Effect of Multiple Feeds on a Termination-Free Polymerization in Continuous Stirred Tank Reactors*

F. G. TEANEY† and R. G. ANTHONY,* *Department of Chemical Engineering, Texas A&M University, College Station, Texas*

Synopsis

The effect of monomer and initiator feeds to each of a series of continuous stirred tank reactors (CSTR) on the molecular weight distributions, average molecular weight, polymer production rate, and initiator and monomer conversions is studied for the termination-free polymerization system. For initiator feed concentrations less than 0.001 mole/liter, the distribution becomes narrower as the polymer progresses from reactor 1 to reactor 3. But for concentrations of initiator of 0.01 mole/liter, the distribution may be broadened from reactor 1 to reactor 3. The broadening of the distribution results in the production of a lower molecular weight polymer.

INTRODUCTION

Many studies have been presented for termination-free polymerizations in batch and continuous stirred tank reactors (CSTR). However, the effect of multiple feeds and monomer and initiator feeds to each reactor on the molecular weight distribution, average molecular weights, and monomer and initiator conversion has not been presented in the literature. Because the molecular weight distribution and average molecular weights affect the physical properties of a polymer, it is desirable to be able to vary operating conditions of a reactor or reactors to produce a polymer of a given molecular weight distribution. For the termination-free polymerization, the distribution can be varied by changing the concentration of the initiator and monomer in a series of CSTR. Determination of the effect of monomer and initiator feed rates, kinetic rate constants, intermediate feeds, and reactor residence time on rate of polymer production and molecular weight distribution in a series of CSTR was the primary objective of this study.

DEVELOPMENT OF MODELS

In the development of the models, the following assumptions were made: mixing is perfect, reactors are operating isothermally at steady state,
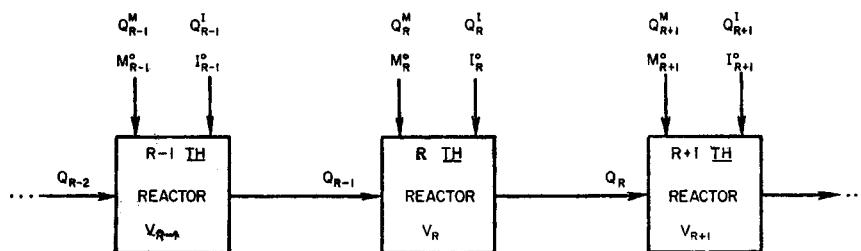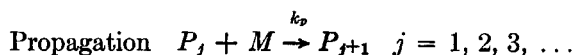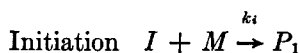

147

Fig. 1. Flow diagram of reactor system.

propagation rate constants are independent of polymer chain length, no chain transfer or termination occurs, and no density change occurs in the reactor.

The following stepwise addition reaction mechanism applies for termination-free polymerization of a monomer:

$$\text{Initiation} \quad I + M \xrightarrow{k_i} P_1$$

$$\text{Propagation} \quad P_j + M \xrightarrow{k_p} P_{j+1} \quad j = 1, 2, 3, \ldots$$

The symbols I, M, P_1, etc., stand for molecular species as well as their concentrations.

Consider a system of R perfectly mixed continuous reactors with influent and effluent rates q_r and volumes V_r as shown in Figure 1. Each reactor has fresh monomer feed $q_r{}^M$ and fresh initiator feed $q_r{}^I$. These fresh feeds in reactors 2 and 3 are referred to as intermediate feeds in the subsequent discussion. The steady state material balances for the rth reactor are:

$$\text{Monomer} \quad f_r M_{r-1} + g_r{}^M M_r{}^0 - M_r[1 + \theta_r k_i I_r + \theta_r k_p \sum_{j=1}^{\infty} P_{j,r}] = 0$$

$$\text{Polymer Species } P_1 \quad f_r P_{1,,r-1} - P_{1,r} + \theta_r k_i M_r I_r - \theta_r k_p M_r P_{1,r} = 0$$

$$\text{Total Polymer} \quad f_r \sum_{j=1}^{\infty} P_{j,r-1} - \sum_{j=1}^{\infty} P_{j,r} + \theta_r k_i M_r I_r = 0$$

$$\text{Initiator} \quad f_r I_{r-1} + g_r{}^I I_r{}^0 - I_r - \theta_r k_i M_r I_r = 0$$

$$\text{Polymer Species } P_j \quad f_r P_{j,r-1} - P_{j,r} - \theta_r k_p M_r[P_{j,r} - P_{j-1,r}] = 0 \quad j \geq 2$$

where $\theta_r = V_r/q_r$, $f_r = q_{r-1}/q_r$, $g_r{}^M = q_r{}^M/q_r$, and $g_r{}^I = q_r{}^I/q_r$.

For each reactor there is an infinite set of material balance equations for P_j. These equations can be solved by stepwise algebraic substitution,[1] but the calculations become unwieldy. This problem is particularly acute when more than one reactor is considered.

An alternate approach is to use the continuous variable technique as proposed by Zeman and Amundson.[1,2] This technique approximates the infinite set of equations for each reactor by a first-order ordinary differen-

tial equation. In this technique the concentration of a particular species of polymer P_j is considered to be a function of a continuous variable $P(j)$ instead of the discrete variable j. Then a function $P(j)$ can be defined such that $P(j) = P_j$.

Now expand the polymer concentration in a backward Taylor series considering only linear terms, as follows:

$$P(j-1) = P(j) - \frac{dP(j)}{dj}\,\Delta j.$$

Higher-order terms could have been retained in the Taylor series expansion. However, Zeman and Amundson[1] state that the first-derivative continuous variable technique becomes a very good approximation as the degree of polymerization becomes large.

For our case, $\Delta j = 1$. Therefore,

$$P(j) - P(j-1) = \frac{dP(j)}{dj}.$$

Also let $P_T = \sum_{j=1}^{\infty} P_j$.

The material balance equations in terms of continuous variables become:

$$M_r = \frac{f_r M_{r-1} + {}^M r\, g^0{}_r M}{1 + \theta_r k_i I_r + \theta_r k_p P_{T,r}} \qquad r = 1\ to\ R,\, M_0 = 0 \tag{1}$$

$$P(1)_r = \frac{f_r P(1)_{r-1} + \theta_r k_i M_r I_r}{1 + \theta_r k_p M_r} \qquad r = 1\ to\ R,\, P(1)_0 = 0 \tag{2}$$

$$P_{T,r} = f_r P_{T,r-1} + \theta_r k_i M_r I_r \qquad r = 1\ to\ R,\, P_{T,0} = 0 \tag{3}$$

$$I_r = \frac{f_r I_{r-1} + g_r{}' I_r{}^0}{1 + \theta_r k_i M_r} \qquad r = 1\ to\ R,\, I_0 = 0 \tag{4}$$

$$\frac{dP(j)_r}{dj} + \alpha_r P(j)_r = \gamma_r P(j)_{r-1} \qquad r = 1\ to\ R,\, P(j)_0 = 0, j \geq 2 \tag{5}$$

$$\alpha_r = \frac{1}{\theta_r k_p M_r}; \quad \gamma_r = \frac{f_r}{\theta_r k_p M_r}$$

Equations (1) through (4) can be solved simultaneously for M_r, $P(1)_r$, $P_{T,r}$, and I_r using the Newton-Raphson iterative procedure. A solution for each reactor is obtained by a stepwise procedure starting with reactor 1.

Equation (5) is a set of linear simultaneous first-order differential equations and can be written in the following matrix form:

$$\frac{d\bar{P}(j)}{dj} + \bar{A}\,\bar{P}(j) = 0 \tag{6}$$

where

$$\bar{P}(j) = \begin{bmatrix} P(j)_1 \\ P(j)_2 \\ \cdot \\ \cdot \\ \cdot \\ P(j)_R \end{bmatrix}; \quad \bar{A} = \begin{bmatrix} \alpha_1 & 0 & 0\ldots\ldots.0 \\ -\gamma_2 & \alpha_2 & 0\ldots\ldots0 \\ 0 & -\gamma_3 & \alpha_3 \;\; 0\ldots 0 \\ \cdot & & \\ \vdots & & \\ 0\ldots\ldots\ldots & -\gamma_R & \alpha_R \end{bmatrix}$$

with initial condition

$$\bar{P}(1) = \begin{bmatrix} P(1)_1 \\ P(1)_2 \\ \cdot \\ \cdot \\ \cdot \\ P(1)_R \end{bmatrix}$$

The solution of eq. (6) is[2,3]

$$\bar{P}(j) = \sum_{k=1}^{R} \frac{\bar{y}_k^T \bar{P}(1)}{\bar{y}_k^T \bar{x}_k} \, \bar{x}_k \, e^{-\lambda_k(J-1)}$$

where λ_k is the eigenvalue of the matrix $\bar{A}$, and $\bar{x}_k$ and $\bar{y}_k^T$ are modal columns and rows of the matrix adj $[\bar{A} - \lambda_k \bar{I}]$. The eigenvalues of $\bar{A}$ are $\lambda_k = \alpha_k$.

Therefore for two reactors in series,

$$P(j)_1 = P(1)_1 \, e^{-\alpha_1(J-1)}$$

and

$$P(j)_2 = \frac{\gamma_2 \, P(1)_1}{\alpha_2 - \alpha_1} \, e^{-\alpha_1(J-1)} + \frac{\gamma_2 P(1)_1 + P(1)_2(\alpha_1 - \alpha_2)}{\alpha_1 - \alpha_2} \, e^{-\alpha_2(J-1)}.$$

DISCUSSION OF RESULTS

The procedure which was used for the study of the effect of monomer and initiator concentrations and for the ratio of the rate constants on conversions, MWD and molecular weights was as follows. Fresh monomer and initiator were fed to each reactor and the effluent from reactor 1 was fed to reactor 2 and effluent from reactor 2 was fed to reactor 3. The residence time in the three reactors was held constant at approximately 200, 145, and 125 min. If an initiator concentration of 0.01 mole/liter was fed to reactor 1, this same concentration was used to provide fresh initiator (intermediate feeds) to reactors 2 and 3. The concentration of monomer to each reactor was approximately 5 moles/liter, 1 mole/liter, and 0.4 mole/liter for reactors 1, 2, and 3, respectively. These concentrations of fresh feeds were calculated on the basis of total volume fed (effluent from previous reactor plus fresh feed) to each reactor. Hence, variation of the

TABLE I
Typical Model Results

	Case 1[a]			Case 2[a]		
	reactor 1	2	3	reactor 1	2	3
Fresh monomer concentration on total feed basis, g-moles/liter	5.000	1.073	0.405	4.950	1.055	0.395
Fresh initiator concentration on total feed basis, g-moles/liter	0.00001	0.00001	0.00001	0.00100	0.00100	0.00100
Residence time, min	200	146	127	198	144	124
Outlet monomer concentration, g-moles/liter	4.997	4.752	4.488	4.695	4.174	3.658
Outlet initiator concentration, g-moles/liter	2.309×10^{-6}	3.537×10^{-6}	4.513×10^{-6}	2.416×10^{-4}	3.876×10^{-4}	5.287×10^{-4}
Outlet concentration of polymer of length one, g-moles/liter	2.093×10^{-8}	3.209×10^{-8}	4.096×10^{-8}	2.190×10^{-6}	3.515×10^{-6}	4.796×10^{-6}
Outlet total polymer concentration, g-moles/liter	7.690×10^{-6}	1.378×10^{-5}	2.046×10^{-5}	7.485×10^{-4}	1.319×10^{-3}	1.928×10^{-3}
Total polymer production, g/hr	288	777	1465	26363	67664	120556
Conversion of monomer on cumulative basis, %	0.06	0.12	0.20	5.17	10.26	16.63
Conversion of initiator on cumulative basis, %	76.91	79.57	81.93	75.60	77.29	78.48
Number-average degree of polymerization, $\bar{D}_n$	358	392	428	335	354	370
Weight-average degree of polymerization, $\bar{D}_w$	684	723	764	647	668	687
$\bar{D}_w/\bar{D}_n$	1.912	1.843	1.781	1.929	1.887	1.857

[a] $k_i = 0.02$; $k_p = 22$.

initiator and monomer concentrations was a variation of monomer and initiator feed rate in moles/hr to each reactor. If no intermediate feeds were utilized, no fresh monomer or initiator was fed to reactors 2 and 3. An alternate case would be to have fresh monomer fed to reactors 2 and 3, but no initiator would be fed to reactors 2 and 3 or vice versa.

A typical set of data for computer simulation at steady state of this reaction system is listed in Table I. Selected plots of molecular weight distributions (MWD) are shown in Figures 8 to 10. The effects of the independent variables on conversions, molecular weights, and MWD are discussed below.

Fresh Initiator Feed Concentration and k_p/k_i

Figure 2 shows the effect of these variables on monomer and initiator conversion for reactor 1 at constant feed rates. Additional reactors in series show similar results. The fresh initiator feed concentration has little effect on monomer conversion at low initiator concentrations. However, as the feed concentration increases (and the number of moles of initiator feed increases), monomer conversion increases rapidly. This effect is even more pronounced as the ratio of propagation to initiation rate constants (k_p/k_i) decreases.

Initiator conversion decreases as the initiator feed concentration increases especially at high k_p/k_i ratios. At a constant initiator feed concentration, the initiator conversion increases as k_p/k_i decreases.

Figure 3 shows that both number-average degree of polymerization $(\bar{D}_n)$ and weight-average degree of polymerization $(\bar{D}_w)$ decrease as the initiator feed concentration increases. Higher initiator concentration in the reactor
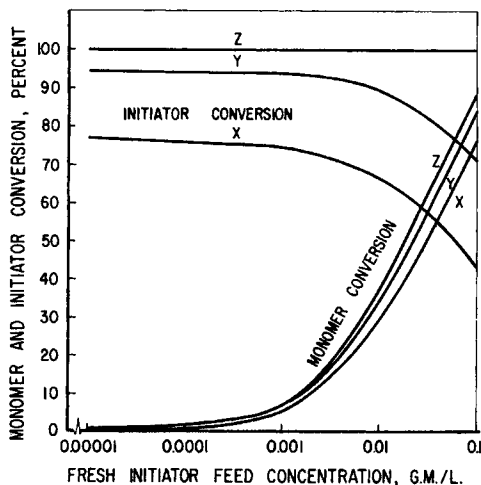

Fig. 2. Effect of fresh initiator feed concentration on monomer and initiator conversion. Reactor 1: $x = k_p/k_i = 110$; $y = k_p/k_i = 22$; $z = k_p/k_i = 0.022$; $[M°] = 5$ g-moles/·liter; $\theta = 200$ min; $k_p = 22$ L/g-mole hr.
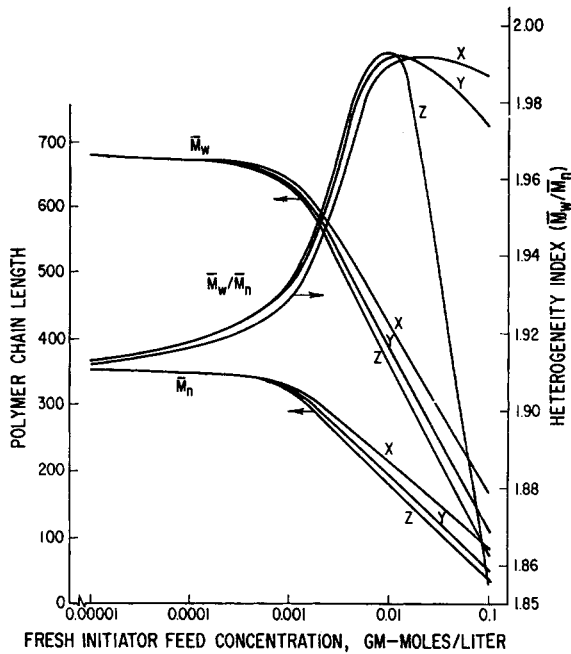
Fig. 3. Effect of fresh initiator feed concentration on polymer molecular weights. Reactor 1: $x = k_p/k_i = 110$; $y = k_p/k_i = 22$; $z = k_p/k_i = 0.022$; $[M°] = 5\,\text{g-moles/-}$ liter; $\theta = 200\,\text{min}$; $k_p = 22\,L/\text{g-mole hr}$.

produces more new short polymer chains which reduce the molecular weights. The ratio of weight-average to number-average degree of polymerization ($\bar{D}_w/\bar{D}_n$) for reactor 1 passes through a maximum as the initiator feed concentration increases. The peak of this curve is much more pronounced as k_p/k_i decreases.

Figure 4 shows the effect of increasing initiator feed concentration on $\bar{D}_n$, $\bar{D}_w$, and $\bar{D}_w/\bar{D}_n$ for reactor 2. Both $\bar{D}_n$ and $\bar{D}_w$ decrease as in reactor 1. However, $\bar{D}_w/\bar{D}_n$ continues to increase for the initiator concentration range investigated instead of passing through a maximum. The effect on reactor 3 is similar to that shown for reactor 2.

Figures 8 and 9 show that the molecular weight distribution (MWD) becomes narrower as the initiator feed concentration decreases. With an increase of initiator concentration from 0.001 mole/liter to 0.01 mole/liter at constant residence time, the number-average of degree of polymerization in reactor 3 is less than that of reactor 1, whereas for initiator concentration of 0.001 mole/liter, the degree polymerization increases with reactor number. One also notes that $\bar{D}_w/\bar{D}_n$ decreases slightly with each reactor at initiator concentrations of 0.001 mole/liter, but it increases slightly with reactor number at 0.01 mole/liter.

Figure 5 shows how the $\bar{D}_w/\bar{D}_n$ varies from reactor to reactor as the initiator feed concentration changes. At low initiator feed concentrations
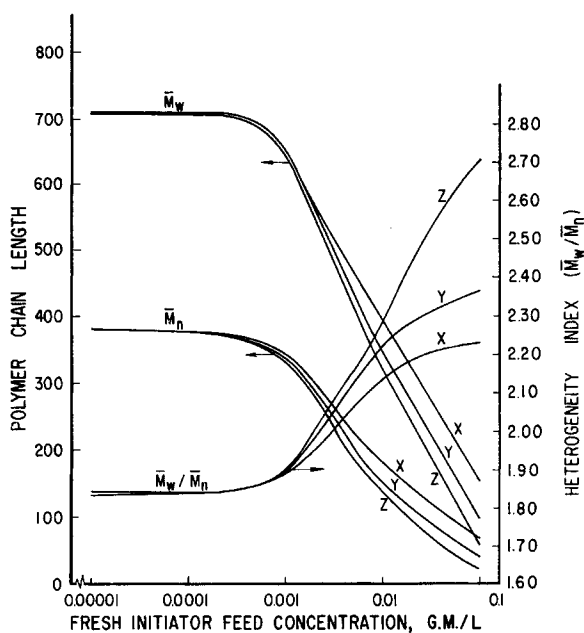
Fig. 4. Effect of fresh initiator feed concentration on polymer molecular weights. Reactor 2: $x = k_p/k_i = 110$; $y = k_p/k_t = 22$; $z = k_p/k_i = 0.022$; $[M°] = 1.073$ g-moles/liter; $\theta = 146$ min; $k_p = 22$ L/mole hr.
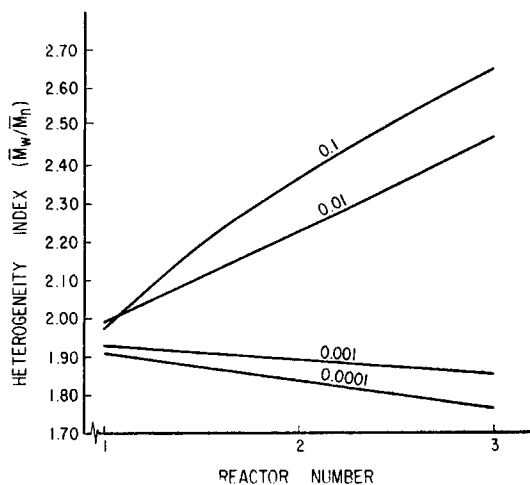

Fig. 5. Variation of $\bar{M}_w/\bar{M}_n$ with reactor number $k_p/k_i = 22$.

$\bar{D}_w/\bar{D}_n$ decreases, while at high concentrations $\bar{D}_w/\bar{D}_n$ increases. This effect was obtained at all values of k_p/k_i studied.

Fresh Monomer Feed Concentration

Figure 6 illustrates the effects of fresh monomer feed concentration (on a total feed basis) for reactor 1. Monomer and initiator conversions in-
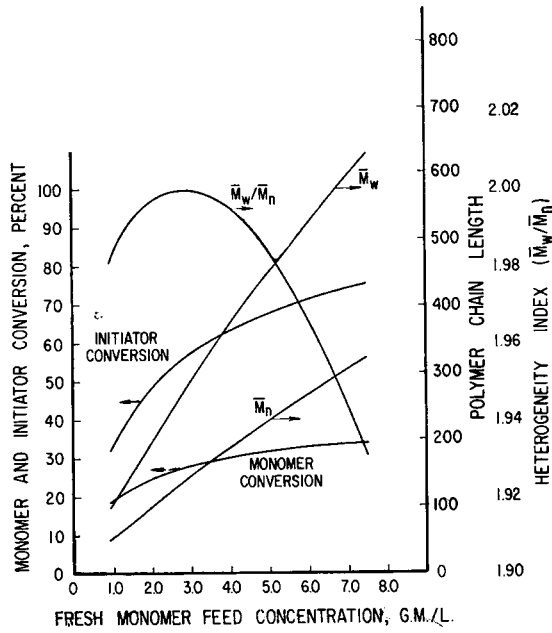
Fig. 6. Effect of fresh monomer feed concentration.   Reactor 1:   initiator concentration
= 0.01 gram-moles/liter; k_p/k_i = 110; θ = 200 min; k_v = 22.

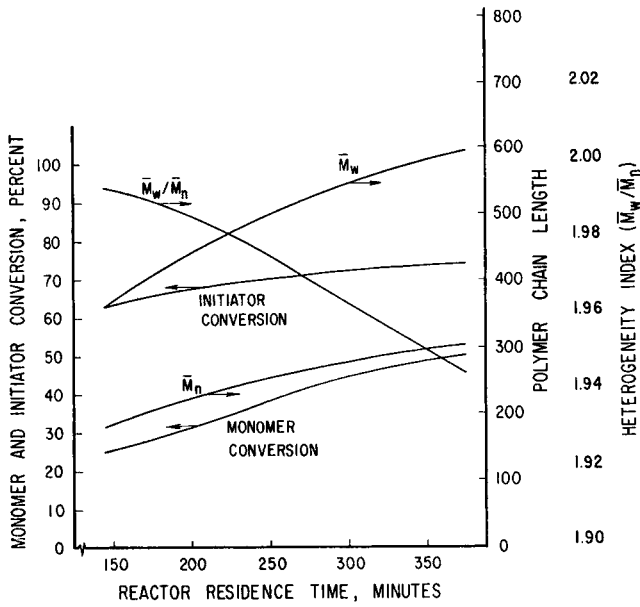Fig. 7. Effect of reactor residence time.   Reactor 1:   fresh initiator feed concentration
= 0.01 gram-moles/liter; k_p/k_i = 110.

crease as monomer feed concentration increases due to the increased driving force for reaction $\bar{D}_n$ and $\bar{D}_w$ increase as monomer feed concentration increases, but $\bar{D}_w/\bar{D}_n$ passes through a maximum. However, for reactors 2 and 3, $\bar{D}_w/\bar{D}_n$ continues to increase as monomer feed concentration increases.

Figure 7 shows the effects of reactor residence time on reactor 1. Monomer conversion, initiator conversion, $\bar{D}_n$, and $\bar{D}_w$ all increase as residence time increases. $\bar{D}_w/\bar{D}_n$ decreases as residence time increases. For reactors 2 and 3, however, $\bar{D}_w/\bar{D}_n$ increases as residence time increases.

No Initiator in the Intermediate Feeds

Figure 10 illustrates the effect of no initiator in the intermediate feeds to reactors 2 and 3. The removal of the initiator feed results in a decrease in monomer conversion and in the mass of polymer produced.

$\bar{D}_n$ and $\bar{D}_w$ decrease from reactor 1 to reactor 3 for intermediate feeds. Since additional initiator is fed to reactors 2 and 3, a substantial number of new polymer chains are formed which results in low average molecular weights. For no intermediate initiator feeds, however, the absence of
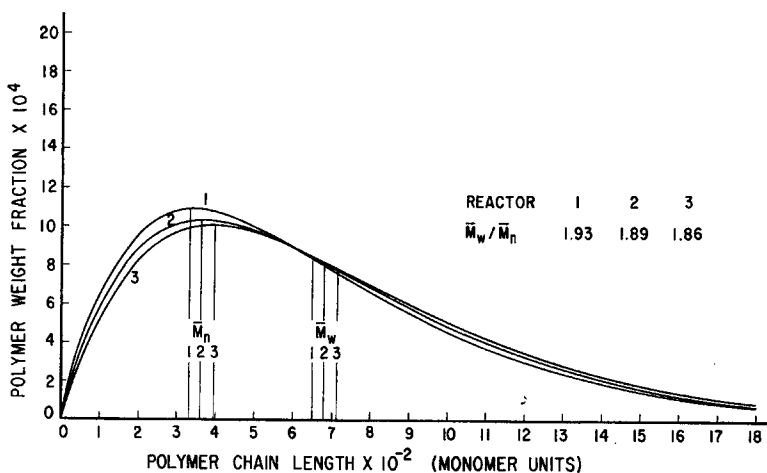

Fig. 8. Molecular weight distribution. $I^{\circ} = 0.001$ g-moles/liter; $k_p/k_i = 110$.

additional fresh initiator results in few new chains being formed. Since no termination reactions occur, the existing chains become longer, which increases the average molecular weights. $\bar{D}_w/\bar{D}_n$ increases with reactor number for $I_r^0 = 0.01$ mole/liter for intermediate initiator feeds but decreases with reactor number for no intermediate initiator feeds.

Figures 9 and 10 illustrate the effect of fresh feeds on the MWD and number-average degree of polymerization for reactors 2 and 3. For the case of fresh initiator feed to reactors 2 and 3, the degree of polymerization decreases from reactors 1 to 3 and $\bar{D}_w/\bar{D}_n$ increases. But for no fresh
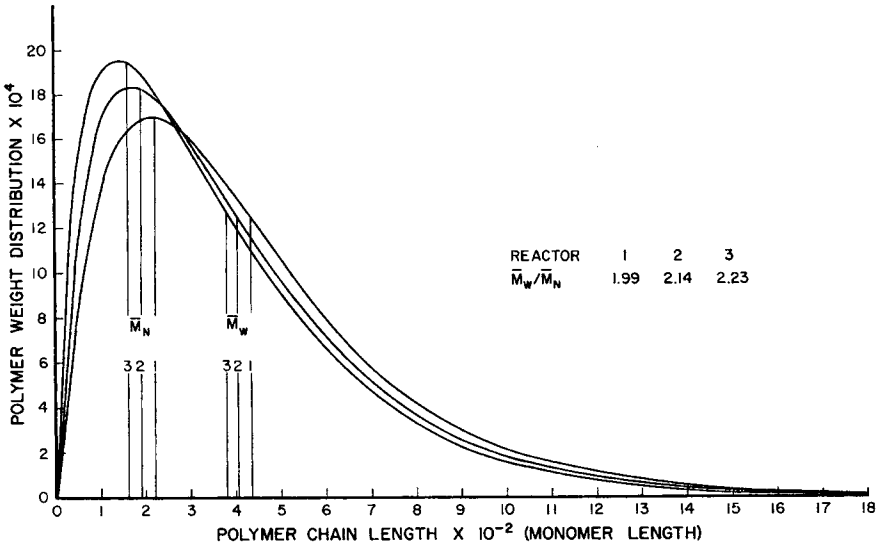
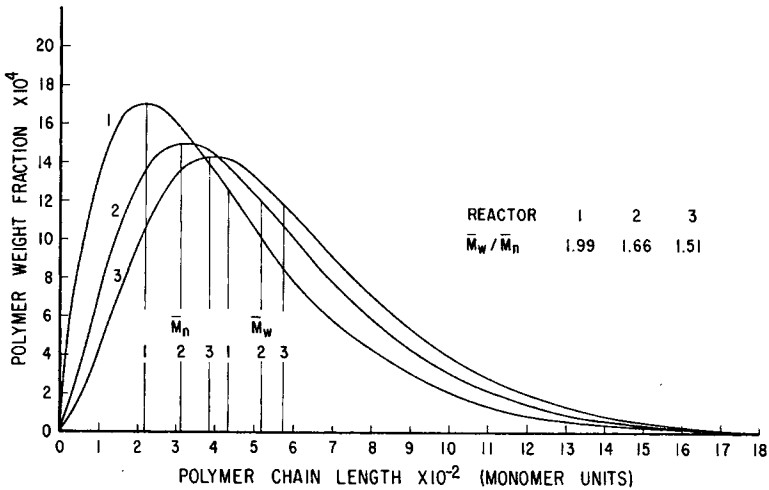Fig. 9. Molecular weight distribution. $I° = .01$ g-moles/liter; $k_p/k_i = 110$.

Fig. 10. Molecular weight distribution. $I° = 0.01$ g-moles/liter; $k_p/k_i = 110$; no fresh feeds to reactors 2 or 3.

initiator feed to reactors 2 and 3, the degree of polymerization increases from reactors 1 to 3 and $\bar{D}_w/\bar{D}_n$ decreases.

For no fresh feeds to reactors 2 and 3, monomer conversion increases but the grams of polymer produced decreases compared to the same problem with intermediate feeds. This is due to the lower total fresh monomer feed. Molecular weight distribution, also, becomes more symmetrical when intermediate feeds are removed.

CONCLUSIONS

Investigation of this polymerization system has shown that initiator feed concentration is the single most important independent variable. It significantly affects conversions and polymer molecular weights. In general, high initiator feed concentrations cause low molecular weight polymers with an increase in $\bar{D}_w/\bar{D}_n$.

High molecular weight polymers with moderate $\bar{D}_w/\bar{D}_n$ can be produced by using high monomer feed concentrations. However, this also causes relatively low monomer conversions.

High molecular weight polymers with moderate $\bar{D}_w/\bar{D}_n$ can also be produced by using high reactor residence times. This can be done by increasing reactor volumes or by reducing total flow rates. For an existing reactor system, reactor volumes are fixed and a reduction in total flow rates reduces total polymer make. Therefore, the preferred method of producing this type of polymer is to use high monomer feed concentrations.

A reactor system with no intermediate feeds can be used to produce either low or high molecular weight polymers. If a high initiator feed concentration is used, a low molecular weight polymer with a very narrow molecular weight distribution is produced. If a low initiator concentration is used, a high molecular weight polymer with a very low $\bar{D}_w/\bar{D}_n$ can be produced. This is especially true if a large number of reactors are used.

Nomenclature

$\bar{D}_w/\bar{D}_n$ = the heterogeneity index
$f_r = q_{r-1}/q_r$
$g_r^I = q_r^I/q_r$
$g_r^M = q_r^M/q_r$
I = concentration of initiator in reactor, gram-moles/liter
I^0 = concentration of fresh initiator feed, gram-moles/liter
k_p = absolute reaction rate constant for propagation reaction, liters/gram-mole hr
k_i = absolute reaction rate constant for initiation reaction, liters/gram-mole hr
M = monomer concentration in reactor, gram-moles/liter
M^0 = concentration of fresh monomer feed, gram-moles/liter
$\bar{M}_w/\bar{M}_n$ = the heterogeneity index
$P_j = P(j)$ = concentration of polymer of length j monomer units, gram-moles/liter
P_T = total polymer concentration, gram-moles/liter
q = flow rate out of reactor, liters/hr
q^I = flow rate of fresh initiator feed, liters/hr
q^M = flow rate of fresh monomer feed, liters/hr
V = volume of reactor, liters
$\theta = V/q$ = residence time of reactor, hr

References

1. R. J. Zeman and N. R. Amundson, *Chem. Eng. Sci.*, **20**, 331 (1965).

2. R. J. Zeman and N. R. Amundson, *Amer. Inst. Chem. Eng. J.*, **9**, 297 (1963).

3. N. R. Amundson, *Mathematical Methods in Chemical Engineering*, Prentice-Hall, Englewood Cliffs, N. J., 1966.

4. S. Bywater, *Polymerization Initiated by Lithium and Its Compounds*, National Research Council of Canada No. 8044.

5. O. Levenspiel, *Chemical Reaction Engineering*, Wiley, New York, 1962.