$(C_i)_{\text{pure component}}$ = lb.-moles of component i adsorbed in the presence of pure component i in the gas phase per 100 lb. adsorbent

C_T = parameter in Equation (2), total lb.-moles of adsorption sites per 100 lb. of adsorbent; C_T^σ has the same meaning except that it is based on a unit of adsorption surface area rather than 100 lb. of adsorbent

$\overline{f}_i^v$ = fugacity of component i in a mixture of vapors, lb./sq. in. abs.

f_i^v = fugacity of pure component i, lb./sq. in. abs.

K_{ji} = adsorption equilibrium constant for pure component i in layer j (see reference *6*)

ν = parameter as defined by Equation (1); see also reference *6*

$\phi = \sum_{i=1}^{c} K_{1i}\overline{f}_i^V$, where $\overline{f}_i^V$ is the fugacity of component i in the gas phase at the conditions of the experiment.

Subscripts

c = total number of component in a given mixture

i = component number, $(1 \leq i \leq c)$

j = number of layers, $(1 \leq j \leq n)$

n = total number of adsorbed layers

LITERATURE CITED

1. Day, J. J., Ph.D. dissertation, Univ. Oklahoma (1965).
2. Eberly, P. E., *J. Phys. Chem.*, **65**, 1261 (1961).
3. Edmister, W. C., "Applied Hydrocarbon Thermodynamics," pp. 8, 218–285, Gulf Publishing Co., Houston, Texas (1961).
4. Etherington, L. D., R. E. D. Haney, W. A. Herbst, and H. W. Scheeline, Scheeline, *AIChE J.*, **2**, 65 (1956).
5. Gilmer, H. B., and Riki Koboyashi, *ibid.*, **10**, 797 (1964); **11**, 702 (1965).
6. Gonzalez, A. J., and C. D. Holland, *ibid.*,
7. Gonzalez, A. J., dissertation, Texas A&M Univ. (1969).
8. Grant, R. J., and M. Mannes, *Ind. Eng. Chem. Fundamentals*, **5**, 497 (1966).
9. ———, and S. B. Smith, *AIChE J.*, **8**, 403 (1962).
10. Humphries, L. C., Mobil Research and Development Corporation, personal communication.
11. Kapfer, W. H., M. Marlow, J. Happel, and C. J. Marsel, *AIChE J.*, **2**, 456 (1956).
12. Langmuir, I., *J. Am. Chem. Soc.*, **40**, 1361 (1918).
13. Lewis, W. K., E. R. Gilliland, B. Chertow, and W. P. Cadogan, *Ind. Eng. Chem.*, **42**, 1320 (1950); **42**, 1326 (1950).
14. Mason, J., and C. E. Cooke, Jr., *AIChE J.*, **12**, 1097 (1966).
15. Menon, P. G., *Chem. Rev.*, **68**, 277 (1968).
16. Othmer, D. F., and F. G. Sawyer, *Ind. Eng. Chem.*, **35**, 1267 (1943).
17. Othmer, D. F., and J. Josefowitz, *ibid.*, **40**, 723 (1948).
18. Payne, H. K., dissertation, Rice Univ. (1964).
19. Ray, G. C., and O. E. Box, Jr., *Ind. Eng. Chem.*, **42**, 1315 (1950).
20. Sturdevant, G. A., dissertation, Rice Univ. (1966).

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Polymerization in a Tubular Reactor

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A mathematical model has been developed to predict the variations in temperature, velocity, and composition which occur during anionic polymerization in laminar flow in a tubular reactor. It is found that very large radial gradients in all three are to be expected when a solution containing only solvent and monomer is polymerized. Recycle of part of the product or prepolymerization in stirred-tank reactors may be used to reduce greatly the distortion of the radial profiles.

The concept of the tubular reactor for polymerization, in which monomer enters at one end (either pure or in a solvent) and leaves as polymer at the other end, is attractive because of its simplicity and potential low cost. Marring this picture is the tendency for polymer to form a thick layer on the tube wall, reducing the capacity of the reactor or even rendering it unworkable. It is therefore of interest to be able to predict the conditions under which operation of a tubular reactor would be expected to be feasible before initiating developmental work on such a reactor in the pilot plant.

While a large number of papers have appeared on the subject of polymerization reactors, these have usually been concerned with reaction systems in which the viscosity of the solution and problems of heat transfer have not been of direct concern. A good example of this type of treatment is the work of Kenat et al. (*6*). At least two papers (*2*, *11*) have appeared in recent years which treated the effect of a changing viscosity on the velocity profiles and heat transfer coefficients for liquids in laminar flow. One paper (*12*) estimates concentration and temperature profiles in a tubular reactor, but treats the case of a fluid with invariant properties in laminar flow. Since the change in fluid viscosity with polymer concentration which occurs during polymerization is frequently much greater than that due either to thermal or shear effects, this previous work is not sufficient to allow one to predict the behavior during polymerization in a tubular reactor.

Qualitatively, there are three important factors to be examined in analyzing the behavior of a tubular reactor: flow instability, heat transfer, and variation in residence time. Flow instability occurs when a reactor can no longer be operated, either because it has been plugged with polymer or because the monomer is coming through largely unreacted due to channeling. Problems in heat transfer arise because the low thermal conductivity of polymer solutions makes transfer of the heat of reaction quite difficult. Variation in residence time is important when side reactions (such as crosslinking) might occur in material remaining in the reactor many times the average residence time.

There are several ways in which polymerization may be initiated—thermally, via free radicals, or ionically. The method of initiation may be of great importance in determining the physical properties of the product, but it is of secondary importance in its effect on reactor behavior. In the following analysis, polymerization following the model of idealized anionic initiation was studied. The kinetic and viscosity relationships are based primarily on published studies of the butadiene/butyl lithium system. However, the method of analysis is felt to be applicable to most systems for which the required data are available.

THE PROBLEM FOR STUDY

In the proposed reactor the monomer, solvent, and anionic polymerization initiator are mixed just before entering a long tube. There are no concentration gradients initially. One assumes that all of the initiator molecules start reacting with the monomer simultaneously. This is a reasonable assumption for the overall polymerization rate of butadiene (*9*), but of doubtful validity with respect to the predicted molecular weight dispersion. The rate of polymerization of the monomer is then a function of the temperature, monomer concentration, and the initial initiator concentration. One assumes there are no chain-terminating reactions.

As the solution flows through the tubular reactor, a radial concentration gradient develops because the material near the center is moving faster than the material near the wall and hence will not have reacted as much in traveling a given distance down the tube. The viscosity of the solution increases rapidly with polymer content; the material near the wall therefore moves still more slowly and the material near the center goes faster. This process continues until the rate of polymerization of the material near the wall drops to a relatively low value due to depletion of the monomer. Then as the concentration of polymer near the center increases and the viscosity gradient decreases, the velocity profile once again approaches parabolic. Whether the flow becomes unstable or not depends on how great the ratio of viscosities between wall and center is allowed to become.

As the monomer polymerizes, heat is liberated. In vinyl-type polymerizations, the heat of reaction is from 12 to 18 kcal./mole, depending on the monomer. This heat will either raise the temperature of the material or be transferred to the wall of the reactor. Since the thermal conductivity of most polymers is rather low, a tubular reactor will not in general act as a satisfactory heat exchanger. It is usually necessary to consider the reaction to be adiabatic and to add sufficient solvent to keep the temperature within the desired limits.

Because of the flow pattern described above, the material moving near the wall will be in the reactor several times as long as the material moving near the center. During most of this time its concentration of monomer will be very low. Whether this long residence time will have an undesirable effect will depend on what, if any, side reactions, such as crosslinking or thermal degradation, can occur under these conditions. No general statement can be made about these effects since they will depend on the monomer, solvent system, and type of polymerization.

These qualitative considerations require quantitative estimation to determine their importance for a given reaction system. The question of flow stability can only be answered by the construction of a fairly elaborate mathematical model, such as is the subject of this paper, or by building a full-scale prototype and trying it.* The question of heat transfer is answered simultaneously by the model, although a reasonable idea of average temperatures can be obtained with a less involved treatment. The variation in residence time can be estimated from the model, but laboratory experiments will be required to determine whether side reactions such as crosslinking result from the very long residence times encountered.

THE MATHEMATICAL MODEL

Constructing the mathematical model for a tubular reactor in laminar flow at steady state involves setting up the differential equations which describe the flow, determining the boundary conditions, and solving.

Three equations of change were used to describe the flow of the reacting fluid:

$$U\frac{\partial C_M}{\partial x} - \mathfrak{D}_M\left(\frac{\partial^2 C_M}{\partial r^2} + \frac{1}{r}\frac{\partial C_M}{\partial r}\right) + R_p = 0 \qquad (1)$$

$$\frac{\partial C_M}{\partial r} = 0 \quad \text{at} \quad r = 0,\ R_0 \qquad (\text{B.C.1})$$

$$U\frac{\partial N_p}{\partial x} + \frac{N_p}{C_P}\mathfrak{D}_M\left(\frac{\partial^2 C_M}{\partial r^2} + \frac{1}{r}\frac{\partial C_M}{\partial r}\right) = 0 \qquad (2)$$

$$\frac{\partial N_p}{\partial r} = 0 \quad \text{at} \quad r = 0,\ R_0 \qquad (\text{B.C.2})$$

$$U\frac{\partial T}{\partial x} - D_T\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) - \frac{\Delta H_M}{c_{ps}\rho}R_p = 0 \qquad (3)$$

$$\frac{\partial T}{\partial r} = 0 \quad \text{at} \quad r = 0,\ \frac{\partial T}{\partial r} = \frac{h_{av}(T_w - T_c)}{k_s} \quad \text{at} \quad r = R_0 \qquad (\text{B.C.3})$$

In these equations radial velocities and the axial diffusion of heat and mass were assumed negligible. Equa-

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*The scale-up of pilot-plant reactors of this type presents unusual problems which will be discussed in a later section.

tion (1) shows the effects of convection, diffusion, and rate of reaction on the concentration of monomer. $\mathfrak{D}_M$, the effective binary diffusivity of the monomer in the solution, would normally be expected to be a function of temperature and possibly of composition. For reasons which will be mentioned later, a constant, relatively high value was assumed. Equation (2) is a first-order approximation of the movement of polymer molecules toward the center of the reactor which is caused by the diffusional flux of monomer toward the wall. In view of the magnitude of the diffusional effect, which is discussed below, a more exact treatment of the highly complex, multicomponent diffusional system actually obtaining in reactors of this type was not deemed necessary. Equation (3) describes the changes in temperature resulting from conduction, convection, and the heat of reaction.

Velocity profiles were calculated by assuming the reacting solution to behave as a Newtonian fluid whose viscosity is a function of temperature, polymer concentration, and molecular weight.

$$\tau = -\mu \frac{\partial U}{\partial r} = \tau_w \frac{r}{R_0} \tag{4}$$

Radial pressure gradients were assumed negligible, so that the shear stress varies linearly from zero at the tube center to τ_w at the wall. Since the total mass flow at any cross section is a constant, one may write

$$R_0^2 \rho_0 U_0 = 2 \int_0^{R_0} \rho U r dr \tag{5}$$

When Equation (4) is integrated and combined with Equation (5), one obtains an expression for the velocity at any point.

$$\frac{U}{U_0} = \frac{\rho_0 R_0^2 \int_{R_0}^{r} \frac{r}{\mu} dr}{2 \int_0^{R_0} \rho r \int_{R_0}^{r} \frac{r}{\mu} dr dr} \tag{6}$$

Equation (6) allows calculation of the velocity profile in the tube when the viscosity is known as a function of position. If the viscosity is also a function of the shear stress this dependence can be allowed for. By an iterative method of calculation Equation (4) can be used to allow the effect of shear stress on viscosity to be incorporated in the solution of Equation (6). However, in the present case the viscosity was assumed to be Newtonian, in part because the distortion in the velocity profiles was found to be greatest where the shear stress was relatively low.

The rate of polymerization is a function of the concentration of monomer and ionic radicals and of the temperature. The expression used

$$R_p = [N_p][C_M] \left\{ 4{,}940 \exp\left[\frac{4{,}200}{1.986}\left(\frac{1}{323} - \frac{1}{T + 273}\right)\right]\right\} \tag{7}$$

was developed from published information (*7* to *10*, *14*) using the following assumptions:

1. The rate of initiation in the case of butadiene is very rapid with respect to the rate of propagation.
2. Association of ionic radicals can be neglected over the temperature range of interest in this work.
3. The heat of association in butadiene polymerization is essentially the same as that observed in isoprene polymerization.

This last assumption is used to obtain the activation energy from the observed overall value for simultaneous association and propagation (*5*, *8*, *9*).

Experimental verification of Equation (7) is lacking in the temperature range of interest here. Therefore, in view of extent of extrapolation and of the assumptions involved, the results obtained by the use of Equation (7) cannot be presented as truly representing the kinetics of the polymerization of butadiene. Rather, it is presented here as a realistic example of an equation to use in illustrating the method of analysis.

The viscosity expression used is a complex function of the polymer concentration, weight-average molecular weight, and the temperature:

$$\ln (\mu \text{ solution}/\mu \text{ solvent})$$

$$= \frac{0.00856\, M_w^{0.76}\, C_P}{\exp\, [(C_P/\rho)^{0.46}(1.219 + 0.0000342\, M_w^{0.76} - 0.0013T)} \tag{8}$$

This expression is adapted from equations proposed by others (*4*, *5*) to give a reasonable fit to data from various sources (*1*, *4*, *13*). The quantity M_w in Equation (8) is set equal to the product of the molecular weight ratio (M_w/M_n) and the number average molecular weight M_n. A factor is included in the coefficients of M_w to account for the observation that measured values of (M_w/M_n) differ from the values predicted by the kinetic model, Equation (7) (*1*, *4*, *5*). This factor was assigned a constant value of about 1.7. Since direct experimental verification of this value is lacking, Equation (8) is used here only for purposes of illustration.

Because of the highly nonlinear expression for the viscosity of the solution, numerical methods were used to evaluate Equation (6). For the same reason, the finite-difference forms of Equations (1) to (3) were solved explicitly (*2*). The radius of the tube was divided into a grid of ten equal segments, and five-point expressions were used for the first and second derivatives with respect to r. Variable-length segments were used in the axial direction to avoid instability of the solution on the one hand and excessive computing time on the other. The temperature calculations at the radial grid point next to the wall were found to be the most sensitive to instability. It was further found that the values of $\partial T/\partial x$ at this point began to fluctuate several profiles before the onset of oscillations in the value of T itself. These fluctuations could be damped out by greatly reducing the length of the axial increments in the critical region. In less sensitive areas much larger increments were used.

The program written in ALGOL to do these calculations computes profiles of temperature, monomer and polymer concentration, polymer molarity, and velocity along the length of the tubular reactor. In addition, the pressure drop and molecular weights (M_n and M_w) are determined. Typically, 500 to 700 sets of profiles are calculated in 40 to 60 sec. of machine time for a given case. A Burroughs 5500 computer was used. Copies of the program may be obtained from the authors.

RESULTS

Four cases have been selected to illustrate the effect of various parameters when a solution of pure monomer is polymerized. These parameters are listed in Table 1. The coolant temperatures were not varied in the cases tabulated here, but by making the heat transfer coefficient very small the effect of insulating the reactor is obtained. The pressure drops listed in the table were computed, rather than being input parameters, but are listed here for convenience. The large range of values will be discussed below.

Case I: The first case considered simulates a reactor made of a jacketed $\frac{3}{4}$-in. pipe 80 ft. long. In Figure 1 profiles of velocity, temperature, and polymer concentration

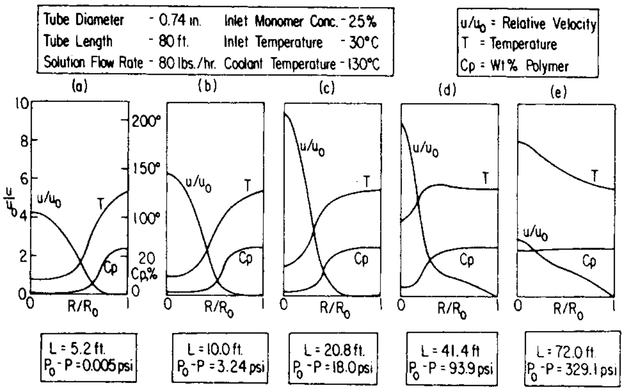

Fig. 1. Radial profiles in a tubular polymerizer (Case I).

are shown at irregular intervals along the reactor. The inlet velocity profile was assumed to be parabolic, with U/U_0 at the center line equal to 2.0 (hydrodynamic entrance effects were neglected). The inlet temperature and concentration were assumed uniform across the tube. At 5.2 ft. down the tube, the monomer closest to the wall is already almost completely polymerized. The temperature wave extends further into the tube than the concentration wave since the thermal diffusivity of the solution is much greater than its molecular diffusivity. At $L = 10.0$ ft. the outer 40% of the tube radius, which represents the outer 64% of the tube area, is occupied by material which is very nearly stagnant. At $L = 20.8$ ft. the center line velocity has risen still further, but because of the increased drag of the fast-moving core, the velocity of the material near the wall has begun to increase as well.

At $L = 29.25$ ft. the center line velocity reaches its maximum value, which is more than ten times the average value in the tube. At $L = 41.1$ ft. the temperature wave continues to penetrate the core of the flowing stream, and as the polymerization continues the center line velocity drops back toward its initial value. At $L = 63.8$ ft. the center line temperature reaches its maximum value, 192°C. At $L = 72.0$ ft. the polymerization is nearly complete, even at the center, and the velocity profile is only slightly distorted from the original parabola. The pressure gradient continues to increase because of the increasing viscosity of the polymer solution. The temperature at the center line is 181°, while the wall temperature is about 131°. When it is remembered that the distance between them is only 0.371 in., it is difficult to imagine measuring this temperature profile experimentally.

Case II: The second case, shown in Figure 2, is a direct scale-up of the first. The 40-fold higher flow rate is coupled with an increase in cross-sectional area of a factor of 15.3 and a 2.5 times greater length. In addition, the inlet temperature is 80°C. instead of 30°. The sharpness of the temperature wave is much more pronounced in Case II than it was in Case I because the larger diameter of the tube makes the transfer of heat by thermal conduction relatively much smaller. For the same reason a smaller fraction of the total heat of reaction can be conducted to the wall. This and the higher inlet temperature lead to substantially higher peak temperatures in the larger reactor.

The maximum temperature reached at the center line, 252°C, is well above the 240° one would calculate for an adiabatic reaction. This apparently anomalous result is caused by the material in the center having been heated by conduction from the reacting solution surrounding it in addition to having its temperature raised by its own heat of polymerization. The buildup of polymer on the walls is quite similar in the two cases, although the maximum relative center line velocity in the larger tube is somewhat lower than in the smaller.

Case III: The third case, Figure 3, is identical to the second except that the wall is insulated. There is remarkably little difference in the maxima of the temperature waves at comparable cross sections for the two cases. The maximum center line velocity is slightly higher for Case III, the relative value being nearly identical to that in Case I. The concentration profiles are also very similar at comparable cross sections.

The feed temperature is the same (80°C.) in Case III as in Case II. Since the reactor in the former case is adiabatic, whereas in the latter case it is jacketed with an oil kept at 130°, one might expect the reaction to proceed faster in Case II. This indeed happens in the region closest to the entrance. However, the reaction rate at 80° is fast enough to be appreciable and in the adiabatic case the material near the wall can heat itself unimpeded by the coolant in the jacket. By the time the 12-ft. profile is reached, the material near the wall is completely reacted in both cases.

It seems surprising at first that the pressure drop is somewhat higher in Case III than in Case II. The higher overall temperature in Case III makes the viscosity somewhat lower. The reason for the higher pressure drop is the greater distortion of the velocity profile noted above. The center line velocity is relatively greater in Case III for each profile from $L = 25$ ft. through $L = 100$ ft. This produces a higher shear and hence a higher pressure drop.

Case IV: In this case, Figure 4, the extreme situation was studied of the relatively squat reactor configuration with insulated walls. Qualitatively the concentration and velocity profiles are similar to those found in the previous cases. The temperature profiles are quite rounded in Case IV where the ratio of length to cross-sectional area is by far the smallest of all the cases studied. It should also be

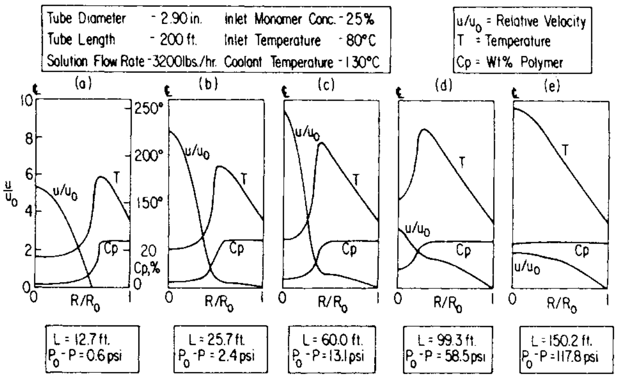

Fig. 2. Radial profiles in a tubular polymerizer (Case II).

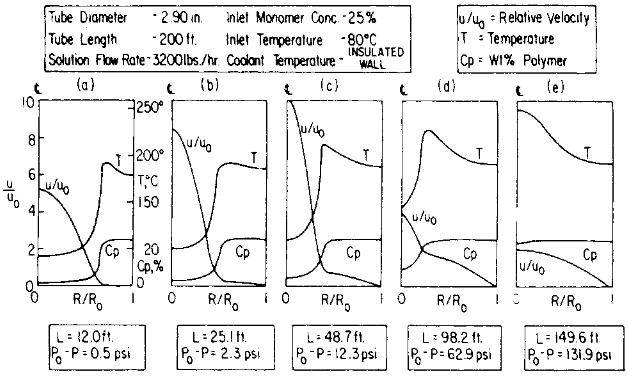

Fig. 3. Radial profiles in a tubular polymerizer (Case III).

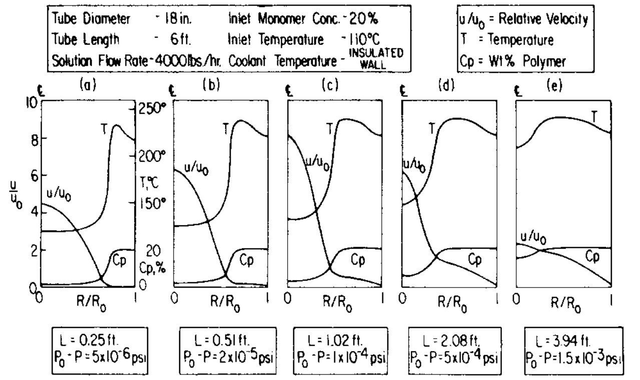

Fig. 4. Radial profiles in a tubular polymerizer (Case IV).

noted that the inlet monomer concentration for this case is only 20%, compared to 25% for the first three. The inlet temperature was raised accordingly to keep the final temperatures in all the cases about the same. The error caused by neglecting heat conduction in the direction of flow will be greater in this case, but is still not large enough to affect the general conclusions.

In simple viscous flow in a tube, with no change in viscosity occurring, the pressure drop is proportional to the flow rate times the length divided by the fourth power of the diameter. In other words the term $\Delta P \cdot D^4/\mathring{m}L$ is a constant. It is remarkable that there is so little variation in this term, which is tabulated in Table 1 for the four cases, considering the vast departure from the parabolic velocity profile which occurs, not to mention the lower polymer concentration (and hence lower viscosity) at the outlet in the last case.

TABLE 1. INPUT PARAMETERS FOR TUBULAR REACTORS WITHOUT POLYMER IN FEED

Case	I	II	III	IV
Tube diameter, in. I.D.	0.742	2.90	2.90	18
Tube length, ft.	80	200	200	6
Solution flow rate, lb./hr.	80	3200	3200	4000
Inlet monomer, wt. fract.	0.25	0.25	0.25	0.25
Inlet temperature, °C.	30°	80°	80°	110°
Coolant temperature, °C.	130°	130°	130°	130°
Heat transfer coefficient, B.t.u./(hr.)(sq. ft.)(°F., pipe to coolant)	50	50	0.001	0.001
Pressure drop across reactor, lb./sq. in.	398	167	200	0.0026
$D^4\ \Delta P/\mathring{m}L$	0.0188	0.0194	0.0221	0.0114

Variation in Molecular Weight

In Table 2 are given the calculated relative molecular weights as a function of radial position at the outlet of the reactor for Cases I and III. The variation is due to molecular diffusion which results from the concentration gradient that is established in the flow through the reactor. A relatively high value was assumed for the molecular diffusivity, 10^{-5} sq. cm./sec., so the calculated variation represents the extreme that might be expected. Although the variation is appreciable for the small reactor, it was found to be insignificant for the larger one. Even for the small reactor, the variation is not large when integrated over the flow, as is done for the last column. It can be concluded that molecular diffusion per se will not cause an appreciable molecular weight dispersion in plant-scale reactors of this sort. It should be recognized that molecular weight dispersion which occurs because of departure from the idealized kinetics assumed for these calculations will be an important factor in reactor design. Only the effect of molecular diffusion may be safely neglected. In general the molecular weight dispersion for each streamline leaving a tubular reactor will be about the same as in a batch reaction which has followed the same time-temperature history. Estimation of the dispersion for a free-radical polymerization, while more difficult than the case studied here, does not present an insuperable computational problem.

TABLE 2. NUMBER-AVERAGE MOLECULAR WEIGHT VARIATION AT REACTOR OUTLET

Radial position	0	0.2	0.4	0.6	0.8	1.0	Mw/Mn
Case I	52,600	70,800	121,800	140,100	135,100	147,100	1.08
Case III	113,200	117,200	129,800	129,500	128,400	130,000	1.001

Longitudinal Pressure Profiles

The variation of pressure with distance along the length of the reactor is shown in Figure 5 for Cases I and III. As would be expected from the velocity profiles, the pressure drop is quite small until the point is reached where a large part of the polymerization is complete. The pressure gradient then rises steadily, reaching a nearly constant value where the polymerization is complete. In each case in the front 25% or so of the reactor the pressure gradient is quite low. It is in these regions that natural convection due to thermal and concentration gradients could appreciably alter the calculated profiles.

Flow Stability

In all of the cases studied it was found that stable flow would result, in the sense that extreme channeling of the flow through the center did not occur. There are a number of reasons for having reservations about this conclusion, however. In the first place, by assuming the flow to be Newtonian, it was guaranteed that the flow would be stable if the reactor were long enough. The possibility that side reactions such as crosslinking might cause the flow in some parts of the reactor to stop completely instead of moving very slowly was not put into the program. Furthermore, the possibility of "slubs" being torn off the slow-moving, thick film was not included. Such blobs would be swept to the center of the tube by the effect of viscous shear. There additional monomer could diffuse into them and they would emerge from the reactor having perhaps a

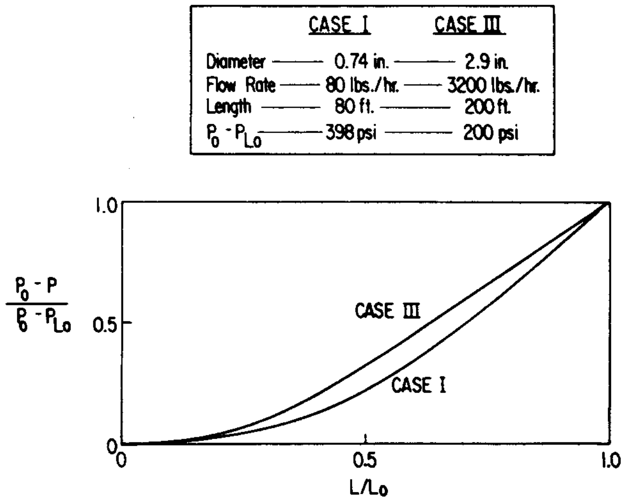

Fig. 5. Comparison of pressure profiles in tubular reactors.

substantially higher molecular weight, even though not necessarily crosslinked, than the bulk of the reactor effluent.

In the second place, no possibility for natural convection was provided in the computation. This effect is probably minor in the long reactors, but might have serious consequences in Case IV where there are large temperature gradients and the pressure drops across the reactor are quite small.

Finally, these calculations are for steady state flow. With such large variations in residence time occurring, the transient period at startup might be quite long.

Alternative Reactor Configurations

These uncertainties led us to consider other designs in which the distortion of the velocity profiles would be substantially reduced. This distortion arises because of the very small ratio of the viscosities of the solutions before and after polymerization. For the cases in Table 1 this ratio is about 1/170 and the viscosity of the entering solution was 0.2 centipoise. The viscosity of the polymer solution can be reduced by operating at a lower concentration, but only at a significant cost in increased solvent handling. Alternatively, the viscosity of the feed can be increased by adding polymer to it. This polymer may be supplied by recycling product (which has first been "killed" to prevent further chain growth), or by carrying out the initial phase of the polymerization in one or more cascaded stirred-tank reactors. The choice would be determined by the relative cost of the two methods and also by the nature of the desired product.

Anionic polymerization which proceeds according to the idealized kinetics hypothesized above yields a weight-average/number-average molecular weight ratio of unity in a batch reaction. As is shown in Table 2, the tubular reactor of Case III gives an Mw/Mn ratio which is also very close to one. It can readily be shown that in a cascade of stirred-tank reactors, this kinetics leads to the ratio given by the expression

$$(Mw/Mn = (N + 1)/N)$$

where N is the number of reactors in the cascade, if the fraction of monomer polymerized in each reactor is the same.

For a cascade of stirred-tank reactors preceding a tubular reactor in which molecular diffusion is negligible, the expression for the final product is

$$(Mw/Mn = (N + f_0^2)/N)$$

where f_0 is the fraction of monomer converted to polymer in the solution leaving the cascade. Again, the fraction of monomer polymerized in each stirred-tank reactor is assumed constant.

The desired value of Mw/Mn depends upon the physical properties required of the product. Where these properties correspond to an extremely narrow molecular weight distribution, polymer recycle may be the only practical way to operate. However, when the desired distribution is only moderately narrow, prepolymerization is more likely to be the choice.

Three additional cases were considered to demonstrate the effects of having polymer in the feed to a tubular reactor. All were modifications of Case III, the insulated 3-in. pipe. A summary of the variable parameters for these cases is given in Table 3.

Pairs of profiles for each of the three cases from Table 3 are shown in Figures 6, 7, and 8. In each figure the velocity, temperature, and composition profiles on the left are taken at the reactor length where the maximum distortion of the velocity profile near the wall occurs. The right-hand profiles in each figure were taken at the position of maximum center line velocity. The velocity profiles are much less distorted from the normal parabolic shapes than were those for Cases I to IV. Case VII shows the least distortion and Case VI shows the most, as one would expect from the respective initial solution viscosities and the similarity of the solution viscosities after polymerization. The temperature and composition profiles also show much smaller radial gradients. This is due partly to the lower inlet monomer concentration and partly to the higher inlet temperatures and correspondingly higher initial reaction rates of the material in the central portion of the reactor.

TABLE 3. INPUT PARAMETERS FOR TUBULAR REACTORS WITH POLYMER IN FEED

Case	V	VI	VII
Tube diameter, in. I.D.	2.90	2.90	2.90
Tube length, ft.	160	150	138
Solution flow rate, lb./hr.	3200	3200	3200
Inlet monomer, wt. fract.	0.15	0.15	0.10
Inlet polymer, wt. fract.	0.10	0.10	0.15
Inlet polymer, molecular weight	126,500	71,000	88,100
Inlet solution viscosity, centipoise	2.33	1.03	2.25
Polymer source	Recycle	2 Tanks	4 Tanks
Inlet temperature, °C.	125°	132°	154°
Mw/Mn of product	1.00	1.08	1.09
Pressure drop, lb./sq. in.	170	188	176

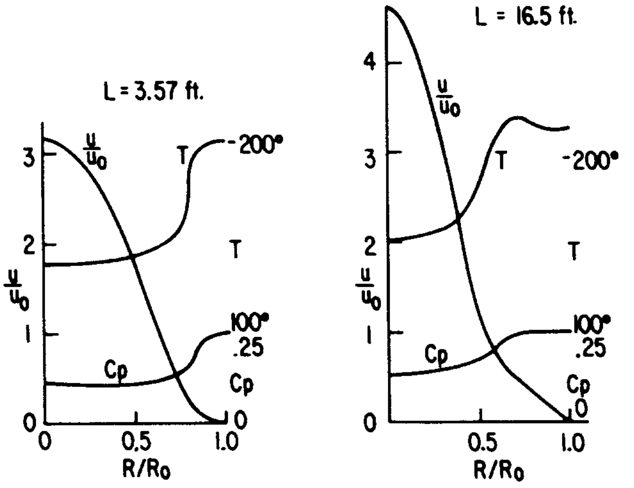

Fig. 6. Effect of recycling polymer on reactor profiles (Case V).

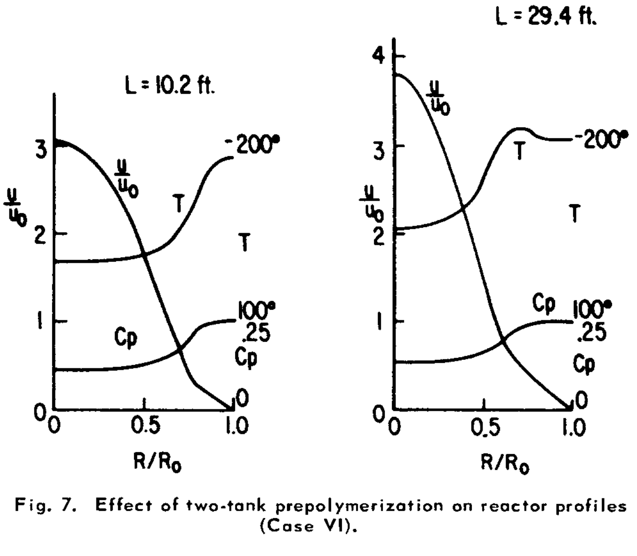

Fig. 7. Effect of two-tank prepolymerization on reactor profiles (Case VI).

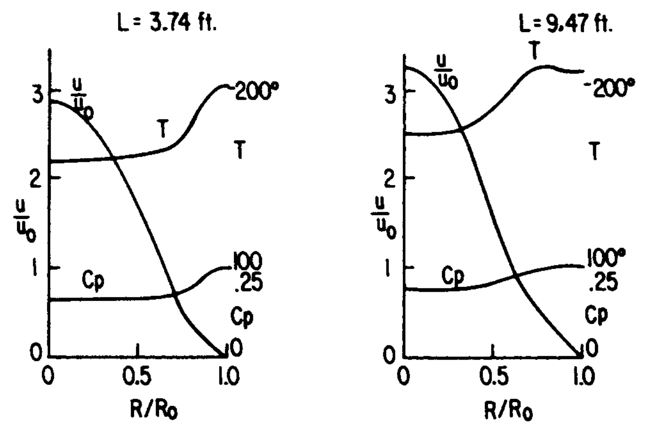

Fig. 8. Effect of four-tank prepolymerization on reactor profiles (Case VII).

Reactor Scale-Up

Examination of the basic differential equations of diffusion and heat transfer [Equations (1) and (3)] shows that when the diameter of a tubular reactor is held constant, the change of concentration or temperature with distance at any point is solely a function of the velocity. If the velocity is reduced by a factor of 10, the longitudinal gradients of concentration and temperature are increased by a factor of 10, so that a given conversion is accomplished in a reactor one-tenth as long. This relationship will hold as long as the assumptions of negligible axial diffusion and conduction are valid and as long as natural convection is negligible. (The assumption of negligible axial diffusion and conduction is valid when axial gradients of concentration and temperature are less than 10% of the radial gradients at the same point.)

It follows from these considerations that the best method of building a pilot-plant reactor of this type for obtaining design data is to duplicate the proposed diameter of the large reactor, and scale down only the length and flow rate. The results obtained from a reactor of small diameter can be used only with caution, since the relatively high heat transfer and greater effect of diffusion will be lost on scale-up.

CONCLUSIONS

A mathematical model has been constructed for computing velocity, temperature, and concentration profiles in a tubular polymerization reactor. In addition, pressure drop and molecular weight distribution were calculated. The calculations indicate stable flow behavior for a variety of flow rates and configurations. Two types of design were shown to minimize the very large concentration and temperature gradients which may develop in reactors of this sort. The effect of molecular diffusion on molecular weight dispersion was found to be small, especially for reactor diameters of 3 in. and above.

While an attempt should be made to use reasonably good values for the various physical properties employed in this method of computation, the results will not be highly accurate because of the numerous assumptions and approximations which were made. However, relatively large changes in the values used would have little effect on the qualitative conclusions which one would reach. The major value of such calculations is to indicate the conditions under which satisfactory reactor performance is either a good probability or quite unlikely. Highly accurate reactor simulation would necessarily need to be coupled with an experimental program on the system concerned to obtain the necessary physical data.

While these calculations were based on data for an anionic polymerization, the method is applicable to any type of polymerization for which sufficient information regarding reaction kinetics, solution viscosity, and molecular weight distribution are known.

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NOTATION

C_M = concentration of monomer, g./cc.
C_P = concentration of polymer, g./cc.
C_{ps} = heat capacity of solution, cal./(g.)(°C.)
$\mathfrak{D}_M$ = molecular diffusivity of monomer, sq. cm./sec.
D_T = thermal diffusivity of solution, sq. cm./sec.
ΔH_M = heat of reaction, cal./g.
h_{av} = average heat transfer coefficient, cal./(sq. cm.)(sec.)
k_s = thermal conductivity of solution, cal./(g.)(sec.)(°C.)
L = distance from tube inlet, cm. or ft.
L_0 = length of tube, cm. or ft.
M_n = number-average molecular weight
M_w = weight-average molecular weight
$\overset{\circ}{m}$ = mass flow rate of solution, g./sec. or lb./hr.
N_p = molal concentration of polymer, moles/cc.
P = pressure, dynes/sq. cm. or lb./sq. in.
P_0 = pressure at reactor inlet, dynes/sq. cm. or lb./sq. in.
P_{L0} = pressure at reactor outlet, dynes/sq. cm. or lb./sq. in.
r = radial variable, cm.
R_0 = radius of tube, cm.
R_p = rate of polymerization, g. monomer/(sec.)(cc.)
T = temperature of solution, °C.
T_c = temperature of coolant in jacket, °C.
T_w = temperature of solution at $r = R_0$, °C.
U = velocity, cm./sec.
U_0 = average velocity at inlet, cm./sec.
x = variable in direction of flow, cm.

Greek Letters

μ = viscosity of solution, poise
ρ = density of solution, g./cc.
ρ_0 = density of feed solution, g./cc.
τ = shear stress in solution, dynes/cc.
τ_w = shear stress at wall, dynes/cc.

LITERATURE CITED

1. Bates, S. I., Dow Chemical Co., private communications.
2. Christiansen, E. B., G. E. Jensen, and F. S. Tao, *AIChE J.*, **12**, 1196 (1966).
3. Forsythe, G. E., and W. R. Wasow, "Finite-Difference Methods for Partial Differential Equations," Wiley, New York (1960).
4. Gruver, J. T., and G. Kraus, *J. Polymer Sci.*, **A2**, 797 (1964).
5. Johnson, R. L., Dow Chemical Co., private communications.
6. Kenat, T. A., R. I. Kermode, and S. L. Rosen, *Ind. Eng. Chem. Proc. Design Develop.*, **6**, 323 (1967).
7. Morton, M., E. E. Bostick, and R. Livigni, *Rubber Plastics Age*, **42**, 397 (1961).
8. ———, and L. J. Fetters, *J. Polymer Sci.*, **A1**, 1735 (1963).
9. Morton, M., L. J. Fetters, and E. E. Bostick, *ibid.*, **C1**, 311 (1963).
10. Morton, M., and L. J. Fetters, *ibid.*, **A2**, 3311 (1964).
11. Rosenberg, D. E., and J. E. Hellums, *Ind. Eng. Chem. Fundamentals*, **4**, 417 (1965).
12. Rothenberg, R. I., and J. M. Smith, *AIChE J.*, **12**, 213 (1966).
13. Seely, G. R., *ibid.*, **10** (1), 56 (1964).
14. Worsfold, D. J., and S. Bywater, *Can. J. Chem.*, **38**, 1891 (1960).

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