

Determination of Optimal Reactor System Configuration for Polymerization Reactions. I. Free-Radical Polymerization at Constant Temperature

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Synopsis

A systematic procedure was developed for selecting the type of reactors or a reactor system configuration for polymerization reactions. Two different mechanisms were investigated, and the "best" reactor system to give the desired quality of the product was determined using a systems synthesis technique. The behavior of the system in the neighborhood of the optimal solution was explored, and the effect of variation in the rate constants and the initial concentrations of the catalyst and the monomer on the optimal reactor system was examined. Recycle streams were introduced and their effect on the system performance was investigated, and finally the applicability of the systems synthesis technique to other polymer reactor design problems was discussed.

INTRODUCTION

Many continuous processes for bulk-polymerizing styrene have been developed in recent years. One of the first continuous processes for mass or bulk polymerization of styrene was developed by the German plastic industry¹ and is schematically represented in Figure 1. In this process the styrene monomer is continuously fed into a tank-type reactor (prepolymerizer) and prepolymerized to the extent of about 30-35% conversion. From the prepolymerizer the intermediate product is fed continuously to a tower polymerizer in which the temperature is gradually increased from the entrance to the exit to reach a conversion level in the range of 95-100%. The final product is extruded, cooled, and ground. This work explores this process, its advantages, and the optimality of the reactor configuration.

While continuous processes have also been developed for solution, emulsion, and suspension polymerization of styrene, mass or bulk polymerization of pure styrene appears to be the simplest process yielding the product with the minimum contamination. However, due to the highly exothermic nature of the radical chain polymerization of styrene, its high activation energy and the tendency to form gel make the heat dissipation a very difficult problem. This, coupled with the increase in viscosity, renders bulk polymerization a cumbersome process to control and may in extreme cases

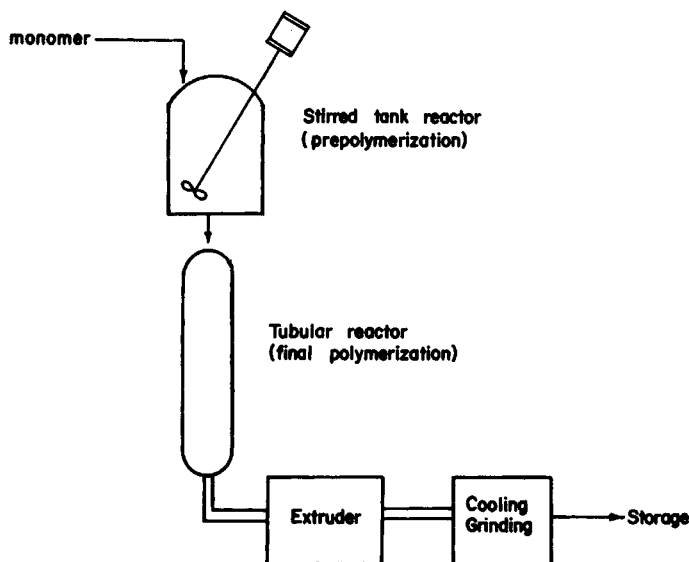


Fig. 1. The German tower process for the polymerization of styrene.

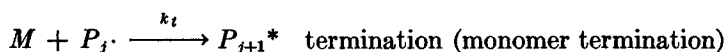
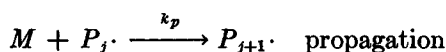
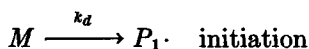
lead to "runaway reactions" or degradation and discoloration of the polymer. The possibility also exists that the molecular weight distribution may be affected owing to chain transfer to the polymer in an uncontrolled bulk polymerization.

Recent advances in control theory, computer applications, chemical instrumentation, and basic understanding of polymer processes have made it possible to develop sophisticated control loops for mass or bulk polymerizations and most of the problems encountered in this type of polymerization can now be handled. It has been reported² that the bulk polymerization processes may stage a "drastic comeback" in the near future. It is possible to reach almost 98–100% conversion in bulk polymerization, and this reduces or eliminates the necessity for purification and extraction.

Interestingly, all the continuous processes developed so far for bulk or solution polymerization are of the stagewise configurations to circumvent the heat dissipation problem. Generally, the preliminary stage is a tank-type reactor (CSTR) which is well stirred, and the final stage is a tubular or tower-type reactor (plug flow reactor). It appears that conventionally the types of reactors and the mode of their interconnection have been arbitrarily or empirically determined. This is not always desirable. The types of polymerization reactors and the reactor system configuration or arrangement can significantly influence the conversion and exit molecular weight distribution of the product polymer. Hence, a definite need exists for a systematic procedure for selecting the types of reactors and the reactor system configuration which optimizes the desired conversion and the desired quality of product. A nonlinear process system synthesis technique which can be used to optimize not only the system performance but also the sys-

tem configuration or structure is presented in this paper. This technique is briefly described below under "Systems Synthesis Technique."

It has been well established that the plug flow or batch reactor yields higher conversion than the tank-type reactor for many polymerization mechanisms. This implies that, from the standpoint of maximizing conversion alone, a plug flow (or batch) reactor is the best. One of the frequently used mechanisms of polymerization can be written as follows (Mechanism I):



Calculation of conversion, molecular weight distributions, and the corresponding moments for batch and continuous polymerizations obeying the above mentioned mechanism has been shown to be straightforward.^{3,4} Liu and Amundson³ have demonstrated that for this mechanism a plug flow (or batch) reactor yields higher conversion than a CSTR of identical volume. Molecular weight distributions (MWD) of the product polymers from these two reactors can be easily calculated, and the MWD of the polymer from the plug flow reactor can be shown to be always narrower than the MWD from the CSTR of identical volume (Fig. 2). If it is desired to produce a polymer with the narrowest MWD possible and at the same time increase the monomer conversion, the plug flow reactor would be the logical choice for Mechanism I (in this work the variance of the MWD is used as a measure of the "spread" of the MWD).

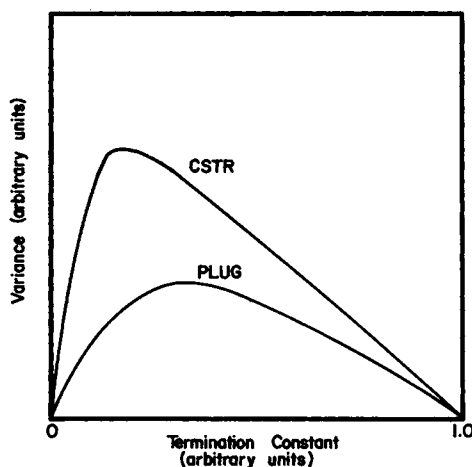
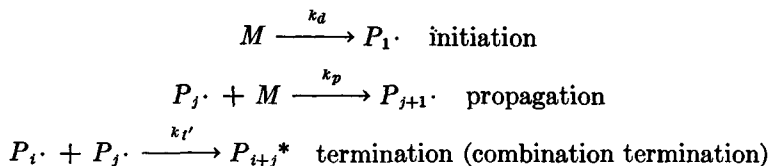


Fig. 2. Variances of MWD in CSTR and Plug flow reactors for mechanism I.

If the termination mechanism is changed (from monomer termination to combination termination),



to obtain a different polymerization sequence (Mechanism II), the choice of the reactor becomes more difficult to make.⁵ The plug flow reactor, again, yields a higher conversion than the stirred tank reactor; but a narrower MWD and hence a lower variance is obtained in the CSTR.⁵ This gives rise to the problem of optimally selecting and determining the types of reactors and their arrangement because the plug flow reactor yields a higher conversion than the CSTR, but the CSTR produces a polymer with narrower MWD.

As many physical properties of a polymer are directly related to its MWD, it is necessary that any process developed for polymerization must yield a product with a MWD as close to the specification as possible. But one cannot ignore conversion of the monomer because the higher the conversion, the lower the cost of purification and extraction and the higher the productivity of the reactor. This leads to the reactor and configuration selection problem without even introducing the temperature.

The problem investigated in this research is concerned with optimal design and selection of the reactor system to produce the desired quality of the polymer. It was assumed that the desired polymer product should have a MWD with a fixed mean, the variance of the MWD should be as small as possible, and monomer conversion should be as large as possible. These three variables are simultaneously optimized in this study.

It was assumed that all reactors in the system were maintained at one constant temperature. Since introduction of the temperature as a decision variable increases considerably the difficulty of the problem, this will be considered in a later publication. It should be noted that in this study, the chain transfer to the monomer and the gel effect which results from the diffusion control of termination reaction are not included in the model. These effects are, however, considered in a later publication (part II of this work). Under these assumptions, an objective function was formulated, minimization of which led to improvement in the product quality and in the reactor system productivity (as measured by conversion). The techniques used for formulating the objective function and for affecting the minimization are discussed next.

THE SYSTEM SYNTHESIS TECHNIQUE

A system is composed of a set of elements (subsystems) which are designed and connected to perform the necessary tasks imposed on the system.

The way in which the subsystems are connected to form the system is called the system structure. In system synthesis, one determines the optimal system structure and the subsystem performance simultaneously from a large number of possible system structures and subsystem performances. Thus, optimization is an essential part of systems synthesis.⁷⁻¹¹

Rudd and his co-workers^{8,9} have developed several methods for systems synthesis by utilizing an approximate objective function in the function space of dynamic programming, a heuristic approach and the branch and bound method. These approaches involved solution of mathematical problems written in the form of a combinatorial problem which requires one to find the best combination among all the possible combinations of subsystems to determine the systems structure. Ichikawa and his co-workers^{7,11,12} avoided these difficulties by formulating the system synthesis problem in the Euclidian space and utilizing one of the conventional optimization methods. This method, which is a structural parameter approach was used in this investigation.

One can write an input-output relation for the i th subsystem as follows (Fig. 3a):

$$y_i = \phi_i(x_i, d_i) \quad i = 1, 2, \dots, N \quad (1)$$

in which x_i = input vector = $[x_{i1}, x_{i2}, \dots, x_{is}]$, y_i = output vector = $[y_{i1}, y_{i2}, \dots, y_{it}]$, and d_i = decision vector in the design of the i th subsystem. For a so-called homogeneous system, all the subsystem performance equations, ϕ_i , $i = 1, 2, \dots, N$ in eq. (1), are identical. On the other hand, for heterogeneous systems, at least one of the equations is different from the

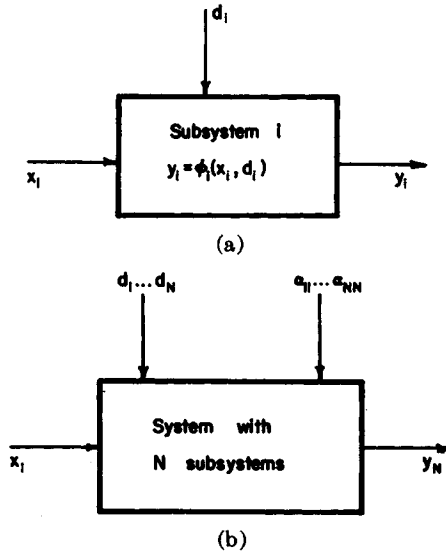


Fig. 3(a). Schematic representation of the subsystem i . (b) Schematic representation of the system with N subsystems.

rest. Several constraints can be imposed on these subsystems; these can be expressed as

$$g_k(x_i, y_i, d_i) \leq 0 \quad i = 1, 2, \dots, N$$

$$k = 1, 2, \dots, K$$
(2)

These constraints usually imply physical limitations on the system or on the variables. Nonnegativeness of the monomer concentrations and an upper bound for the temperature are some examples of such constraints. In the approach suggested by Ichikawa and his co-workers,^{7,10,11} the process system with N subsystems is considered to have an input vector x_1 and an output vector y_N with structural parameters α_{ij} 's representing the fraction of the output of the j th subsystem, y_j , fed to the subsystem i (Fig. 3b). For a system with N subsystems, the relationships between x_i , y_i , and α can be expressed in terms of a system matrix:

	y_1	$y_2 \dots y_j \dots y_N$	
x_1	0	0 ... 0 ... 0	
x_2	α_{21}	$\alpha_{22} \dots \alpha_{2j} \dots 0$	
.	.	.	.
.	.	.	.
x_i	α_{i1}	$\alpha_{i2} \dots \alpha_{ij} \dots 0$	
.	.	.	.
.	.	.	.
x_N	α_{N1}	$\alpha_{N2} \dots \alpha_{Nj} \dots 0$	

(3)

It can be seen from eq. (3) and Figure 4 that these parameters do characterize the structure of the system and that the α -matrix serves as the necessary and sufficient condition to determine the system structure. The input

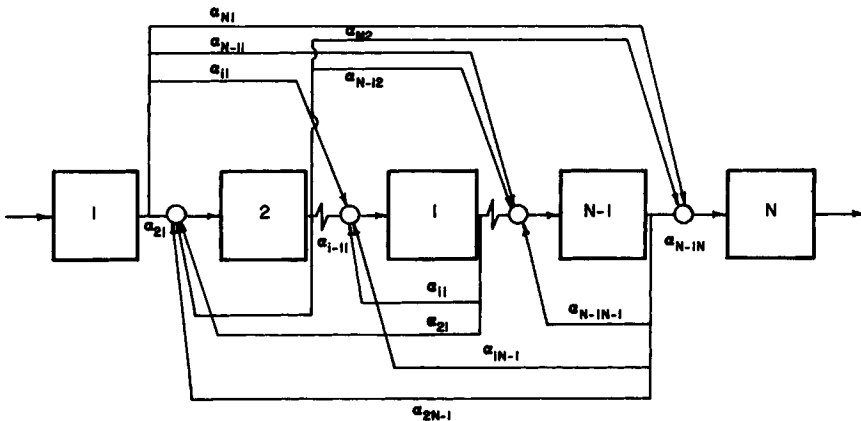


Fig. 4. Schematic diagram of a system with N subsystems showing the α parameters.

stream to the i th subsystem can now be expressed by using eq. (3) in the form

$$x_i = \sum_j \alpha_{ij} y_j \quad i = 1, 2, \dots, N \quad (4)$$

As α_{ij} 's are parameters related to the stream x_i (Fig. 4), the following relations must be valid for α 's:

$$\sum_i \alpha_{ij} = 1.0 \quad j = 1, 2, \dots, N \quad (5)$$

and

$$0 \leq \alpha_{ij} \leq 1 \quad i, j = 1, 2, \dots, N \quad (6)$$

The desired outcome of the process is now written in terms of an objective function which is

$$J = f(x_i, y_i, d_i, \alpha) \quad i = 1, 2, \dots, N \quad (7)$$

The overall system synthesis problem for minimization of J , therefore, consists of minimizing eq. (7) subject to constraints of eqs. (1), (2), (4), (5), and (6). Thus, by using the α -matrix, the combinatorial problem in function space can be transformed into the ordinary Euclidian space optimization problem. It may be possible to preassign or fix some of the α -parameters based on the designer's experience to reduce the dimensionality of the problem.

MATHEMATICAL MODEL FOR POLYMERIZATION REACTOR SYSTEM

The system which was considered is shown schematically in Figure 5. The two reactors in this figure are a CSTR and a PFR. Depending on the α_{ij} values, the system covers all possible ways in which a CSTR and a PFR can be connected (Fig. 5). The total volume of the system (V_T) was as-

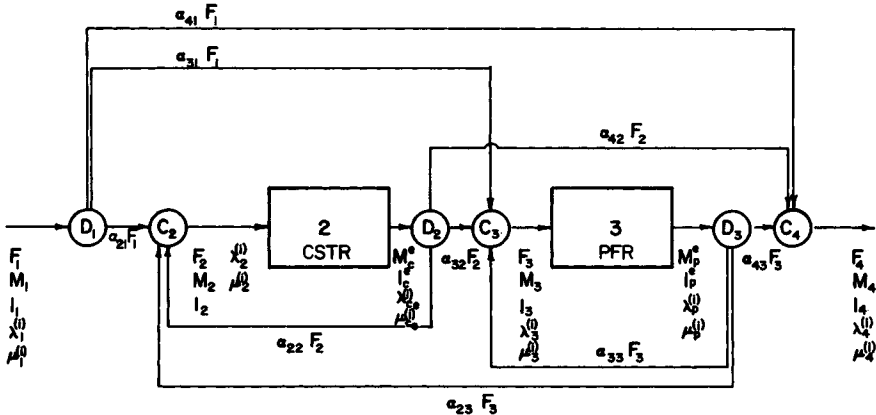
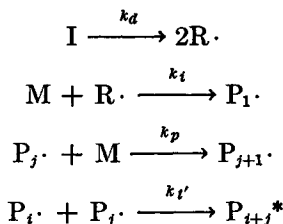


Fig. 5. Process variables at various points in the system ($i = 0, 1, 2$).

sumed to be known, and the fraction of this volume to be apportioned to each reactor was determined by process systems synthesis.

Kinetic Model

The first step in modeling continuous polymerization reactors is to understand the mechanism of polymerization and to derive the corresponding batch kinetic expressions. In the current investigation, the following batch kinetic model developed by Katz and Sidel¹² was used:



This mechanism is very similar to the one presented earlier (Mechanism II), the only apparent difference being the initiation step. The one-step initiation step is replaced by a two-step sequence to include the concentration of the initiator in the model. The batch kinetic expressions for this model are¹² (in deriving this model it was assumed that monomer consumed by initiation step is negligible compared to the monomer consumed by propagation reaction)

$$\frac{dI}{dt} = -k_a I \quad I(0) = I_0 \quad (8)$$

$$\frac{d\lambda^{(0)}}{dt} = 2k_a I - k_t' [\lambda^{(0)}]^2 \quad \lambda^{(0)}(0) = 0 \quad (9)$$

$$\frac{dM}{dt} = -k_p M \lambda^{(0)} \quad M(0) = M_0 \quad (10)$$

$$\frac{d\lambda^{(k)}}{dt} = k k_p M \lambda^{(k-1)} - k_t' \lambda^{(0)} \lambda^{(k)} \quad \lambda^{(k)}(0) = 0 \quad k = 1, 2, \dots \quad (11)$$

$$\frac{d\mu^{(k)}}{dt} = \frac{k_t'}{2} \sum_{j=0}^k \binom{k}{j} \lambda^{(j)} \lambda^{(k-j)} \quad \mu^{(k)}(0) = 0 \quad k = 0, 1, 2, \dots \quad (12)$$

In these equations, I = concentration of the initiator, k_a = initiation rate constant, M = concentration of the monomer, k_p = propagation rate constant, k_t' = termination rate constant, $\lambda^{(k)}$ = k th moment for the active polymer distribution, and $\mu^{(k)}$ = k th moment for the dead polymer distribution. The moments are defined as

$$\lambda^{(k)}(t) = \int_0^\infty j^k P \cdot(j, t) dj \quad (13)$$

and

$$\mu^{(k)}(t) = \int_0^{\infty} j^k P^*(j,t) dj \quad (14)$$

where j is the chain length, and $P(j,t)$ and $P^*(j,t)$ are the size distributions of the active polymer and the dead polymer, respectively. In this paper, the generic name MWD is used to refer to these size distributions, although these size distributions have sometimes been called chain length distributions.

Material Balances

In Figure 5, D_1 , D_2 , and D_3 represent the distributors; C_2 , C_3 , and C_4 represent the mixers; and R_2 and R_3 represent the reactors. Nine different process variables were considered in formulating the objective function; these were I , $\lambda^{(0)}$, M , $\lambda^{(1)}$, $\lambda^{(2)}$, $\mu^{(0)}$, $\mu^{(1)}$, $\mu^{(2)}$, and flow rate F . Values of these process variables at various points in the system are shown in Figure 5.

Material balance equations can be written at each mixing point (mixers). These are

At mixer C_2 :

$$F_2 = \alpha_{21}F_1 + \alpha_{22}F_2 + \alpha_{23}F_3 \quad (15)$$

$$F_2I_2 = \alpha_{21}F_1I_1 + \alpha_{22}F_2I_c^e + \alpha_{23}F_3I_p^e \quad (16)$$

$$F_2M_2 = \alpha_{21}F_1M_1 + \alpha_{22}F_2M_c^e + \alpha_{23}F_3M_p^e \quad (17)$$

$$F_2\lambda_2^{(k)} = \alpha_{21}F_1\lambda_1^{(k)} + \alpha_{22}F_2\lambda_{ce}^{(k)} + \alpha_{23}F_3\lambda_{pe}^{(k)} \quad k = 0, 1, 2 \quad (18)$$

$$F_2\mu_2^{(k)} = \alpha_{21}F_1\mu_1^{(k)} + \alpha_{22}F_2\mu_{ce}^{(k)} + \alpha_{23}F_3\mu_{pe}^{(k)} \quad k = 0, 1, 2 \quad (19)$$

At mixer C_3 :

$$F_3 = \alpha_{31}F_1 + \alpha_{32}F_2 + \alpha_{33}F_3 \quad (20)$$

$$F_3I_3 = \alpha_{31}F_1I_1 + \alpha_{32}F_2I_c^e + \alpha_{33}F_3I_p^e \quad (21)$$

$$F_3M_3 = \alpha_{31}F_1M_1 + \alpha_{32}F_2M_c^e + \alpha_{33}F_3M_p^e \quad (22)$$

$$F_3\lambda_3^{(k)} = \alpha_{31}F_1\lambda_1^{(k)} + \alpha_{32}F_2\lambda_{ce}^{(k)} + \alpha_{33}F_3\lambda_{pe}^{(k)} \quad k = 0, 1, 2 \quad (23)$$

$$F_3\mu_3^{(k)} = \alpha_{31}F_1\mu_1^{(k)} + \alpha_{32}F_2\mu_{ce}^{(k)} + \alpha_{33}F_3\mu_{pe}^{(k)} \quad k = 0, 1, 2 \quad (24)$$

At mixer C_4 :

$$F_4 = \alpha_{41}F_1 + \alpha_{42}F_2 + \alpha_{43}F_3 \quad (25)$$

$$F_4I_4 = \alpha_{41}F_1I_1 + \alpha_{42}F_2I_c^e + \alpha_{43}F_3I_p^e \quad (26)$$

$$F_4M_4 = \alpha_{41}F_1M_1 + \alpha_{42}F_2M_c^e + \alpha_{43}F_3M_p^e \quad (27)$$

$$F_4\lambda_4^{(k)} = \alpha_{41}F_1\lambda_1^{(k)} + \alpha_{42}F_2\lambda_{ce}^{(k)} + \alpha_{43}F_3\lambda_{pe}^{(k)} \quad k = 0, 1, 2 \quad (28)$$

$$F_4\mu_4^{(k)} = \alpha_{41}F_1\mu_1^{(k)} + \alpha_{42}F_2\mu_{ce}^{(k)} + \alpha_{43}F_3\mu_{pe}^{(k)} \quad k = 0, 1, 2 \quad (29)$$

in which I_p^e , M_p^e , $\lambda_{pe}^{(k)}$, and $\mu_{pe}^{(k)}$ = process variables at the exit of the plug flow reactor, and I_c^e , M_c^e , $\lambda_{ce}^{(k)}$, and $\mu_{ce}^{(k)}$ = process variables at the exit of the stirred tank reactor. Moments from two different populations can be added as was done in these material balance equations if the populations have identical distributions.¹³

To determine the fraction of the total volume to be allocated to the plug flow reactor (PFR), decision variable η was defined as follows:

$$\eta = \frac{V_{\text{PLUG}}}{V_T} \quad (30)$$

and therefore

$$1 - \eta = \frac{V_{\text{CSTR}}}{V_T} \quad (31)$$

The performance of each polymerization reactor depends on the mean residence time of the process fluid in the reactor; the residence time in the CSTR is

$$\tau_{\text{CSTR}} = \frac{V_{\text{CSTR}}}{F_2} \quad (32)$$

and in the plug flow reactor is

$$\tau_{\text{PLUG}} = \frac{V_{\text{PLUG}}}{F_3} \quad (33)$$

Subsystems Performance

The performance equations for the subsystems R_2 and R_3 can be easily written by taking a material balance for each of the process variables. Since the system was assumed to be under a steady-state condition, the flow rate remained constant in the system, and no accumulation took place in the subsystems and the system. The other process variables, however, changed only as functions of the position in the system because polymerization occurred in the reactors. Balances for I , M , $\lambda^{(0)}$, $\lambda^{(1)}$, $\lambda^{(2)}$, $\mu^{(0)}$, $\mu^{(1)}$, and $\mu^{(2)}$ around the CSTR are

$$F_2 I_2 - F_2 I_c^e - k_d I_c^e V_{\text{CSTR}} = 0 \quad (34)$$

or

$$I_c^e = \frac{I_2}{1 + k_d \tau_{\text{CSTR}}}$$

$$F_2 M_2 - F_2 M_c^e - V_{\text{CSTR}} k_p M_c^e \lambda_{ce}^{(0)} = 0 \quad (35)$$

or

$$M_c^e = \frac{M_2}{1 + k_p \lambda_{ce}^{(0)} \tau_{\text{CSTR}}}$$

$$F_2 \lambda_2^{(0)} - F_2 \lambda_{ce}^{(0)} + 2V_{\text{CSTR}} k_d I_c^e - V_{\text{CSTR}} k_t' [\lambda_{ce}^{(0)}]^2 = 0 \quad (36)$$

OR

$$\lambda_{ce}^{(0)} = \frac{-1 + \sqrt{1 + 4\tau_{\text{CSTR}}k_i'(\lambda_2^{(0)} + 2\tau_{\text{CSTR}}k_d I_c^e)}}{2\tau_{\text{CSTR}}k_i'}$$

$$F_2\lambda_2^{(1)} - F_2\lambda_{ce}^{(1)} + V_{\text{CSTR}}[k_p M_c^e \lambda_{ce}^{(0)} - k_i' \lambda_{ce}^{(0)} \lambda_{ce}^{(1)}] = 0 \quad (37)$$

OR

$$\lambda_{ce}^{(1)} = \frac{\lambda_2^{(1)} + k_p M_c^e \lambda_{ce}^{(0)} \tau_{\text{CSTR}}}{1 + k_i' \lambda_{ce}^{(0)} \tau_{\text{CSTR}}}$$

$$F_2\lambda_2^{(2)} - F_2\lambda_{ce}^{(2)} + V_{\text{CSTR}}[2k_p M_c^e \lambda_{ce}^{(1)} - k_i' \lambda_{ce}^{(0)} \lambda_{ce}^{(2)}] = 0 \quad (38)$$

OR

$$\lambda_{ce}^{(2)} = \frac{\lambda_2^{(2)} + 2k_p M_c^e \lambda_{ce}^{(1)} \tau_{\text{CSTR}}}{1 + k_i' \lambda_{ce}^{(0)} \tau_{\text{CSTR}}}$$

$$\mu_2^{(0)} F_2 - F_2 \mu_{ce}^{(0)} + \frac{V_{\text{CSTR}} k_i' (\lambda_{ce}^{(0)})^2}{2} = 0 \quad (39)$$

OR

$$\mu_{ce}^{(0)} = \mu_2^{(0)} + \frac{\tau_{\text{CSTR}} k_i' (\lambda_{ce}^{(0)})^2}{2}$$

$$\mu_2^{(1)} F_2 - F_2 \mu_{ce}^{(1)} + V_{\text{CSTR}} k_i' \lambda_{ce}^{(0)} \lambda_{ce}^{(1)} = 0 \quad (40)$$

OR

$$\mu_{ce}^{(1)} = \mu_2^{(1)} + \tau_{\text{CSTR}} k_i' \lambda_{ce}^{(0)} \lambda_{ce}^{(1)}$$

$$\mu_2^{(2)} F_2 - F_2 \mu_{ce}^{(2)} + V_{\text{CSTR}} k_i' [\lambda_{ce}^{(0)} \lambda_{ce}^{(2)} + \lambda_{ce}^{(1)} \lambda_{ce}^{(1)}] = 0 \quad (41)$$

OR

$$\mu_{ce}^{(2)} = \mu_2^{(2)} + \tau_{\text{CSTR}} k_i' [\lambda_{ce}^{(0)} \lambda_{ce}^{(2)} + \lambda_{ce}^{(1)} \lambda_{ce}^{(1)}].$$

Exit concentrations from the plug flow reactor could be calculated by integrating the differential eqs. (8) through (12) with the initial conditions given by eq. (42):

$$\begin{aligned} I(0) &= I_3 \\ \lambda^{(0)}(0) &= \lambda_3^{(0)} \\ M(0) &= M_3 \\ \lambda^{(1)}(0) &= \lambda_3^{(1)} \\ \lambda^{(2)}(0) &= \lambda_3^{(2)} \\ \mu^{(0)}(0) &= \mu_3^{(0)} \\ \mu^{(1)}(0) &= \mu_3^{(1)} \\ \mu^{(2)}(0) &= \mu_3^{(2)}. \end{aligned} \quad (42)$$

Equation (8) can also be solved analytically with the initial condition given in eq. (42) to yield the exit concentration of the initiator. The solution is

$$I_p^e = I_3 e^{-k_{dr} \tau_{\text{PLUG}}} \quad (43)$$

It is clear that eqs. (15) through (42) completely describe the system under investigation. The system consists of seven decision variables (η , α_{21} , α_{32} , α_{31} , α_{33} , α_{23} , and α_{22}) and nine state variables (F ; M ; I ; $\lambda^{(i)}$, $i = 0, 1, 2$; and $\mu^{(i)}$, $i = 0, 1, 2$).

Weighting Factors

It is apparent from the section on "Systems Synthesis Technique" that the appropriate objective function for optimization of the system to be synthesized was of the form

$$J = (W_1)M_4 + (W_2)(\sigma_4 - \sigma_d)^2 + (W_3)(\Delta_4 - \Delta_d)^2 \quad (44)$$

in which M_4 = exit monomer concentration, σ_4 = standard deviation of the exit MWD, Δ_4 = mean of the exit MWD, σ_d = desired standard deviation of the exit MWD, Δ_d = desired mean of the exit MWD, and W_1 , W_2 , and W_3 = weighting factors. Minimization of this objective function could force the mean of the MWD to approach Δ_d , the variance to σ_d , and maximize the conversion (by minimizing the exit monomer concentration). It should be noted here that nominal values of the weighting factors (W_1 , W_2 , and W_3) not only could make each of the three terms in the objective function approximately the same order of magnitude but also could unify the dimensions of these terms. By changing the weighting factors appropriately about their nominal values, it was possible to make any of the three terms that make up the objective function dominate the other two terms. For example, if W_1 was increased to about 100 times the nominal value, the conversion of the monomer dominates the other two terms and the optimal design obtained favored higher conversion from the system.

Once the moments of active and dead polymer radicals are determined the mean and variance of the MWD can be calculated from the following equations:

$$\Delta = \frac{\lambda^{(1)} + \mu^{(1)}}{\lambda^{(0)} + \mu^{(0)}} \quad (45)$$

$$\sigma^2 = \frac{\lambda^{(2)} + \mu^{(2)}}{\lambda^{(0)} + \mu^{(0)}} - \Delta^2. \quad (46)$$

COMPUTATIONAL

In essence the original systems synthesis problem was recast into a non-linear optimization problem by employing the structural parameter method, in which values of η and α_{12} were to be found to minimize J . In carrying out this optimization, certain simplifications could be made in the structure based on past experience. The fraction of the feed bypassing both the

reactors, α_{41} , was assumed to be zero. Recycling over a well-stirred tank reactor does not increase its productivity, and, therefore, α_{22} was set equal to zero. The optimization problem was made very complex because of recycles (α_{23} and α_{33}) from the plug flow reactor. It would involve a two-level search: (i) to determine the values of process variables to satisfy the material balance equations, and (ii) to determine the values of the decision variables η , α_{21} , and α_{32} to "optimize" the system. This two-level search would consume a lot of computational time. Because of these reasons, recycles from the plug flow reactor were assumed to be zero. In summary, the following structural parameters vanished:

$$\begin{aligned}\alpha_{41} &= 0.0 \\ \alpha_{22} &= 0.0 \\ \alpha_{23} &= 0.0 \\ \alpha_{33} &= 0.0\end{aligned}\tag{47}$$

and the system simplified to the one shown in Figure 6. The following computational scheme was used for this problem:

(i) Select appropriate values for the rate constants k_d , k_p , and k_i' and total volume V_{total} ; also select the process variables in feed, M_1 , $\lambda_1^{(0)}$, $\lambda_1^{(1)}$, $\lambda_1^{(2)}$, $\mu_1^{(0)}$, $\mu_1^{(1)}$, $\mu_1^{(2)}$, I_1 , and the feed flow rate F_1 .

(ii) Choose initial estimates of η , α_{21} , α_{32} (only three decision variables are left after simplification).

(iii) Solve eqs. (15), (20), and (25) and determine F_2 , F_3 , and F_4 . Check if F_4 is equal to F_1 .

(iv) Solve eqs. (16), (21), (26), (34), and (43) to find values for I_2 , I_3 , I_c^e , and I_p^e .

(v) Solve eqs. (8)–(12), (17), (18), (19), (22)–(24), (27)–(29), and (30)–(42) simultaneously to determine the remaining process variables.

(vi) Determine the objective function J_2 by choosing appropriate weights.

(vii) Check if the objective function has reached the minimum. If not, use the simplex pattern search to improve the estimates of η , α_{21} , and α_{32} (for description of this direct search technique, the readers are referred to the existing literature^{14,15}), return to step (iii), and repeat the calculations.

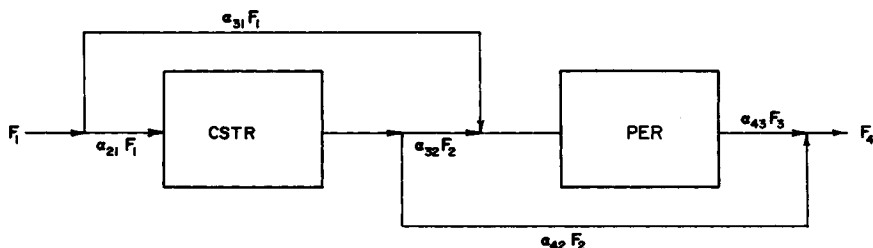


Fig. 6. Simplified system diagram.

(viii) Stop the computations when the minimum is reached, and print out the results.

It should be noted here that for steps (iii) and (iv), an IBM subroutine SIMQ was used; and for solving the differential equations, subroutine RKGS was used. The two-level search was avoided as the recycle streams (α_{23} and α_{33}) from the plug flow reactor were omitted from the analysis. Later in this publication, some of the results obtained through the multilevel search are presented.

RESULTS AND DISCUSSION

The rate constants used in this investigation and the other relevant data are presented in Table I. The nominal weighting factors used were

$$\begin{aligned} W_1 &= 100 \\ W_2 &= 1.0 \times 10^{-7} \\ W_3 &= 1.0 \times 10^{-4} \end{aligned} \quad (48)$$

The desired mean of the exit MWD was assumed to be 1500.0, and the desired variance (square of the standard deviation σ_d) was assumed to be zero. With these values for Δ_d and σ_d , the objective function J of eq. (44) can be written as

$$J' = 100M_4 + 1.0 \times 10^{-7}\sigma_4^2 + 1.0 \times 10^{-4}(\Delta_4 - 1500.0)^2 \quad (44')$$

It was advisable to carefully select the initial estimates of the decision variables to avoid lengthy computational times. As all three decision variables were in the range of 0 to 1, this selection was not difficult. A large number of simulation results was obtained, and the results are shown in Table II. It can be seen that increasing the flow into the CSTR (results 5 and 7) reduced the conversion, increased the variance, and increased the mean of the MWD. The objective function increased considerably from 7.57 to 32.14. Increasing the fraction flowing into the plug flow reactor (results 2 to 6) increased the conversion and decreased the mean of the

TABLE I
Parameter Values Chosen for Computation

Parameters	Symbol	Value
Initiation constant	k_d	1.0
Propagation constant	k_p	1.0×10^5
Termination constant	k_t	1.0×10^6
Total volume	V	50 liters
Inlet flow rate	F_1	100 liters/hr
Inlet monomer	M_1	1.0 gmoles/l.
Inlet moments of active polymer	$\lambda_1^{(i)}, i = 1,2,3$	0.0
Initial moments of dead polymer	$\mu_1^{(i)}, i = 1,2,3$	0.0
Inlet catalyst	I_1	1.0×10^{-3} gmoles/l.

TABLE II
Simulation Results for $w_1 = 100.0$, $w_2 = 10^7$ and $w_3 = 10^{-4}$

No.	Decision Variables			Residence Times		Flow Rates		Objective Function	Exit Properties			
	η	α_{21}	α_{32}	CSTR	PLUG	F_2	F_3		M_4	$I_4 \times 10^{-3}$	A_4	$\sigma_4^2 \times 10^{-7}$
1	0.318	0.600	0.318	0.568	.270	60.0	59.1	19.97	0.176	0.350	1637.7	0.180
2	0.60	0.318	0.318	0.629	0.383	31.8	78.31	9.19	0.089	0.175	1513.5	0.160
3	0.60	0.318	0.50	0.629	0.357	31.8	84.1	8.42	0.082	0.165	1472.4	0.162
4	0.60	0.318	0.60	0.629	0.343	31.8	87.28	8.05	0.077	0.160	1455.0	0.161
5	0.60	0.318	0.80	0.629	0.320	31.8	93.64	7.35	0.0674	0.151	1430.0	0.148
6	0.60	0.318	1.001	0.629	0.314	31.8	100.00	6.75	0.0548	0.138	1398.0	0.145
7	0.60	0.80	0.80	0.25	0.357	80.0	83.99	32.04	0.186	0.485	1860.0	0.237
8	0.80	0.10	1.00	1.00	0.40	10.0	100.0	13.09	0.0173	0.0334	1163.0	0.106
9	0.90	0.10	1.00	0.50	0.45	10.0	100.0	9.81	0.0235	0.042	1227.0	0.3097
10	0.90	0.318	1.00	0.157	0.45	31.8	100.0	8.40	0.0768	0.1734	1566.0	0.226
11	0.00	0.318	1.00	0.572	0.00	31.8	100.0	10.04	0.0596	0.1236	1300.0	0.103
12	0.50	0.500	0.50	0.50	0.333	50.0	75.0	15.07	0.1374	0.285	1604.5	0.181
Opt. Pt.	0.547	0.318	0.968	0.7402	0.276	31.8	98.8	6.62	0.0552	0.144	1397.6	0.118

MWD. Eliminating the plug flow reactor completely (results 6 and 11) reduced the variance, reduced mean of the MWD, and reduced the conversion. The decision variables from the sixth simulation ($\eta = 0.600$, $\alpha_{21} = 0.318$ and $\alpha_{32} = 1.00$) were chosen as the initial estimates, and the objective function of eq. (44') was minimized. The optimum values are also shown in Table II. In practical situations, α_{32} may be taken as 1.0 instead of 0.968, for this change would not affect the optimal results significantly.

Initially, the weighting factors were chosen so that each of the three terms making up the objective function contributes approximately equally. If W_1 was reduced to 10.0, the contribution from the conversion term becomes less significant and the objective function changed to

$$J'' = 10.0M_4 + 1.0 \times 10^{-7} \sigma_4^2 + 1.0 \times 10^{-4} (\Delta_4 - 1500.0)^2. \quad (44'')$$

The objective function could be recalculated in the same simulation run (the other results of course remain identical to ones obtained for $W_1 = 100.0$ as far as simulation is concerned). The values of these objective functions are shown in Table III. Unlike the previous case ($W_1 = 100.0$), an increase in α_{32} resulted in an increase of objective function. Increasing the size of the plug flow reactor reduced the objective function for low values of η , but the objective function increased as η changed from 0.40 to 1.0. Optimal results for this case are also presented in Table III. The significance of the variance term could be further increased if W_2 was changed to 1.0×10^{-6} ; this made the objective function

$$J''' = 10.0M_4 + 1.0 \times 10^{-6} \sigma_4^2 + 1.0 \times 10^{-4} (\Delta_4 - 1500.0)^2. \quad (44''')$$

Simulation results for this case ($W_1 = 10.0$, $W_2 = 10^{-6}$, and $W_3 = 10^{-4}$) are reported in Table IV. For this case, an increase in α_{21} increased the objective function considerably, indicating that a low value of α_{21} is desirable. Again, optimal results for this case are also presented in Table IV.

TABLE III
Simulation Results for $W_1 = 10.0$, $W_2 = 10^{-7}$, and $W_3 = 10^{-4}$

No.	η	α_{21}	α_{32}	Objective function
1	0.600	0.318	0.600	1.332
2	0.600	0.318	1.000	2.02
3	0.600	0.318	0.800	1.494
4	0.600	0.800	0.800	15.45
5	0.600	0.318	0.318	1.294
6	0.318	0.318	0.318	2.721
7	0.400	0.400	0.400	1.400
8	0.100	0.318	1.00	5.346
9	0.100	0.600	1.00	2.18
10	0.400	0.400	1.00	1.43
11	0.100	0.400	1.00	2.87
Opt. point	0.400	0.600	0.275	1.262

TABLE IV
Simulation Results for $W_1 = 10.0$, $W_2 = 10^{-6}$, and $W_3 = 10^{-4}$

No.	η	α_{21}	α_{32}	Objective function
1	0.600	0.318	0.600	4.58
2	0.600	0.318	1.00	5.130
3	0.600	0.318	0.800	4.64
4	0.600	0.800	0.800	20.73
5	0.510	0.318	0.318	4.61
6	0.600	0.318	0.318	4.71
7	0.318	0.318	0.318	6.77
Opt. point	0.294	0.336	0.704	4.560

The optimal results of all three cases are compared in Table V. It can be seen that the selection of the reactor system for polymerization depends on the weighting factors used in the objective function. As a CSTR produces a polymer with a low variance in comparison with a PFR, increasing the weighting factor for σ^2 increased the residence time for the CSTR. On the other hand, if the weighting factor for monomer conversion was increased, a higher holding time was obtained for the plug flow reactor. If the terms related to MWD (mean and variance) were omitted from the objective function, only a plug flow reactor of volume V_T was best suited. In the foregoing system synthesis, the values of rate constants and the initial (feed) concentrations were assumed to be constant. The effect of varying some of these parameters on the optimality was also examined in this investigation. The results of such examination can be used to determine the sensitivity of the optimal solution with respect to these parameters.

Effect of Variation in the Rate Constants

Weighting factors of the last case reported ($W_1 = 10.0$, $W_2 = 10^{-6}$, and $W_3 = 10^{-4}$) were used for exploring the performance of the system near the optimal point. The effect of variation in k_d on the system performance is shown in Figure 7. This variation may be caused by a change in temperature, a change in the nature of the catalyst, or any other means. It can be seen that the objective function decreased as k_d increased and reached a minimum at $k_d = 1.0$. The effect of increasing k_d was to reduce the variance of the MWD and the monomer concentration in the exit stream, but this increase in k_d caused the absolute difference between the mean of the exit MWD and 1500.0 (the desired mean of the exit MWD) to exhibit a minimum. The effect of variation in k_p , the propagation constant, was also investigated and the results are presented in Figure 8. A low value of k_p yielded the product polymer with a very low variance but reduced the conversion, and the exit of the mean of the MWD fell far below the desired value of 1500.0. This rendered the value of the objective function very high. Increasing the k_p value increased the variance and the mean of the MWD, but reduced the monomer concentration; the net effect was a re-

TABLE V
Optimal Results for the Three Cases Investigated

No.	Decision Variables			Residence Times		Flow Rates			No.	Objective Function	Weighting Factors			Exit Properties			
	η	c_{21}	σ_{32}	CSTR	PLUG	F_2	F_3	F_3			W_1	W_2	W_3	M_4	$I_4 \times 10^3$	Δ_4	$\sigma_4^2 \times 10^{-7}$
1	0.547	0.318	0.968	0.740	0.276	31.8	98.8	98.8	1	6.820	100.0	10^{-7}	10^{-4}	.0552	0.144	1397.6	0.118
2	0.400	0.600	0.275	0.500	0.254	60.0	73.7	73.7	2	1.262	10.0	10^{-7}	10^{-4}	.104	0.316	1593.3	0.180
3	0.294	0.336	0.704	0.604	0.329	33.6	90.0	90.0	3	4.560	10.0	10^{-6}	10^{-4}	.0773	0.168	1462.8	0.165

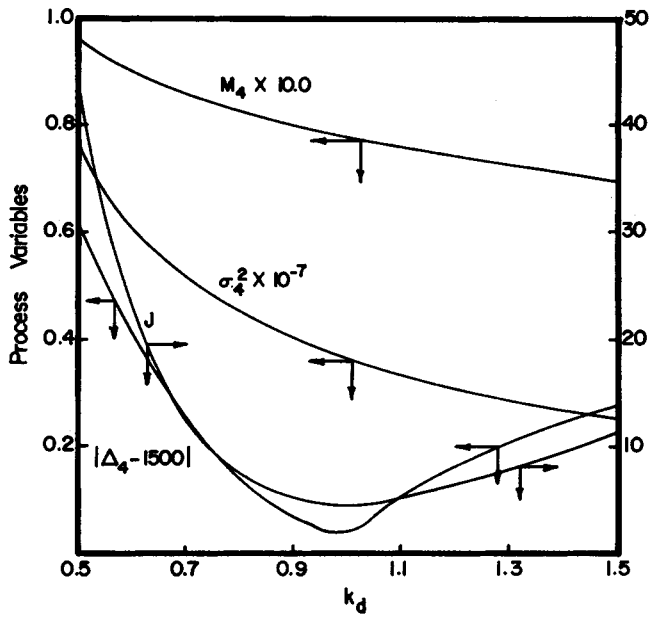


Fig. 7. Effect of k_d on process variables at the optimal point $\eta = 0.294$, $\alpha_{21} = 0.336$, and $\alpha_{32} = 0.704$.

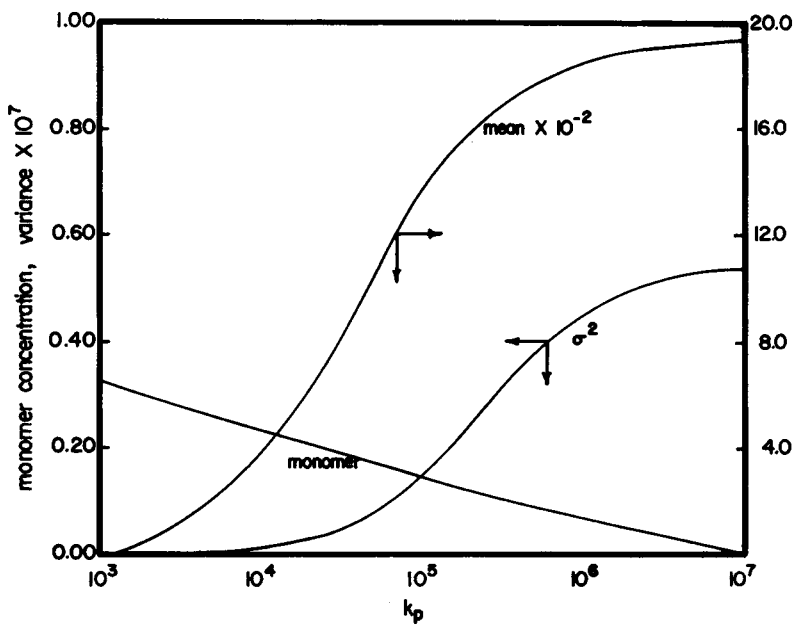


Fig. 8. Effect of k_p on the process variables for the optimal solution $\eta = 0.294$, $\alpha_{21} = 0.336$, and $\alpha_{32} = 0.704$.

duction in the objective function. A minimum value of J''' was obtained for $k_p = 10^6$; any increases beyond this again increased the objective function. Reduction in the value of the termination (Fig. 9) constant, k_t' , reduced the rate at which the polymer radicals combine with the monomer; this increased the conversion. Increasing k_t' (say, from 10^3 to 10^5) increased the variance of the MWD and reduced the conversion; both are undesirable. But this increase in k_t' caused a reduction in the objective function as the mean of the MWD moved closer to 1500.0. Further increase in k_t' from 10^6 , however, reduced the variance and the mean of the MWD.

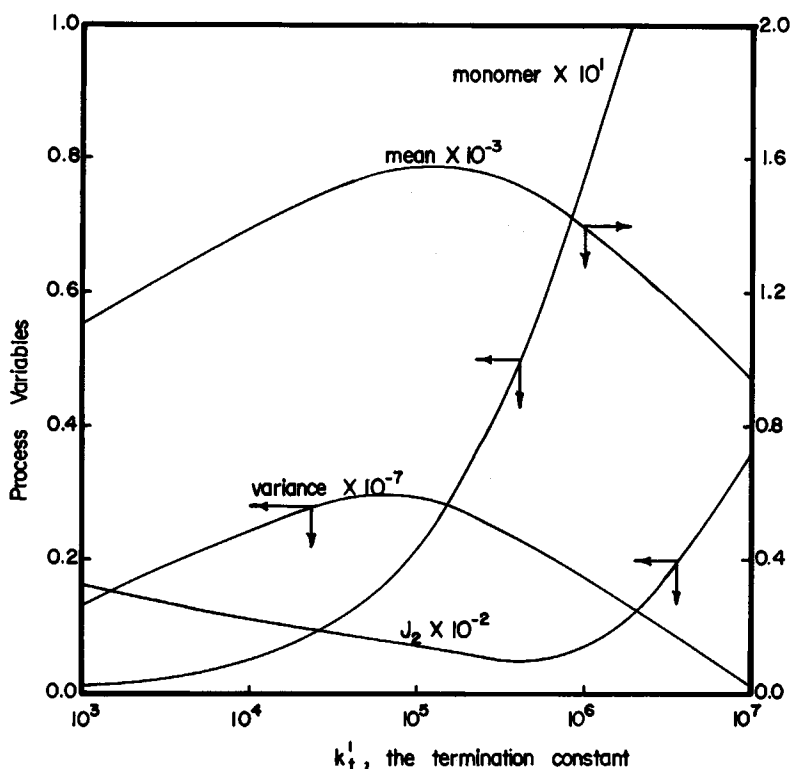


Fig. 9. Effect of k_t' on the optimal solution, $\eta = 0.294$, $\alpha_{21} = 0.336$, $\alpha_{32} = 0.704$.

In fact, both the variance and the mean reached maxima around 10^5 . The monomer concentration increased, which is equivalent to a reduction in conversion. The objective function became a minimum around a k_t' value of 4.0×10^5 . Polymer with narrower MWD was obtained for k_t' values of 10^7 and higher, but such high values of the termination rate constant yielded very low conversions and very low values of the mean of the MWD. It should, however, be emphasized that the previous analysis was carried out only to explore the sensitivity of the system around the optimal point.

Effect of Variation in Initial Concentrations

The effect of variation in initial concentrations I_1 and M_1 was also examined in this work. These results are presented in Tables VI and VII. The conversion of monomer at the optimal solution was independent of the monomer concentration. The conversion remained unchanged for all feed monomer concentrations. Reducing the feed monomer reduced the mean and variance of the MWD; the mean was reduced proportionately. Changing M_1 from 1.0 to 0.01 changed the mean from 1462.5 to 14.62. For the same change in M_1 , however, the variance dropped from 0.16×10^7 to 0.16×10^3 , that is, the variance changed parabolically. Table VI summarizes these results. Increasing I_1 , however, increased the conversion and reduced the mean and variance of the MWD. A low value of 10^{-7} for I_1 produced a polymer with a high average molecular weight and a high variance (mean 49,872.5, variance 0.379×10^{10}) but yielded a low conversion of monomer. These results are presented in Table VII.

TABLE VI
Effect of M_1 on Optimal Solution $\eta = 0.294$, $\alpha_2 = 0.336$, $\alpha_{32} = 0.704$

M_1	J_2	Δ_4	σ_4^2	M_4	I_4
0.01	220.64	14.62	0.165×10^3	0.000773	0.167×10^{-3}
0.10	183.37	146.2	0.165×10^6	0.00773	0.167×10^{-3}
1.00	4.56	1462.5	0.165×10^7	0.0773	0.167×10^{-3}

TABLE VII
Effect of I_1 on Optimal Solution $\eta = 0.294$, $\alpha_{21} = 0.336$, $\alpha_{32} = 0.704$

I_1	J_2	Δ_4	$\sigma_4^2 \times 10^{-7}$	M_4	I_4
10^{-7}	239,782	49,872.0	0.43×10^3	0.335	0.167×10^{-7}
10^{-6}	166,281	41,845.0	0.24×10^3	0.3231	0.167×10^{-6}
10^{-5}	48,329	23,222	0.738×10^2	0.280	0.167×10^{-5}
10^{-4}	3,894	7,654	0.618×10	0.1860	0.167×10^{-4}
10^{-3}	4.56	1,462.0	0.16	0.0773	0.167×10^{-3}
10^{-2}	172.92	185.2	0.408×10^{-2}	0.01839	0.167×10^{-2}

EFFECT OF RECYCLE

The recycles from the plug flow reactor ($\alpha_{33}F_3$ and $\alpha_{23}F_3$) were originally assumed to be zero to simplify the analysis. The results presented here were obtained by including the recycle stream in the systems synthesis routine. Results of simulation in which α_{33} and α_{23} were varied from 0 to 1.0 are presented first, and then the results of synthesis with recycles are presented.

If recycles were not assumed to be zero, the material balance equations could not be solved directly. A modified computational scheme was de-

vised for simulation and optimization of the system with recycle. The computational scheme used is as follows:

(i) Assume a value for M_3 . Integrate the plug flow equation to obtain M_p^e .

(ii) Calculate M_2 using eq. (19); noting that $\alpha_{22} = 0.0$, calculate M_c^e using eq. (37).

(iii) Check if these values of M satisfy eq. (24). If this equation is not satisfied, redefine the value of M_3 and iterate until eq. (24) is satisfied. A golden section search (one-dimensional) routine was used as a root-finding routine to determine values of M which would satisfy eq. (24).

(iv) If eq. (24) is satisfied, repeat similar searches for other variables, $\lambda_3^{(i)}$ and $\mu_3^{(i)}$, $i = 0, 1, 2$.

It should be noted here that equations for I , the initiator concentration, eqs. (18), (23), (28), (37) and (45), can be solved simultaneously in matrix terms for I_2, I_3 , and I_4 ; the solution is

$$\begin{bmatrix} I_2 \\ I_3 \\ I_4 \end{bmatrix} = \begin{bmatrix} F_2 & F_3 \alpha_{23} e^{-k_d \tau_{\text{PLUG}}} & 0 \\ \frac{-\alpha_{32} F_2}{1 + k_d \tau_{\text{CSTR}}} & F_3 (1 - \alpha_{33} e^{-k_d \tau_{\text{PLUG}}}) & 0 \\ \frac{-\alpha_{42} F_2}{1 + k_d \tau_{\text{CSTR}}} & F_3 \alpha_{43} e^{-k_d \tau_{\text{PLUG}}} & F_4 \end{bmatrix}^{-1} \begin{bmatrix} \alpha_{21} I_1 F_1 \\ \alpha_{31} I_1 F_1 \\ \alpha_{41} I_1 F_1 \end{bmatrix} \quad (51)$$

This scheme was used with the scheme described earlier for simulating the process system; α_{33} represents the fraction of the exit flow from the plug flow reactor which was fed back to the same reactor. Any increase in α_{33} (from a nominal value of zero) reduced the residence time in the plug flow reactor and, therefore, reduced the conversion of the monomer to polymer. Recycling, however, caused polymers of different chain lengths to intermix and grow further, thus reducing the variance of the molecular weight distribution. Because of this intermix, the average molecular weight increased only slightly. Table VIII presents these results; α_{23} represents the fraction of the exit flow from the plug flow reactor which was fed to the stirred tank reactor. Residence times in both the CSTR and the plug flow reactor were reduced when α_{23} was increased from its nominal value of zero. This increased the exit monomer concentration, lowering the conversion. An increase in α_{23} also caused the variance to decrease, thus making the product more desirable. These results are shown in Table IX.

Synthesis with Recycle

This modified computational scheme was combined with the optimizing routine of the computational section (the simplex pattern search) to determine the optimal structure when recycle loops were present in the system. Results of this optimization are presented in this section.

It is apparent that high recycle flow rates are not advantageous because these increase the objective function considerably. The computational schemes of the computational section and the previous subsection could be coupled to include five decision variables (α_{21} , α_{32} , α_{23} , α_{33} , and η) instead

TABLE VIII. Effect of Recycle (α_{22}) on the Process Variables at the Optimal Solution $\eta = 0.294$, $\alpha_{21} = 0.336$, $\alpha_{23} = 0.704$

α_{33}	Residence Time		Monomer Concentrations				Initiator Conc.		Flow Rates		MWD		
	CSTR	PLUG	M_c^e	M_3	M_2	M_p^e	M_e	$I_c^e \times 10^3$	$I_p^e \times 10^3$	F_2	F_3	Mean $\times 10^{-4}$	Variance $\times 10^{-7}$
0.0	0.604	0.329	0.324	0.0851	1.00	0.0560	0.0773	0.623	0.113	33.56	90.08	0.1462	0.1652
0.1	0.604	0.294	0.324	0.762	1.00	0.233	0.245	0.623	0.649	33.56	100.07	0.1472	0.1518
0.2	0.604	0.263	0.324	0.709	1.00	0.258	0.265	0.623	0.654	33.56	112.58	0.1488	0.1426
0.3	0.604	0.230	0.324	0.656	1.00	0.269	0.274	0.623	0.657	33.56	128.66	0.1502	0.1380
0.4	0.604	0.197	0.324	0.610	1.00	0.291	0.294	0.623	0.660	33.56	150.11	0.1511	0.1336
0.5	0.604	0.164	0.324	0.561	1.00	0.300	0.303	0.623	0.663	33.56	180.13	0.1520	0.1287
0.6	0.604	0.132	0.324	0.513	1.00	0.308	0.310	0.623	0.660	33.56	225.17	0.1535	0.1224
0.7	0.604	0.099	0.324	0.480	1.00	0.334	0.334	0.623	0.669	33.56	300.22	0.1552	0.1145
0.8	0.604	0.066	0.324	0.434	1.00	0.337	0.337	0.623	0.672	33.56	450.33	0.1569	0.1102
0.9	0.604	0.032	0.324	0.372	1.00	0.342	0.342	0.623	0.674	33.56	900.66	0.1587	0.1037

TABLE IX. Effect of Recycle (α_{22}) on the Process Variables at the Optimal Solution, $\eta = 0.294$, $\alpha_{21} = 0.330$, $\alpha_{23} = 0.704$

α_{33}	Residence Time		Monomer Concentrations				Initiator Conc.		Flow Rates		MWD		
	CSTR	PLUG	M_c^e	M_3	M_2	M_p^e	M_e	$I_c^e \times 10^3$	$I_p^e \times 10^3$	F_2	F_3	Mean $\times 10^{-4}$	Variance $\times 10^{-7}$
0.0	0.604	0.329	0.324	0.0851	1.00	0.0560	0.0773	0.623	0.113	33.56	90.08	0.1462	0.1652
0.1	0.469	0.306	0.316	0.785	0.830	0.244	0.253	0.627	0.650	43.24	96.89	0.1468	0.1603
0.2	0.372	0.283	0.310	0.747	0.712	0.252	0.261	0.631	0.651	54.52	108.82	0.1475	0.1538
0.3	0.299	0.261	0.306	0.709	0.625	0.259	0.268	0.635	0.653	67.81	114.18	0.1484	0.1475
0.4	0.242	0.236	0.306	0.674	0.566	0.276	0.283	0.638	0.655	83.71	125.37	0.1493	0.1398
0.5	0.196	0.213	0.305	0.637	0.516	0.282	0.289	0.642	0.657	103.05	138.99	0.1508	0.1305
0.6	0.159	0.190	0.304	0.600	0.476	0.287	0.294	0.645	0.658	127.12	155.93	0.1521	0.1236
0.7	0.129	0.167	0.311	0.570	0.453	0.305	0.308	0.648	0.660	57.86	177.57	0.1537	0.1176
0.8	0.102	0.144	0.312	0.534	0.425	0.309	0.311	0.652	0.661	198.52	206.20	0.1552	0.1117
0.9	0.079	0.121	0.313	0.499	0.402	0.311	0.313	0.655	0.663	254.79	245.81	0.1568	0.1053

of three (α_{21} , α_{32} , and η) as used in the previous optimization. The starting values chosen for these decision variables were

$$\begin{aligned}\alpha_{21} &= 0.336 \\ \alpha_{32} &= 0.704 \\ \alpha_{23} &= 0.1 \\ \alpha_{33} &= 0.2 \\ \eta &= 0.594.\end{aligned}\tag{52}$$

The objective function of eq. (44''') was minimized; the computation times were almost 2–2.5 times the computational times for the case with three variables because of the two-level search involved. However, no substantial improvement was found in the performance, and the final values for the decision variables obtained were

$$\begin{aligned}\alpha_{21} &= 0.3374 \\ \alpha_{32} &= 0.700 \\ \alpha_{23} &= 0.0018 \\ \alpha_{33} &= 0.004 \\ \eta &= 0.594.\end{aligned}\tag{53}$$

The reduction in variance was offset by an increase in the exit monomer concentration. The objective function was reduced from 4.56 to 4.537. A low recycle, as was obtained in this synthesis, is very impractical to maintain and should be removed from the system in practice. It can be concluded, therefore, that for the problem under consideration recycle does not improve the performance and can be omitted from the analysis. Very low recycle flow rates were also obtained under the optimal conditions for the other two objective functions considered, eqs. (44') and (44''). This implies that the optimal structure contains no recycles. Results from this synthesis study are summarized in Table X.

TABLE X
Results of Optimization with Recycle

No.	Recycle		Exit monomer	Objective function	Exit MWD	
	α_{23}	α_{33}			Mean	Variance $\times 10^{-7}$
1	0.1	0.1	0.2478	4.614	1469.5	0.1534
2	0.2	0.1	0.2486	4.638	1478.0	0.1485
3	0.1	0.2	0.2573	4.764	1473.8	0.1506
4	0.2	0.2	0.2622	4.815	1491.8	0.1398
5	0.05	0.05	0.2345	4.603	1465.0	0.1568
6	0.01	0.01	0.1841	4.585	1464.8	0.1596
7	0.002	0.005	0.1358	4.543	1463.3	0.1618
8	0.002	0.004	0.1238	4.537	1463.0	0.1638
Op. pt.	0.0018	0.004	0.1235	4.5368	1462.6	0.1641

CONCLUDING REMARKS

A systematic procedure was developed for selecting the reactor system configuration for polymer processes. The procedure is fairly general and can be employed in a number of situations related to the polymer industry. If the performance functions and economic data for two different types of polymer reactors (say, bulk and solution) are available, the synthesis technique can be used to select the right type of processing units for a specific operation. In selecting between the two types of polymerization processes, it may be necessary to include not only the reactors but also the separation unit, extraction unit, and other recovery units.

In the investigation presented in this paper, the temperature effect was neglected. Temperature influences the system performance in many ways. An increase in temperature increases the rate constants and the rates of reactions and thus produces additional products per unit time. As the polymerization reactions are generally exothermic, an increase in the rate of reaction increases the amount of heat to be removed to maintain isothermal conditions and thus increases the coolant flow rate and area required for heat transfer. These temperature effects were neglected in this work but will be examined later (part II).

Additional effects due to the diffusional control of termination processes¹⁶⁻¹⁸ and due to the chain transfer to the monomer can be incorporated in the model employed in the present work. These would relax some of the assumptions made in this work and change the system equations. Effects of these processes on the system performance is considered in part II of this paper. It is hoped that the technique presented in this paper would lead to more systematic design and selection of polymerization reactor systems.

Nomenclature

CSTR	continuous stirred tank reactor
d_i	decision variables for subsystem i
F	flow rate of the processing fluid in the system
g_i	constraints imposed on the system
I	initiator concentration
J, J', J'', J'''	objective function to be minimized as defined by eq. (44)
k_d	rate constant for decomposition of the initiator
k_i	rate constant for initiation
k_p	rate constant for propagation
k_t, k_t'	rate constant for termination
M	concentration of the monomer
MWD	molecular weight distribution
N	number of subsystems in the system
PFR	plug flow reactor
P_j	concentration of the active polymer of chain length j
P_j^*	concentration of the dead polymer of chain length j
R	intermediate in initiation step

t	time
V_{CSTR}	volume of the stirred tank reactor
V_{PLUG}	volume of the plug flow reactor
V_T	$V_{\text{PLUG}} + V_{\text{CSTR}}$
W_i	weighting factors
x_i	input vector for subsystem i
y_i	output vector for subsystem i
Δ_d	desired mean of the exit MWD
Δ_A	actual mean of the exit MWD
$\lambda^{(k)}$	k th moment of the active polymer chain length (size) distribution
$\mu^{(k)}$	k th moment of the dead polymer chain length (size) distribution
τ_{CSTR}	residence time in the plug flow reactor
τ_{PLUG}	residence time in the stirred tank reactor
σ_d	desired standard deviation of the exit MWD
σ_A	actual standard deviation of the exit MWD
η	fractional of the total volume apportioned to the plug flow reactor

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