$f(v)$ = normalized Gaussian function to curve fit the leading half of the chromatogram of the polymer standards

h = instrumental spreading correction parameter, counts^{-2}

h_c = instrumental spreading correction parameter obtained from the leading half of the chromatogram, counts^{-2}

M_i = calibration molecular weight at a particular elution volume

$\overline{M}$ = cup averaged molecular weight, or molecular weight

$\overline{M}(h)$ = corrected chromatogram molecular weight

$\overline{M}(\infty)$ = chromatogram molecular weight

T_w = wall temperature of the tubular reactor, °K

v = elution volume from the chromatograph, counts

v_p = elution volume at the peak of the polystyrene standard, counts

$\overline{X}$ = cup averaged conversion

Subscripts

n = number average

w = weight average

z = z average

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Continuous Production of Polystyrene In A Tubular Reactor: Part II

An analysis of the bulk polymerization of styrene by azobisisobutyronitrile in a tubular reactor was made. Rigorous models were developed and verified. A diffusion model gave predictions of molecular weights and conversions that were 2% higher on the average than the experimental values. Another model, a plug flow contraction of the diffusion model, predicted molecular weights and conversions that were 6% higher on the average than the experimental values.

The diffusion model showed that optimal conversions could be obtained by proper reactor operation. Tentative studies for optimal conversion with minimal molecular weight dispersion indicated the reactor should be operated at a wall temperature 5° to 10°C below that required for optimal conversion.

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SCOPE

More than half of today's polystyrene comes from a two-stage bulk polymerization process. The first stage, often called a *prepolymerizer*, consists of stirred-batch kettles. Here conversion of the monomer goes to 30 to 40% completion. Because of viscosity considerations and energy requirements for the mixers, the syrup is transferred to other processes to complete the polymerization.

Despite the widespread use of the kettles, a disadvantage is the relatively larger capital outlay and higher operating costs incurred in comparison with those of a tubular reactor system. Even with a seeming economic advantage, the tubular reactor is little used for commercial polystyrene production (Bishop, 1971), apparently because a large temperature gradient across the tube diameter causes uneven polymerization rates, resulting in poor control of the final product molecular weight distribution. According to Boundy et al. (1970), this temperature rise should be restricted to 10° to 20°C.

The purpose of this study is to investigate the reactor diameter—temperature gradient—product quality functionality by mathematical models which have been verified with experimental data. Also studied are optimal reactor conditions for maximum conversion with minimal molecular weight dispersion.

CONCLUSIONS AND SIGNIFICANCE

From this study it was found that rigorous mathematical models could describe the bulk polymerization of styrene initiated by azobisisobutyronitrile in a tubular reactor. The predicted conversions and molecular weights compared very well with experimental results. Radial diffusion was found to be of little significance in the model. A plug flow contraction of a diffusion model also gave close agreement with experimental values. This study showed optimal conversions can be obtained with proper reactor operation and that proper choice of wall temperature, initiator concentration, and reactor radius was needed to control the molecular weight distribution.

Consequently there appears to be no technical reason why a tubular reactor system should not replace the presently used stirred-batch kettles as the first stage in the bulk polymerization of styrene. In general, it is probable that other polymer systems can and should be investigated in a similar manner. The findings would then be used to upgrade and improve existing polymerization processes.

There is moderate interest in the modeling of polymerization processes, but much of this interest is channeled into the analysis of batch, or continuous stirred-tank reactors. [A compendium of sample references is listed by Wallis (1973.] There has been little development in the modeling of polymerization in tubular reactors as the following discussion shows.

Lynn and Huff (1971) analyzed numerically an anionic polymerization in a laminar flow tubular reactor. Unfortunately they used a relatively large diameter tube for their simulations. This condition was, in fact, the cause of the runaway reactions shown in their simulations. Yet they failed to relate the runaway reaction to their choice of a large tube diameter and a high reactor wall temperature. Despite these distorted temperature and velocity profiles, they did not calculate its effect on the average monomer conversion or the average molecular weights of the polymer.

Merrill and Hamrin (1970) showed that radial diffusion had little effect on conversion. This was verified in this study.

Cintron-Cordero et al. (1968) and Cintron-Cordero (1971) simulated homogeneous free-radical polymerization processes. From their results it can be concluded that moderately distorted velocity profiles have little effect on the average polymer properties. Consequently, the assumption of a parabolic velocity profile is used later to simplify the model.

Biesenberger et al. (1972) considered homogeneous free-radical polymerization of styrene initiated by AIBN in a numerical simulation study. Their results from a plug flow model were of little value to the industrial processor because high initiator concentrations used in the simulation led to the prediction of low molecular weight polymers (10,000 to 15,000), not of industrial quality.

Among all of the simulations discussed:

1. None are compared with experimental data, and
2. There is little emphasis on the effects of various operating conditions on the conversion of monomer and the molecular weights of the polymer product. On the other hand, industry requires such information and especially the key parameters, conversion and molecular weight distribution.

KINETIC MODEL

The kinetic scheme for free-radical polymerization is reasonably well understood (Ham, 1967; Odian, 1970; Bamford et al., 1958; Flory, 1953); it consists of three phases: initiation, propagation, and termination of the free radical.

The scheme used is (Wallis, 1973):

Initiation:

$$I \xrightarrow{k_I} 2R_I\cdot \tag{1}$$

$$R_I\cdot + M \xrightarrow{fk_I} R_1\cdot \tag{2}$$

Propagation:

$$R_n\cdot + M \xrightarrow{k_p} R_{n+1}\cdot \tag{3}$$

Termination:

$$R_r\cdot + R_s\cdot \xrightarrow{k_t} P_{r+s} \tag{4}$$

Chain Transfer:

$$R_n\cdot + M \xrightarrow{k_{trm}} P_n + M\cdot \tag{5}$$

Styrene will also polymerize solely by heating in the absence of any added initiator. This rate is a few tenths of a percent per hour at 90°C, but it increases sharply with temperature. The mechanism for this is not well understood and the reader is directed to Boundy et al. (1970), Ham (1967), and Hui and Hamielec (1972) for views. However, in the temperature range 60° to 120°C, the bulk thermal polymerization is well represented by Boundy et al. (1970)

$$R_{pt} = k_{mt}\, C_m \tag{6}$$

Since the equipment was operated in the 60° to 120°C range, the thermal polymerization as defined by Equation (6) was used in the model.

The two independent rates of initiation, thermal and initiator, may be combined to give a general expression for the polymerization reaction. This expression is

$$R_p = (R_{pI}^2 + R_{pt}^2)^{1/2} \tag{7}$$

DESCRIPTION OF THE POLYMER PRODUCT

The kinetic reactions and their respective rate expressions may be used to generate the instantaneous molecular weights of the polymer. These instantaneous quantities are later utilized to obtain an overall description of the final product.

The results that follow for the number and weight average molecular weights were adapted from Biesenberger and Tadmor (1968). Wallis (1973) developed the expression for the Z average molecular weight. All details are reported by Wallis (1973).

$$X_n = \frac{1 + \bar{P}_c}{1 - p} \tag{8}$$

$$X_w = \frac{\bar{P}_{tr}}{1 + \bar{P}_c}\,\frac{(1 + p)}{(1 - p)} + \frac{\bar{P}_c}{1 + \bar{P}_c}\,\frac{(4 + 2p)}{(1 - p)} \tag{9}$$

$$X_z = \frac{\dfrac{\overline{P}_{tr}}{1+\overline{P}_c}\,\dfrac{(1+4p+p^2)}{(1-p)^2} + \dfrac{\overline{P}_c}{1+\overline{P}_c}\,\dfrac{(8+14p+2p^2)}{(1-p)^2}}{X_w} \tag{10}$$

The average chain lengths X_n, X_w, and X_z are evaluated from three kinetic rates:

1. Polymer propagation,
2. Termination by combination, and
3. Chain transfer to monomer

since the parameters p, $\overline{P}_{tr}$, and $\overline{P}_c$, which define the chain lengths, are directly related to the stated rates (see Notation).

It is emphasized that X_n, X_w, and X_z are instantaneous values which depend on the kinetic rates. The method for determining the overall average molecular chain lengths of the polymer product is presented in the section on the mathematical model.

Molecular chain lengths can be converted to molecular weights by multiplying the chain lengths by 104.14, the molecular weight of a monomer unit of styrene.

CHOICE OF KINETIC DATA

The following expressions and kinetic rate data were used for the study (Wallis, 1973):

Initiation:

$$-\frac{dC_I}{dt} = k_I C_I \quad \text{m/l-s} \tag{11}$$

$$R_I = 2fk_I C_I \quad \text{m/l-s} \tag{12}$$

$$f = 0.62 \tag{13}$$

$$k_I = 1.58 \times 10^{15} \exp(-30.8/RT) \quad \text{s}^{-1} \tag{14}$$

Monomer polymerization:

$$R_p = (R_{pI}^2 + R_{pt}^2)^{1/2} \quad \text{m/l-s} \tag{15}$$

$$R_{pI} = k_m C_m (fC_I)^{1/2} \quad \text{m/l-s} \tag{16}$$

$$k_m = 1.665 \times 10^{10} \exp(-21.63/RT) \quad \text{s}^{-1} \tag{17}$$

$$R_{pt} = k_{mt} C_m \quad \text{m/l-s} \tag{18}$$

$$k_{mt} = 9.87 \times 10^5 \exp(-19.2/RT) \quad \text{s}^{-1} \tag{19}$$

Monomer transfer:

$$C_{trm} = \frac{k_{trm}}{k_p} = 0.22 \exp(-5.6/RT) \tag{20}$$

Matheson et al. (1951), Tobolsky et al. (1960), and Hamielec (1972) have shown that k_m depends on conversion for conversions exceeding 30%. This phenomena is called the *gel effect*. Since this study was concerned with conversions below 30 to 35%, the gel effect was not expected to be a major factor, and it was excluded from the model.

While an expression may be developed for the rate of thermal initiation R_{It} (Wallis, 1973), it can be shown that R_{It} is negligibly small in comparison with R_I (Wallis, 1973). Hence R_{It} was assumed equal to zero for the purposes of the model.

MATHEMATICAL MODEL

While Wallis (1973) has shown that a constant density model adequately predicts polymer reactor performance, the model presented here accounts for changing density. Other assumptions are listed ahead. The bases for these assumptions are given by Wallis (1973).

Assumptions:

1. Heat capacity, thermal conductivity, heat of reaction, and diffusion coefficients are constant.
2. The diffusion coefficient for AIBN and styrene diffusion are equal.
3. The polymer does not diffuse.
4. The velocity profile is parabolic (a plug profile is used for the plug flow model).
5. Axial mass and energy diffusion are small.
6. Radial velocities are zero.
7. The reactor wall temperature is constant based on experimental reactor wall temperature control.
8. The density of the reacting medium is given by

$$\begin{aligned}\rho &= [.845 - .001\,(T-353)] \\ &\quad + [0.2 + .001\,(T-353)]\,x_m \\ &= a + bx_m\end{aligned} \tag{21}$$

Diffusion Model

The following equations were obtained by using the assumptions just listed:

$$V_{zo}\frac{\partial x_I}{\partial z} = k_I(1-x_I)\,\frac{(a+bx_m)}{\rho_o} + \frac{D}{r}\,\frac{\partial}{\partial r}\left(r\,\frac{\partial x_I}{\partial r}\right) \tag{22}$$

$$V_{zo}\frac{\partial x_m}{\partial z} = R_p + \frac{D}{r}\,\frac{\partial}{\partial r}\left(r\,\frac{\partial x_m}{\partial r}\right) \tag{23}$$

$$\rho_o C_p V_{zo}\frac{\partial T}{\partial z} = -\,\Delta H_r R_p + \frac{k}{r}\,\frac{\partial}{\partial r}\left(r\,\frac{\partial T}{\partial r}\right) \tag{24}$$

$$R_p = C_{mo}(1-x_m)\left[k_m^2(1-x_m)^2\left(\frac{a+bx_m}{\rho_o}\right)^3 fC_{Io}(1-x_I) + k_{mt}^2\left(\frac{a+bx_m}{\rho_o}\right)^2\right]^{1/2} \tag{25}$$

The boundary conditions were

$$\frac{\partial x_I(0,z)}{\partial r} = \frac{\partial x_m(0,z)}{\partial r} = \frac{\partial T(0,z)}{\partial r} = 0$$

$$x_I(r,0) = 0$$

$$x_m(r,0) = 0$$

$$T(r,0) = T_{\text{in}}$$

$$\frac{\partial x_I(R,z)}{\partial r} = \frac{\partial x_m(R,z)}{\partial r} = 0$$

$$T(R,z) = T_w$$

Equations (22) to (24) were reduced to a set of ordinary differential equations through the use of second-order finite differences. The resultant initial value set of ordinary differential equations were integrated by means of a fourth-order Runge-Kutta-Gill routine on a CDC 6400 computer. The grid spacing was sufficiently small to eliminate discretization error. The effective reactor length, 610 cm, was calculated from equipment dimensions by assuming the region from the initiator injection point to the reactor sample valve represented the zone of polymer reaction. The experimental data were reported in Part I and are not listed here.

Plug Flow Model

The use of the concept of a heat transfer coefficient h between the tube wall and reacting fluid permitted development of the following equations from basic principles:

$$V_o \frac{dx_I}{dz} = k_I(1 - x_I)\,\frac{(a + bx_m)}{\rho_o} \qquad (26)$$

$$V_o \frac{dx_m}{dz} = R_p \qquad (27)$$

$$\rho_o C_p V_o \frac{dT}{dz} = -\,\Delta H_r R_p - \frac{2h}{R}\,(T - T_w) \qquad (28)$$

The initial conditions were

$$x_I(0) = 0$$

$$x_m(0) = 0$$

$$T(0) = T_{\text{in}}$$

The heat transfer coefficient used in Equation (28) was estimated with the aid of the following equation (Holman, 1963):

$$\frac{h(2R)}{k} = 4.364 \qquad (29)$$

Substituting the value of h given by Equation (29) into Equation (28) gives

$$\rho_o C_p V_o \frac{dT}{dz} = -\,\Delta H_r R_p + \frac{4.364\,k}{R^2}\,(T - T_w) \qquad (30)$$

Equations (26), (27), and (30) were integrated on a CDC 6400 computer by a Runge-Kutta-Gill routine.

MOLECULAR WEIGHT CALCULATION

Integration of Equations (22) to (24), or Equations (26), (27), and (30), gives x_I, x_m, and T as functions of radius and axial position. The polymer properties may be evaluated from these. The instantaneous number, weight, and Z average chain lengths are given in Equations (8) to (10). These chain lengths are averaged along each reactor streamline to obtain streamline average chain lengths. The latter are used to develop a cup averaged set of molecular weights for the polymer leaving the reactor.

The molecular weights averaged along a streamline are calculated by Equations (31) to (33). The quantity $\bar{x}_{mi}$ is defined by the following:

$$\bar{x}_{mi} = (\bar{x}_{m,i+1} - x_{m,i}) = -\,R_p\,\Delta z/V_z$$

where $\bar{x}_{mi}$ represents the amount of dead polymer formed by reaction in the axial increment i to $i + 1$. The variable $\bar{x}_{m,i+1}$ represents the monomer concentration that results at axial position $i + 1$ after monomer reaction without diffusion in the axial increment i to $i + 1$. By assuming that the arithmetic average of the molecular weights at axial positions i and $i + 1$ is representative of the molecular weight in that increment, the expressions for the streamline molecular weights for N axial increments are

$$M_{ns} = \frac{\Sigma w_i}{\Sigma \dfrac{w_i}{M_i}} = \frac{\sum_{i=0}^{N} \bar{x}_{mi}}{\sum_{i=0}^{N} \dfrac{2\bar{x}_{mi}}{(M_{n,i} + M_{n,i+1})}} \qquad (31)$$

$$M_{ws} = \frac{\Sigma w_i M_i}{\Sigma w_i} = \frac{\sum_{i=0}^{N} (M_{w,i} + M_{w,i+1})\,\bar{x}_{mi}}{2\sum_{i=0}^{N} \bar{x}_{mi}} \qquad (32)$$

$$M_{zs} = \frac{\Sigma w_i M_i^2}{\Sigma w_i M_i} = \frac{\sum_{i=0}^{N} (M_{z,i} + M_{z,i+1})^2\,\bar{x}_{mi}}{\sum_{i=0}^{N} 2\,(M_{z,i} + M_{z,i+1})\,\bar{x}_{mi}} \qquad (33)$$

The streamline averaged properties at the reactor exit, defined by Equations (31) to (35), were used to calculate the cup averaged properties which follow. All integrals were evaluated by Simpson's Rule.

$$\overline{M}_n = \frac{2\pi \int_0^R rV_z\,(\Sigma\bar{x}_{mi})\,dr}{2\pi \int_0^R \dfrac{rV_z\,(\Sigma\bar{x}_{mi})\,dr}{M_{ns}}} \qquad (34)$$

$$\overline{M}_w = \frac{2\pi \int_0^R rV_z\,(\Sigma\bar{x}_{mi})\,M_{ws}\,dr}{2\pi \int_0^R rV_z\,(\Sigma\bar{x}_{mi})\,dr} \qquad (35)$$

$$\overline{M}_z = \frac{2\pi \int_0^R rV_z\,(\Sigma\bar{x}_{mi})\,M_{zs}^2\,dr}{2\pi \int_0^R rV_z\,(\Sigma\bar{x}_{mi})\,M_{zs}\,dr} \qquad (36)$$

The cup averaged conversion was determined from the following equation:

$$\overline{X}_m = \frac{2\pi \int_0^R rV_z\,(1 - C_m/C_{mo})\,dr}{2\pi \int_0^R rV_z\,dr} \qquad (37)$$

Equations (34) to (37) were developed by Wallis (1973); it is noteworthy that Equations (34), (35), and (37) were subsequently confirmed and presented in a recent publication by Kwon and Evans (1973).

The dispersity ratio was calculated by taking the ratio of the cup averaged weight average molecular weight to the cup averaged number average molecular weight.

The plug flow model gave adequate predictions of reactor performance (Wallis, 1973). However, superior predictions were obtained by arbitrarily doubling the heat transfer coefficient given by Equation (29). The more realistic predictions by this modified model (Table 1) were a result of the higher rate of heat removal brought about by the increased value of the heat transfer coefficient. Considering the actual complexity of the polymer system a plug flow model, even with an adjusted heat transfer coefficient, would be useful for process description as evidenced by the results.

The diffusion model predicts reactor performance even better than the modified plug flow model. Table 1 shows that the agreement between the diffusion model and the experimental results is excellent.

It should be mentioned that the error in ascertaining experimental values was about 5 to 10% and that reactor simulations using the kinetic data from Matheson et al. (1951) for k_p and k_t in k_m rather than the value given for k_m [Equation (17)] gave results almost 10% lower than these simulation studies. However, the data of Matheson et al. (1951) were taken for temperatures to 60°C and the mathematical expressions suggested in the reference have been extrapolated to the temperature range 70° to 100°C.

It should be noted that the high standard deviations for the ratios $\overline{M}_w/\overline{M}_w(h)$ and $\overline{D}_n/\overline{D}_n(h)$ in Table 1 were caused by minute thermal polymerization in two of the experiments. This was due to an excessive rate of inhibitor removal prior to polymerization (see Wallis, 1973). Because of this fact, of all predictions, the ratios given for $\overline{M}_n/\overline{M}_n(h)$ and $\overline{X}/\overline{X}$(expt.) are believed to be more indicative of the true accuracy of the model predictions since both $\overline{M}_n(h)$ and $\overline{X}$(expt.) are unaffected by small amounts of thermal polymerization.

Simulations showed radial diffusion of monomer and initiator had little effect on the model predictions of conversion and molecular weights; see Wallis (1973) for details.

MODEL COMPARISONS

While there were no experimental/model comparisons for liquid polymerization in tubular reactors, Duerksen and Hamielec (1968) and Duerksen et al. (1967) have modeled styrene polymerization in a CSTR. The earlier work gave comparisons for a single tank.

In the later study, Duerksen and Hamielec (1968) presented model and experimental results for three CSTR's in series. They determined optimal initiator efficiencies and termination rate constants by minimizing the following expression:

$$[\overline{M}_n(\text{exp.}) - \overline{M}_n(\text{model})]^2 + [\overline{M}_w(\text{exp.}) - \overline{M}_w(\text{model})]^2$$

The results in Table 2 were calculated from their data by Wallis (1973).

The results given in Tables 1 and 2 are grouped together in Table 3 for the purpose of comparison.

From Table 3 it is seen that the accuracies of the tubular reactor models of this study compare very favorably with the accuracies of the CSTR models developed by other researchers for both parameter average value and standard deviation. In addition, the diffusion model is more accurate than the plug flow model.

REACTOR STABILITY AND PERFORMANCE

The diffusion model has been used to generate typical graphs of reactor operation under various conditions. Based on these graphs, several aspects of reactor stability and performance may be discerned.

The use of the diffusion model developed in this study

Table 1. A Comparison of Tubular Reactor Models With Experimental Results

$\frac{\text{Model}}{\text{expt.*}} = x_m \pm \sigma$	Plug flow model	Diffusion model	Experimental range
$\frac{\overline{M}_n}{M_n(h)} =$	1.05 ± .027	1.02 ± .045	$50{,}000 < \overline{M}_n < 80{,}000$
$\frac{\overline{M}_w}{M_w(h)} =$	1.0 ± .10	0.98 ± .095	$80{,}000 < \overline{M}_w < 140{,}000$
$\frac{\overline{D}_n}{D_n(h)} =$	0.95 ± .09	0.98 ± .08	$1.5 < \overline{D}_n < 2$
$\frac{\overline{X}}{X\ (\text{expt.*})} =$	1.06 ± .03	1.02 ± .028	$10\% < \overline{X} < 35\%$

* Expt. = experimental values.

Table 2. A Comparison of CSTR Predictions With Experimental Results

$\frac{\text{Model}}{\text{expt.*}} = x_m \pm \sigma$	Single CSTR	Experimental range	Multiple CSTR	Experimental range
$\frac{\overline{M}_n}{\overline{M}_n(h)} =$	0.96 ± .08	$47{,}000 < \overline{M}_n < 76{,}000$	0.96 ± .08	$15{,}000 < \overline{M}_n < 52{,}000$
$\frac{\overline{M}_w}{\overline{M}_w(h)} =$	0.93 ± .07	$73{,}000 < \overline{M}_w < 116{,}000$	0.95 ± .04	$26{,}000 < \overline{M}_w < 90{,}000$
$\frac{\overline{D}_n}{\overline{D}_n(h)} =$	0.98 ± .01	$1.5 < \overline{D}_n < 1.7$	0.99 ± .05	$1.5 < \overline{D}_n < 2.8$
$\frac{\overline{X}}{\overline{X}\ (\text{expt.*})} =$	0.93	$10\% < \overline{X} < 30\%$	1.01 ± .05	$14.7\% < \overline{X} < 50\%$

* Expt. = experimental.

TABLE 3. A COMPARISON OF VARIOUS MODELS WITH EXPERIMENTAL RESULTS

	Plug flow tubular reactor	Diffusion model	CSTR model	Optimized CSTR model
$\frac{\overline{M}_n}{\overline{M}_n(h)}$	1.05 ± 0.027	1.02 ± 0.045	0.96 ± 0.08	0.96 ± 0.08
$\frac{\overline{M}_w}{\overline{M}_w(h)}$	1.0 ± 0.10	0.98 ± 0.095	0.93 ± 0.07	0.95 ± 0.04
$\frac{\overline{D}_n}{\overline{D}_n(h)}$	0.95 ± 0.09	0.98 ± 0.08	0.98 ± 0.01	0.99 ± 0.05
$\frac{\overline{X}}{\overline{X}\,(\text{expt.}^*)}$	1.06 ± 0.03	1.02 ± 0.028	0.93	1.01 ± 0.05

* Expt. = experimental.

gives the relationships between tubular reactor radii, wall temperature, and the maximum temperature rise between the tube center and the tubular reactor wall. These relationships are shown in Figure 1.

From Figure 1 it is seen that:

1. For a given maximum temperature rise the reactor radius decreases with increasing wall temperature. This implies that production capacity decreases with higher reactor operating temperatures.
2. For a given maximum temperature rise the reactor radius decreases with increasing initiator concentration. This implies that production capacity decreases with increased initiator concentration.
3. There is a maximum "maximum temperature rise" for given reactor conditions. Since this maximum is considerably greater than the 20°C that would be allowed in practice, it has little industrial significance.

However, the trends indicated in points 1 and 2 above may be offset by increased monomer conversion. In designing a reactor for polymer production, a temperature rise of 15°C would probably provide a reasonable compromise between throughput and product quality. Figures similar to Figure 1 could be used to determine a suitable reactor radius.

The initiator concentrations listed on the figure are inlet values and some are experimental values; see Part I for the data. The inlet temperature used to derive Figure 1 is 80°C. The influence of inlet temperature, for differences of approximately 20°C or less between the inlet and the reactor wall, is very small in comparison with the influence of wall temperature.

PRODUCT QUALITY AND REACTOR OPERATION

The experimental residence times and initiator concentrations of experiments 1 and 4 were used to generate Figures 2 to 4. An inlet temperature of 80°C was used throughout the simulation series. These figures were intended as a guide to show the usefulness of a reliable reactor model in determining suitable reactor operating conditions. The model could be used to generate similar curves for any specific set of conditions.

While throughput from an industrial standpoint increases with reactor radius, Figure 2 shows that an increase in conversion is also possible with increased reactor radius due to the increased temperatures at the tube center. However, if the reactor wall temperature is increased beyond some maximum level, it is also possible to obtain a decrease in conversion for a given reactor radius since higher wall temperatures cause the initiator to react more rapidly without a corresponding increase in polymer production. Increased initiator concentration for a given reactor radius and reactor wall temperature increases monomer conversion.

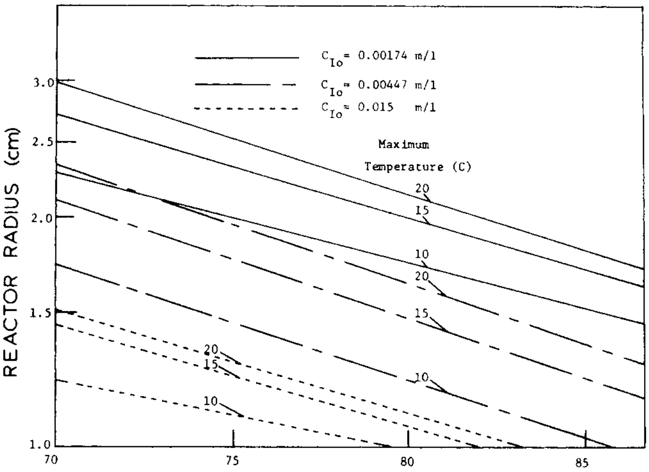

Fig. 1. Critical radii for maximum differential temperatures between tube center and reactor wall.

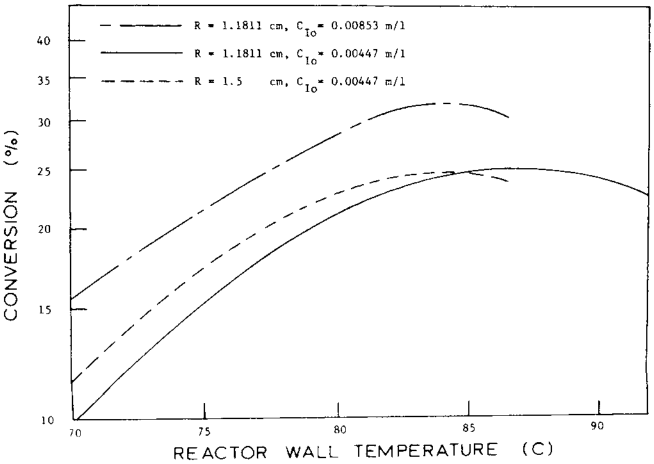

Fig. 2. Effect of radius and reactor wall temperature on monomer conversion.

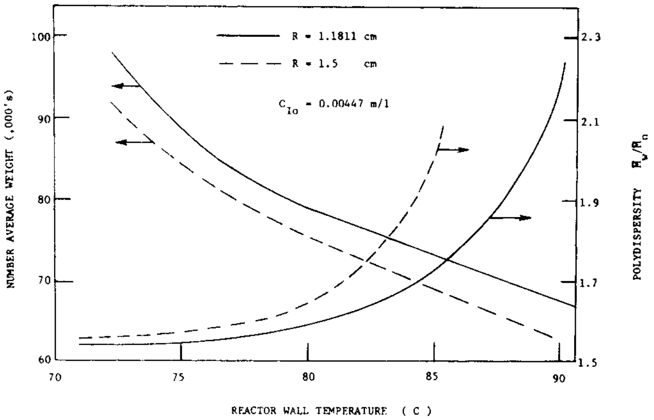

Fig. 3. Effect of radius and reactor wall temperature on number average weight and polydispersity.

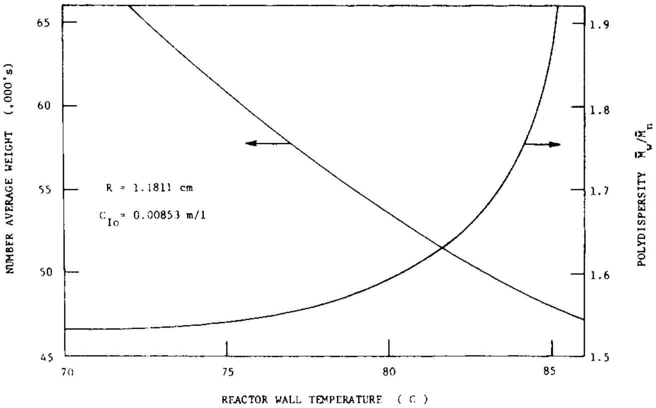

Fig. 4. Effect of reactor wall temperature on number average weight and polydispersity.

Figure 3 shows that the polymer formed in the larger diameter tube is lower in molecular weight and poorer in quality, that is, it has higher polydispersity. A higher wall temperature also results in a decrease in molecular weight and an increase in polydispersity, shown by the curves in Figures 3 and 4. The decrease in molecular weight and increase in polydispersity is caused by the high rate of initiator removal; the formation of small chain molecules is followed by the formation of long chain molecules as the initiator is depleted. The formation of both types of chains results in a very disperse product having a low number average molecular weight. Inspection of Figures 3 and 4 shows that for given reactor conditions increasing initiator concentration causes a decrease in molecular weight and an increase in polydispersity. If initiator concentration at the reactor inlet is fixed and the wall temperature varied, the average molecular weight decreases and the polydispersity increases with increasing reactor wall temperature. The increase in polydispersity may be equated to a decrease in product quality.

The above discussion of Figures 2 to 4 shows that increasing reactor wall temperature, or initiator concentration, or reactor radius causes:

1. Conversion to increase to a maximum value,
2. Number average molecular weight to decrease, and
3. Polydispersity to increase, implying a decrease in product quality.

The implication for industrial production is that a compromise has to be made between product quality, molecular weight, and plant capacity.

Based on Figures 2 to 4, a reasonable compromise is the operation of the reactor at 5° to 10°C below the optimal reactor wall temperature required for maximum conversion. Further increases in conversion may be obtained by having two reactors in series, the second reactor being operated at a higher wall temperature. This increase in wall temperature would be needed since the initiator solution would consist of two initiators, one of which would only decompose significantly at a higher temperature. Clearly, the more temperature sensitive initiator would decompose in the first reactor.

Industrial product capacity could be obtained from 1000 or more parallel tubes (for example, heat exchanger bundle) approximately 2.5- to 4-cm I.D.

CONCLUSIONS

An analysis was made of the bulk polymerization of styrene initiated by azobisisobutyronitrile in a tubular reactor. Rigorous mathematical models were developed and verified.

The model simulations carried out on a CDC 6400 computer showed:

1. Predictions of molecular weights and conversions compared very favorably with those produced in the experimental program.
2. A diffusion model predicted molecular weights and conversions 2% higher on the average than experimental values on a relative basis.
3. Radial diffusion of the monomer and the initiator had little effect on the model predictions of conversion and molecular weights.
4. A plug flow contraction of the diffusion model, predicted molecular weights and conversion 6% higher on the average than the experimental values on a relative basis.
5. The diffusion model showed that optimal conversions can be obtained by proper reactor operation.
6. The diffusion model showed that increased wall temperature, and/or initiator concentration, and/or reactor radius, caused broad molecular weight distributions.
7. Tentative model studies for optimal conversion with minimal molecular weight dispersion indicated the reactor should be operated at a wall temperature of 5° to 10°C below that required for optimal conversion.
8. Further numerical and experimental studies are required to establish if the production of adequate quality polystyrene in a tubular reactor is compatible with a conversion greater than 35%.
9. The development of a two-stage reactor operated at different wall temperatures and using different initiators to realize conversion greater than 35% is needed.

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NOTATION

a = styrene density, g/cc
b = coefficient for polymer correction to styrene density, g/cc
C = concentration, g-mol/l
C_p = heat capacity, 0.45 cal/g-°K
C_{trm} = transfer to monomer constant, the ratio of transfer to monomer rate constant to propagation rate constant
D = diffusion coefficient, 2×10^{-5} cm^2/s
$\overline{D}_n$ = polydispersity ratio, ratio of weight average to number average molecular weight

$\overline{D}_n(h)$ = experimental polydispersity ratio
f = initiator efficiency
fk_I = rate constant for the initiation reaction, s^{-1}
h = heat transfer coefficient, cal/cm^2-s-°K
I = initiator molecule
k = thermal conductivity, 3×10^{-4} cal/cm-s-°K
k = rate constant
k_{mt} = thermal rate constant for monomer usage, s^{-1}
M = monomer molecule
$M\cdot$ = monomer radical obtained by monomer transfer
$M_{n,i}$ = number average molecular weight at axial position i at any streamline
M_{ns} = number average molecular weight for a streamline at the reactor exit
$M_{w,i}$ = weight average molecular weight at axial position i at any streamline
M_{ws} = weight average molecular weight for a streamline at the reactor exit
$M_{z,i}$ = Z average molecular weight at axial position i at any streamline
M_{zs} = Z average molecular weight for a streamline at any reactor exit
$\overline{M}$ = cup averaged molecular weight, or molecular weight
$\overline{M}(h)$ = experimental molecular weight
p = probability of an active polymer chain propagating, $1/(1 + R_I/R_p + C_{trm})$
P = polymer molecule
$\overline{P}_c$ = probability of a combination of polymer radicals instead of monomer transfer, $1/(1 + 2C_{trm}R_p/R_I)$
$\overline{P}_{tr}$ = probability of a monomer transfer occurring instead of radical combination, $1/(1 + R_I/(2R_pC_{trm}))$
r = radius inside a tube, cm
R = radius of a tube to the inner wall surface, cm
R = gas constant, 1.987 cal/g-mole-°K
R = reaction rate
$R\cdot$ = radical
R_p = rate of polymerization
T = temperature, °K
T_{in} = inlet temperature of the reacting stream, °K
T_w = wall temperature of the tubular reactor, °K
V_z = velocity of the reacting stream, cm/s
V_o = average velocity at reactor inlet, cm/s
w_i = weight of polymer of chain length i
X = instantaneous polymer chain length
x = conversion
$\overline{X}$ = cup averaged conversion
x_m = arithmetic mean
$x_{m,i}$ = conversion of monomer to polymer at axial position i at any streamline
$\overline{x}_{m,i+1}$ = conversion of monomer to polymer at axial position $i + 1$ that would occur solely by reaction if the conversion at axial position i was $x_{m,i}$
$\overline{x}_{mi}$ = incremental change in monomer conversion from axial position i to $i + 1$, caused solely by reaction if the conversion at position i was $x_{m,i}$
z = axial distance along the tubular reactor, cm
Z = Z average

Subscripts

I = initiator
m = monomer
n = number average
o = inlet
p = propagation
pI = polymerization due to initiator
pt = polymerization due to thermal effects
t = termination by combination
trm = transfer to monomer
w = weight average
z = axial distance along the tubular reactor, cm
Z = Z average

Greek Letters

ΔH_r = heat of reaction due to polymerization, −16.7 Kcal/g-mole
ρ = density of reacting mixture, g/cc
σ = standard deviation

Some of the symbols with localized meaning are defined in the text.

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