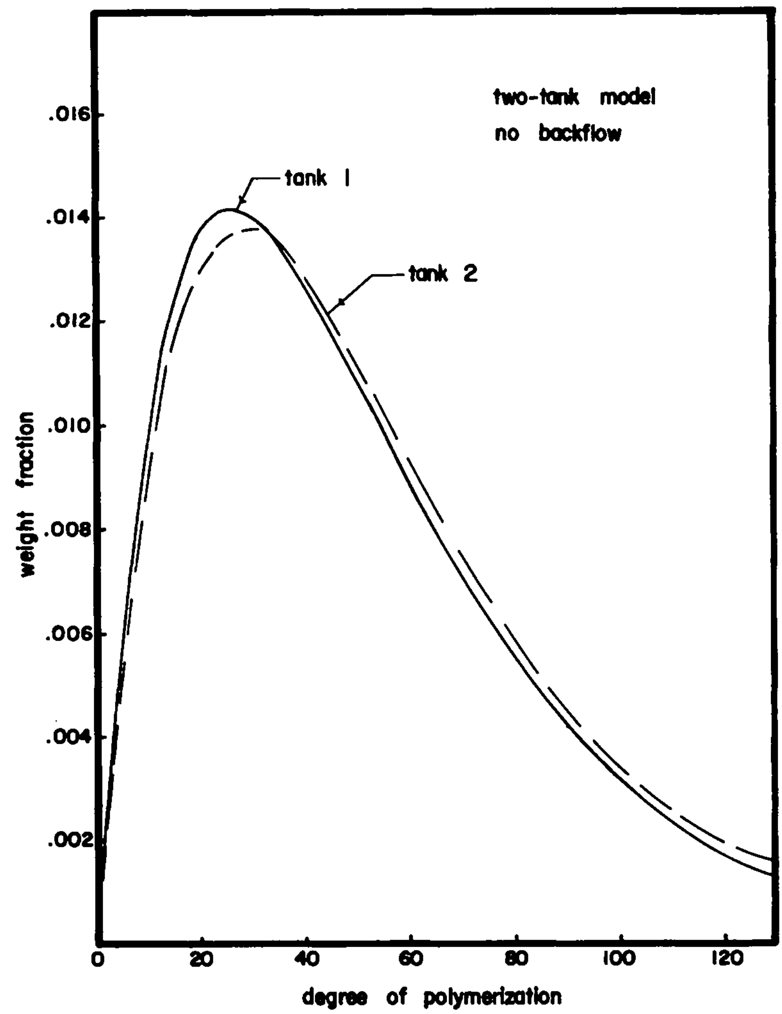


Fig. 6. Molecular weight distribution in the 2-tank model for free-radical polymerization.

desirable. Increase in backflow, however, shifts the peak to the left and thus decreases the mean of the MWD. For the mechanisms under investigation, an increase in backflow yields a wider MWD; and thus, backflow is not desirable.

## Modified Mechanism

It has been shown that an infinite number of tanks without backflow (plug flow without dispersion) gives the maximum conversion and the narrowest MWD. However, if the termination mechanism is modified to

$$P_i + P_j \rightarrow M_{i+j}$$

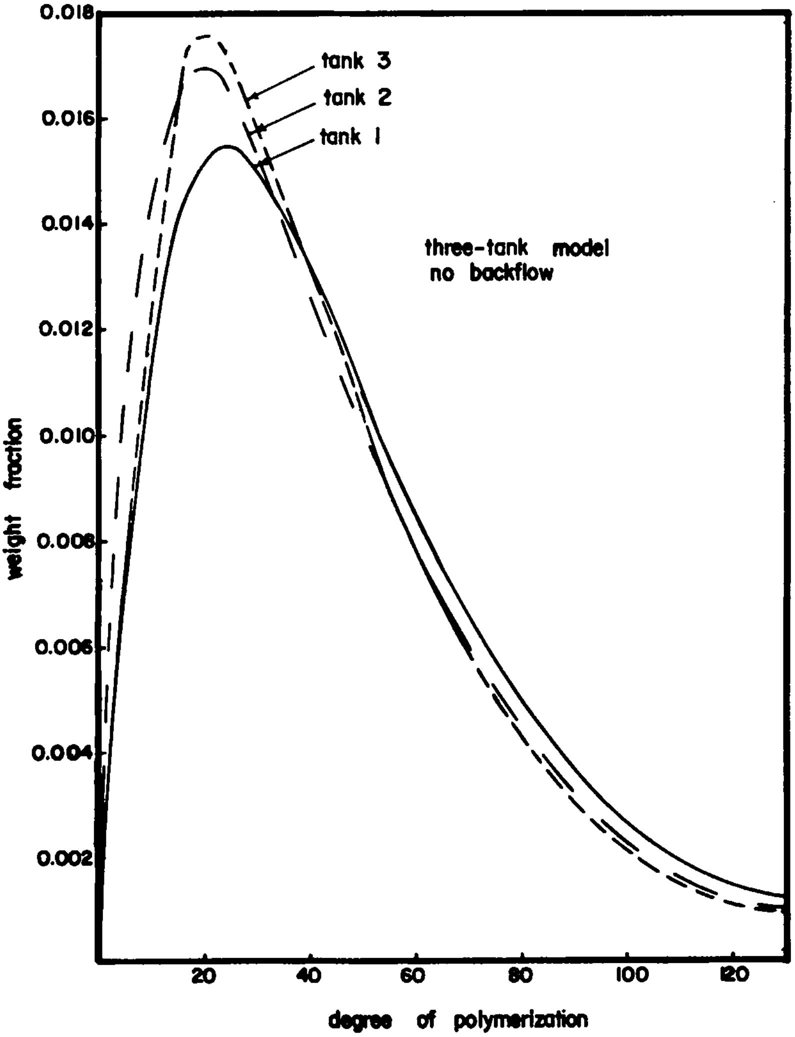


Fig. 7. Molecular weight distribution in the 3-tank model free-radical polymerization.

TABLE III
Effect of Backflow on Conversion and Molecular Weight Distribution (MWD) for the Two-Tank Model

| Backflow Parameter | Monomer concentration | | MWD | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Mean | | Variance | | Peak | |
| | Tank 1 | Tank 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| 0 | 0.4083 | 0.1438 | 42.89 | 44.19 | 592.78 | 589.97 | 26 | 26 |
| 10 | 0.2613 | 0.2279 | 44.79 | 44.80 | 611.23 | 611.15 | 28 | 28 |
| 20 | 0.2515 | 0.2338 | 44.86 | 44.80 | 612.01 | 611.92 | 28 | 28 |

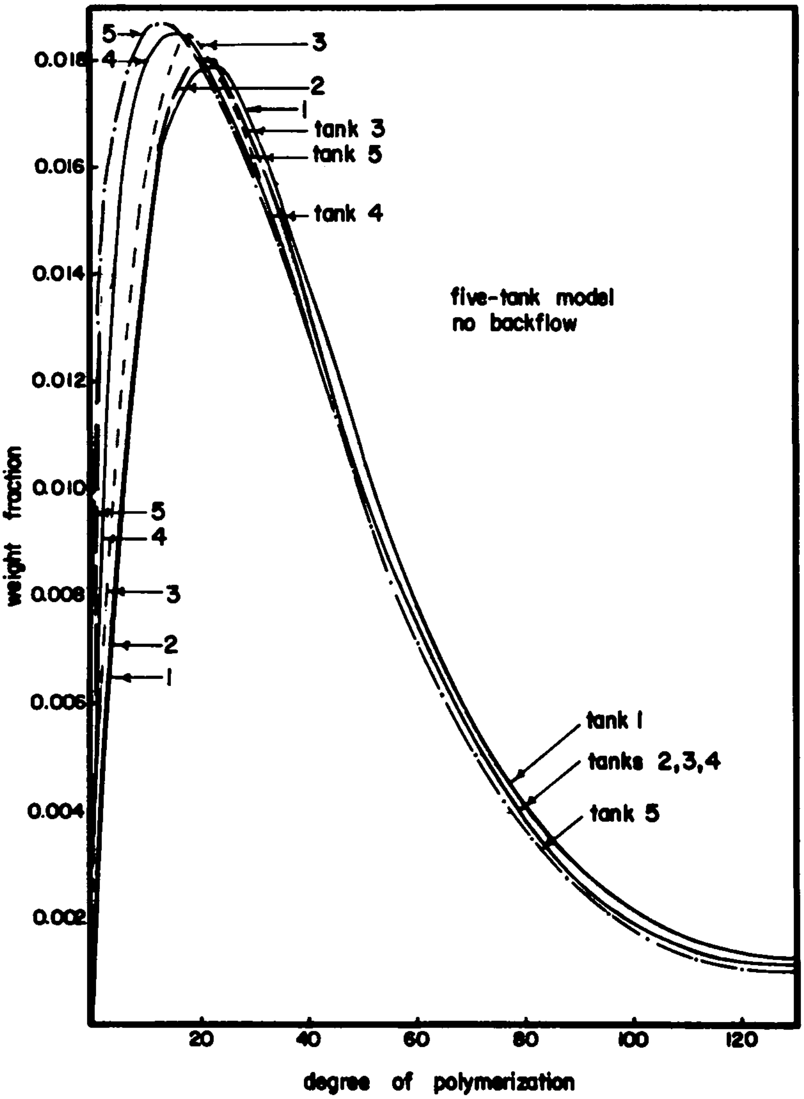


Fig. 8. Molecular weight distribution in the 5-tank model for free-radical polymerization.

the one-tank model would yield the narrowest distribution and backflow would be more desirable. From the conversion standpoint, the plug-flow reactor would be superior to the CSTR for this modified mechanism.

## Comparison with "Dispersion" Model

It should be noted that a correspondence exists between the tanks-in-series model and the "axial dispersion" model often used to model non-ideal flow behavior.[16] Elementary processes visualized for these models are similar in that fluid can move upstream by both dispersion and by

TABLE IV
Effect of Backflow on Conversion and Molecular Weight Distribution (MWD) for the Three-Tank Model

| Backflow parameter | Monomer concentration | | | MWD | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Mean | | | Variance | | | Peak | | |
| | Tank 1 | Tank 2 | Tank 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| 0 | 0.5294 | 0.1839 | 0.0633 | 40.90 | 38.36 | 38.73 | 569.96 | 564.98 | 549.58 | 24 | 19 | 20 |
| 10 | 0.2766 | 0.2332 | 0.2114 | 44.37 | 44.38 | 44.39 | 607.34 | 607.36 | 607.16 | 28 | 28 | 28 |
| 15 | 0.2654 | 0.2350 | 0.2198 | 44.48 | 44.47 | 44.47 | 609.89 | 609.66 | 609.13 | 28 | 28 | 28 |
| 20 | 0.2573 | 0.2381 | 0.2208 | 44.71 | 44.58 | 44.82 | 611.81 | 611.71 | 610.10 | 28 | 28 | 28 |

TABLE V
Effect of Backflow on Conversion and Molecular Weight Distribution (MWD) for the Five-Tank Model

| Backflow parameter | Monomer concentration | | | | | MWD | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Mean | | | | | Variance | | | | | Peak | | | | |
| | Tank 1 | Tank 2 | Tank 3 | Tank 4 | Tank 5 | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 | 5 |
| 0 | 0.6862 | 0.3645 | 0.1530 | 0.0516 | 0.0174 | 37.03 | 37.50 | 36.17 | 34.80 | 34.60 | 515.74 | 519.00 | 528.46 | 541.66 | 540.82 | 21 | 21 | 18 | 15 | 13 |
| 5 | 0.3451 | 0.2605 | 0.1989 | 0.1583 | 0.1380 | 43.08 | 43.04 | 43.00 | 42.97 | 42.97 | 602.68 | 603.81 | 604.70 | 605.33 | 605.28 | 25 | 25 | 25 | 25 | 25 |
| 7.5 | 0.3183 | 0.2556 | 0.2093 | 0.1785 | 0.1630 | 43.51 | 43.50 | 43.48 | 43.46 | 43.44 | 612.38 | 611.02 | 611.53 | 611.32 | 611.03 | 26 | 26 | 26 | 26 | 26 |
| 10 | 0.2965 | 0.2464 | 0.2191 | 0.1848 | 0.1727 | 44.68 | 44.67 | 44.66 | 44.67 | 44.69 | 611.43 | 611.55 | 612.02 | 612.00 | 612.63 | 27 | 27 | 27 | 27 | 27 |

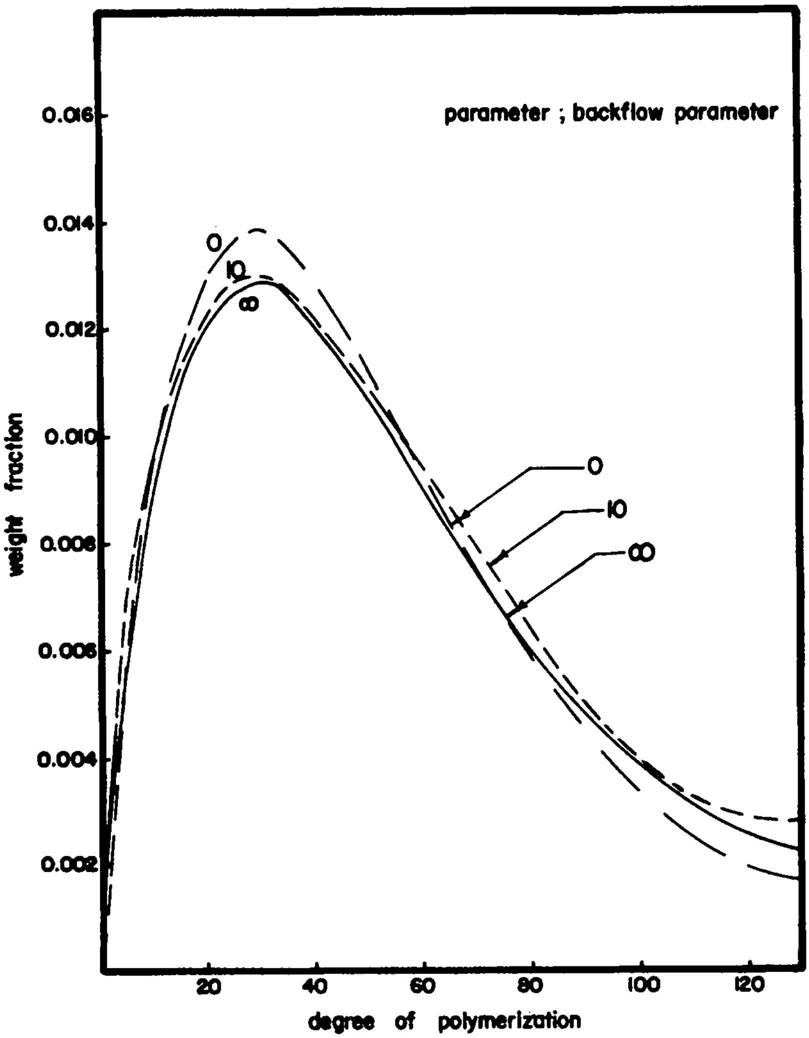


Fig. 9. Effect of the backflow parameter on the molecular weight distribution for the 2-tank model.

backflow. A comparison is presented here between the two models and the limitations of the comparison are pointed out.

Examine the $N$ tanks-in-series model; the unsteady concentration ($C$) of a reacting species in tank $n$ may be written as

$$\frac{V}{N}\frac{\partial C_n}{\partial t} = Bq_0(C_{n+1} - 2C_n + C_{n-1}) + q_0(C_{n-1} - C_n) + r_n\left(\frac{V}{N}\right) \quad (28)$$

or

$$\frac{\partial C_n}{\partial t} = \frac{Bq_0N}{V}(C_{n+1} - 2C_n + C_{n-1}) - \frac{q_0N}{V}(C_n - C_{n-1}) + r_n. \quad (28a)$$

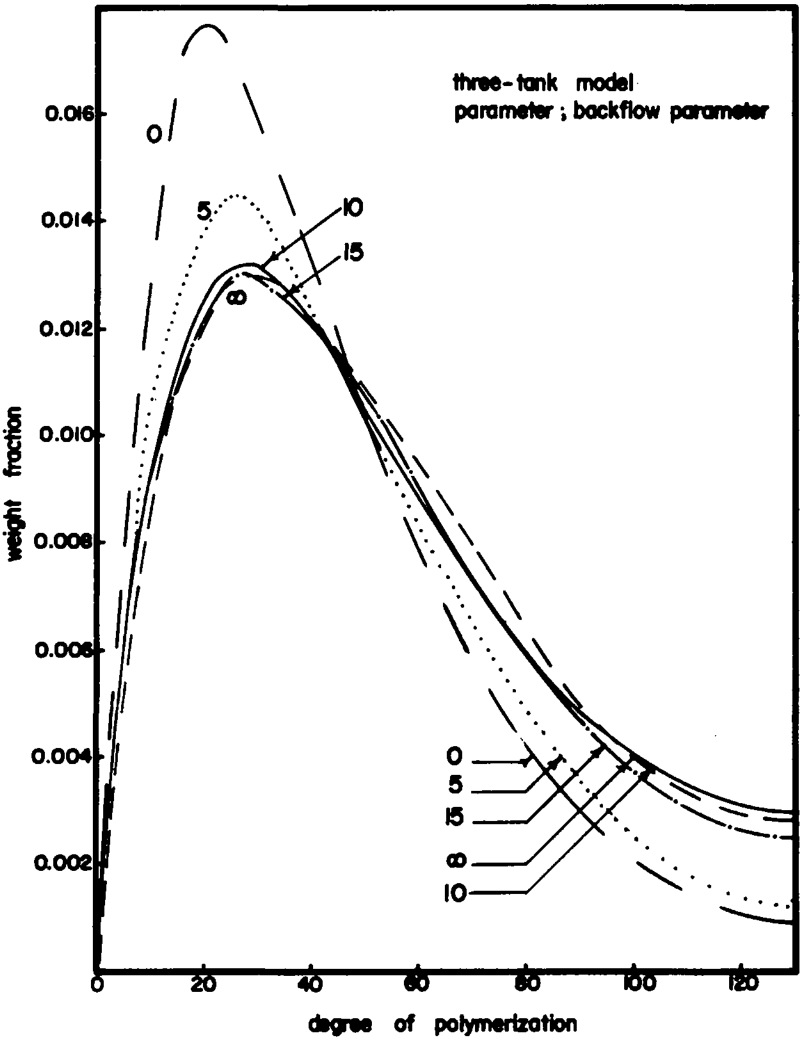


Fig. 10. Effect of the backflow parameter on the molecular weight distribution for the 3-tank model.

The material balance for the dispersion model is

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - U \frac{\partial C}{\partial z} + r \tag{29}$$

in which $D_z$ = axial dispersion coefficient and $U$ = linear velocity. By means of the Taylor series expansion, the dispersion model equation can be transformed into a finite difference form as follows:

$$\frac{\partial C_n}{\partial t} = D_z \left[\frac{(C_{n+1} - C_n) - (C_n - C_{n-1})}{(\Delta z)^2}\right] - U \left(\frac{C_n - C_{n-1}}{\Delta z}\right) + r_n \tag{30}$$

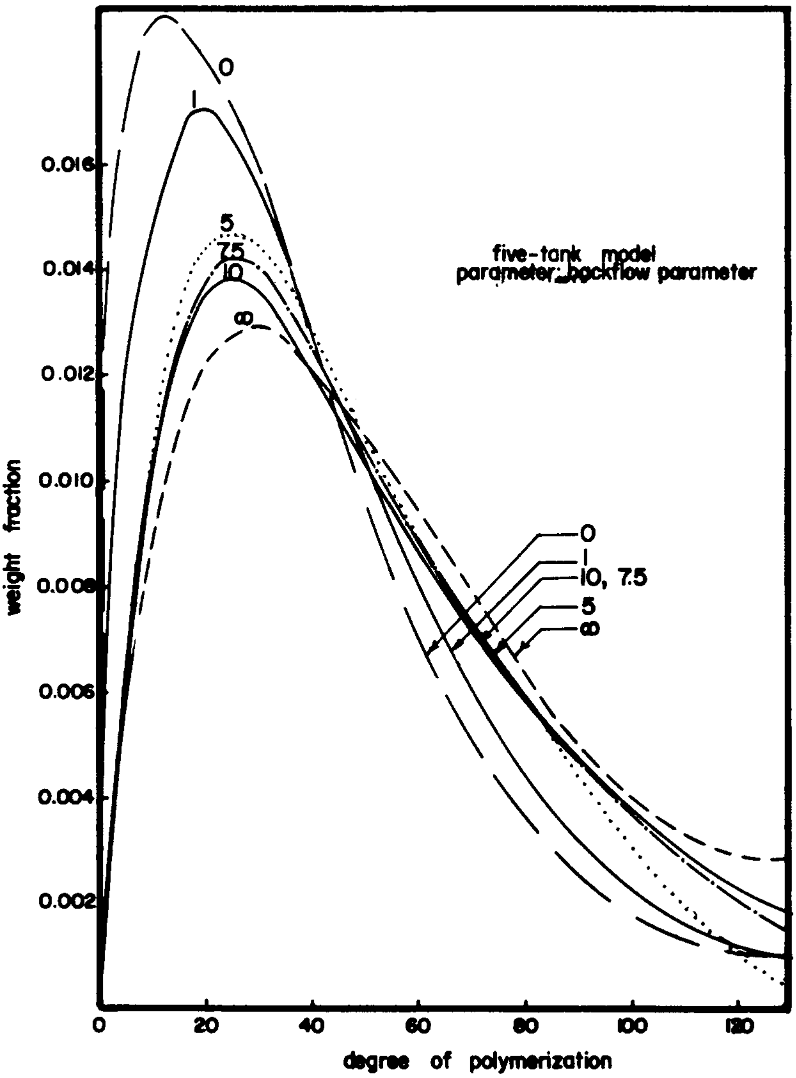


Fig. 11. Effect of the backflow parameter on the molecular weight distribution for the 5-tank model.

or

$$\frac{\partial C_n}{\partial t} = \frac{D_z}{\Delta z^2}(C_{n+1} - 2C_n + C_{n-1}) - \frac{U}{\Delta z}(C_n - C_{n-1}) + r_n. \qquad (30a)$$

Comparing eqs. (28a) and (30a), the approximate equivalence of the models can be found to be

$$\frac{D_z}{\Delta z^2} \doteq \frac{Bq_0N}{V}. \qquad (31)$$

And if $\Delta z = L/N$, the equivalence becomes

$$D_z \doteq \frac{L^2Bq_0}{NV}. \tag{32}$$

It is evident that this equivalence is not valid for either very low values of $N$ or very low values of $B$. As $N \to 1$, $D_z$ of eq. (32) approaches a finite value; however, $D_z$ should approach infinity as $N \to 1$ because this represents the one CSTR model. For low values of $B$, the model reduces to the $N$ tanks-in-series without backflow, and $D_z$ should not vanish if $B \to 0$ as predicted by eq. (32).

Meaningful results can be obtained from this equivalence for infinitely large $N$ or $B$. As $N \to \infty$ (if $B$ is finite), $D_z$ tends to zero; and, hence, $N_{Pe}$ ($= UL/D_z$) becomes infinitely large. This corresponds to the plug-flow model. On the other hand, if $B \to \infty$ (for a finite $N$), $D_z \to \infty$ and the model approaches the one-tank model. For $B$ and $N$ simultaneously tending to infinity, $D_z$ is indeterminate according to eq. (32).

Similarly, the following approximate equivalence exists between the tanks-in-series model without backflow and the dispersion model[15]:

$$D_z \doteq \frac{L^2q_0}{NV}. \tag{33}$$

Again, this equivalence does not hold good for very low values of $N$. As $N \to 1$, there is only one tank in the model, and $D_z$ should approach infinity; but according to eq. (33), $D_z$ approaches a finite value. These approximate equivalences for both the models (tanks-in-series with backflow and tanks-in-series model without backflow) are summarized in Table VI.

TABLE VI
Comparison of Dispersion Model with Tanks-in-Series Model With and Without Backflow

| Number of tanks | Backflow parameter | Dispersion coefficient | Peclet number | Model approaches |
|---|---|---|---|---|
| $N \to \infty$ | no backflow | $D_z \to 0$ | $N_{Pe} \to \infty$ | plug flow |
| $N \to 1$ | no backflow | $D_z \to$ finite | $N_{Pe} \to$ finite | — |
| $N \to \infty$ | $B$ finite | $D_z \to 0$ | $N_{Pe} \to \infty$ | plug flow |
| $N$ finite | $B \to \infty$ | $D_z \to 0$ | $N_{Pe} \to 0$ | CSTR |
| $N \to \infty$ | $B \to \infty$ | — | — | — |
| $N \to 1$ | $B \to 0$ | — | — | — |

## Comparison with Tubular Reactors with Laminar Flow

Denbigh[17] has investigated the residence time distributions in a tubular reactor with laminar flow and has shown that the exit age distribution is given by

$$E_p(t) = \frac{2t_0^2}{t^3} \tag{34}$$

in which $t_0$ = residence time (time of passage) of the fluid element at the tube axis and $t$ = residence time for any radial position $r$. Exit age distributions and degree of segregation ($J$) can be calculated from eq. (34) and compared with age distributions and $J$ from the tanks-in-series model with backflow. From this comparison, values of $N$ (number of tanks) and $B$ (backflow parameter) for the tanks-in-series model with backflow can be determined that would approximate the tubular reactor with laminar flow.

### Applicability of Results

The tanks-in-series with backflow model and the procedures developed here can be used to investigate the effect of mixing on the conversion and molecular weight distribution of polymerization reactors. The optimum mixing pattern as determined from the model study may be transformed into an optimum tubular reactor design, for example, by proper use of the equivalence between the dispersion model and the tanks-in-series with backflow model. The optimum values at the mixing parameters fix the geometry of the tubular reactor.

## CONCLUSIONS

Material balance equations for the tank-in-series model were derived and solved by an iterative method. The results were compared with the extreme cases of the plug flow and CSTR models. Molecular weight distributions were calculated, and it was found that backflow is not desirable from the MWD standpoint for the mechanism investigated.

The tanks-in-series with backflow model can be used to model a wide variety of polymerization reactors. Axial dispersion in tubular reactors can be modeled using this model. When the flow parameters $N$ and $B$ are large, a meaningful equivalence between the tanks-in-series with backflow model and the dispersion model in finite difference form exists.

## APPENDIX I

### Derivation of Eqs. (2), (3), and (4)

Consider the system shown in Figure 1 with $N = 3$. Let an impulse input of a tracer be added to tank 1. The unsteady-state material balance for the tracer concentration ($C$) is

$$V_1 \frac{dC_1}{dt} + (q_0 + q')C_1 = q_0C_0 + q'C_2 \tag{I-1}$$

$$V_2 \frac{dC_2}{dt} + (q_0 + q')C_2 + q'C_2 = (q_0 + q')C_1 + q'C_3 \tag{I-2}$$

$$V_3 \frac{dC_3}{dt} + (q_0 + q')C_3 = (q_0 + q')C_2 \tag{I-3}$$

in which $Vi$ = volume of the tank $i$, and $Ci$ = concentration of the tracer in tank $i$. If all the tanks are of the same volume ($V_i = V/3$), these equations can be rewritten after taking the Laplace transform as follows:

$$\frac{S}{3}\bar{C}_1 + (1 + B)\bar{C}_1 = \bar{C}_0 + B\bar{C}_2 \quad \text{(I-4)}$$

$$\frac{S}{3}\bar{C}_2 + (1 + B)\bar{C}_2 + B\bar{C}_2 = (1 + B)\bar{C}_1 + B\bar{C}_3 \quad \text{(I-5)}$$

$$\frac{S}{3}\bar{C}_3 + (1 + B)\bar{C}_3 = (1 + B)\bar{C}_2 \quad \text{(I-6)}$$

in which $\bar{C}_0$, $\bar{C}_1$, $\bar{C}_2$, and $\bar{C}_3$ are Laplace transforms of $C_0$, $C_1$, $C_2$, and $C_3$, respectively. Solving eqs. (I-4) through (I-6) for $\bar{C}_1$, $\bar{C}_2$, and $\bar{C}_3$, the following relations can be obtained:

$$\bar{C}_3 = \frac{27(1 + B)^2\bar{C}_0}{\{S + 3(1 + B)\}\{S^2 + 3S(2 + 3B) + 9(1 + B)\}} \quad \text{(I-7)}$$

$$\bar{C}_2 = \frac{9(1 + B)\bar{C}_0}{S^2 + 3S(2 + 3B) + 9(1 + B)} \quad \text{(I-8)}$$

and

$$\bar{C}_1 = \frac{\bar{C}_0 + \dfrac{9(1 + B)\bar{C}_0 B}{S^2 + 3S(2 + 3B) + 9(1 + B)}}{\left(\dfrac{S}{3} + 1 + B\right)}. \quad \text{(I-9)}$$

Taking inverse Laplace transforms, expressions for RTD as presented in the text are obtained.

## Appendix II

## Calculation of J

$J$ can be calculated if the RTD and state of micromixing are known.[12,13] Consider the three tanks-in-series model without backflow and with RTD given by

$$E(t) = \frac{27t^2}{\bar{t}^3} e^{-3t/\bar{t}}. \quad \text{(II-1)}$$

It has been shown that var $\alpha$ and var $\alpha_p$ required to calculate $J$, eq. (5), can be computed by

$$\text{var } \alpha = \frac{\overline{t^3}}{3\bar{t}} - \frac{\overline{t^2}}{4\bar{t}^2} \quad \text{(II-2)}$$

$$\text{var } \alpha_p = \text{var } \alpha - \text{var } \alpha \text{ within the points} \quad \text{(II-3)}$$

and

$$\text{var } \alpha \text{ within the points} = (\text{var } \alpha_p)_1 + (\text{var } \alpha_p)_2 + (\text{var } \alpha_p)_3. \quad \text{(II-4)}$$

Now,

$$\overline{t^3} = \int_0^\infty t^3E(t)dt = \frac{20}{9}\bar{t}^3 \quad \text{(II-5)}$$

and

$$\overline{t^2} = \int_0^\infty t^2E(t)dt = \frac{4}{3}\bar{t}^2. \quad \text{(II-6)}$$

Substituting these values for $\bar{t}^3$ and $\bar{t}^2$ in eq. (II-2),

$$\text{var}\ \alpha = \frac{8}{27}\bar{t}^2. \tag{II-7}$$

## Calculation of (var $\alpha_p$)$_1$

$\alpha_{p1}$ is the mean age within the points in tank 1. This can be calculated by noting that

$$E_1(t) = I_1(t) = \frac{3}{\bar{t}}\, e^{-3t/\bar{t}} \tag{II-8}$$

in which $I_1(t)$ = internal age distribution of the fluid elements. Now for the first tank,

$$\alpha_{p1} = \int_0^\infty \frac{3}{\bar{t}}\, e^{-3\alpha/\bar{t}} \alpha d\alpha = \frac{\bar{t}}{3} \tag{II-9}$$

and

$$(\text{var}\ \alpha_p)_1 = \frac{V}{3}\int_V dV \int_0^\infty \frac{3}{\bar{t}}\, e^{-3\alpha/\bar{t}}\left(\alpha - \frac{\bar{t}}{3}\right)^2 d\alpha = \frac{\bar{t}^2}{27}. \tag{II-10}$$

Along the same lines for tanks 2 and 3,

$$\alpha_{p2} = \int_0^\infty \frac{9\alpha}{\bar{t}^2}\, e^{-3\alpha/\bar{t}} \alpha d\alpha = \frac{2\bar{t}}{3} \tag{II-11}$$

$$(\text{var}\ \alpha_p)_2 = \frac{V}{3}\int_V dV \int_0^\infty \frac{9}{\bar{t}^2}\, e^{-3\alpha/\bar{t}}\left(\alpha - \frac{2\bar{t}}{3}\right)^2 d\alpha = \frac{2}{27}\bar{t}^2 \tag{II-12}$$

$$(\alpha_p)_3 = \int_0^\infty \frac{27\alpha^2}{\bar{t}^3}\, e^{-3\alpha/\bar{t}}\, \alpha d\alpha = \bar{t} \tag{II-13}$$

and

$$(\text{var}\ \alpha_p)_3 = \frac{V}{3}\int_V dV \int_0^\infty \frac{27\alpha^2}{\bar{t}^3}\, e^{-3\alpha/\bar{t}}(\alpha - \bar{t})^2 d\alpha = \frac{3\bar{t}^2}{27}. \tag{II-14}$$

From eqs. (II-2), (3), (4), (10), (12), and (14),

$$J = \frac{\text{var}\ \alpha_p}{\text{var}\ \alpha} = \frac{2/27}{8/27} = 0.25.$$

By using the appropriate RTD, $J$ values for this and other cases of the tank-in-series model can be computed.

## Nomenclature

| | |
|---|---|
| $B$ | backflow parameter |
| $C_n$ | concentration of the reacting species in tank $n$, g moles/l. |
| $D_z$ | axial dispersion coefficient, an$^2$/sec |
| $E_i(t)$ | exit age distribution from tank $i$ |
| $J$ | degree of segregation |
| $M(1,i)$ | monomer concentration in tank $i$, g moles/l. |
| $M(j,i)$ | concentration of dead polymer of chain length $j$ in tank $i$, g moles/l. |
| $N$ | number of tanks in the series |
| $P(j,i)$ | concentration of active polymer of chain length $j$ in tank $i$, g moles/l. |
| $P_T$ | total active polymer concentration, g moles/l. |

| | |
|---|---|
| $U$ | linear velocity, cm/sec |
| $V$ | volume of the tank, liters |
| $W(j,i)$ | weight fraction of polymer with chain length $j$ in tank $i$ |
| $a, a_0, a_1, b, c$ | constants defined for eq. (4) |
| $k_{in}$ | initiation rate constant, $hr^{-1}$ |
| $k_p$ | propagation rate constant, l./g mole hr |
| $k_t$ | termination rate constant, l./g mole hr |
| $q_0$ | influent flow rate to reactor system, l./hr |
| $q'$ | backflow rate, l./hr |
| $r$ | reaction term, g mole/l. hr |
| $t$ | time, hr |
| $\bar{t}$ | mean residence time for the system $\left(= \frac{V}{q_0}\right)$ |
| $z$ | distance along the tubular reactor, cm |
| $\alpha$ | age of a fluid element, hr |
| $\alpha_p$ | mean age of a molecular within a point, hr |
| $\alpha_{bi}$ | $\frac{q'}{V_i}$ = backflow space velocity, $hr^{-1}$ |
| $\alpha_{fi}$ | $\frac{q_0}{V_i}$ = influent flow space velocity, $hr^{-1}$ |
| $\alpha_{Ti}$ | $\alpha_{bi} + \alpha_{fi} = \frac{q_0 + q'}{V_i}$ |

This work was partially supported by the Agricultural Experiment Station, Kansas State University.

## References

1. K. G. Denbigh, *Trans. Faraday Soc.*, **43**, 648 (1947).
2. R. J. Zeman and N. R. Amundson, *Chem. Engl. Sci.*, **20**, 331 (1965).
3. R. J. Zeman and N. R. Amundson, *Chem. Eng. Sci.*, **20**, 637 (1965).
4. J. H. Duerksen, A. E. Hamielec, and J. W. Hodgins, *A.I.Ch.E. J.*, **13**, 1081 (1967).
5. J. H. Duerksen and A. E. Hamielec, *J. Polym. Sci. C*, **25**, 155 (1968).
6. A. E. Hamielec, J. W. Hodgins, and K. Tebbins, *A.I.Ch.E. J.*, **13**, 1087 (1967).
7. M. Harada, K. Tanaka, W. Eguchí, and S. Nagata, *J. Chem. Eng. Japan*, **1**, 148 (1968).
8. R. L. Lawrence and G. Vasudevan, *Ind. Eng. Chem., Process Des. Develop.*, **7**, 281 (1968).
9. S. Lynn and J. E. Huff, *A.I.Ch.E. J.*, **17**, 475 (1971).
10. W. H. Ray, *Ind. Eng. Chem., Process Des. Develop.*, **7**, 422 (1968).
11. R. Shinnar and P. Noar, *Chem. Eng. Sci.*, **22**, 1369 (1967).
12. T. N. Zwietering, *Chem. Eng. Sci.*, **11**, 1 (1969).
13. B. I. Tsai, Ph.D. Dissertation, Kansas State University, Manhattan, Kansas, 1970.
14. Z. Tadmor and J. A. Biesenberger, *Ind. Eng. Chem., Fundam.*, **5**, 336 (1966).
15. S. L. Liu and N. R. Amundson, *Rubber Chem. Technol.*, **34**, 995 (1961).
16. C. Y. Wen and L. T. Fan, *Modeling of Flow Systems*, Gordon and Breach, New York, in press.
17. K. G. Denbigh, *Chemical Reactor Theory*, Cambridge University Press, Cambridge, Great Britain, 1966.

Received September 11, 1972
Revised October 20, 1972