

Determination of Optimal Reactor System Configuration for Polymerization Reactions. II. Effect of Chain Transfer, Autoacceleration, and Temperature Profile

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

Synopsis

The effect of chain transfer, diffusion control, and temperature on the optimal design and selection of polymerization reactors was investigated. Chain transfer to the monomer was examined and a parametric study of the corresponding rate constant was carried out. The Trommsdorff effect was included in the model by using a diffusion-controlled termination process. An optimum temperature sequence was determined for this modified model by incorporating the effect of temperature on the rate constants and on the amount and rate of heat removal. Furthermore, the concept of dividing the plug flow reactor into several constant temperature zones was considered, and the effect of "zoning" on the system performance was determined.

INTRODUCTION

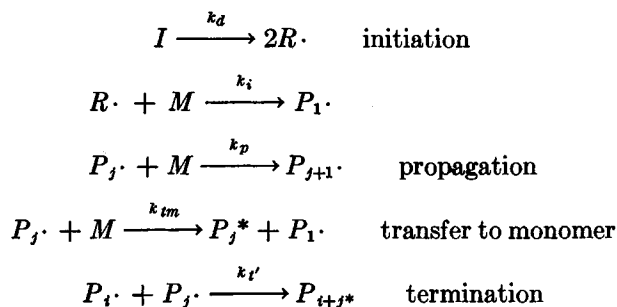
The selection of reactor type and configuration for polymerization reactors was considered in a previous paper.¹ The systems synthesis technique was used to obtain the "best" possible reactor system configuration which minimized an objective function incorporating the conversion of the monomer and mean and variance of the molecular weight distribution (MWD) to produce the desired quality of the product polymer. The investigation considered effects of variation in rate constants, in the feed monomer concentration, and in the initiator concentration on the optimal solution and on the process variables such as exit monomer concentration, variance, and mean of the exit MWD. The effect of recycling the exit stream from the plug flow reactor was also examined, and it was shown that recycling does not improve the performance of the system.

The polymerization mechanism used in the previous paper¹ did not take into account chain transfer to the monomer and the effect of diffusion on the termination processes. Also, in the previous investigation, the entire system was considered to have one uniform temperature. The chain transfer effect was incorporated in the current investigation, and the effect of chain transfer on the optimum system structure from reference 1 was determined. The Trommsdorff effect (autoacceleration effect or the gel

effect) was included in the mathematical model by considering the termination reaction as a diffusion controlled process and using a chain length-dependent termination constant. Nonisothermal conditions were considered in the second part of the investigation. The optimal reactor system configuration (structure of the system) used for optimal synthesis was the same as the one examined in the previous paper (Fig. 5, reference 1). The system components consisted of a completely mixed flow reactor and a plug flow reactor. Results of these investigations are reported in this paper.

CHAIN TRANSFER

In the previous paper,¹ the effect of chain transfer to the monomer was neglected. This phenomenon of chain transfer was first recognized by Flory² who investigated the possibility of transferring reactivity from one species to another; this reaction involves the transfer of an atom between the radical and the molecule. In transfers to the solvent (or any saturated molecule), the atom is transferred to the radical, whereas in transfers involving unsaturated species (such as monomer itself), the atom can go in either direction. Chain transfers to polymer or monomer lead to the formation of branched polymers, and chain transfers to saturated molecules result in termination. They may also result in the formation of additional polymer molecules. Only chain transfer to the monomer was considered in this investigation. The modified polymerization mechanism obtained by including this effect can be written as follows³:



The batch kinetic expressions for this mechanism can be obtained in terms of the initiator concentration, monomer concentration, and the moments of size distributions. These are³

$$\frac{dI}{dt} = -k_d I \quad (1)$$

$$\frac{dM}{dt} = -(k_p + k_{im})M\lambda^{(0)} \quad (2)$$

$$\frac{d\lambda^{(0)}}{dt} = 2k_d I - k_t' \lambda^{(0)} \lambda^{(0)} \quad (3)$$

$$\frac{d\lambda^{(1)}}{dt} = k_p M \lambda^{(0)} - k_{tm} M (\lambda^{(1)} - \lambda^{(0)}) - k_i' \lambda^{(0)} \lambda^{(1)} \quad (4)$$

$$\frac{d\lambda^{(2)}}{dt} = 2 k_p M \lambda^{(1)} - k_{tm} M (\lambda^{(2)} - \lambda^{(1)}) - k_i' \lambda^{(0)} \lambda^{(2)} \quad (5)$$

$$\frac{d\mu^{(0)}}{dt} = k_{im} M \lambda^{(0)} + \frac{k_i'}{2} \lambda^{(0)} \lambda^{(0)} \quad (6)$$

$$\frac{d\mu^{(1)}}{dt} = k_{im} M \lambda^{(1)} + k_i' \lambda^{(0)} \lambda^{(1)} \quad (7)$$

$$\frac{d\mu^{(2)}}{dt} = k_{im} M \lambda^{(2)} + k_i' (\lambda^{(2)} \lambda^{(0)} + \lambda^{(1)} \lambda^{(1)}). \quad (8)$$

The notations used in these equations are defined at the end of this paper (also, see Fig. 5, reference 1, for structural notation).

Material balance equations for each of the process variables can be written for the CSTR (see Subsystems Performance, reference 1); these are presented in Table I. For the plug flow reactor, the material balance equations

TABLE I
Expressions for Exit Concentrations from the Stirred Tank Reactor

Symbol	Variable description	Exit from CSTR
I	initiator concentration	$I_c = \frac{I_2}{1 + \tau_{\text{CSTR}} k_d}$
M	monomer concentration	$M_c = \frac{M_2}{1 + (k_p + k_{tm}) \tau_{\text{CSTR}} \lambda_c^{(0)}}$
$\lambda^{(0)}$	0-th moment of active radical distribution	$\lambda_c^{(0)} = \frac{-(1 + (1 + 4[\lambda_2^{(0)} + 4\tau_{\text{CSTR}} k_d I_c] \tau_{\text{CSTR}} k_i')^{1/2})}{2\tau_{\text{CSTR}} k_i'}$
$\lambda^{(1)}$	1st moment of active radical distribution	$\lambda_c^{(1)} = \frac{\lambda_2^{(1)} + k_p M_c \lambda_c^{(0)} \tau_{\text{CSTR}} + k_{tm} M_c \lambda_c^{(0)} \tau_{\text{CSTR}}}{1 + k_i' \lambda_c^{(0)} \tau_{\text{CSTR}} + k_{tm} M_c \tau_{\text{CSTR}}}$
$\lambda^{(2)}$	2nd moment of active radical distribution	$\lambda_c^{(2)} = \frac{\lambda_2^{(2)} + 2k_p M_c \lambda_c^{(1)} \tau_{\text{CSTR}} + k_{tm} M_c \lambda_c^{(1)} \tau_{\text{CSTR}}}{1 + k_i' \lambda_c^{(0)} \tau_{\text{CSTR}} + k_{tm} M_c \tau_{\text{CSTR}}}$
$\mu^{(0)}$	0-th moment of polymer distribution	$\mu_c^{(0)} = \mu_2^{(0)} + k_{im} M_c \lambda_c^{(0)} \tau_{\text{CSTR}} + \frac{k_i'}{2} \lambda_c^{(0)} \lambda_c^{(0)} \tau_{\text{CSTR}}$
$\mu^{(1)}$	1st moment of polymer distribution	$\mu_c^{(1)} = \mu_2^{(1)} + k_{im} M_c \lambda_c^{(1)} \tau_{\text{CSTR}} + k_i' \lambda_c^{(0)} \lambda^{(1)} \tau_{\text{CSTR}}$
$\mu^{(2)}$	2nd moment of polymer distribution	$\mu_c^{(2)} = \mu_2^{(2)} + k_{im} M_c \lambda_c^{(1)} \tau_{\text{CSTR}} + k_i' \tau_{\text{CSTR}} \{ \lambda_c^{(0)} \lambda_c^{(2)} + \lambda_c^{(1)} \lambda_c^{(1)} \}$

are the same as those for the batch system, eqs. (1) through (8), with the initial conditions given below:

$$\begin{aligned}
 I(0) &= I_3 & \lambda^{(2)}(0) &= \lambda_3^{(2)} \\
 M(0) &= M_3 & \mu^{(0)}(0) &= \mu_3^{(0)} \\
 \lambda^{(0)}(0) &= \lambda_3^{(0)} & \mu^{(1)}(0) &= \mu_3^{(1)} \\
 \lambda^{(1)}(0) &= \lambda_3^{(1)} & \mu^{(2)}(0) &= \mu_3^{(2)}
 \end{aligned} \tag{9}$$

The material balance equations for the process variables I , F , M , $\lambda^{(0)}$, $\lambda^{(1)}$, $\lambda^{(2)}$, $\mu^{(0)}$, $\mu^{(1)}$, and $\mu^{(2)}$ at the mixing points C_2 , C_3 , and C_4 are the same as those presented in the previous paper,¹ eqs. (17) through (35). A computational scheme similar to the one employed in the previous paper was devised to simulate the present system, and the effect of chain transfer to the monomer on the process variables was determined. For this simulation, the recycle streams from the plug flow and CSTR were removed and the remaining α -values were fixed by using the optimal results of the previous paper:

$$\left. \begin{aligned}
 \alpha_{22} &= 0.0 & \alpha_{21} &= 0.336 \\
 \alpha_{23} &= 0.0 & \alpha_{32} &= 0.704 \\
 \alpha_{33} &= 0.0 & \alpha_{41} &= 0.0
 \end{aligned} \right\} \tag{10}$$

The volume ratio V_P/V_T was assumed to be equal to 0.294. The nominal values of parameters used in investigating the effect of chain transfer are presented in Table II. The model system used in this investigation was same as the optimal solution of Table IV presented in the previous paper.

TABLE II
Nominal Values of Parameters Used in the Analysis

Symbol	Parameter description	Nominal value
V_T	total volume	100
q_f	feed flow rate	100
M_0	initial monomer conc.	1.0
k_i	initiation rate constant	0.7719
k_p	propagation rate constant	0.216×10^6
k_t	termination rate constant	0.50×10^6
k_{tm}	rate constant for transfer to monomer	1.0

Effect of Variation in Rate Constant

To determine the effect of chain transfer to the monomer, simulation was carried out using various values of k_{tm} . The results are shown in Table III. It can be seen that as long as k_{tm} was very much smaller than k_p , the effect of k_{tm} on the monomer concentration was negligibly small. At higher values of k_{tm} , however, the influence of k_{tm} on the exit monomer concentration was appreciable. Furthermore, at lower values of k_{tm} , the reduction

TABLE III

Effect of Chain Transfer to Monomer on the Exit Monomer Concentration, the Exit Solvent Concentration, and the Exit MWD for $\eta = 0.294$, $\alpha_{21} = 0.336$, $\alpha_{32} = 0.704$

k_{tm}	Exit monomer	Exit MWD	
		Mean	Variance $\times 10^{-6}$
0.001	0.1398	818.56	0.1297
0.01	0.1398	818.27	0.1297
0.1	0.1398	815.50	0.1299
1.0	0.1398	788.70	0.1314
10.0	0.1397	593.67	0.1201
100.0	0.1393	171.50	0.0220
1000.0	0.1355	21.99	0.000446

in mean and variance was very small because the propagation rate constant, k_p , was predominant. But at higher values of k_{tm} , the chain transfer to monomer became significant and a large number of branched molecules were formed. This drastically reduced both the mean and the variance. For example, increasing k_{tm} from 100.0 to 1000.0 caused the mean of the MWD to drop from 171.50 to 21.88 and the variance from 0.02×10^6 to 0.00044×10^6 ; the monomer concentration, however, was reduced from 0.1393 to 0.1355.

TROMMSDORFF EFFECT

Radical chain polymerizations are often characterized by the presence of an autoacceleration effect (the Trommsdorff, or gel effect) in the polymerization rate as the reaction proceeds. This effect causes the rate of polymerization in a batch reactor to increase with time even though the concentration of the monomer (and also the initiator) decreases. Interest in this phenomenon has been maintained since Norrish and Smith⁴ and later Trommsdorff et al.⁵ suggested that the autoacceleration or gel effect observed in many free-radical polymerizations was due to diffusion control of the termination process. As the polymerization proceeds, the viscosity of the system increases, and this causes a reduction in the termination rate constant.

It was once assumed that the autoacceleration effect in the rate of polymerization was only important near the end of a polymerization. However, experiments by Oster et al.⁶ and other investigators^{7,8,9} showed that the rate of polymerization was viscosity dependent even at zero conversion. In a review published recently, North¹⁰ analyzed the diffusion control of free-radical reactions and presented several theories for it.

In the experimental investigation of methyl methacrylate polymerization, North and Reed¹¹ discovered that the termination rate constant could be expressed as a power series in the total polymer concentration as

$$\frac{k_t}{k_{t0}} = \frac{\eta_0'}{\eta'} \{1 + A'P_T + A''(P_T)^2 + \dots\} \quad (11)$$

in which k_{t0} = termination constant at zero conversion, η' = average "microviscosity" presented to the polymer chain end throughout the diffusion process; η_0' = average "microviscosity" at zero conversion, A' , A'' = constants, and $P_{T\cdot} = \Sigma P_{i\cdot}$ = total active polymer concentration. Duerksen and Hamielec¹² found that an increase in viscosity increased the conversion and average molecular weight for the free-radical solution polymerization of styrene. They obtained experimental data with a single CSTR and regressed the data to obtain the following relationship between the viscosity and the catalyst efficiency, eq (12), and the viscosity and the termination rate constant, eq. (13):

$$\log f/f_0 = .022 \log (1 + \kappa) - .0285 [\log (1 + \kappa)]^2 \quad (12)$$

$$\log k_t/k_{t0} = .060 \log (1 + \kappa) - .0934 [\log (1 + \kappa)]^2 \quad (13)$$

where κ = viscosity of the reactor contents, f = catalyst efficiency, and f_0 = catalyst efficiency at zero conversion. Evidence of the gel effect in styrene polymerization was also discovered experimentally by O'Driscoll and White^{13,14} who found that $k_p/k_t^{1/2}$ increased with the conversion for the benzoyl peroxide-initiated polymerization of styrene at 90°C. Recent experimental investigations by Hamielec and coworkers^{15,16,17} on the kinetics of homopolymerization of the monomers styrene, vinyl chloride, methyl methacrylate, and acrylamide showed that diffusion-controlled kinetics (gel effect) can significantly affect the rate of polymerization and average molecular weights. Hamielec and co-workers^{15,16,17} developed a mathematical model for gel effect which includes the effect of viscosity on the termination rate constant. Benson and North¹⁸ considered the overall kinetics of free-radical homopolymerization without chain transfer in which the propagation rate constant was assumed to be independent of chain length, but the termination reaction was considered diffusion controlled. The termination rate constant derived by considering the diffusional control mechanism is

$$k_t = k_{t0}(1 + N_L^{1/2})^{-1}[1 + N_L^{1/8} d] \quad (14)$$

where k_{t0} = termination constant at zero conversion, N_L = chain length, and $d = [k_{t0}^{1/2}(2fk_dI)^{1/2}]/(k_pM)$.

For homopolymerization with chain transfer to the monomer and diffusional control of the termination process, North and Reed¹¹ obtained the following expression for the termination rate constant:

$$k_t = k_{t0} \left[\frac{8\pi(\nu + \nu_f)^2}{\nu\nu_f(2\nu + \nu_f)} \right]^{-1/2} \quad (15)$$

in which ν = mean kinetic chain length (rate of propagation/rate of initiation) and ν_f = mean kinetic chain length for the transfer reaction (rate of propagation/rate of transfer to the monomer).

Equation (14) was used in this work to model the effect of chain length on the termination rate constant when chain transfer to the monomer was

not present. For kinetic models which included chain transfer to the monomer, however, the chain length dependence of k_t was given by eq. (15).

EFFECT OF TEMPERATURE PROFILE

In the previous paper,¹ the entire system, including both the CSTR and the plug flow reactor, was assumed to be under isothermal conditions. Temperature effects are very important in polymer reactor systems as the extent of polymerization and the quality of the polymer product depend on the temperature level in the reactor. In this work, the system considered in the previous paper was reexamined by including the effect of temperature. The effects due to chain transfer to the monomer and diffusional control of the termination process were also included.

Thermodynamically, temperature defines the polymerization-depolymerization equilibrium; this equilibrium temperature is often called the ceiling temperature. Above this temperature, depolymerization is more favorable. Since the activation energy for depolymerization is very high, depolymerization becomes increasingly important at higher temperatures even though it is not significant at lower temperature. Again, as most polymerization reactions are exothermic in nature, high temperatures result in low equilibrium conversions. Temperature also affects the rate of polymerization; as all the rate constants (initiation, propagation, termination, and chain transfer) increase exponentially with temperature, the overall effect of temperature is to increase the rate of polymerization. The level of temperature also determines the amount of cooling water required or the surface area required for cooling. High temperatures increase the rate of polymerization and thus increase the rate at which of heat is liberated due to the exothermic reaction. Therefore, to maintain a constant temperature, the heat transfer rate must increase with temperature.

In the current investigation, it was assumed that temperature levels in the reactor were well below the critical ceiling temperature, and hence the depolymerization effect could be neglected. This effect can be included by considering the propagation as a reversible reaction. The increase in the values of the rate constants with temperature can be expressed as

$$k_a = A_a \exp(-E_a/RT) \quad (16)$$

$$k_p = A_p \exp(-E_p/RT) \quad (17)$$

$$k_{t0} = A_t \exp(-E_t/RT) \quad (18)$$

$$k_{tm} = A_{tm} \exp(-E_{tm}/RT) \quad (19)$$

in which E_a, A_a = activation energy and frequency factor for initiation, E_p, A_p = activation energy and frequency factor for propagation, E_t, A_t = activation energy and frequency factor for termination, and E_{tm}, A_{tm} = activation energy and frequency factor for chain transfer to the monomer.

It should be noted that the termination rate constant, k_{t0} , represents the value at zero conversion; for any other value of conversion, k_t can be deter-

mined by using one of the relations presented in the section on the Trommsdorff effect. It was assumed in this investigation that the heat of polymerization was independent of temperature. Under these conditions, the heat to be removed from the reactor can be expressed as

$$Q = (\Delta H)_p X \quad (20)$$

in which $(\Delta H)_p$ = heat of polymerization, kcal/gmole; X = conversion of monomer to polymer per hour, hr⁻¹; and Q = heat to be removed per hour, kcal/hr.

As the temperature increased, the consumption of monomer increased, and the amount of heat to be removed to maintain constant temperature increased. This heat can be removed by increasing the flow of the coolant fluid. The cost of this cooling was incorporated in the objective function by adding a term to the previous objective function (eq. (44), reference 1), the new objective function used was

$$J = W_1 M_4 + W_2 (\sigma_4 - \sigma_d)^2 + W_3 (\Delta_4 - \Delta_d)^2 + W_4 (q_{\text{CSTR}} + q_{\text{PLUG}}) \quad (21)$$

in which W_1 , W_2 , W_3 , and W_4 = weighting factors; σ_4 = standard deviation of the MWD; σ_d = desired value of the standard deviation; Δ_4 = mean of the exit MWD; Δ_d = desired mean; q_{CSTR} = coolant flow rate for CSTR, l./hr; and q_{PLUG} = coolant flow rate for plug flow reactor, l./hr. The weighting factors were chosen to make each of the four terms in the objective function dimensionless and approximately the same order of magnitude. The objective function J was an implicit function of temperature as the four process variables (M , Δ , σ^2 , and q), namely, the monomer concentration, mean, and variance of the MWD, and coolant flow rate were functions of the reactor temperature. As temperature increases, the rate of polymerization increases; this reduces the exit monomer concentration and the value of the objective function. An increase in temperature, however, generates additional heat in the polymerization reactor, which requires a higher coolant flow rate. This causes an increase in the objective function. The system considered here was the same as the one examined in the previous paper¹ (Fig. 5, reference 1). Two different examples were considered. In the first example, the effect of chain transfer to the monomer was neglected. Under these conditions, the kinetic and the material balance equations, eqs. (15) through (43) of the previous paper,¹ were used with eqs. (14), (16), (17), (18), (20), and (21) presented above to determine the system performance. The chain transfer to the monomer was included in the second example; and to account for this effect, modified kinetic equations, eqs. (1) through (8) and equations presented in Table I, were used. For both these examples, however, the gel effect was included in the polymerization model by considering the termination as a diffusional process.

COMPUTATIONAL ASPECTS

The methodology used in formulating the objective function was presented in the previous paper¹ and is not repeated here. In this study, the

objective function of eq. (21) was minimized with respect to the following decision variables: (1) α_{21} ; (2) α_{32} ; (3) η , fraction of the total reactor volume to be apportioned to the plug flow reactor; (4) T_{CSTR} , temperature in the CSTR; and (5) T_{PLUG} , temperature in the plug flow reactor.

Since the recycle from the plug flow reactor (fractions α_{23} and α_{33}) did not improve the isothermal performance of the system,¹ these flows were assumed to be zero in this analysis. The computational procedure again involved the use of the simplex pattern search technique for optimization and was similar to the one used in the previous paper. Since the number of decision variables increased from 3 to 5, the optimization involved a five-dimensional search. Once the temperatures in the reactors were chosen according to the search pattern, the rate constants in both the reactors could be determined from eqs. (16) through (19). It should be noted that the values of the rate constants could have different values in the reactors. Values of some of the constants used in this work are presented in Table IV. As the Trommsdorff effect was included in the model, it was necessary to calculate the termination rate constant at each iteration by using the appropriate equation from the section on the Trommsdorff effect above.

TABLE IV
Kinetic Constants Used in The Temperature Study

Symbol	Parameter description	Numerical value
A_i	preexponential factor	2.12×10^6
E_i	activation energy for initiation	15,000
A_p	preexponential factor	1.05×10^7
E_p	activation energy for propagation	4,100
A_{tm}	preexponential factor	2.30×10^6
E_{tm}	activation energy for chain transfer	6,200
A_t	preexponential factor	1.25×10^9
E_t	activation energy for termination	904

RESULTS AND DISCUSSION

No Chain Transfer

As the first reactor in the system was a CSTR, a uniform steady-state temperature was maintained in it; this was T_{CSTR} . However, in the plug flow reactor, a nonuniform temperature profile could be maintained. In industrial polymerizations, prepolymerization is carried out in a CSTR, and 30–35% polymer is fed to a relatively larger plug flow reactor (PFR) in which temperature is gradually increased in zones (see Figure 1).

Case I: One Zone in PFR. In this case, two temperatures (T_{CSTR} and T_{PLUG}) were used as decision variables along with two structural parameters (α_{21} and α_{32}) and the volume fraction (η). Simulation results were obtained

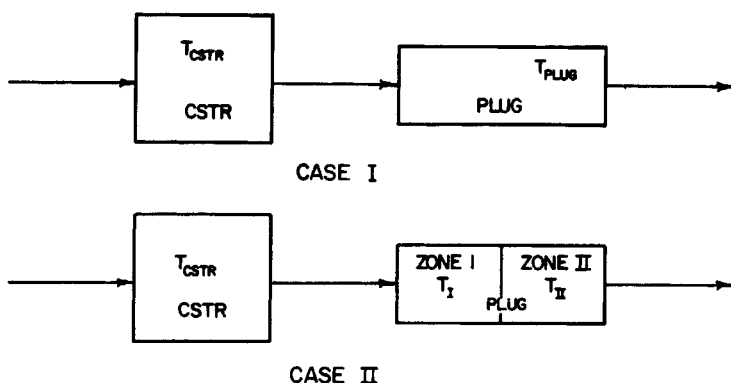


Fig. 1. Reactor conditions for determining the temperature effect.

to select an appropriate starting point for optimization and also to observe the system behavior. These results are summarized in Table V. As η was increased from 0.78 to 0.88, keeping the other decision variables constant, the variance of the MWD increased from 0.283×10^7 to 0.304×10^7 . In contrast, the exit monomer concentration decreased from 0.0063 to 0.0048 and the mean of MWD decreased from 1218.0 to 1130.0. When almost the entire volume (V_T) was allocated to the PFR (that is, $\eta = 0.96$), the system yielded a polymer with a low mean ($\Delta_4 = 986.0$) and a moderate variance ($\sigma_4^2 = 0.32 \times 10^7$). As α_{21} (simulations 1 and 2) was decreased, the fraction of the feed stream fed to the plug flow reactor increased. This resulted in an increase in the variance of the MWD from 0.312×10^7 to 0.328×10^7 . However, the exit monomer concentration decreased from 0.018 to 0.0083.

Increasing α_{32} increased the fraction of the exit stream from the CSTR to the PFR; this reduced the variance of the MWD from 0.319×10^7 to 0.283×10^7 . As both the reactors were assumed to be at constant but different temperatures, these temperatures determined the values of the rate constants and also the coolant flow rate required.

For optimizing this system, two different starting points corresponding to simulation runs 1 and 6 were used. The following constraints were imposed on the decision variables:

$$\left. \begin{aligned} 0 &\leq \alpha_{21} \leq 1.0 \\ 0 &\leq \alpha_{32} \leq 1.0 \\ 0 &\leq \eta \leq 1.0 \\ 290 &\leq T_{\text{CSTR}} \leq 500 \\ T_{\text{CSTR}} &\leq T_{\text{PLUG}} \leq 500 \end{aligned} \right\} \quad (22)$$

The last constraint on T_{PLUG} was necessary as it was not practical to cool the exit stream from the CSTR before feeding it to the PFR. Both the starting points yielded the same optimal point. The optimal results are shown in Table V. The volume of the CSTR required was very small because only 20% of the feed was processed in the CSTR. The performance index at the optimal point was recalculated with the termination rate con-

TABLE V
Results of Systems Synthesis—Case I

Run no.	Decision variables					Objective function
	α_{21}	α_{22}	η	T_{CSTR}	T_{PLUG}	
1	0.43	0.53	0.78	375.2	380.5	5.32
2	0.16	0.53	0.78	375.2	380.5	3.53
3	0.16	0.75	0.78	375.2	380.5	0.5068
4	0.16	0.85	0.78	375.2	380.5	0.4832
5	0.16	0.85	0.88	375.2	380.5	1.083
6	0.16	0.85	0.96	375.2	380.5	3.563
7	0.16	0.85	0.70	375.2	380.5	0.2935
Opt. point	0.20	0.84	0.66	381.5	390.3	0.2385

stant assumed independent of the chain length (k_t was taken equal to k_{t0} for all the values of the chain length). In other words, the Trommsdorff effect was neglected. Results of these computations are presented in Table IX and are compared with the other results reported in this table. It can be seen from these results that the inclusion of the gel effect increased considerably the conversion of the monomer, the mean of the MWD, and the variance of the MWD.

Case II: Two Zones in PFR. It is necessary, in practice, to sectionalize the PFR to facilitate efficient heat transfer. In this case, it was assumed that two zones were necessary in the PFR. The purpose was to show that two zones in the reactor yielded a better quality of polymer, improved the system performance, and lowered the objective function. For these calculations, the last constraint presented in eq. (22) was modified to

$$\begin{aligned} T_{\text{CSTR}} &\leq T_{\text{I}} \leq 500 \\ T_{\text{CSTR}} &\leq T_{\text{II}} \leq 500 \end{aligned} \quad (23)$$

According to these constraints zone II can have either a higher or lower temperature than zone I. The computational scheme was modified, as the PFR was divided into two sections each with a residence time of $\tau_{\text{PLUG}}/2.0$ and the material from the first section was fed to the second section. To simulate this, the integration of differential equations was stopped at $\tau_{\text{PLUG}}/2.0$ the rate constants were changed corresponding to the temperature level in zone II, and the integration was restarted. Results of these simulations and optimization are presented in Tables VI and IX. It can be seen that "zoning" the PFR improved the system performance considerably. The average molecular weight at the optimum increased from 1490 to 1496 if two zones were introduced. Variance dropped considerably and at the optimal point the variance was $.1834 \times 10^7$ for case II as compared to $.2134 \times 10^7$ for case I. Sectionalizing the PFR also improved the conversion and lowered the level of the temperature required in both the reactors. The volume of the CSTR was very small, and the plug flow reactor alone may be enough for efficient performance. The area required for heat transfer,

TABLE VI
Results of Systems Synthesis—Case II

Run no.	Decision variables					T_{PLUG}		Objective function
	α_{21}	α_{22}	η	T_{CSTR}	I	II		
1	0.43	0.53	0.78	375.2	380.5	385.5	4.86	
2	0.43	0.70	0.78	375.2	380.5	385.5	3.416	
3	0.43	0.80	0.78	375.2	380.5	385.5	2.165	
4	0.43	0.90	0.78	375.2	380.5	385.5	1.034	
5	0.30	0.90	0.78	375.2	380.5	385.5	0.5834	
6	0.20	0.90	0.78	375.2	380.5	385.5	0.3234	
Opt. point	0.22	0.90	0.64	370.5	375.0	378.0	0.1835	

the mixing effects, and the capital costs were not included in the objective function. Inclusion of these factors may yield an optimal structure different from the one obtained in this work.

Effect of Chain Transfer

To include the effect of chain transfer on the systems synthesis, the modified kinetic equations, eqs. (1) through (8) and equations in Table I, were used. Again, two different cases were examined.

Case III: One Zone in PFR. Simulation results for this case are presented in Table VII. The effect of chain transfer to the monomer on the optimal systems synthesis can be seen by comparing the results cases I and III in Tables V, VII, and IX. It is well known that transfer to monomer with subsequent polymerization of the double bond leads to the formation of branched molecules. Each transfer reaction adds a branch point to the molecule, and the branch grows causing an increase in the molecular weight. However, the probability of branching is approximately proportional to the weight-average molecular weight. Hence, branched molecules tend to become more highly branched and still larger. The net result is that the

TABLE VII
Results of Systems Synthesis—Case III

Run no.	Decision variables					Objective function
	α_{21}	α_{32}	η	T_{CSTR}	T_{PLUG}	
1	0.43	0.53	0.78	375.2	380.5	5.98
2	0.43	0.63	0.78	375.2	380.5	3.83
3	0.43	0.73	0.78	375.2	380.5	2.38
4	0.43	0.83	0.78	375.2	380.5	0.8363
5	0.30	0.83	0.78	375.2	380.5	0.5832
6	0.20	0.83	0.78	375.2	380.5	0.4176
7	0.20	0.83	0.60	375.2	380.5	0.4322
Opt. point	0.18	0.88	0.75	386.5	393.5	0.3086

molecular weight distribution is widened and it has space along high molecular weight tail. This effect can be seen by examining the mean and variance of the molecular weight distribution for cases I and III.

Case IV: Two Zones in PFR. Introducing the chain transfer effect and having two temperature zones in the PFR again improved the system performance over the case with only one zone in the PFR (case III). These results are presented in Table VIII. Results for this case indicated that at the optimum, the value of η required was smaller than case III and that a larger fraction of the feed was fed to the CSTR.

Results from all the four cases are compared in Table IX.

TABLE VIII
Results of Systems Synthesis—Case IV

Run no.	Decision variables				T_{PLUG}		Objective function
	α_{21}	α_{37}	η	T_{CSTR}	I	II	
1	0.43	0.53	0.78	375.2	380.5	385.5	5.63
2	0.43	0.75	0.78	375.2	380.5	385.5	3.27
3	0.43	0.95	0.78	375.2	380.5	385.5	8.63
4	0.30	0.85	0.78	375.2	380.5	385.5	0.6338
5	0.20	0.85	0.78	375.2	380.5	385.5	0.4336
6	0.20	0.85	0.75	375.2	380.5	385.5	0.4133
Opt. point	0.23	0.83	0.70	381.5	385.5	390.0	0.2903

TABLE IX
Comparison of Optimal Results for Five Different Cases

Case examined	Trommsdorff effect	Chain transfer	Objective function	Exit properties		
				M_w	$\Delta_w \times 10^4$	$\sigma_w^2 \times 10^7$
Case I	yes	no	0.2385	0.0023	1490.0	0.2134
Case II	yes	no	0.1835	0.0018	1496.0	0.1834
Case III	yes	yes	0.3086	0.0027	1510.4	0.2343
Case IV	yes	yes	0.2903	0.0027	1506.4	0.2035
Case V*	no	no	1.530	0.0034	1538.0	0.3108

* At optimal values of case I.

CONCLUDING REMARKS

The effects of chain transfer, autoacceleration (gel or Trommsdorff effect), and the temperature profile on the synthesis of a polymerization reaction system were considered. The results indicate that the autoacceleration effect improves the conversion of the monomer but is detrimental to the molecular weight distribution of the polymer. In other words, the variance of the MWD increases, causing a wider spread of polymer molecules.

In the current investigation, the semiempirical model developed by Benson and North¹⁸ was used to model the autoacceleration in the polymerization reactor system. It is worth noting that the diffusional control of the polymerization process can also be modeled by expressing k_t/k_p^2 in terms of conversion of the monomer. A semiempirical correlation along these lines was proposed by Hui and Hamielec,¹⁷ who employed the following empirical relationship:

$$\frac{k_t}{k_p^2} = \left(\frac{k_t}{k_p^2} \right)_0 \exp [C_1 X_M + C_2 X_M^2 + C_3 X_M^3] \quad (25)$$

where X_M = conversion of the monomer; and C_1, C_2, C_3 = arbitrary constants to be determined from experimental data.

In investigating the effect of temperature or, more specifically, the temperature profile it was shown that sectionalizing the plug flow reactor improves the system performance and facilitates efficient heat transfer. Only two sections were assumed in the current investigation; an optimum number of sections can be obtained by carrying out a one-dimensional search on the number of sections or by including the number of sections in the list of decision variables. As the optimum temperature obtained for zone II was at least equal to or greater than the optimum temperature for zone I, it can be concluded that similar results could be obtained by modifying the constraints of eq. (23) to

$$\begin{aligned} T_{\text{CSTR}} &\leq T_1 \leq 500 \\ T_1 &\leq T_{\text{II}} \leq 500 \end{aligned} \quad (24)$$

Nomenclature

C_i	mixer i
D_i	distributor i
E_d	activation energy for decomposition of the initiator
E_p	activation energy for propagation
E_t	activation energy for termination
F_i	flow rate into the out of the mixer i , l./hr
I	initiator concentration, g/l.
J	objective function to be minimized
M	monomer concentration, g/l.
P_i'	concentration of active radical of chain length i , g/l.
P_i^*	concentration of the dead polymer of chain length i , g/l.
Q	quantity of heat to be removed, kcal/hr
T_{CSTR}	temperature in the CSTR, °K
T_{PLUG}	temperature in the PFR, °K
T_I	temperature in zone I of the PFR
T_{II}	temperature in zone II of the plug flow reactor
W_i	weighting factor
X	conversion per hour, hr ⁻¹

k_d	rate constant for the decomposition of the initiator, sec^{-1}
k_p	rate constant for propagation, liter/gm mole sec.
k_{t0}	rate constant for termination at zero conversion, l./g mole sec
k_i	rate constant for initiation
k_{tm}	rate constant for chain transfer to the monomer, l./g mole sec
k_t	rate constant for termination
q_{CSTR}	coolant flow rate for the CSTR, l./hr
q_{PLUG}	coolant flow rate for the PFR, l./hr
α_{ij}	fraction of the flow from the distributor j that is fed to the mixer i
Δ_A	actual exit mean of the MWD
Δ_d	desired exit mean of the MWD
$\mu^{(i)}$	i th moment of the dead polymer distribution
$\lambda^{(i)}$	i th moment of the active polymer distribution
η	fraction of the total volume to be apportioned to the plug flow reactor, dimensionless
σ_A	actual value of the standard deviation at the exit
σ_d	desired value of the standard deviation at the exit
ν	kinetic chain length
κ	viscosity of the reactor contents
η_0'	average microviscosity at zero conversion
η'	average microviscosity presented to the polymer chain end throughout the diffusion process

References

1. J. S. Shastry, L. T. Fan and L. E. Erickson, *Appl. Polym. Sci.*, **17**, 3101 (1973).
2. P. J. Flory, *J. Amer. Chem. Soc.*, **59**, 241 (1937).
3. S. Katz and G. M. Saidel, *A.I.Ch.E. J.*, **13**, 319 (1967).
4. R. G. W. Norrish and R. R. Smith, *Nature*, **150**, 566 (1942).
5. E. Trommsdorff, H. Kohle and P. Lagally, *Makromol. Chem.*, **1**, 169 (1947).
6. G. K. Oster, G. Oster, and G. Prati, *J. Amer. Chem. Soc.*, **79**, 595 (1957).
7. J. N. Atherton and A. M. North, *Trans. Faraday Soc.*, **58**, 2049 (1962).
8. A. M. North and D. Postlethwaite, *Polymer*, **5**, 237 (1964).
9. G. M. Burnett and G. L. Duncan, *Makromol. Chem.*, **51**, 154 (1962).
10. A. M. North, in *Progress in High Polymers*, Vol. 2, J. C. Robb and F. W. Peaker, Eds., CRC Press, Cleveland, Ohio (1968).
11. A. M. North and G. A. Reed, *Trans. Faraday Soc.*, **57**, 859 (1961).
12. J. H. Duerksen and A. E. Hamielec, *J. Polym. Sci. C*, 155 (1968).
13. K. F. O'Driscoll and P. J. White, *J. Polym. Sci.*, **B1**, 597 (1963).
14. K. F. O'Driscoll and P. J. White, *J. Polym. Sci.*, **A3**, 283 (1965).
15. A. E. Hamielec, Gel Effect in Vinyl Polymerization, presented at the Polymer Reactor Engineering Symposium, Quebec City, Quebec, Canada, 1972.
16. A. Abdel-Alim and A. E. Hamielec, *J. Appl. Polym. Sci.*, **16**, 789 (1972).
17. A. W. T. Hui and A. E. Hamielec, *J. Appl. Polym. Sci.*, **16**, 749 (1972).
18. S. W. Benson and A. M. North, *J. Amer. Chem. Soc.*, **84**, 935 (1962).

Received November 22, 1972

Revised March 6, 1973