MULTI-CRITERIA ANALYSIS AND OPTIMIZATION

OF CHAIN PROPAGATION WITH MONOMER TERMINATION

POLYMERIZATION IN A BATCH REACTOR

by

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B.S., Kansas State University, Manhattan, Kansas, 1981

A MASTER'S THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

CHEMICAL ENGINEERING

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1984

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ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. L. T. Fan for his encouragement and guidance during the course of this reserach and the writing of this thesis. Thanks are due to Drs. W. P. Walawender and L. E. Erickson for serving as the supervisory committee members. The author wishes to thank Snehal A. Patel for his assistance in this research. The author was financially supported by the Engineering Experiment Station, Kansas State University, during the course of this research.

TABLE OF CONTENTS

INTRODUCTION

Polymerization is a multi-billion dollar industry, and thus, a slight improvement in an operating system can result in a great deal of cost savings. For this reason, polymerization systems have been studied extensively (see, e.g., Han, 1977). In this paper, analysis and optimization of polymerization are carried out by resorting to multi-criteria techniques.

Two of the parameters that are considered to be most important in evaluating the performance of a polymer reactor system are the molecular weight distribution, MWD, of the polymer produced and the conversion of monomer. The MWD of a polymer is of principle importance in determining its physical properties. A graphical representation of MWD is simply a plot of the weight fraction of polymer at a specific chain length against the chain length; strictly speaking, it is discrete in nature. The MWD can be characterized largely by its mean and variance or standard deviation, and therefore, it is highly desirable that in producing a polymer, its mean and standard deviation be constrained within desirable ranges. This helps assure that the polymer will have the desired physical characteristics. A high conversion will lower or eliminate the cost of separating unreacted monomer for recycling.

The need for multi-criteria analysis or optimization arises since the mean and standard deviation of the MWD of the polymer produced in a reactor change simultaneously as the extent of monomer conversion increases. If nearly all the monomer is allowed to react, the mean and standard deviation are likely to become excessively high. If the standard deviation is to be kept low, the mean and extent of conversion will also probably be low. In general, an improvement in one criterion tends to give rise to a detrimental change in at least one of the other criteria.

In a conventional single-criterion approach, different criteria are combined after they are weighed somewhat subjectively with respect to their relative importance; this tends to mask details of structure of the criteria space of the system under consideration, which is a batch reactor for polymerization via isothermal chain propogation with monomer termination in the present work. In contrast, by resorting to a multi-criteria approach, we gain an insight into such structure.

MODELING

Governing Equations

The polymerization mechanism of the system under consideration is (Liu and Amundson, 1961; also see Appendix A)

$$M \xrightarrow{k_i} P_1^{\bullet} \qquad ; \text{ initiation}$$

$$P_j^{\bullet} + M \xrightarrow{k_p} P_{j+1}^{\bullet} \qquad ; \text{ propagation}$$

$$P_j^{\bullet} + M \xrightarrow{k_m} P_{j+1}^{*} \qquad ; \text{ termination}$$

The corresponding batch kinetic equations are

$$\frac{dM}{dt} = -k_i M - (k_p + k_m)\, M\, P_T^{\bullet} \tag{1}$$

$$\frac{dP_1^{\bullet}}{dt} = k_i M - (k_p + k_m)\, M\, P_1^{\bullet} \tag{2}$$

$$\frac{dP_j^{\bullet}}{dt} = k_p M (P_{j-1}^{\bullet} - P_j^{\bullet}) - k_m\, M\, P_j^{\bullet}\ ,\ j \geq 2 \tag{3}$$

$$\frac{dP_j^{*}}{dt} = k_m M\, P_{j-1}^{\bullet},\ j \geq 2 \tag{4}$$

Addition of Eqs. 2 and 3 leads to

$$\frac{dP_T^{\bullet}}{dt} = k_i M - k_p\, M\, P_T^{\bullet} \tag{5}$$

By resorting to the eigenzeit transformation (Postal, 1935)

$$d\tau = M dt, \tag{6}$$

Eqs. 1 through 5 can be transformed, respectively, as

$$\frac{dM}{d\tau} = k_i - (k_p + k_m)\, P_T^{\bullet} \tag{7}$$

$$\frac{dP_1^{\bullet}}{d\tau} = k_i - (k_p + k_m)\, P_1^{\bullet} \tag{8}$$

$$\frac{dP_j^{\bullet}}{d\tau} = k_p(P_{j-1}^{\bullet} - P_j^{\bullet}) - P_j^{\bullet}\ , \ j \geq 2 \tag{9}$$

$$\frac{dP_j^{*}}{d\tau} = k_m\, P_{j-1}^{\bullet}\ , \ j \geq 2 \tag{10}$$

$$\frac{dP_T^{\bullet}}{d\tau} = k_i - k_m\, P_T^{\bullet} \tag{11}$$

Notice that these equations form a set of linear equations. While Eqs. 7, 8, and 11 can easily be solved analytically, this is not the case for Eqs. 9 and 10, because both Eqs. 9 and 10 represent infinite sets of equations, one for each chain length, j (also see Appendix B).

Decision Variable

The two variables which seem most natural in determining the MWD are batch reaction or retention time and temperature. The length of time the reaction is allowed to continue will obviously affect the MWD. For convenience, the transformed time, τ, is employed. The temperature of the reaction mixture will affect the reaction rates and thus both the equilibrium point and the time necessary to reach equilibrium. This will definitely affect the MWD. While other variables could be considered as decision variables, we shall focus our attention only to these two in this study.

Criteria

For the reasons mentioned previously, the conversion, mean, and standard deviation are chosen as the parameters characterizing the present system. For ease of analysis or optimization, it is desirable to express the criteria in such a way that all three are minimized toward zero. The conversion, X, can be subtracted from its maximum value of 1 to yield the first criterion, f_1, defined as

$$f_1 = (1-X) \tag{12}$$

The desired mean, μ_d, and the desired standard deviation, σ_d, are frequently specified by the consumer of the polymer; the mean, μ, and the standard deviation, σ, are, forced to approach these values. This gives rise to the second criterion, f_2, defined as

$$f_2 = |(\mu-\mu_d)| \tag{13}$$

and the third criterion, f_3, defined as

$$f_3 = |(\sigma-\sigma_d)| \tag{14}$$

SIMULATION

To obtain the MWD and the corresponding criterion functions, the governing equations of the model need be solved or simulated. Three methods are attempted in this study, including numerical solution, continuous variable approximation and discrete exact approach.

Numerical Solution

The MWD can be obtained in a strictly numerical fashion by solving Eqs. 8 through 10 using an ordinary differential equation (ODE) integrating program; the GEAR package developed by Hindmarsh (Hindmarsh, 1974) has been used. The results of simulation are shown in Figure 1.

Continuous Variable Approximation

This approach introduces a simplifying assumption of continuity for the MWD (see, e.g., Rosenbrock, 1966). Although, in reality, the polymer can only take on integral values of chain length, letting the chain length take on non-integral values should not introduce excessive error if the mean chain length is fairly high. By introducing the new independent, continuous variable, j, the two infinite sets of equations are collapsed into two partial differential equations (PDE), which, in principle, can be solved by the method of characteristics (Lapidus, 1962; also see Appendix C)

Using the continuous variable approximation, Eq. 9 can be rewritten as

$$\frac{\partial P^{\bullet}(j,\tau)}{\partial \tau} = k_p[P^{\bullet}(j-1,\tau) - P^{\bullet}(j,\tau)] - k_m P^{\bullet}(j,\tau) \qquad (15)$$

It is further assumed that $P^{\bullet}(j-1,\tau)$ may be expanded into a truncated Taylor series as

$$P^{\bullet}(j-1,\tau) = P^{\bullet}(j,\tau) - \frac{\partial}{\partial j} P^{\bullet}(j,\tau) \qquad (16)$$

Thus, Eq. 15 may be rewritten as

$$\frac{\partial P^{\cdot}(j,\tau)}{\partial \tau} + k_p \frac{\partial P^{\cdot}(j,\tau)}{\partial j} = -k_m \, P^{\cdot}(j,\tau) \tag{17}$$

with

$$\text{I.C.: } P^{\cdot}(j,0) = 0$$

and

$$\text{B. C.: } P^{\cdot}(1,\tau) = P_1^{\cdot}(\tau)$$

Equation 17 is a first order linear hyperbolic PDE which can be solved by the method of characteristics to obtain (Lapidus, 1962)

$$P^{\cdot}(j,\tau) = \frac{k_i}{k_p + k_m} [e^{-\frac{k_m}{k_p}(j-1)} - e^{(j-1)-(k_p+k_m)\tau}] \text{ for } j \leq 1 + k_p \tag{18}$$

$$P^{\cdot}(j,\tau) = 0 \qquad \text{for } j > 1 + k_p \tag{19}$$

Similarly, by means of the continuous variable approximation, we obtain the solution for $P^*(j,\tau)$ from Eq. 10 as

$$P^*(j,\tau) = \frac{k_m k_i}{k_p+k_m} [(\tau - \frac{j-2}{k_p} + \frac{1}{k_p+k_m}) e^{-(j-2)k_m/k_p} - \frac{e^{(j-2)-(k_p+k_m)\tau}}{k_p+k_m}] \tag{20}$$

The resultant MWD's are illustrated in Figure 2.

Discrete Exact Approach

This approach solves the transformed governing equations, Eqs. 8 through 10, in a stepwise fashion, giving rise to an exact expression for the MWD for the system under consideration. The solution to Eq. 8 can be easily written as (see Appendix D)

$$P_1^{\cdot} = \frac{k_i}{k_p+k_m}\left[1 - e^{-(k_p+k_m)\tau}\right] \tag{21}$$

I.C.: $P_j^{\cdot}=0$ when $\tau=0$

Inserting this solution into Eq. 9 for j=2, i.e.,

$$\frac{dP_2^{\cdot}}{d\tau} = k_p(P_1^{\cdot} - P_2^{\cdot}) - k_m P_2^{\cdot} , \tag{22}$$

we obtain

$$P_2^{\cdot} = \frac{k_p k_i}{k_p+k_m}\left[\frac{1}{k_p+k_m} - e^{-(k_p+k_m)\tau}\left(\tau + \frac{1}{k_p+k_m}\right)\right] \tag{23}$$

This solution can then be inserted into Eq. 9 for j=3 yielding

$$P_3^{\cdot} = \frac{k_i k_p^2}{k_p+k_m}\left[\frac{1}{(k_p+k_m)^2} - e^{-(k_p+k_m)\tau}\left(\frac{\tau^2}{2} + \frac{\tau}{k_p + k_m} + \frac{1}{(k_p + k_m)^2}\right)\right] \tag{24}$$

Repeating this procedure, we see that a general solution has the following format;

$$P_j^{\cdot} = \frac{k_i}{k_p+k_m}\left\{a^{j-1} - e^{-(k_p+k_m)\tau}\, a^{j-1}\sum_{i=1}^{j}\frac{[(k_p+k_m)\tau]^i}{(i-1)!}\right\} \tag{25}$$

where

$$a = \frac{k_p}{k_p+k_m}$$

Similarly, Eq. 21 can be inserted into Eq. 10 for j=2

$$\frac{dP_2^*}{d\tau} = \frac{k_m}{k_p} P_1^* \ , \tag{26}$$

$$\text{I.C. : } P_j^* = 0 \quad \text{when } \tau = 0$$

to obtain

$$P_2^* = \frac{k_i\ k_m}{k_p+k_m} [\tau - \frac{1}{k_p+k_m} + \frac{e^{-(k_p+k_m)\tau}}{k_p + k_m}] \tag{27}$$

and Eq. 23 can be inserted into Eq. 10 for j=3 to obtain

$$P_3^* = \frac{k_i\ k_m}{k_p+k_m} \{a\tau - \frac{2a}{k_p+k_m} + \frac{e^{-(k_p + k_m)\tau}}{k_p + k_m} a[2 + (k_p+ k_m)\tau] \tag{28}$$

This procedure can be continued to obtain a general solution

$$P_j^* = \frac{k_i\ k_m}{k_p+k_m} [\tau\ a^{j-2} - \frac{(j-1)a^{j-2}}{k_p + k_m} + \frac{e^{-(k_p+k_m)\tau} a^{j-2}}{k_p + k_m} \sum_{i=1}^{j-1} \{ (j-i)\frac{[(k_p+k_m)\tau]^{i-1}}{(i-1)!}\}], \ j \geq 2 \tag{29}$$

The MWD's computed from Eqs. 25 and 29 are given in Figure 3. Furthermore, these equations yield analytical expressions for the criterion functions.

The mean and standard deviation can be related to the first and second moments of the MWD. The general expression for the n-th moment is

$$E[j^n] = \sum_{j=1}^{\infty} W(j)j^n \tag{30}$$

where

$$W(j) = \frac{j(\dot{P}_j + P_j^*)}{M_o - M}$$

Note that $E[j]$ is the first moment and $E[j^2]$ is the second moment.

Eqs. 25 and 29 can be substituted into Eq. 30 for n=1 to obtain an expression for the first moment

$$E[j] = \frac{k_i}{k_p+k_m} [\sum_{j=1}^{\infty} a^{j-1}\{j^2 + k_m\tau(j+1)^2-(1-a)(j+1)^2 j\} - e^{-(k_p+k_m)\tau} \sum_{i=0}^{\infty} \frac{b^i}{i!} \sum_{k=1}^{\infty} a^{k-1}\{(k+i)^2 - k(k+i+1)^2 (1-a)\}]/(M_0-M) \tag{31}$$

The infinite summations can be reduced with a great deal of effort to

$$E[j] = \frac{k_i}{k_p+k_m} [\frac{k_m\tau(4-3a+a^2) - (a+3)}{(1-a)^3} + e^{-k_m\tau}\{\frac{2b}{(1-a)^2} + \frac{a+3}{(1-a)^3}\}]/(M_0-M) \tag{32}$$

where

$$b = k_p\tau$$

Note that the mean is equal to the first moment.

A similar process can be repeated for n=2 to obtain the second moment as

$$E(j^2) = \frac{k_i}{k_p+k_m} [\frac{k_m\tau(8-5a+4a^2-a^3) - (7+10a+a^2)}{(1-a)^4} + e^{-k_m\tau}\{\frac{3(b^2+b)}{(1-a)^2} + \frac{3b(a+3)}{(1-a)^3} + \frac{7+10a+a^2}{(1-a)^4}\}]/(M_0-M) \tag{33}$$

The standard deviation is given by

$$\sigma = \{E[j^2] - E[j]^2\}^{1/2} \tag{34}$$

TRADE-OFF AMONG THE CRITERIA

The trade-off surface is the sector or region of the criteria or objective space where no criterion can be decreased without increasing another criterion. The three criteria, given in Eqs. 12 through 14, are simple enough to allow a large number of repeated evaluations necessary for tracing out the trade-off surface.

Traditionally, we would have to start in the decision space and then proceed to the criterion space (i.e., we must first choose values of the independent or decision variables and then calculate the criterion functions). However, because of the simplicity of the criterion equations, we can easily perform the inverse operation, i.e., we can choose values for the criteria and then calculate the decision variables using a root finding technique.

Knowing that all three criteria represented by Eqs. 12 through 14 are being minimized to zero, the following procedure can be used to determine the trade-off surface as shown in Figure 4. (For illustration, let M_o=0.4, μ_d=25 and σ_d=11.)

a. Set f_1 and f_2 to zero and compute the corresponding value of f_3, thus locating point A in the figure.

b. Maintain f_1 at zero and increase f_2 along line segment AB until f_3 equals zero, i.e. point B.

c. Increase f_1 along line BC with f_3 kept at zero until f_2 equals zero, thus locating point C.

d. With f_2 at zero increase f_3 along CA until f_1 is zero at point A.

It can be shown that the portion of the criteria surface traced inside the lines, AB, BC and CA, is the only region which satisfies the definition of a trade-off surface.

Configuration of Figure 4 indicates that the trade-off surface is a portion of a plane described by

$$\frac{f_1}{f_{10}} + \frac{f_2}{f_{20}} + \frac{f_3}{f_{30}} = 1 \tag{35a}$$

where

$$f_1, f_2, f_3 \geq 0 \tag{35b}$$

Normalizing the criterion functions as

$$\bar{f}_1 = \frac{f_1}{f_{10}}$$

$$\bar{f}_2 = \frac{f_2}{f_{20}}$$

and

$$\bar{f}_3 = \frac{f_3}{f_{30}} ,$$

equations (35a) and (35b) can be rewritten as

$$\bar{f}_1 + \bar{f}_2 + \bar{f}_3 = 1, \qquad 0 \leq \bar{f}_1, \bar{f}_2, \bar{f}_3 \leq 1 \tag{36}$$

The assumption that the trade-off surface is planar, described by Eqs. 35a and 35b, can now be tested by applying Eq. 36 to points on this surface. In fact, all points on the surface sum to 1 within 1 percent error. This would suggest that a triangular coordinate plot might be useful in representing the surface. Figure 5 shows constant temperature lines or isotherms on the trade-off surface with the values of τ shown at each end. Intermediate values of τ can be found by interpolation. Constant τ lines could also be drawn on the same figure; however, we have not done so because they are so close to the isotherms that to do so would overcrowd the plot.

In Figure 5, we see that it is possible to chart both the two-dimensional criteria space and the three-dimensional criteria space on the same plot. Thus, there is a straight-forward point to point correspondence between the two spaces. This simplicity would allow us to proceed from one space to the other without any elaborate calculations. Due to the linearity of the two spaces, it would now be possible to resort to simple analytical techniques to calculate the preferred decision instead of using complex numerical search procedures.

PREFERRED DECISION FOR ECONOMIC OPTIMIZATION

The trade-off surface consists of the non-inferior decisions, and thus, every point on this surface is a possible solution to the multi-criteria optimization problem. To select a preferred decision (or optimal solution) from the non-inferior decisions, the relative importance of each criterion need be considered. Two methods are described in this paper; they are the value function approach and the ε-constraint method.

Value Function Approach

The value function approach involves weighting each criterion by assigning a relative importance to it and minimizing the sum of the weighted objectives, V (Kuhn, 1951). This yields (see Appendix E)

$$a\bar{f}_1 + b\bar{f}_2 + c\bar{f}_3 = V \tag{37}$$

where a, b, and c are weights. It can be shown that V has a minimum on the interior of the surface only if a = b = c; then, V = a at every point on the trade-off surface. If the condition, a = b = c, is not satisfied, the optimum will be on the boundary.

Since the value function given by Eq. 37 does not yield useful or meaningful results, we shall consider an objective of the quadratic form

$$a(\bar{f}_1)^2 + b(\bar{f}_2)^2 + c(\bar{f}_3)^2 = V \tag{38}$$

At a critical point, we have

$$\left(\frac{\partial V}{\partial \bar{f}_2}\right)_{\bar{f}_3} = \left(\frac{\partial V}{\partial \bar{f}_3}\right)_{\bar{f}_2} = 0 \tag{39}$$

and furthermore, we have from Eq. 36

$$\bar{f}_1 = 1 - \bar{f}_2 - \bar{f}_3 \,, \tag{40}$$

Obviously, $\bar{f}_1$ is dependent on $\bar{f}_2$ and $\bar{f}_3$. It can be shown that

$$\left(\frac{\partial V}{\partial \bar{f}_2}\right)_{\bar{f}_3} = -2a\bar{f}_1 + 2b\bar{f}_2 \tag{41}$$

or

$$(a+b)\bar{f}_2 + a\bar{f}_3 = a \tag{42}$$

and

$$\left(\frac{\partial V}{\partial \bar{f}_3}\right)_{\bar{f}_2} = -2a\bar{f}_1 + 2c\bar{f}_3 \tag{43}$$

or

$$a\bar{f}_2 + (a+c)\bar{f}_3 = a \tag{44}$$

Solving Eqs. 40, 42 and 44 simultaneously, we obtain

$$\left.\begin{aligned} \bar{f}_1 &= \frac{bc}{ac+ab+bc} \\ \bar{f}_2 &= \frac{ac}{ac+ab+bc} \\ \bar{f}_3 &= \frac{ab}{ac+ab+bc} \end{aligned}\right\} \tag{45}$$

At the critical point, we have

$$\frac{\partial^2 V}{\partial \bar{f}_2^{\,2}} = 2a + 2b = A \tag{46}$$

$$\frac{\partial^2 V}{\partial \bar{f}_3^{\,2}} = 2a + 2c = C \tag{47}$$

$$\frac{\partial^2 V}{\partial \bar{f}_2 \partial \bar{f}_3} = 2a = B \tag{48}$$

Since

$$A > 0$$

and

$$AC - B^2 = 4(ab+ac+bc) > 0 \; ,$$

this critical point is the minimum point.

ε-Constraint Method

As applied to the present problem, the ε-constraint method involves restricting two criteria or objectives within a range of their minima and then minimizing the third in this range (see, e.g., Cohon, 1975). This is probably a much more realistic approach than the value function approach for this polymerization problem. Often, it will be critical to keep the mean and standard deviation within ranges in order to meet specifications.

The problem now becomes that of minimizing $\bar{f}_1$ while maintaining $\bar{f}_2$ and $\bar{f}_3$ within a range of zero. For example, let us impose the following constraints on $\bar{f}_2$ and $\bar{f}_3$; (see Appendix F)

$$\bar{f}_2 \leq 0.2 \quad \text{and} \quad \bar{f}_3 \leq 0.3$$

Obviously, from the condition that

$$\bar{f}_1 = 1 - \bar{f}_2 - \bar{f}_3 \; ,$$

we have

$$\bar{f}_1 \geq 0.5$$

Thus, the minimum value of $\bar{f}_1$ is obtained as

$$\bar{f}_1 = 0.5$$

DISCUSSION

Isothermal chain propagation with monomer termination in a batch reactor is considered in this work for two reasons: its relative simplicity permits a relatively complete mathematical analysis, and available literature information provides a basis for comparison and evaluation of the merits of the present approach.

Several MWD's obtained by the numerical solution are shown in Figure 1 as mentioned earlier. The drawback of this technique is that the computational effort required is excessive. We see that it is necessary to solve on the order of 100 equations, two for each value of j from two to fifty to obtain the results given in Figure 1, which are essentially in agreement with those obtained by Liu and Amundson (Liu, 1961). After the MWD is calculated, its mean and standard deviation must then be calculated numerically.

Computing time will indeed multiply if this procedure is to be employed repeatedly for a multi-criteria analysis problem of the type under consideration. Therefore, no attempt has been made to resort to this approach in conjunction with subsequent multi-criteria analysis.

The continuous MWD's calculated from Eqs. 18 and 20 are shown for several values of τ and temperature in Figure 2 as stated earlier. Note that each MWD curve is significantly different from the corresponding MWD curve obtained from the numerical solution (see Figure 1). While the means and standard deviations of these curves are not too different, the skewness and kurtoses almost certainly would be. This would lead us to suspect that the continuous variable approximation solution may not be a sufficiently accurate representation of the discrete MWD for the purpose of conducting a multi-criteria analysis or optimization. Even if the inaccuracies resulting from this method are acceptable, substantial computational effort is still necessary to determine the mean and standard deviation of the MWD.

The exact MWD's have been calculated from Eqs. 25 and 29 for various values of τ and temperature by means of the discrete exact approach developed in this work. The shape of the MWD's agree well with that of the MWD's obtained by the numerical solution, as expected. This approach is slightly more time consuming than the continuous variable approximation. Fortunately, it is not necessary to solve for the MWD since the mean and standard deviation can be calculated directly, as shown previously. While mathematical manipulations involved in the discrete exact approach seem to be cumbersome, the resultant solutions in terms of the mean and standard deviation of the MWD are in relatively simple forms. This reduces the time and effort necessary to determine the mean and standard deviation to a minimum without affecting their accuracy. The coefficients of skewness and kurtosis can be similarly obtained and be included in the multi-criteria analysis or optimization if necessary.

The trade-off relation among the monomer conversion, and the mean and standard deviation of the MWD has been detailed explicitly. It has been found that the criterion or objective space and the decision space for the present system can be sketched on a single graph. This simplifies the computations necessary to obtain an approximate solution, greatly facilitating the determination of operating conditions in response to the change in relative importance of the criteria for the optimization.

It should be noted that although the approximation of the surface by

$$\bar{f}_1 + \bar{f}_2 + \bar{f}_3 = 1$$

is reasonable, results with improved accuracy can be easily obtained by taking the approximate solution as a starting point for search.

CONCLUDING REMARKS

The model equations for a batch reactor for chain propagation polymerization with monomer termination have been solved exactly by a newly proposed discrete method; it has yielded relatively simple analytical expressions. The availability of such expressions have greatly facilitated multi-criteria analysis and optimization of the system.

Nomenclature

k_i = rate constant for the initiation reaction, s^{-1}

= $7.29 \times 10^5 \exp(-5102/T)$

k_m = rate constant for the termination reaction, L/(gmol)(s)

= $1.0 \times 10^{10} \exp(-6908/T)$

k_p = rate constant for the propagation reaction, L/(gmol)(s)

= $4.667 \times 10^{10} \exp(-6142/T)$

j = polymer chain length

M = monomer concentration at any given time, gmol/L

M_o = initial concentration of monomer, gmol/L

$P_j^{\bullet}$ = active polymer concentration, with chain length j, gmol/L

P_j^{*} = dead polymer concentration, with chain length j, gmol/L

$P_T^{\bullet}$ = total active polymer concentration, gmol/L

t = time in conventional units, s

T = reactor temperature, K

τ = representation for time in the eigenzeit space, s gmol/L

X = conversion of monomer

= M/M_o

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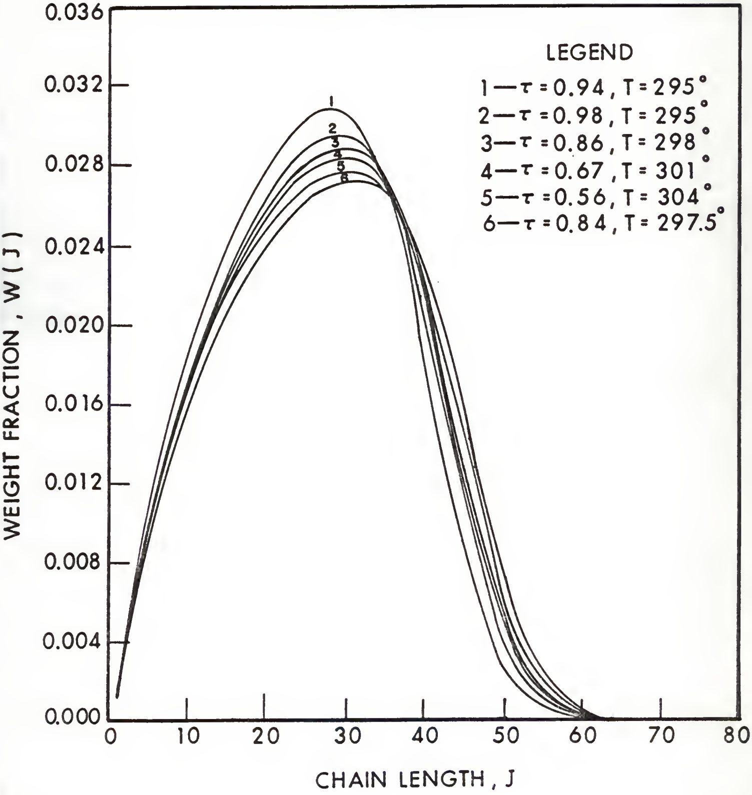


Figure 1. MWD obtained from numerical solution.

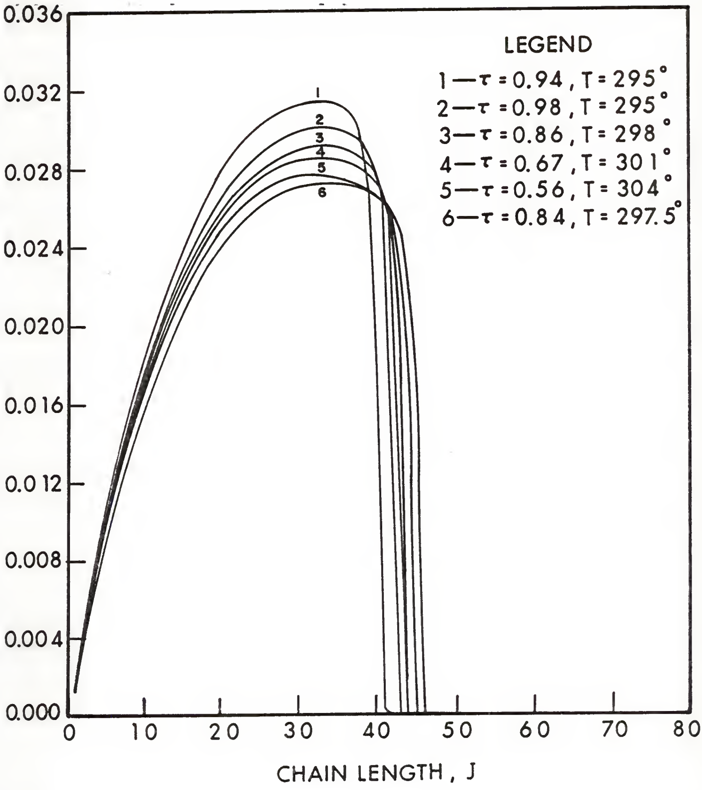


Figure 2. MWD obtained from continuous variable approximation

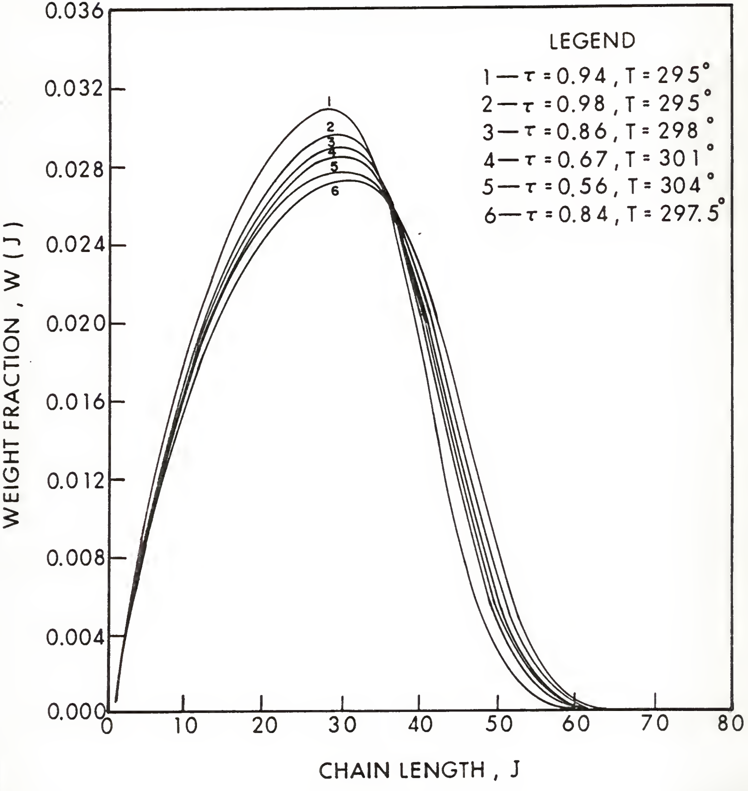


Figure 3. MWD obtained from discrete exact approach.

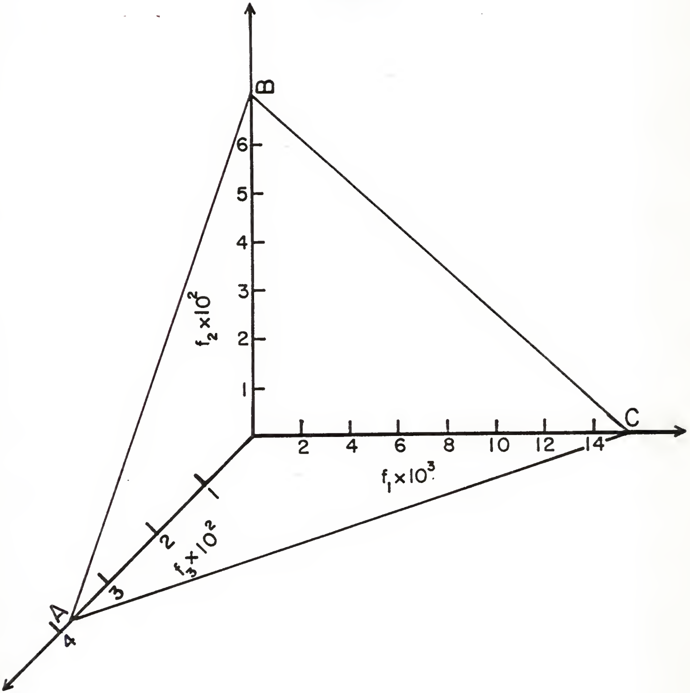


Figure 4. 3–D plot of the trade-off surface.

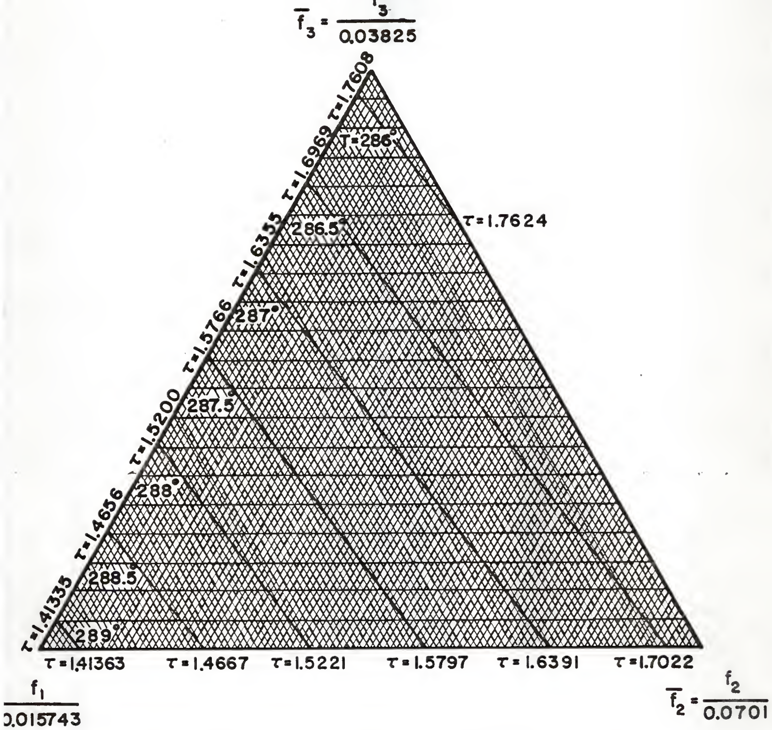


Figure 5. Plot of the trade-off surface with isotherms.

APPENDICES

APPENDIX A

CONSERVATION EQUATIONS FOR BATCH POLYMERIZATION WITH MONOMER TERMINATION

An isothermal batch polymerization reactor is considered, in which the rate constants for propagation and termination are independent of chain length. The polymerization mechanism considered is:

$$M \longrightarrow P_i^{\bullet} \qquad \text{initiation}$$

$$P_j^{\bullet} + M \xrightarrow{k_1} P_{j+1}^{\bullet} \qquad \text{propagation} \tag{A-1}$$

$$P_j^{\bullet} + M \xrightarrow{k_m} P_{j+1}^{*} \qquad \text{termination}$$

MASS BALANCE ON MONOMER

generation − consumption = accumulation

$$0 \quad - k_i M + \sum_{j=1}^{\infty} (k_p + k_m)\, MP_j^{\bullet} = \frac{dM}{dt}$$

Let

$$\sum_{j=1}^{\infty} P_j^{\bullet} = P_T$$

Thus,

$$\frac{dM}{dt} = -k_i M - (k_p + k_m)\, MP_T^{\bullet} \tag{A-2}$$

MASS BALANCE ON ACTIVE POLYMER

(i) active polymer of chain length one:

generation - consumption = accumulation

$$k_i M - (k_p + k_m)\, MP_i^{\bullet} = \frac{dP_1}{dt}$$

or

$$\frac{dP_1^{\bullet}}{dt} = k_i M - (k_p + k_m)\, MP_1^{\bullet} \qquad \text{(A-3)}$$

(ii) active polymer of chain length $j \geq 2$:

generation - consumption = accumulation

$$k_p MP_{j-1}^{\bullet} - (k_p + k_m)\, MP_j^{\bullet} = \frac{dP_j}{dt}$$

or

$$\frac{dP_j}{dt} = k_p M\,(P_{j-1}^{\bullet} - P_j) - k_m MP_j^{\bullet}, \quad j \geq 2 \qquad \text{(A-4)}$$

MASS BALANCE ON DEAD POLYMER

generation - consumption = accumulation

$$k_m MP_{j-1}^{\bullet} - \quad 0 \quad = \frac{dP_j^{*}}{dt}$$

or

$$\frac{dP_j^{*}}{dt} = k_m MP_{j-1}^{\bullet} \qquad \text{(A-5)}$$

$$\frac{dP_1^{\bullet}}{dt} + \sum_{j=2}^{\infty} \frac{dP_j^{\bullet}}{dt} = k_i M - (k_p + k_m)\ MP_1^{\bullet} + k_p M \sum_{j=2}^{\infty} (P_{j-1}^{\bullet} - P_j^{\bullet})$$

$$- k_m M \sum_{j=2}^{\infty} P_j^{\bullet}$$

or

$$\frac{d}{dt}\,[P_1^{\bullet} + \sum_{j=2}^{\infty} P_j^{\bullet}] = k_i M - (k_p + k_m)\ MP_1^{\bullet} + \sum_{j=2}^{\infty} P_j^{\bullet} + k_p M \sum_{j=2}^{\infty} P_{j-1}^{\bullet}$$

But

$$\sum_{j=2}^{\infty} P_{j-1}^{\bullet} = \sum_{j=1}^{\infty} P_j = P_T^{\bullet}$$

and thus,

$$\frac{dP_T^{\bullet}}{dt} = k_i M - (k_p + k_m)\ MP_T^{\bullet} + k_p MP_T^{\bullet}$$

or

$$\frac{dP_T^{\bullet}}{dt} = k_i M - k_m MP_T^{\bullet} \qquad \text{(A-6)}$$

APPENDIX B

ANALOG SOLUTIONS TO M, P_T AND T

INTRODUCTION

The main advantage of using an analog approach to solving differential equations is the ease with which the various parameters in the equations can be varied. For the polymerization problem, the rate constants are taken as constants in the differential equations resulting from the three reactions. This is true for given temperature, however, the temperature itself needs to be optimized. Such a situation is ideal for the use of an analog computer.

EQUATIONS DESCRIBING THE SYSTEM*

$$\frac{dM}{dt} = -k_i M - k_p P_T M - k_m P_T M \qquad \text{(B-1)}$$

$$\frac{dP_T}{dt} = k_i M - k_m P_T M \qquad \text{(B-2)}$$

$$\frac{dT}{dt} = M \qquad \text{(B-3)}$$

SOLUTION PROCEDURE

(i) scaling table for magnitude scaling:

Problem* variable	Estimated max. value	Scale Factor	Computer variable
M	0.4	2.5	$[2.5M]$
P_T	0.04	25	$[25P_T]$
$\dot{M}$	0.4	2.5	$[2.5\dot{M}]$
$\dot{P}_T$	0.04	25	$[25\dot{P}_T]$

*see Appendix A for details

(ii) scaled equations

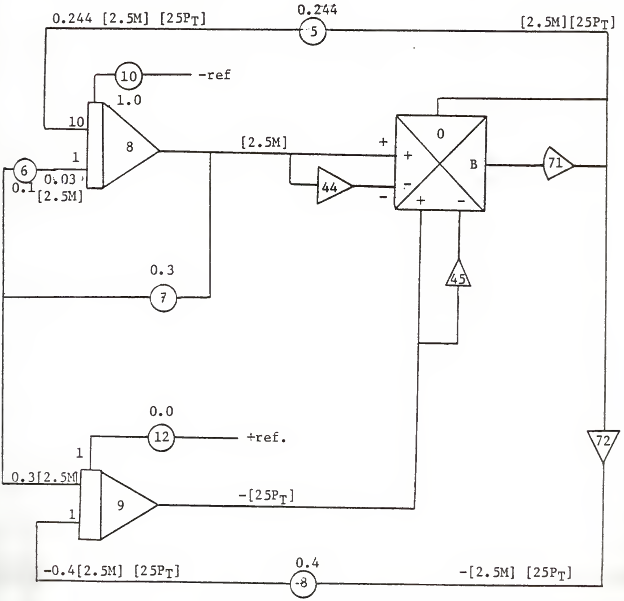
$$[\dot{2.5M}] = -k_i[2.5M] - \frac{k_p}{25}[25P_T][2.5M] - \frac{k_m}{25}[25P_T][2.5M] \qquad \text{(B-4)}$$

$$[\dot{25P_T}] = 10k_i\,[2.5M] - \frac{k_p}{2.5}[25P_T]\,[2.5M] \qquad \text{(B-5)}$$

τ = Mdt (since this is a simple integral, no elaborate scaling is done for τ).

Note that a dot on the variable indicates the first derivative with respect to time.

(iii) Computer circuit:



(i) computer components assignment:

POTS	PARAMETER	AMPS	USE	OUTPUT PARAMETER
5	(kp+km)/250	8		+[2.5M]
6	0.2	9		$-[25P_T]$
7	10ki	44	I	-[2.5M]
8	km/2.5	45	I	$+[25P_T]$
10	[2.5Mo]	71	H	$[2.5M][25P_T]$
12	$[25P_{To}]$	72	I	$[2.5M][25P_T]$

After a static check on the system, the values of M and P_T were plotted for various temperature settings. The potentiometer settings for the various temperatures are shown below. For this problem,

$$M_o = 0.4$$

$$P_{To} = 0$$

$$k_i = 7.29 \times 10^5 \exp(-5102/T)$$

$$k_p = 4.667 \times 10^{10} \exp(-6142/T)$$

$$k_m = 10 \times 10^{10} \exp(-6908/T)$$

Potentiometer settings:

Temp(°K)	5	6	7	8	10	12
280	0.0563	0.10	0.0890	0.0772	1.00	0
285	0.0828	0.10	0.1225	0.1190	1.00	0
290	0.1201	0.10	0.1668	0.1877	1.00	0
295	0.1721	0.10	0.2247	0.2705	1.00	0
300	0.2437	0.10	0.2998	0.3997	1.00	0
305	0.3411	0.10	0.3962	0.5830	1.00	0
310	0.4724	0.10	0.5189	0.8400	1.00	0
315	0.6474	0.10	0.6738	1.1965	1.00	0

The plots for M, P_T' and τ versus time for the various temperatures are presented in Figures C1 through C3.

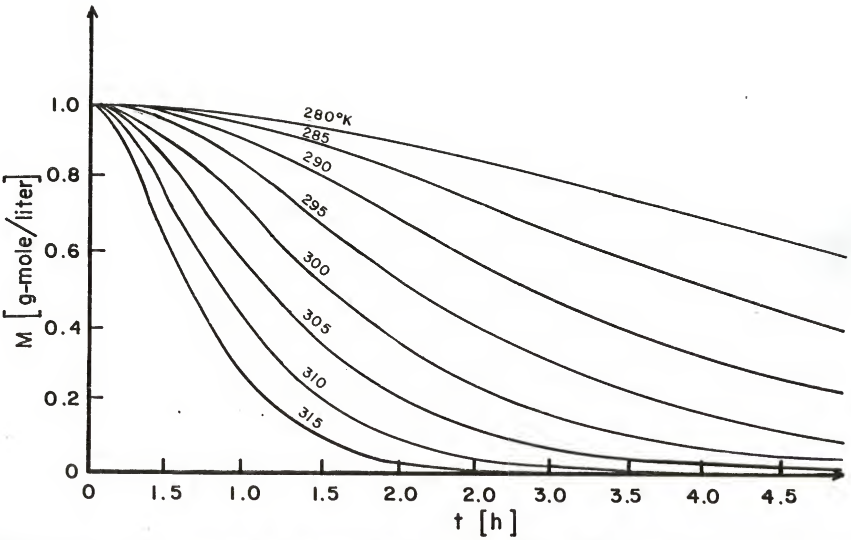


Figure B-1. Monomer concentration vs. time.

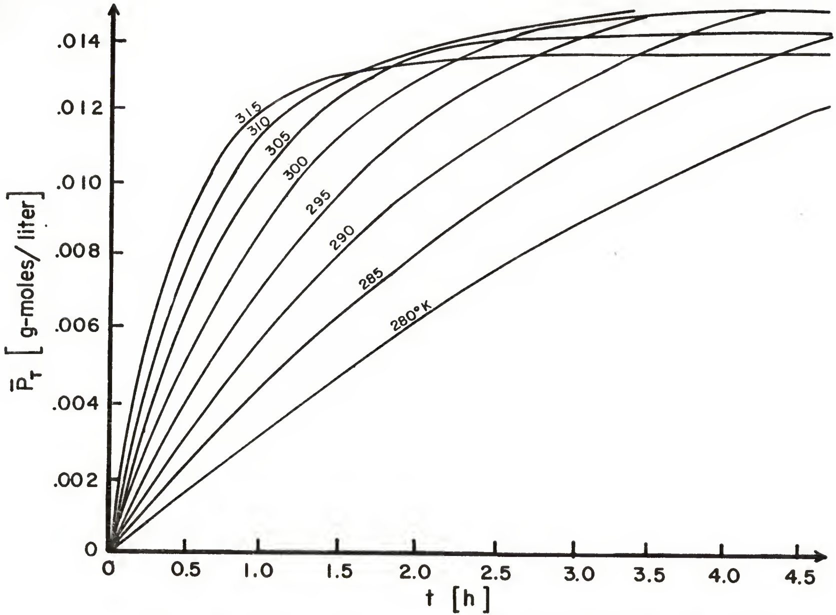


Figure B-2 . Total active polymer concentration vs. time.

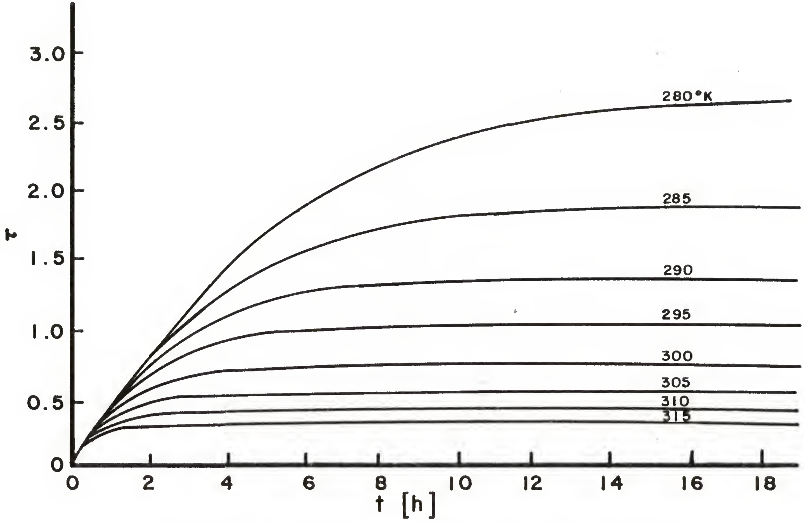


Figure B-3. Transformed time vs. actual hours.

APPENDIX C

CONTINUOUS APPROACH FOR OBTAINING MOLECULAR WEIGHT DISTRIBUTION IN BATCH POLYMERIZATION WITH MONOMER TERMINATION

In the continuous variable approach, the discrete molecular weight distribution (MWD) is approximated by a continuous one, and j is allowed to take on nonintegral values. We let

$$\left.\begin{aligned} P^{\bullet}_{(j)} &= P^{\bullet}_{j} \\ P^{*}_{(j)} &= P^{*}_{j} \end{aligned}\right\} \text{ for integral values of } j \qquad \text{(C-1)}$$

$$P^{\bullet}_{(j)} \text{ and } P^{*}_{(j)} = \text{interpolated values for } j \text{ integer} \qquad \text{(C-2)}$$

This transformation will collapse the set of infinite number of equations (one for each polymer species) into a single equation with the chain length as an independent variable.

CONSERVATION EQUATIONS

$$\frac{dM}{dt} = -k_i M - (k_p + k_m)\, P^{\bullet}_T M \qquad M(0) = M_0 \qquad \text{(C-3)}$$

$$\frac{dP^{\bullet}_1}{dt} = k_i M - (k_p + k_m)\, \dot{P}_1 M \qquad P^{\bullet}_1(0) = 0 \qquad \text{(C-4)}$$

$$\frac{dP^{\bullet}_j}{dt} = k_p M\, (P^{\bullet}_{j-1} - P^{\bullet}_j) - k_m M P^{\bullet}_j \qquad P^{\bullet}_j(0) = 0 \qquad \text{(C-5)}$$

$$\frac{dP^{*}_j}{dt} = k_m M P^{\bullet}_{j-1} \qquad P^{*}_j(0) = 0 \qquad \text{(C-6)}$$

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* See Appendix A for derivation of these equations.

$$\frac{dP_T^\bullet}{dt} = k_i M = k_m P_T^\bullet M \qquad P_T^\bullet(0) = 0 \qquad \text{(C-7)}$$

EIGENZEIT TRANSFORMATION

At this stage it would be convenient to introduce the eigenzeit transformation

$$d\tau = M(t)dt \quad \text{or,} \quad \tau = \int_0^t M(t)dt$$

into Equations (C-3) through (C-7) to obtain

$$\frac{dM}{d\tau} = -k_i - (k_p + k_m)\, P_T^\bullet, \quad M(0) = M_0 \qquad \text{(C-8)}$$

$$\frac{dP_1^\bullet}{d\tau} = k_i - (k_p + k_m)\, P_1^\bullet, \quad P_1^\bullet(0) = 0 \qquad \text{(C-9)}$$

$$\frac{dP_j^\bullet}{d\tau} = k_p(P_{j-1}^\bullet - P_j^\bullet) - k_m P_j^\bullet \qquad P_j^\bullet(0) = 0, \; j \geq 2 \qquad \text{(C-10)}$$

$$\frac{dP_j^*}{d\tau} = k_m\, P_{j-1}^\bullet \qquad P_j^*(0) = 0 \quad j \geq 2 \qquad \text{(C-11)}$$

$$\frac{dP_T^\bullet}{d\tau} = k_i - k_m P_T^\bullet \qquad P_T^\bullet(0) = 0 \qquad \text{(C-12)}$$

SOLUTIONS OF TRANSFORMED EQUATIONS

Solution for $P^{\bullet}_T$

$$\frac{dP^{\bullet}_T}{d\tau} = k_i - k_m P^{\bullet}_T$$

or

$$\frac{dP^{\bullet}_T}{d\tau} + k_m P^{\bullet}_T = k_i$$

Multiplying both sides of this expression by $e^{k_m \tau}$, we have

$$e^{k_m \tau} \frac{dP^{\bullet}_T}{d\tau} + e^{k_m \tau} k_m P^{\bullet}_T = e^{k_m \tau} k_i$$

or

$$\frac{d}{d\tau} [P^{\bullet}_T e^{k_m \tau}] = e^{k_m \tau} k_i$$

or

$$P^{\bullet}_T = e^{-k_m \tau} [\frac{e^{-k_m \tau} k_i}{k_m}] \Bigg|_0^{\tau}$$

$$= e^{-k_m \tau} [\frac{e^{-k_m \tau} k_i}{k_m} - \frac{k_i}{k_m}]$$

or

$$P^{\bullet}_T = \frac{k_i}{k_m} [1 - e^{-k_m \tau}] \qquad \text{(C-13)}$$

Solution for M

$$\frac{dM}{dt} = -k_i - (k_p + k_m)\ P_T^{\bullet}$$

Using Equation (B-13) for P_T we obtain:

$$\frac{dM}{dT} = -k_i - (k_p + k_m)\ \frac{k_i}{k_m}\ [1 - e^{-k_m \tau}]$$

or

$$M - M_0 = -k_i\tau - \frac{(k_p + k_m)k_i}{k_m}\ [\tau + \frac{e^{-k_m \tau}}{k_m}]\Big|_0^{\tau}$$

$$= -k_i\tau - (\frac{(k_p + k_m)k_i}{k_m})\ [\tau + \frac{e^{k_m}}{k_m} - \frac{1}{k_m}]$$

or

$$M = M_0 - k_i\tau - (\frac{k_p + k_m}{k_m})\ k_i[\tau + \frac{e^{-k_m \tau}}{k_m} - \frac{1}{k_m}] \tag{C-14}$$

Solution for $P_1^{\bullet}$

$$\frac{d}{dT}\ (P_1^{\bullet}) = k_i - (k_p + k_m)\ P_1^{\bullet}$$

or

$$\frac{dP_1^{\bullet}}{d\tau} + (k_p + k_m)\ P_1^{\bullet} = k_i$$

Multiplying both sides of this expression by $e^{(k_p + k_m)\tau}$, we have

$$e^{(k_p + k_m)\tau}\ \frac{dP_1^{\bullet}}{d\tau} + e^{(k_p + k_m)\tau}\ (k_p + k_m)P_1^{\bullet} = e^{(k_p + k_m)\tau}\ k_i$$

or

$$\frac{d}{d\tau}\left[P_1^{\bullet}\, e^{(k_p + k_m)\tau}\right] = k_i\, e^{(k_p + k_m)\tau}$$

or

$$P_1^{\bullet} = e^{-(k_p + k_m)\tau}\left[\frac{k_i\, e^{(k_p + k_m)\tau}}{k_p + k_m}\right]\Bigg|_0^{\tau}$$

or

$$P_1^{\bullet} = \frac{k_i}{k_p + k_m}\left[1 - e^{-(k_p + k_m)\tau}\right] \tag{C-15}$$

Solution for $P_j^{\bullet}$

The solution for $P_j^{\bullet}$ is obtained from [1] and is reproduced here. Using the continuous approximation, Equation (C-5) may be rewritten as:

$$\frac{d\dot{P}(j,t)}{dt} = k_p M[\dot{P}(j-1,t) - \dot{P}(j,t)] - k_m M\dot{P}(j,t) \quad P(j,0) = 0,\ j \geq 2 \tag{C-16}$$

We may now assume that $\dot{P}(j-1,t)$ may be expanded into a truncated Taylor series as

$$P^{\bullet}(j-1,t) = P^{\bullet}(j,t) - \frac{\partial}{\partial j} P(j,t)$$

Equation (C-16) may now be reduced to:

$$\frac{\partial \dot{P}(j,t)}{\partial t} + k_p M \frac{\partial P(j,t)}{\partial j} = -k_m MP^{\bullet}(j,t)\ , \quad j \geq 2 \tag{C-17}$$

Boundary conditions are:

B.C.1 $\quad \dot{P}(j,0) = 0$

B.C.2 $\quad \dot{P}(1,t) = \dot{P}_1(t)$

Equation (C-17) may be solved using the method of characteristics (Lapidus, 1962) [6]. Since $P_{(j,t)}$ is a function of both j and t, the total differential of $P_{(j,t)}$ can be written as

$$\frac{\partial \dot{P}(j,t)}{\partial t} dt + \frac{\partial \dot{P}(j,t)}{\partial j} dj = d\dot{P}(j,t) \tag{C-18}$$

Any solution of Equation (C-17) must staisfy Equation (C-18) so by comparing terms of the two equations we have the following set of two ordinary differential equations;

$$\frac{dj(t)}{dt} = k_p \; M(t) \tag{C-19}$$

and

$$\frac{dP(j(t),t)}{dt} = -k_m M(tP(j(t),t)) \tag{C-20}$$

Using the eigenzeit transformation, Equations (C-19) and (C-21) become

$$\frac{dj(\tau)}{d\tau} = k_p \tag{C-21}$$

and

$$\frac{d\dot{P}(j(\tau),\tau)}{d\tau} = -k_m \dot{P}(j(\tau),\tau) \tag{C-22}$$

The solution to Equation (C-21) using the initial condition $j = 1$ when $\tau = 0$ is

$$j = 1 + k_p \tau_j \qquad \text{(C-23)}$$

The solution to Equation (C-22) is

$$\int_{P(1,\tau-\tau_j)}^{P(j,\tau)} \frac{dP^{\bullet}_{(j(\tau),\tau)}}{P_{(j(\tau),\tau)}} = -k_m \int_{\tau-\tau_j}^{T} d\tau$$

or

$$P^{\bullet}_{(j,\tau)} = P^{\bullet}_{(1,\tau-\tau_j)}\, e^{-k_m \tau_m} \quad , \qquad j \geq 1, \qquad \tau \geq \tau_j \qquad \text{(C-24)}$$

Substituting for $P^{\bullet}_1$ from Equation (C-15) results in

$$P^{\bullet}_{(j,\tau)} = \frac{k_i}{k_p + k_m} \left[e^{-k_m \tau_j} - e^{k_p \tau_j - (k_p + k_m)\tau} \right] \qquad \text{(C-25)}$$

T_j may be eliminated from Equation (C-25) using Equation (C-23) to give

$$P^{\bullet}_{(j,\tau)} = \frac{k_i}{k_p + k_m}\, e^{-\frac{k_m}{k_p}(j-1)} - e^{(j-1) - (k_p + k_m)\tau} \quad , \qquad \text{(C-26)}$$

$$j \leq 1 + k_p$$

$$P^{\bullet}_{(j,\tau)} = 0 \; , \quad j \leq 1 + k_p$$

We now have a workable solution for $P^{\bullet}$.

Solution for P_j^*

Using the continuous approximation, Equation (B-11) may be rewritten as:

$$\frac{dP^*_{(j,\tau)}}{d} = k_m P^{\bullet}_{(j-1,\tau)} \qquad \text{for a given value of } j \qquad \text{(C-27)}$$

A single integration will give us an equation for $P^*_{(j,\tau)}$, since $P_{(j,\tau)}$ can be replaced with its value from Equation (C-26). From Equation (C-26) we also know that the chain length of $P^{\bullet}$ is constrained so that the minimum value is 1 and the maximum value is $1+k_p\tau$. Applying this constraint to Equation (C-27), we arrive at the following inequality constraint:

$$1 \leq j-1 \leq 1 + k_p\tau$$

or

$$\frac{j-2}{k_p} \leq \tau \qquad \text{which gives us the lower limit for} \quad .$$

The lower limit for P^* is 0 (its initial value). The justification for using the boundary condition of $P^* = 0$ when $\tau = \frac{j-2}{k_p}$ follows from the fact that at this value of τ, $P^{\bullet} = 0$ and since P^* is formed from P, P^* has to be zero.

$$\int_0^{P^*} dP^* = \frac{k_m k_i}{k_p + k_m} \int_{\frac{j-2}{k_p}}^{\tau} [e^{-\frac{k_m}{k_p}(j-2)} - e^{(j-2) - (k_p + k_m)\tau}] \, d\tau$$

$$= \frac{k_m k_i}{k_p + k_m} [\tau e^{-\frac{k_p}{k_m}(j-2)} \frac{-e^{(j-2) - (k_p + k_m)\tau}}{k_p + k_m}] \Bigg|_{\frac{j-2}{k_m}}^{\tau}$$

$$= \frac{k_m k_i}{k_p + k_m} [(\tau - \frac{j-2}{k_p}) e^{-\frac{k_m}{k_p}(j-2)} \frac{-e^{(j-2) - (k_p + k_m)\tau}}{k_p + k_m}]$$

$$+ \frac{e^{(j-2) - \frac{(j-2)}{k_p}(k_p + k_m)}}{k_p + k_m}]$$

$$P^*_{(j,\tau)} = \frac{k_m k_i}{k_p + k_p} [(\tau - \frac{j-2}{k_p} + \frac{1}{k_p + k_m}) e^{-(j-2)\frac{k_m}{k_p}} - \frac{e^{(j-2) - k_p + k_m)\tau}}{k_p + k_m}] \quad \text{(C-28)}$$

REMARKS

The M.W.D. equation is not written due to its complexity. The various moments are not derived here because it would be much easier to numerically obtain these moments for given values of k_i, k_p, k_m and M_0, using a computer.

APPENDIX D

DISCRETE APPROACH FOR OBTAINING MOLECULAR WEIGHT DISTRIBUTION IN BATCH POLYMERIZATION WITH MONOMER TERMINATION

The molecular weight distribution (MWD) in a polymerization mixture is discrete since only whole numbers of monomer units can add themselves to a growing polymer chain. The chain length, j, of the polymer can therefore take on only integral values. Discreteness of MWD also implies that the concentrations of active and dead polymer species, $P_j^{\bullet}$ and P_j^{*} respectively, are defined only for integral values of j. The approach used here solves the set of infinite number of equations (one for each polymer species) by the method of induction. Thus, the solutions presented here are exact for the given system of differential equations. However, it must be borne in mind that this technique may not necessarily be as effective for another set of differential equations.

CONSERVATION EQUATIONS

$$\frac{dM}{dt} = -k_i M - (k_p + k_m)\, P_T^{\bullet} M, \qquad M(0) = M_0 \tag{D-1}$$

$$\frac{dP_1}{dt} = k_i M - (k_p + k_m)\, P_1^{\bullet} M\ , \qquad P_1^{\bullet}(0) = 0 \tag{D-2}$$

$$\frac{dP_j^{\bullet}}{dt} = k_p M\, (P_{j-1}^{\bullet} - P_j^{\bullet}) - k_m M P_j^{\bullet}, \qquad P_j^{\bullet}(0) = 0 \quad j \geq 2 \tag{D-3}$$

---

*For derivation of these equations see APPENDIX A.

$$\frac{dP_j^*}{dt} = k_m M P_{j-1}^{\bullet} , \qquad P_j^*(0) = 0, \quad j \geq 2 \tag{D-4}$$

$$\frac{dP_T^{\bullet}}{dt} = k_i M - k_m P_T^{\bullet} M , \qquad P_T^{\bullet}(0) = 0 \tag{D-5}$$

EIGENZEIT TRANSFORMATION

At this stage it would be more convenient to introduce the eigenzeit transformation

$$d\tau = M(t)\ dt \quad \text{or} \quad \tau = \int_0^t M(t)\ dt$$

into Equations (D-1) through (D-5) to obtain the following set of equations into the τ space.

$$\frac{dM}{dT} = -k_i - (k_p + k_m)\ P_T' \qquad M(0) = M_o \tag{D-6}$$

$$\frac{dP_1'}{d\tau} = k_i - (k_p + k_m)\ P_1' \qquad P'(0) = 0 \tag{D-7}$$

$$\frac{dP_j'}{d\tau} = k_p\ (p_{j-1}' - P'_j) - k_m P_j' \qquad P_j'(0) = 0\ ,\ j \geq 2 \tag{D-8}$$

$$\frac{dP_j^*}{d\tau} = k_m P_{j-1}' \qquad P_j^*(0) = 0\ ,\ j \geq 2 \tag{D-9}$$

$$\frac{dP_T'}{d\tau} = k_i - k_m P_T' \qquad P_T'(0) = 0 \tag{D-10}$$

SOLUTIONS OF TRANSFORMED EQUATIONS

Solutions for equations (D-6), (D-7) and (D-10) are relatively simple and are given below.*

$$M = m_o - k_i\tau - \frac{k_p + k_m}{k_m} \cdot k_i[\tau + \frac{e^{-k_m\tau}}{k_m} - \frac{1}{k_m}] \qquad \text{(D-11)}$$

$$P_1' = \frac{k_i}{k_p + k_m}[1 - e^{-(k_p + k_m)\tau}] \qquad \text{(D-12)}$$

$$P_T' = \frac{k_i}{k_m}[1 - e^{-k_m\tau}] \qquad \text{(D-13)}$$

Equations (D-8) and (D-9) are more complex than other equations and call for different solution procedures.

Solution for P_j':

j = 1

$$P_1' = (1 - e^{-(k_p + k_m)\tau})\frac{k_i}{k_p + k_m} \qquad \text{(D-14)}$$

j=2

$$\frac{dP_2'}{d\tau} = k_p(P_1' - P_2') - k_m P_2'$$

or

$$\frac{dP_2'}{d\tau} + (k_p + k_m)P_2' = k_p P_1'$$

*Details of these solutions are presented in Appendix C.

Substituting for P_1' from Equation (D-14) we obtain:

$$\frac{dP_2'}{d\tau} + (k_p + k_m)\, P_2' = \frac{k_p\, k_i}{k_p + k_m}\,(1 - e^{-(k_p + k_m)})$$

or

$$\frac{d}{d\tau}[e^{(k_p + k_m)\tau} - P_2'] = e^{(k_p + k_m)\tau} - \frac{k_p\, k_i}{k_p + k_m}\,(1 - e^{-(k_p + k_m)\tau})$$

Integration of both sides will result in:

$$e^{(k_p + k_m)\tau} - P_2' = \frac{k_p\, k_i}{k_p + k_m}\,\frac{e^{(k_p + k_m)}}{k_p + k_m} - \tau + C$$

At $\tau = 0$, $P_2' = 0$; thus,

$$C = -\frac{k_p\, k_i}{(k_p + k_m)^2}$$

$$P_2' = \frac{k_p\, k_i}{k_p + k_m}\,[\frac{1}{k_p + k_m} - e^{-(k_p + k_m)\tau}(\tau + \frac{1}{k_p + k_m})]$$

$j = 3$

$$P_3' = \frac{k_i\, k_p^2}{k_p + k_m}\,[\frac{1}{(k_p + k_m)^2} - e^{-(k_p + k_m)\tau}(\tau^2/2 + \frac{\tau}{k_p + k_m} + \frac{1}{(k_p + k_m)^2})]$$

$j = 4$

$$P_4' = \frac{k_i\, k_p^3}{k_p + k_m}\,[\frac{1}{(k_p + k_m)^3} - e^{-(k_p + k_m)\tau}(\frac{\tau^3}{3!} + \frac{\tau^2}{2!(k_p + k_m)} + \frac{\tau}{(k_p + k_m)^2} + \frac{1}{(k_p + k_m)^3})]$$

By inductive reasoning, a general solution to Equation (D-8) may now be written as

$$P_j' = \frac{k_i}{k_p + k_m} \left[\left(\frac{k_p}{k_p + k_m}\right)^{j-1} - e^{-(k_p + k_m)\tau} \sum_{i=1}^{j} \left(\frac{k_p}{k_p + k_m}\right)^{j-1} \frac{[\tau(k_p + k_m)]^i}{(i - 1)!} \right]$$

Check for validity of Equation (D-14)

If Equation (D-14) is valid, it should be possible to obtain Equation (D-13) (i.e., solution for $\dot{P}_T = \sum_{j-1}^{\infty} P_j'$) from it.

$$\sum_{j=1}^{\infty} P_1' = \left[\sum_{j=1}^{\infty} a^{j-1} - e^{-(k_p + k_m)\tau} \sum_{j=1}^{\infty} \left(a^{j-1} \sum_{i=1}^{j} \frac{[\tau(k_p + k_m)]^i}{(i - 1)!}\right)\right] \frac{k_i}{k_p + k_m}$$

where,

$$a = \frac{k_p}{k_p + k_m}$$

$$\sum_{j=1}^{\infty} a^{j-1} = 1 + a + a^2 + \ldots . = \frac{1}{1-a} \qquad \text{since } a < 1$$

$$\sum_{j=1}^{\infty} \left(a^{j-1} \sum_{i=1}^{j} \frac{[\tau(k_p + k_m)]^2}{(i - 1)!}\right) = \frac{1}{1-a} e^{\tau K_p}$$

Therefore,

$$\sum_{j=1}^{\infty} P_j' = \left[\frac{1}{1-a} - \frac{\exp(-k_p\tau - k_m\tau + k_p\tau)}{1 - a}\right] \frac{k_i}{k_p + k_m}$$

$$= [1 - e^{-\tau k_m}] \frac{k_i}{k_m}$$

which is the same as Equation (D-13).

Solution fo P_j^*

j=2

$$P_2^* = k_m \int_0^\tau P_i d\tau$$

$$= \frac{k_i k_m}{k_p+k_m} [\tau - \frac{1}{k_p+k_m} + \frac{e^{-\tau(k_p+k_m)}}{k_p + k_m}]$$

j=3

$$P_3^* = \frac{k_i k_m}{k_p+k_m} [a\tau - \frac{2a}{k_p+k_m} + \frac{e^{-\tau(k_p+k_m)} a}{k_p + k_m} (2 + \tau(k_p + k_m))]$$

j=4

$$P_4^* = \frac{k_i k_m}{k_p+k_m} [a^2\tau - \frac{3a^2}{k_p + k_m} + \frac{e^{-\tau(k_p+k_m)} a}{k_p + k_m} (3 + \frac{2\tau(k_p+k_m)}{1!} \frac{\tau^2(k_p+k_m)^2}{2!})]$$

j=5

$$P_5^* = \frac{k_i k_m}{k_p+k_m} [a^3\tau - \frac{4a^3}{k_p+k_m} + \frac{e^{-\tau(k_p+k_m)} a^3}{k_p + k_m} (4 + \frac{3\tau(k_p+k_m)}{1!} + \frac{2\tau^2(k_p+k_m)^2}{2!} + \frac{\tau^3(k_p+k_m)^3}{3!})]$$

Once again by inductive reasoning the solution to Equation (D-9) may now be written as

$$P_j^* \frac{k_i k_m}{k_p+k_m} [\tau a^{j-2} - \frac{(j-1)a^{j-2}}{k_p + k_m} + \frac{e^{-\tau(k_p+k_m)} a^{j-2}}{k_p + k_m} \sum_{i=1}^{j-1} (j-2) \frac{[\tau(k_p+k_m)]^{i-1}}{}] , \; j \geq 2 \qquad \text{(D-15)}$$

Finallythe validity of Equation (D-15) is verified.

There is no direct means to check the correctness of the equation for P_j^* so we resort to indirect methods. The molecular weight distribution is:

$$MWD = W(j) = \frac{j\,P_j^{\bullet} + j\,P_j^{*}}{M_0 - M} \qquad \text{(D-16)}$$

The summation of W(j) over all values of j must equal unity if exact equations for $P_j^{\bullet}$, P_j^{*} and M are used. It was shown earlier that equations M and $P_j^{\bullet}$ respectively, so if W(j) equals unity using Equation (D-15) for P_j^{*}, the correctness of this equation is verified. $W(j) = 1$ would also ensure perfect mass balance and in statistical terms would confirm that W(j) is indeed a discrete density function.

$$\sum_{j=1}^{\infty} W(j)$$

$$= \frac{\sum_{j=1}^{\infty} jP_j^{\bullet} + \sum_{j=2}^{\infty} jP_j^{*}}{M_0 - M}$$

$$= \frac{\sum_{j=1}^{\infty} (jP_j^{\bullet} + (j+1)\,P_{j+1}^{*})}{M_0 - M}$$

$$= [\frac{k_i}{k_p+k_m} \sum_{j=1}^{\infty} \{ja^{j-1} - je^{-(k_p+k_m)\tau} a^{j-1} \sum_{i=1}^{j} \frac{[\tau(k_p+k_m)]^{i-1}}{(i-1)!}$$

$$+ \frac{k_i\,k_m}{k_p+k_m} \sum_{j=1}^{\infty} \{\tau a^{j-1}(j+1) - \frac{j(j-1)a^{j-1}}{k_p+k_m} + \frac{(j+1)a^{j-1}e^{-\tau(k_p+k_m)}}{k_p+k_m}$$

$$\cdot \sum_{i=1}^{\infty} (j+1-i) \frac{[\tau(k_p+k_m)]^{i-1}}{(i-1)!} \}]/(M_0-M)$$

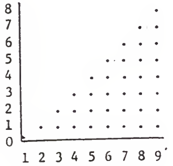
$$= [\frac{k_i}{k_p+k_m} [\sum_{j=1}^{\infty} a^{j-1}\{j+k_m\tau(j+1) - j(j+1)\ (1-a)\}$$

$$- \sum_{j=1}^{\infty} \sum_{i=1}^{j} e^{-\tau(k_p+k_m)} a^{j-1} \frac{[\tau(k_p+k_m)]^{i-1}}{(k-1)!} \quad (j-(j+1)\ (1-a)\ (j+1-i)]]/(M_0-M)$$

$$= \frac{k_i}{k_p+k_m} [\sum_{j=1}^{\infty} a^{j-1}\{j + k_m\tau(j+1) - j(j+1)\ (1-a)\}$$

$$- \sum_{j=1}^{\infty} \sum_{i=1}^{j-1} e^{-\tau(k_p+k_m)} a^{j-1} \frac{[\tau(k_p+k_m)]^{i}}{i!} \quad (j - (j+1)\ (1-a)\ (j-1)]/M_0-M)$$

The summations $\sum_{j=1}^{\infty} \sum_{i=0}^{j-1}$ may be modified such that both summations are in terms of infinite series. This would help in simplifying the analysis. The diagram given below shows the domain of i and j values for the above summations. It is apparent from this figure that for every value of i, j varies from i+1 to ∞.



Thus,

$$\sum_{j=1}^{\infty} (\sum_{i=0}^{j-1}) = \sum_{i=0}^{\infty} (\sum_{j=i+1}^{\infty})$$

A new variable k may be introduced such that $k = j-1$; then

$$\sum_{i=0}^{\infty} \left(\sum_{j=i+1}^{\infty} \right) = \sum_{i=0}^{\infty} \left(\sum_{k=1}^{\infty} \right)$$

or

$$\sum_{j=1}^{\infty} W(j)$$

$$= \frac{k_i}{k_p + k_m} \left[\sum_{j=1}^{\infty} a^{j-1} \{ j + k_m \tau (j+1) - j(j+1)(1-a) \} \right.$$

$$\left. - \sum_{i=1}^{\infty} \sum_{k=1}^{\infty} e^{-\tau(k_p+k_m)} a^{k-1+i} \frac{[\tau(k_p+k_m)]^i}{i!} [(k+i)-(k+i+1)(1-a)k] \right] / M_0 - M)$$

$$= \frac{k_i}{k_p+k_m} \left[\sum_{j=1}^{\infty} a^{j-1} \{ j + k_m \tau (j+1) - j(j+1)(1-a) \} \right.$$

$$\left. - \sum_{i=0}^{\infty} \sum_{k=1}^{\infty} e^{-\tau(k_p+k_m)} a^{k-1} \frac{b^i}{i!} [(k+i)-(k+i+1)(1-a)k] \right] / (M_0 - M)$$

where

$$b = \tau k_p$$

$$\sum_{j=1}^{\infty} (j+1) a^{j-1} = \sum_{j=1}^{\infty} j a^{j-1} + \sum_{j=1}^{\infty} a^{j-1} = \frac{1}{(1-a)^2} + \frac{1}{1-a} = \frac{2-a}{(1-a)^2}$$

$$\sum_{j=1}^{\infty} (j^2+j) a^{j-1} = \sum_{j=1}^{\infty} j^2 a^{j-1} + \sum_{j=1}^{\infty} j a^{j-1} = \frac{1+a}{(1-a)^3} + \frac{1}{(1-a)^2} = \frac{2-a}{(1-a)^2}$$

Thus,

$$\sum_{j=1}^{\infty} W(j)$$

$$= \frac{k_i}{k_p+k_m} \left[\frac{1}{(1-a)^2} + \frac{k_m \tau (2-a)}{(1-a)^2} - \frac{2}{(1-a)^2} + \frac{e^{-\tau k_m}}{(1-a)^2} \right] / (M_0 - M)$$

$$= \frac{k_i}{k_p + k_m} [\frac{k_m \tau (2-a) - 1}{(1-a)^2} + \frac{e^{-\tau k_m}}{(1-a)^2}] / (M_0 - M)$$

$$= [k_i \tau + \frac{k_i}{1-a}(\tau - \frac{1}{k_m} + \frac{e^{-\tau k_m}}{k_m})] / (M_0 - M)$$

The numerator of the last expression above corresponds to the equation for (M_0-M) from Equation (D-11). Thus,

$$\sum_{j=1}^{\infty} W(j) = 1,$$

This verifies the correctness of Equation (D-15).

MOMENTS OF j_i

Any function $F(\cdot)$ with domain the real line and counterdomain [0,1] is defined to be a discrete density function if for some countable set $j_1, j_2, \ldots, j_n, \ldots$

(i) $f(j_2)$ 0 for $i = 1, 2, \ldots$

(ii) $f(j) = 0$ for $j \neq j_i$, $i = 1, 2, \ldots$

(iii) $\Sigma f(j_i) = 1$, where summation is over the points $j_1, j_2, \ldots, j_n$.

The molecular weight distribution, $W(j)$, given by Equation (C-16) satisfies the above three conditions and may, therefore, be treated as a discrete density function.

The moments (or raw moments) of a distribution are the expectations of the powers of the variable which has the given distribution. For the variable j, the rth moment, denoted by $\mu'_r = E(j^r)$, if the expectation exists. Using this definition, the various moments of the variable j may be obtained as

$$\mu'_r = E[j^r] = \sum_{j=1}^{\infty} j^r W(j)$$

or

$$E(j^r) = \frac{k_i}{k_p + k_m}\Big[\sum_{j=1}^{\infty} a^{j-1}\{j^{r+1} + k_m\tau(j+1)^{r+1} - (1-a)(j+1)^{r+1}(j)\}$$

$$-e^{-\tau(k_p + k_m)}\sum_{i=0}^{\infty}\Big(\frac{b^i}{i!}\sum_{k=1}^{\infty} a^{k-1}\{(k+1)^{r+1}$$

$$- k(k+i+1)^{r+1}(1-a)\}\Big)\Big]/(M_0-M) \qquad \text{(D-17)}$$

Table D-1 gives a list of thirteen series summations that will be used while evaluating the first four moments of j.

Table D-1. Series summations used in evaluating moments of j.

$$C_1 = \sum_{j=1}^{\infty} a^{j-1} = \frac{1}{1-a} \qquad C_4 = \sum_{j=1}^{\infty} j^3 a^{j-1} = \frac{1+4a+a^2}{(1-a)^4}$$

$$C_2 = \sum_{j=1}^{\infty} j a^{j-1} = \frac{1}{(1-a)^2} \qquad C_5 = \sum_{j=1}^{\infty} j^4 a^{j-1} = \frac{1+11a+11a^2+a^3}{(1-a)^5}$$

$$C_3 = \sum_{j=1}^{\infty} j^2 a^{j-1} = \frac{1+a}{(1-a)^3} \qquad C_6 = \sum_{j=1}^{\infty} j^5 a^{j-1} = \frac{1+26a+66a^2+26a^3+a^4}{(1-a)^6}$$

$$C_7 = \sum_{j=1}^{\infty} j^6 a^{j-1} = \frac{1+57a+302A^2+302a^3+57a^4+a^5}{(1-a)^7}$$

$$D_1 = \sum_{i=0}^{\infty} b^i/i! = e^b$$

$$D_2 = \sum_{i=0}^{\infty} i b^i/i! = be^b$$

$$D_3 = \sum_{i=0}^{\infty} i^2 b^i/i! = (b^2+b)e^b$$

$$D_4 = \sum_{i=0}^{\infty} i^3 b^i/i! = (b^3+3b^2+b)e^b$$

$$D_5 = \sum_{i=0}^{\infty} i^4 b^i/i! = (b^4+6b^3+7b^2+b)e^b$$

$$D_6 = \sum_{i=0}^{\infty} i^5 b^i/i! = (b^5+10b^4+25b^3+15b^2+b)e^b$$

Mean of the distribution:

Substitution of r=1 into Equation (D-17) results in

$$E(j) = \frac{k_i}{k_p + k_m}\Big[\sum_{j=1}^{\infty}\{a^{j-1}\tau j^2 + k_m\,(j+1)^2 - (1-a)(j+1)^2 j\}$$

$$-e^{-\tau(k_p+k_m)}\sum_{i=0}^{\infty}\Big(\frac{b_i}{i!}\sum_{k=1}^{\infty} a^{k-1}\{(k+i)^2 - k(k+i+1)^2(1-a)\}\Big)\Big]/(M_0-M)$$

$$= \frac{k_i}{k_p + k_m}\Big[\Big\{\frac{1+a}{(1-a)^3} + \frac{k_m\tau(4-3a+a^2)}{(1-a)^3} - \frac{4+2a)}{(1-a)^3}\Big\}$$

$$+e^{-b-\tau k_m}\sum_{i=0}^{\infty}\Big(\frac{b_i}{i!}\Big[\frac{2i}{(1-a)^2} + \frac{a+3}{(1-a)^3}\Big]\Big)\Big]/(M_0=M)$$

note:

$$\sum_{j=1}^{\infty}(j+1)^2 a^{j-1} = \frac{1}{a}\Big[\sum_{k=1}^{\infty} k^2 a^{k-1}\Big] = \frac{4-3a+a^2}{(1-a)^3}$$

$$(1-a)\sum_{j=1}^{\infty}(j+1)^2\, j a^{j-1} = \frac{1-a}{a}\Big[\sum_{k=1}^{\infty} k^3 a^{k-1} - \sum_{r=1}^{\infty} k^2 a^{k-1}\Big] = \frac{4+2a}{(1-a)^3}$$

(k=j+1)

$$E(j) = \frac{k_i}{k_p + k_m}\Big[\frac{k_m\tau(4-3a+a^2)-(a+3)}{(1-a)^3} + e^{-\tau k_m}\Big\{\frac{2b}{(1-a)^2} + \frac{a+3}{(1-a)^3}\Big\}\Big]/(M_0-M)$$

$$\text{mean} = \mu = E(j) \qquad \text{(D-18)}$$

Standard Deviation:

For r=2, Equation (D-17) becomes

$$E(j^2) = \frac{k_i}{k_p+k_m} \left[\sum_{j=1}^{\infty} a^{j-1}\{j^3+k_m\tau(j+1)^3 - (1-a)(j+1)^3(j)\}\right.$$

$$\left. -e^{-b-\tau j_n} \sum_{k=1}^{\infty} a^{k-1}\{(1+1)^3-(k+i+1)^3(k)(1-a)\})\right]/(M_0-M)$$

$$= \frac{k_i}{k_p+k_m} \left[\left\{\frac{1+4a+a^2}{(1-a)^4} + \frac{k_m\tau(8-5a+4a^2-a^3)}{(1-a)^4} - \frac{8+14a+2a^2}{(1-a)^4}\right\}\right.$$

$$\left. +e^{-b-\tau k_m} \sum_{i=0}^{\infty} \left(\frac{b_i}{i!}\ \frac{3i^2}{(1-3)^2} + \frac{3i(a+3)}{(1-a)^3} + \frac{7+10a+a^2}{(1-a)^4}\right\})\right]/(M_0-M)$$

Note that

$$\sum_{j=1}^{\infty} (j+1)^3 a^{j-1} = \frac{1}{a}\left[\sum_{k=1}^{\infty} k^3 a^{k-1} - 1\right] = \frac{8-5a-4a^2-a^3}{(1-a)^4} \qquad (k=j+1)$$

$$(1-a) \sum_{j=1}^{\infty} (j+1)^3 j a^{j-1} = \frac{1-a}{a}\left[\sum_{k=1}^{\infty} k^4 a^{k-1} - \sum_{k=1}^{\infty} k^3 a^{k-1}\right] = \frac{8+14a+2a^2}{(1-a)^4}$$

(k=j+1)

$$E(j^2) = \frac{k_i}{k_p+k_m} \left[\frac{k_m\tau(8-5a+4a^2-a^3) - (7+10a+2a^2)}{(1-a)^4}\right.$$

$$\left. + e^{-\tau k_m} \left\{\frac{3(b^2+b)}{(1-a)^2} + \frac{3b(a+3)}{(1-a)^3} + \frac{7+10a+a^2}{(1-a)^4}\right\}\right]/(M_0-M)$$

$$\text{standard deviation} = \sigma = (E(j^2)-\mu^2)^{1/2} \qquad \text{(D-19)}$$

where μ is the mean and can be obtained using Equation (D-18).

Coefficient of skewness:

For r=3, Equation (D-17) becomes:

$$E(j^3) = \frac{k_i}{k_p + k_m} [\sum_{j=1}^{\infty} a^{j-1}\{j^4 + k_m\tau(j+1)^4 = (1-a)(j+1)^4(j)\}$$

$$= e^{-b- k_m} \sum_{i=0}^{\infty} (\frac{b_i}{i!} \sum_{k=1}^{\infty} a^{k-1}\{(k+1)^4-(k+i+1)^4(k)(1-a)\})]/(M_0-M)$$

$$= \frac{k_i}{k_p + k_m} [\{\frac{1+11a+11a^2+a^3}{(1-a)^5} + \frac{k_m\tau(16+a+11a^2-5a^3+a^4)}{(1-a)^5} = \frac{16+66a+36a^2+2a^3}{(1-a)^5}\}$$

$$+e^{-b-\tau k_m} \sum_{i=0}^{\infty} \{\frac{b_i}{i!} (\frac{4i^3}{(1-a)^2} + \frac{6i^2(a+3)}{(1-a)^3} + \frac{4i(7+10a+a^2)}{(1-a)^4} + \frac{(15+55a+25a^2+a^3)}{(1-a)^5})\}]$$

$$\div (M_0-M)$$

Note that

$$\sum_{j=1}^{\infty} a^{j-1}(j+1)^4 = \frac{1}{a}[\sum_{k=1}^{\infty} k^4 a^{k-1}-1] = \frac{16+a+11a^2-5a^3+a^4}{(1-a)^5} \quad (k=j+1)$$

$$(1-a) \sum_{j=1}^{\infty} (j+1)^4 j a^{j-1} = \frac{1-a}{a} [\sum_{k=1}^{\infty} k^5 a^{k-1} - \sum_{k=1}^{\infty} k^4 a^{k-1}] = \frac{16+66a+36a^2+2a^3}{(1-a)^5} \quad (k=j+1)$$

$$E(j^3) = \frac{k_i}{k_p + k_m}[\frac{k_m\tau(16+a+11a^2-5a^3+a^4) - (15+55a+25a^2+a^3)}{(1-a)^5}$$

$$+e^{-\tau k_m}\{\frac{4(b^3+3b^2+b)}{(1-a)^2} + \frac{6(b^2+b)(a+3)}{(1-a)^3} + \frac{4(b)(7+10a+a^2)}{(1-a)^4}$$

$$+ \frac{(15+55a+25a^2+a^3)}{(1-a)^5}\}]/(M_0-M)$$

$$\text{coefficient of skewness} = \frac{E(j^3)}{\sigma^3} \qquad \text{(D-20)}$$

where σ is the standard deviation and can be estimated using Equation (D-19)

Coefficient of kurtosis:

Setting r=4 in Equation (D-17) results in:

$$E(j^4) = \frac{k_i}{k_p+k_m}\Big[\sum_{j=1}^{\infty} a^{j-1}\{j^5+k_m\tau(j+1)^5 - (1-a)(j+1)^5(j)\}$$

$$-e^{-b-\tau k_m}\sum_{i=0}^{\infty}\Big(\frac{b_i}{i!}\sum_{k=1}^{\infty} a^{k-1}\{(k+i)^5-k(k+i+1)^5(1-a)\}\Big)\Big]/(M_0-M)$$

$$= \frac{k_i}{k_p+k_m}\Big[\Big\{\frac{1+26a+66a^2+25a^3+a^4}{(1-a)^6} + \frac{k_m\tau(32+51a+46a^2-14a^3+6a^4-a^5)}{(1-a)^6}\Big\}$$

$$-\frac{32+262a+342a^2+72a^3+2a^4}{(1-a)^6} + e^{-b-\tau k_m}\sum_{i=0}^{\infty}\Big(\frac{b_i}{i!}\cdot\frac{5i^4}{(1-a)^2}$$

$$+\frac{10i^3(a+3)}{(1-a)^3} + \frac{10i^2(7+10a+a^2)}{(1-a)^4} + \frac{5i(15+55a+25a^2+a^3)}{(1-a)^5}$$

$$+\frac{(31+236a+276a^2+56a^3+a^4}{(1-a)^6}\Big)\Big\}\Big]/(M_0-M)$$

Note that

$$\sum_{j=1}^{\infty} a^{j-1}(j+1)^5 = \frac{1}{a}\Big[\sum_{k=1}^{\infty} k^5a^{k-1}-1\Big] = \frac{32+51a+46a^2-14a^3+6a^4-a^5}{(1-a)^5}$$

$(k=j+1)$

$$(1-a)\sum_{j=1}^{\infty}(j+1)^5ja^{j-1} = \frac{1-a}{a}\Big[\sum_{k=1}^{\infty} k^6a^{k-1} - \sum_{k=1}^{\infty} k^5a^{k-1}\Big]$$

$$= \frac{32+262a+342a^2+72a^3+2a^4}{(1-a)^6} \qquad (k-j+1)$$

$$E(j^4) = \frac{k_i}{k_p+k_m}\left[\frac{k_m\tau(32+51a+46a^2-14a^3+6a^4-a^5)-(31+236a+276a^2+56a^3+a^4)}{(1-a)^6}\right.$$

$$+ e^{-\tau k_m}\{\frac{5(b^4+6b^3+7b^2+b)}{(1-a)^2} + \frac{10(a+3)(b^3+b^3+3b^2+b)}{(1-a)^3}$$

$$+ \frac{10(7+10a+a^2)(b^2+b)}{(1-a)^4} + \frac{5(15+55a+25a^2+a^3)b}{(1-a)^5}$$

$$\left. + \frac{31+236a+276a^2+56a^3+a^4}{(1-a)^6}\}\right]/(M_0-M)$$

$$\text{coefficient of kurtosis} = \frac{E(j^4)}{4} - 3 \qquad \text{(D-21)}$$

where σ is the standard deviation and can be estimated using Equation (D-19).

APPENDIX E

VALUE FUNCTION APPROACH

The objective function is a vector value function in a multi-objective problem, and thus, all feasible decisions cannot be ordered in sequence by the use of the objective function as performed in the case of a uniobjective. We, therefore, need a scalar index representing the decision maker's preference in finally selecting the preferred decision. Alternatively stated, we have introduced a scalar function $v(\underline{f})$, mapping from the objective space to the preference space; the scalar function, $v(\underline{f})$, is termed as a value function.

The form of a value function is chosen subjectively by the decision maker, but it should be a monotonous function with respect to each objective, f_i. In a multiobjective minimization problem, any objective vector, $\underline{f}$, is preferred or indifferent to the objective vector, $\underline{f}+\underline{\delta}$, for any nonnegative vector $\underline{\delta}$. Therefore, it is assumed that the smaller the magnitude of the value function the more preferred it is by the decition maker; thus, the value function, $v(\underline{f})$, must satisfy

$$v(\underline{f}) \leq v(\underline{f}+\underline{\delta}) \quad \text{for} \quad \underline{\delta} \geq \underline{0} \tag{E-1}$$

This condition implies that $v(\underline{f})$ increases monotonically with respect to any component of $\underline{f}$.

Any two objectives, $\underline{f}^1$ and $\underline{f}^2$, are comparable through a value function and satisfy one and only one of the following relationships (Keeney and Faiffa, 1976),

(1) $\underline{f}^1$ is preferred to $\underline{f}^2$ (written $\underline{f}^1 > \underline{f}^2$), i.e., $v(\underline{f}^1) < v(\underline{f}^2)$

(2) $\underline{f}^1$ is indifferent to $\underline{f}^2$ (written $\underline{f}^1 \simeq \underline{f}^2$), i.e., $v(\underline{f}^1) = v(\underline{f}^2)$

(3) $\underline{f}^1$ is less preferred than $\underline{f}^2$ (written $\underline{f}^1 < \underline{f}^2$), i.e, $v(\underline{f}^1) > v(\underline{f}^2)$

Thus, given the value function, $v(\underline{f})$, the preferred decision can be obtained from the following uniobjective minimization problem;

Minimize

$$J = v(\underline{f}(\underline{x})) \qquad \text{(E-2)}$$

In the text, it has been shown that

$$v(\underline{f}) = af_1 + bf_2 + cf_3$$

does not yield a satisfactory solution to the optimization problem. However,

$$v(\underline{f}) = af_1^2 + bf_2^2 + cf_3^2$$

yields a solution. These forms, however, are somewhat arbitrary, and other forms would probably yield a different solution to the optimization problem.

APPENDIX F

ε-CONSTRAINT METHOD

This method is based on the Kuhn-Tucker condition for noninferior decision (Kuhn and Tucker, 1951; Cohon and Marks, 1975). The first equation of the Kuhn-Tucker condition can be written as

$$\left(\frac{\partial f_i}{\partial \underline{x}}\right)^T w_1 + \sum_{i=2}^{n} \left(\frac{\partial f_i}{\partial \underline{x}}\right)^T w_i = 0 \qquad \text{(F-1)}$$

Since only the relative values of the weights are significant, we can assume that w is 1 without loss of generality. Thus, the equation becomes

$$\left(\frac{\partial f_i}{\partial \underline{x}}\right)^T + \left(\frac{\partial \underline{\tilde{f}}}{\partial \underline{x}}\right)^T \underline{\tilde{w}} = 0 \qquad \text{(F-2)}$$

where

$$\underline{\tilde{f}} = [f_2(\underline{x}) \;\; f_3(\underline{x}) \;\; . \; . \; . \;\; f_n(\underline{x})]^T$$

$$\underline{\tilde{w}} = [w_2 \;\; w_3 \;\; . \; . \; . \;\; w_n]^T$$

This equation allows us to interpret w in the second term as a Lagrangian multiplier vector. This interpretation implies that a noninferior decision satisfying the above equation can be obtained by solving the optimization problem:

Minimize

$$J = f_1(\underline{x}) \qquad \text{(F-3)}$$

subject to

$$\underline{\tilde{f}}(\underline{x}) \leq \underline{\varepsilon} \qquad \text{(F-4)}$$

where $\underline{\varepsilon}$ is an (n-1)-dimensional constant vector. $\underline{\varepsilon}$ varies parametrically to yield theset of noninferior decisions. Note that each ε_i must not be smaller than a certain value in order to render the feasible decision set nonempty.

To identify the minimum value of ε_i, the following auxiliary problem with a single objective must be solved.

Minimize

$$J_i = f_i(\underline{x}) \tag{F-5}$$

while other objectives $f_j(\underline{x})$, $j\neq 1$, are entirely neglected. The optimal value of J_i is the minimum value of ε_i.

Though the ε-constraint method appears somewhat intricate, in the main text we have shown how it can be straightforwardly applied to this analysis to yield useful results.

MULTI-CRITERIA ANALYSIS AND OPTIMIZATION
OF CHAIN PROPAGATION WITH MONOMER TERMINATION
POLYMERIZATION IN A BATCH REACTOR

by

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B.S., Kansas State University, Manhattan, Kansas, 1981

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

CHEMICAL ENGINEERING

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1984

ABSTRACT

Most polymerization systems are geared to produce a polymer with a certain molecular weight distribution. It is desirable to produce a polymer with a specified mean and variance while at the same time attaining a high conversion of monomer. Naturally, it is often impossible to attain simultaneously all three objectives and they must be traded off against each other. This introduces the need for multi-criteria analysis and optimization.

To execute such analysis, a numerical representation of the molecular weight distribution need be obtained. This follows directly from a solution of the kinetic equations governing the system. These equations are usually solved either numerically or by resorting to a continuous approximation; however, a new discrete approach is proposed in this work, which requires less computational effort than either of the other methods and gives an exact solution. In the present discrete approach the infinite set of kinetic equations (one for each polymer chain length) is solved by the method of induction. The discrete solution renders a detailed analysis of the trade-off surface possible and the optimization is carried out using the value function approach and the ε-constraint method.