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MATHEMATICAL MODELING OF
UNSTEADY STATE PHOTO-POLYMERIZATION

BY

RONG-FA LIANG

Dissertation submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial fulfillment
of the requirements for the degree of
Doctor of Engineering Science
1984
Title of Thesis:

MATHEMATICAL MODELING OF
UNSTEADY STATE PHOTO-POLYMERIZATION

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Mathematical modeling of unsteady state photopolymerization in an isothermal batch reactor has been investigated. An analytical solution of the distribution of active polymers as a function of reaction time has been determined. It is verified that the quasi-stationary state approximation is valid in the photopolymerization process.

The free radical polymerization of styrene is forced periodically by on-off UV light regulation to the reactor. The effect of operating condition, the ratio of light-off period to light on/off period, on the polydispersity and
molecular weight distribution are theoretically and numerically investigated. Significant broadening on molecular weight distribution can be obtained during the unsteady state process.

Experimental results of polydispersity are compared to a kinetic model of a nonuniformly initiated photopolymerization, which comprises a high dose rate region and a very low dose rate region. Good agreement is obtained between the model and experiments after fitting three parameters.
I wish to express my appreciation to my thesis advisor, Professor Ching-Rong Huang for his skillful guidance and valuable comments on my research. The author is also indebted to other committee members who have given comments of the manuscript.

Gratitude is also extended to my parents, Mr. and Mrs. Yuan-Tsuen Liang, and my wife, Kai-Wan, for their constant encouragement and moral support during my graduate studies.
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CHAPTER 1

INTRODUCTION

The quasi-stationary state approximation (QSSA) for the reactive intermediate species, first introduced by Bodenstein and Lutkemeyer (1), has generally led to essential simplifications in the differential equations which describe the instantaneous behavior of reacting chemical species. In many cases, the use of this approximation has resulted in closed form analytical solutions for simple kinetic schemes which otherwise are mathematically tractable only by numerical techniques.

The errors incurred in free-radical chain addition polymerizations through the use of the popular QSSA are although severe, but fairly common. Biesenberger and Capinpin (2) have concluded that the proposed criteria are reasonably accurate and that in most known free-radical polymerizations only hindered termination might possibly lead to appreciable errors through application of the QSSA. The QSSA is valid virtually over the entire practical range of interest in a chain-addition polymerization from start to finish only when criteria $\sqrt{K_t(T)/K_i} \gg 1$ and $K_t/K_p \gg 1$ are satisfied. If either one is violated, then the QSSA does not apply.

Broadening of a molecular weight distribution (MWD) is of considerable importance. Billmeyer (3) has shown that of two polymers having the same weight average molecular weight the broader distribution material has a more pronounced shear rate-apparent viscosity relation, and the broader distribution
material may be easier to process. Rodriguez (4) showed that the MWD has been important in many diverse applications including flow of melts and solutions, aging and weathering behavior, adhesion, and flocculation. Because of the difficulties involved in measuring a distribution in detail, one shortcut has been to postulate a reasonable mathematical form or model for the distribution and then evaluate the parameters from number and weight-average of polymerization. In general, such a model would give $w_x$, the weight fraction of x-mer, as a function of $x$, $x_w$, $x_n$ and perhaps other parameters.

Thomas and Hagan (5) investigated the effect of MWD on the processing and mechanical properties of polystyrene. With samples taken from injection-molded sheets the narrow distribution was shown to have consistently higher tensile strengths than the broad distribution material. The broad distribution material also exhibited greater anisotropy at all of the molding temperatures. This was attributed to its greater melt elasticity. They also showed that, at constant molecular weight (MW), the rupture elongation of injection-molded polystyrene sheets is increased by narrowing the MWD. They also conducted creep tests at room temperature using a tensile load 5000 psi. Two materials which had the same MW were compared. The total strain in the broad distribution samples exceeded that of the narrow distribution material over most of the test. In addition, the average rupture time of the latter specimens was twice as long as that measured on the broad distribution samples.
Pezzin (6) found a small MWD effect because broadening the distribution tended to increase $n$ when the strain-time relationship was expressed in terms of the Nutting equation: $\varepsilon = kt^n$, where $n$ is an empirical parameter independent of the applied load. Ross (7) investigated the effects of MW and MWD on polypropylene filaments. He found that the crystalline state of undrawn fibers could be correlated with extrusion temperature and MWD; fibers produced from broad distribution resins had a monoclinic structure while the narrow distribution resins gave paracrystalline fibers.

Sato and Ishizuka (8), in an extensive study showed that broad polypropylene samples had a slightly lower melting temperature than fractions with the same viscosity. Narrowing the MWD greatly increases the tear strength when comparisons are made at constant viscosity as shown by Wallach (9). Data show small increases in the heat distortion temperature when the MW is raised and the MWD is reduced (10). Limited data (11) showed that two bimodal narrow distribution polyethylene had much higher burst strengths than a low MW comparison sample which had an unusually broad MWD. Broadening the MWD increased the tensile modulus (12) of polyethylene when comparisons were made at a constant solution viscosity. This was presumably due to the fact that broadening the MWD at constant MW increases the percent crystallinity of a material (13). Notched izod impact strength has been measured on compression-molded polyethylene fraction (14). The results showed that impact strength increases with MW at constant density. It also appeared to increase when
the MWD was reduced because the impact strength of fractions was substantially higher than that measured on whole polymers. Van Schooten et al. (15) have also related the impact strength of polypropylene to MWD. A substantial effect of MWD on the stress cracking of polystyrene was observed (10) because, when comparisons were made at the same MW, it was found that the narrow distribution specimens generally lasted 10-100 times as long as the broad distribution samples.

Most of the work indicates that MW and MWD effects on the modulus and losses of amorphous polymers are quite significant in the rubbery region. Losses normally increased and modulus decreased when low MW or broad distribution materials were tested. Most investigators (17)(18) concluded that broad distributions usually decrease the fold resistance of low MW specimens when comparisons were made between fractions and blends. An MWD effect was noted by Grohn and Friedrich (19) because, at constant viscosity, the flex life of broad distribution samples was shorter than the flex life of fractions.

The molecular weight and the nature of molecular weight distribution significantly affect the physical and rheological properties of a polymer. In a continuous stirred-tank reactor, however, the MWD breadth is fixed by the conversion and the residence time of a reactor present. The effect of widening in MWD can be gotten through mixing polymer streams from different reactors. An alternate approach is to employ an unsteady process in the reactor itself to change the MWD. Cyclic
operation of polymerization reactors, where one or more process inputs are intentionally varied periodically with time, can significantly enlarge the scope of available MWD's beyond those attainable at steady state.

Ray (20) examined the effects of periodic operation of both condensation and free-radical polymerization reactor under sinusoidal perturbations in monomer feed concentration. He has reported a narrowing of the MWD for a condensation polymerization scheme and a broadening of the MWD for a free-radical polymerization scheme, when compared with the steady state. Yu (21) simulated a periodically operated continuous stirred-tank reactor (CSTR) for the thermal polymerization of styrene and found the MWD to increase at low frequencies, but all effects were damped at higher frequencies because of the limited heat transfer relative to the thermal capacitance of commercial reactors. Lawrence and Vasudevan (22) considered the performance of a polymerization reactor in a very slow sinusoidal manner for both simple addition and combination-termination mechanisms. They have observed a broadening of the MWD for variations in either monomer or initiator feed compositions. Konopnicki and Kuester (23) developed a mechanism which includes transfer to both monomer and solvent as well as termination by combination and disproportionation. They examined the influence of non-isothermal operation and viscosity effects on the MWD of the polymer produced as well as induced sinusoidal and square-wave forcing functions on initiator feed concentrations and jacket temperature. The phenomena of gel-effect using correlations valid for solutions of viscosity less than thirty poise
were considered in the mechanism. The patent disclosure of Claybaugh et al. (24) reports experimental data for cyclic operation of a Ziegler catalyzed polypropylene reactor. Besides providing an increase in the polydispersity, periodic variations in the feed concentration of a chain transfer agent hydrogen produced an approximately uniform product.

Based upon the relative value of the period $\tau$ and the characteristic response time $\tau_C$ of the system, four different families of periodic operation may be distinguished (25):

a. Process Life Cycle ($\tau \gg \tau_C$): Providing the full initial capacity is restored, a periodic state is established. The problems here are relatively straightforward unless the operating and maintenance intervals are of similar magnitudes.

b. Quasi-Steady Periodic Operation ($\tau \gg \tau_C$): This class is distinguished from the previous one in that here cycling is intentional. In both, straightforward determination of periodic reactor performance follows by application of the quasi-steady state approximation. Thus, this class is dominated by steady-state operating characteristics.

c. Intermediate Periodic Operation ($\tau \sim \tau_C$): When the period is of the order of the system's dynamic response time, transient behavior assumes significant importance. The analytical Capabilities available for this class are limited; it is consequently one of the most interesting, since the performance shifts caused by transient phenomena are not always expected and are occasionally quite large.
d. Relaxed Steady-State Operation ($\tau \ll \tau_c$): A forced oscillation with very small amplitude often results when the input varies rapidly relative to the response time. Thus, to a good approximation the state of the system may be considered time-independent.

A few investigations of the performance of photochemical reactors have been reported. To predict reactor performance, the light intensity profile throughout the reactor should be specified as well as mass balance considerations regarding the reacting species. Since the radial light model is simple in every respect, it is worthwhile to know under what conditions it may be applied. Matsuura and Smith (26) proposed a diffuse light model to represent the light intensity profile within an elliptical reactor. Harada et al. (27) also pointed out in their study of an elliptical reactor that the radial light model should be carefully employed in the calculation of the light intensity profile, and they presented a two-dimensional light distribution model. Zolner and Williams (28) proposed a three-dimensional light intensity distribution model based on an external, cylindrical sleeve radiation source, within which the reactor is centered. This model contains an adjustable parameter which is the location of the source relative to the reactor. If the emitting source is placed exactly at the reactor surface, then the model predicts an infinite radiation flux at that point.

Jacob and Dranoff (29) reported a further detailed study to determine the quantum efficiency of the photohydrolysis as a function of light intensity and reactant concentration, and analyzed
the reaction data on the basis that the lamp is a normal line source. Cerdá et al. (30) presented an extensive model of the elliptical-reflector reactor light distribution which accounts for the geometric properties of lamp, reflector, and reactor. The radiation arriving at any point within the reactor is traced back to the lamp surface, either via a direct path or by means of a single reflection at the elliptical-reflector surface. Jain, Graessley, and Dranoff (31) considered the reaction of the photo-polymerization of styrene in ethylbenzene solvent. Light in the near ultraviolet was used to promote this reaction with the aid of a suitable photoinitiator. They derived an expression for the intensity as a function of position in the annulus considering radiation emanating in all directions from the lamp taken as a line source.

The complete determination of the kinetic behavior of isothermal photoreactions in the presence of strong absorption of radiation often requires a knowledge not only of chemical rates but also of rates of mixing in the distribution of radiation attenuation. The response to the non-uniform initiation resulting from strong absorption depends on the reaction mechanism and on the relative rates of mass transfer, reaction, and radiation absorption. Depth-dose curves of UV light in polymer solution show a sharp decrease in dose with increasing depth. This leads to a nonuniform distribution of dose rate in the reaction system. Thus only a part of reactor is irradiated.

Yemin and Hill (32) reported that the rate of the nonuniformly
initiated photopolymerization of methylmethacrylate in bulk increases with agitation speed. Chen and Hill (33) carried out a theoretical study on effects of nonuniform initiation on reaction rate and distribution of product in continuous stirred-tank reactors. They assumed the dose rate distribution to be exponential and showed that nonuniformity of dose rate distribution and the radical life time relative to mixing time have large effects. The molecular weight distribution was calculated to be unimodal, and the position of the peak moves to the lower molecular weight with increase of the nonuniformity and/or the mixing time relative to the radical life time.

Muller et al. (34) examined the molecular weight distribution of the polymer to observe a bimodal distribution. They also found that a low molecular weight species was in appreciable relative amount at low stirring speeds, and its amount became smaller with increasing stirring speeds. Kawakami and Isbin (35) reported the effects of agitation on radiolysis of chloral hydrate aqueous solution under nonuniform dose rate distribution. They reported a simplified analysis based mainly on the intermittent irradiation of fluid elements caused by recirculating flow in a stirred-tank reactor. In radiation induced reaction, a control with a higher accuracy can be attained by the dose rate regulation, and because dose rate is easily changed and affects the rate of radical formation directly, the concentration of radical reaches a new steady-state value within a very short time. Since the heat generation is proportional to the radical concentration, the
temperature control by dose rate regulation is expected to give good response.

Continuous flow chemical reactors involving exothermic reactions are often operated autothermally; that is, the operating temperature is sustained entirely by the heat generated by reaction. Van Heerden (36) studied the characteristics of such processes and showed that they may possess multiple steady states and that some steady states are unstable to small perturbations. A number of theoretical studies treating control and start-up problems as well as the general nature of steady and unsteady behavior in various reactor models followed Van Heerden's work. The majority of these were focused on the continuous flow, stirred-tank reactor for reasons of mathematical tractability.

Since all kinds of polymerization are inevitably accompanied by a rapid increase in viscosity, an explosive acceleration in rate is observed by Nishimura (37), especially in bulk polymerizations. The abnormal increases in the rate of conversion, the degree of polymerization, and the mean lifetime of polymer radicals have been inclusively recognized as the gel effect, which usually causes the multiplicity behavior in the polymerization. It is also demonstrated mathematically by Knorr and O'Driscoll (38) that steady-state mass balance solutions are possible at three levels of conversion in free-radical polymerization of a CSTR.

The overall objectives of this study are concerned with the periodic operation of continuous stirred-tank polymerization reactors in an attempt to give more flexibility in the molecular
weight distribution of a polymer. The ultraviolet light on and off regulation to a CSTR is considered. Analytical studies of polydispersity and molecular weight distribution are carried out on the control of a CSTR. A mathematical model is developed to correlate the effects of mixing on nonuniformly initiated polymerization. This model is then verified by data of experiments conducted in a laboratory scale reactor. In order for the quasi-stationary state approximation to be applicable, a theoretical study of free-radical concentration history in a batch reactor must be developed. Emphasis is also placed on the reactor performance characteristics and reactor responses to perturbation from steady states.
CHAPTER 2

ACTIVE POLYMER CONCENTRATION VERSUS TIME
FOR PHOTOPOLYMERIZATION IN BATCH REACTOR

For polymerization the number of reactions involved is conceptually infinite. However, for simulation work, the memory of any computer is finite so that some truncation of the number of reactions to be considered is needed. A method for the calculation of the active polymerization concentrations with respect to reaction time for the photopolymerization is developed in this chapter. The method involves the use of a generating function which reduces the infinite number of differential equations to one differential equation followed by evaluation of an integral.

Theoretical Development

All of the reactor models developed in this investigation employ the following reaction steps in styrene polymerization.

(a) Initiation
By absorption of UV light by sensitizer
\[ S \xrightarrow{I_{as}} 2S^\cdot \]
\[ S^\cdot + M \xrightarrow{K_d} R_1^\cdot \]
By thermal decomposition of monomer
\[ M \xrightarrow{K_i} R_1^\cdot \]

(b) Propagation
\[ R_j^\cdot + M \rightarrow R_{j+1}^\cdot \]
(c) Termination

\[
\begin{align*}
R_j^* + R_i^* & \xrightarrow{K_{tc}} P_{i+j} \\
R_j^* + R_i^* & \xrightarrow{K_{td}} P_j + P_i
\end{align*}
\]

(d) Chain Transfer To the Monomer

\[
R_j^* + M \xrightarrow{K_f} P_j + R_1^*
\]

where \( R_{i,j}, P_{i,j}, S \) and \( M \) are the concentrations of active polymer, dead polymer, sensitizer and monomer, respectively.

In main radical chain polymerizations it is found that the deactivation can occur by two distinct mechanisms, namely, combination and disproportionation. Termination by combination has been shown to be the predominant mechanism for polystyrene. (39) The chain transfer rate constant, \( K_f \), can be neglected due to a very small magnitude as compared to other rate constants.

The active polymer material balances for a batch reactor yield the equations

\[
\begin{align*}
\frac{dR_1^*}{dt} &= \Omega_i - K_p MR_1^* - K_t R_1^* R_1^* \\
\frac{dR_2^*}{dt} &= K_p MR_1^* - K_p MR_2^* - K_t R_2^* R_1^* \\
\frac{dR_3^*}{dt} &= K_p MR_2^* - K_p MR_3^* - K_t R_3^* R_1^*
\end{align*}
\]

(1) (2) (3)
with the additional monomer balance

\[ \frac{dM}{dt} = - \Omega_i - K_p M \sum R_i \]  

(5)

In our system the thermal initiation rate is negligible in comparison to the photosensitized initiation rate, i.e.,

\[ \Omega_i = 2 \phi_s I_{as} \]

where \( \phi_s \) is the quantum yield of sensitizer. Also the termination rate constant can be expressed as

\[ K_t = K_{td} + K_{td} \]

The generating function for this system is defined as

\[ \Phi(w, t) = \sum_{j=1}^{\infty} R_j(t) w^j \]  

(6)

where \( w \) is a parameter. Differentiating equation (6) partially with respect to \( t \) gives

\[ \frac{\partial \Phi}{\partial t} = \frac{dR_1}{dt} w + \frac{dR_2}{dt} w^2 + \frac{dR_3}{dt} w^3 + \ldots \]

Then substitution into equations (1)–(3) yields

\[ \frac{\partial \Phi}{\partial t} = \Omega_i w + (- K_p M + K_p M w - K_t \sum R_i) \phi \]  

(7)

Letting

\[ q_1 = K_p M - K_p M w + K_t \sum R_i \]

and

\[ q_2 = \Omega_i w \]

Equation (7) then becomes

\[ \frac{\partial \Phi}{\partial t} + q_1 \phi = q_2 \]

Multiplying by integrating factor

\[ e^{q_1(t)} \]

\[ Q_1(t) \]
where

\[ Q_1(t) = \int_{t_2=0}^{t} q_1(t_2) \, dt_2 \]

The solution is found to be

\[
\phi(t) = \int_{t_1=0}^{t} q_2(t_1) \, e^{\int_{t_1}^{t} K_{t_1} \, dt_2} \, dt_1
\]

\[
= \int_{t_1=0}^{t} q_2(t_1) \, e^{-\int_{t_1}^{t} (Q_1(t)-Q_1(t_1))} \, dt_1
\]

(8)

and

\[
Q_1(t) - Q_1(t_1) = \int_{t_2=t_1}^{t} q_1(t_2) \, dt_2
\]

By inserting the defined \( q_1 \) and \( q_2 \) into the equation (8), then it can be written

\[
\phi(t) = \int_{t_1=0}^{t} \left\{ \Omega_i \cdot \frac{1}{w} \right\} \, e^{\int_{t_1}^{t} (K_p M + K_t \sum R_i) \, dt_2} \times
\]

\[
\int_{t_1}^{t} K_p M \, dt_2 \}
\]

Also

\[
\int_{t_1}^{t} K_p M \, dt_2 = w \sum_{j=1}^{\infty} \frac{1}{(j-1)!} \left( \int_{t_1}^{t} K_p M \, dt_2 \right)^{j-1} w
\]

Thus, by comparing with the defined equation (6), it follows that

\[
R_j(t) = \int_{t_1=0}^{t} \Omega_i \cdot e^{\int_{t_1}^{t} (K_p M + K_t \sum R_i) \, dt_2} \frac{1}{(j-1)!} \times
\]

\[
\left( \int_{t_1}^{t} K_p M \, dt_2 \right)^{j-1} dt_1
\]

(9)
Thus if one knows the concentration of monomer, $M$, and total active polymer, $\sum R_i$, as a function of the reaction time, these integrals may be evaluated and the concentration $R_j$ of the $j$-th active polymer obtained.

The isothermal batch reactor is assumed to be perfectly mixed and, for the photochemical case, fully illuminated. If $I_o$ is the flux of radiation incident upon the reactor, and the total rate of light absorption is averaged over the path length of the light (42), then

$$I_{as} = I_o \left\{ \frac{\epsilon_s \epsilon_s}{\epsilon_s + \epsilon_m + \sum \epsilon_{Pi} \epsilon_{Pi}} \right\} \{ 1 - e^{-\epsilon_s \epsilon_s + \epsilon_m + \sum \epsilon_{Pi} \epsilon_{Pi}} \} \frac{L}{L}$$

(10)

where $\epsilon_m$, $\epsilon_s$, and $\epsilon_{Pi}$ are the molar absorptivities of monomer, sensitizer, and dead polymer, respectively, and $L$ is the total path length of the light in the reactor. Quantum yield, $\phi_s$, is also estimated to be 0.072 g-moles/Einstein for styrene sensitized by benzoin methyl ether from measured polymerization rates at full illumination and perfect mixing. Assumptions employed in the use of equation (10) are: axial nonuniformities due to light attenuation are negligible, the rates of reaction are uniform throughout the reactor and that the fraction of light absorbed by the monomer and the polymer is constant. In addition, for the present case, the following assumptions are made:

1. The light absorbed by the monomer and the polymer are negligible, i.e., $\epsilon_s \epsilon_s >> \epsilon_m + \sum \epsilon_{Pi} \epsilon_{Pi}$
2. The light intensity absorbed by the sensitizer is assumed to be constant and of the magnitude of order 10, hence, the exponential term in equation (10) may be neglected.
By applying the assumptions (1) and (2), the corresponding relation between the total rate of light absorption and $I_o$ is insensitive to chemical compositions, i.e.,

$$I_{as} = \frac{I_o}{L} = \text{constant}$$

and the initiation rate via absorption of ultraviolet light is

$$\Omega_i = 2\phi_s I_{as} = \frac{2\phi_s I}{L}$$

Combining equations (4) and (5), and using the initial conditions that

$$\sum R_i(t) = 0 \quad \text{at} \quad t = 0$$

$$M(t) = M_o \quad \text{at} \quad t = 0$$

we get

$$\sum R_i(t) = \sqrt{\frac{\Omega_i}{K_t}} e^{2\sqrt{\frac{\Omega_i}{K_t}} t} \left( e^{2\sqrt{\frac{\Omega_i}{K_t}} t - 1} \right)$$

$$\sum R_i(t) = \sqrt{\frac{\Omega_i}{K_t}} e^{2\sqrt{\frac{\Omega_i}{K_t}} t} + 1$$

Since $e^{2\sqrt{\frac{\Omega_i}{K_t}} t}$ >> 1, thus $\sum R_i(t)$ is approximately given by

$$\sum R_i(t) = \sqrt{\frac{\Omega_i}{K_t}}$$  \hspace{1cm} (11)

And then

$$M(t) = \frac{B}{K_p} e^{\frac{\sqrt{\Omega_i / K_t}}{K_p}} e^{-K_p \sqrt{\Omega_i / K_t} t} - \frac{\Omega_i}{K_p \sqrt{K_t / \Omega_i}}$$  \hspace{1cm} (12)

where we define

$$B = \Omega_i + K_p \sqrt{\Omega_i / K_t} \cdot M_o$$
Substituting equations (11) and (12) into (9), one gets

\[ R_j(t) = \frac{\Omega_i}{(j-1)!} \int_{t_1=0}^{t} F(t)G(t) \, dt_1 \quad (13) \]

in which

\[ F(t) = e^{-\int_{t_1}^{t} (K_p M + K_t \sum R_i) \, dt_2} \]

\[ = H(t) e^{-\frac{B K_t}{\Omega_i K_p} e^{-K_p \sqrt{\Omega_i/K_t} t_1}} \]

\[ G(t) = \left( \int_{t_1}^{t} K_p M \, dt_2 \right)^{j-1} \]

\[ = (P(t) + \sqrt{\Omega_i K_t} t_1 + \frac{B K_t}{\Omega_i K_p} e^{-K_p \sqrt{\Omega_i/K_t} t_1})^{j-1} \quad (14) \]

with

\[ H(t) = e^{\frac{B K_t}{\Omega_i K_p} e^{-K_p \sqrt{\Omega_i/K_t} t}} \]

\[ P(t) = \frac{B K_t}{\Omega_i K_p} e^{-K_p \sqrt{\Omega_i/K_t} t} - \sqrt{\Omega_i K_t} t \]

so that the equation (13) may then be written

\[ R_j(t) = \frac{\Omega_i H(t)}{(j-1)!} \int_{t_1=0}^{t} e^{-c_1 t_1} \{ c_3 t_1 + c_1 e^{-c_2 t_1} + P(t) \}^{j-1} \, dt_1 \quad (15) \]

where

\[ c_1 = \frac{B K_t}{\Omega_i K_p} \]

\[ c_2 = K_p \sqrt{\Omega_i/K_t} \]

\[ c_3 = \sqrt{\Omega_i K_t} \]
Equation (15) can be expressed with the series expansion of the exponential function

\[ H(t) = e^{c_1 t} \]

\[ P(t) = -c_1 e^{-c_2 t} - c_3 t \]

Equation (15) can be expressed with the series expansion of

\[
R_j(t) = \frac{\Omega_i H(t)}{(j-1)!} \sum_{n=0}^{\infty} \left( -\frac{c_1 e^{-c_2 t}}{n!} \right) \left\{ c_3 t_1 + c_1 e^{-c_2 t_1 + P(t)} \right\}^{j-1} t_1^{j-1} \int_{t_1=0}^{t} \cdots \int_{t_{j-1}=0}^{t} \cdots \cdots \cdots \int_{t_{j-1}=0}^{t} \right. \]

One can use binomial series to represent equation (16):

\[
R_j(t) = \frac{\Omega_i H(t)}{(j-1)!} \sum_{m=0}^{j-1} \frac{c_3^m c_1^{j-1-m}(j-1)!}{m!(j-1-m)!} \sum_{n=0}^{\infty} \left( -\frac{c_1}{n!} \right)^n \times \]

\[
\times \left( \int_{t_1=0}^{t} \cdots \int_{t_{j-1}=0}^{t} \left( t_1 + P(t) \right)^m e^{-c_2(j-1-m+n)t_1} dt_1 \right) \]

Finally, the active polymer concentration can be expressed as:

\[
R_j(t) = \Omega_i e^{c_1 t} \sum_{m=0}^{j-1} \frac{c_3^m c_1^{j-1-m}}{m!(j-1-m)!} \sum_{n=0}^{\infty} \left( -\frac{c_1}{n!} \right)^n \times \]

\[
\times \left[ e^{-c_2(j-1-m+n)t} \sum_{\gamma=0}^{m} (-1)^\gamma \frac{\frac{c_1}{c_3} e^{-c_2 t}}{m!(m-\gamma)!} (m-\gamma)! \{ c_2^2 (m+1-n) \} \right] \text{ for } m+1-n-j \neq 0 \]

\[
\text{or } \left\{ \left[ \frac{1}{m+1} \left( \frac{c_1}{c_3} e^{-c_2 t} \right)^{m+1} - \left( \frac{c_1}{c_3} e^{-c_2 t} - t \right)^{m+1} \right] \right\} \text{ for } m+1-n-j = 0 \]
The use of the generating function enables one to compute the concentration of any j-mer in the photopolymerization system without calculating the concentration of all of its precursors.

The accuracy of the approximation depends on the number of exponential terms used in the equation (17). From the computational standpoint some remarks must be made. The value $C_1$ in the equation is very large and computation with such large value becomes very tedious and difficult on the computer. Therefore, some calculation techniques should be applied. For large degree $j$ of polymerization, however, Stirling's formula may be used to combine with the other exponential function.

To evaluate a definite integral by formal methods is often difficult, even when the function is of a relatively simple analytical form. For these intractable case, some other approach is necessary. An obvious alternative is to find a function that is both a suitable approximation of a given function and simple to integrate formally.

An integral approximation is employed as follow:

Since $K_p \sqrt{\Omega_i / K_t} >> 1$ and $B \sqrt{K_t / \Omega_i} >> \sqrt{\Omega_i K_t}$, reasonable for the process, then equations (12) and (14) may be written as

$$M(t) = \frac{B \sqrt{K_t / \Omega_i}}{K_p} (1 - K_p \sqrt{\Omega_i / K_t}) - \frac{\Omega_i}{K_p \sqrt{K_t / \Omega_i}}$$

$$= \frac{B \sqrt{K_t / \Omega_i}}{K_p} - B t_2 - \frac{1}{K_p} \sqrt{\Omega_i K_t}$$
The active polymer concentrations with respect to time may thus be written

\[ F(t) = e^{\frac{1}{2}BK_p t^2} - B\sqrt{K_t/\Omega_i}t \times e^{\frac{1}{2}BK_p t^2} \]

\[ G(t) = \left\{ \left(\frac{1}{2}BK_p t_1^2 - B\sqrt{K_t/\Omega_i}t_1\right) + \left(B\sqrt{K_t/\Omega_i}t - \frac{1}{2}BK_p t^2\right) \right\}^{-1} \]

so that equation (13) becomes

\[ R_j(t) = \frac{\Omega_i}{(j-1)!} \int_0^t e^{A_1 t - A_2 t_1 + A_2 t + A_1 t} \left(A_2 t_1^2 + A_1 t t_1 + A_1 t - A_2 t^2\right)^{j-1} dt_1 \]

where

\[ A_1 = B\sqrt{K_t/\Omega_i} \]

\[ A_2 = \frac{1}{2}BK_p \]

Let

\[ y = A_1 t - A_1 t_1 + A_2 t_1^2 - A_2 t^2 \]

then

\[ dt_1 \approx -dy/A_1 \quad (A_1 >> A_2) \]

The active polymer concentrations with respect to time may thus be written

\[ R_j(t) = -\frac{\Omega_i}{A_1 (j-1)!} \int_0^t e^{-y} y^{j-1} dy \]

Which may be integrated, and then it on rearranging becomes

\[ R_j(t) = \frac{\Omega_i}{A_1} \left\{ 1 + e^{-(A_1 t - A_2 t^2)} \sum_{\gamma=0}^{j-1} (-1)^{\gamma+1} \frac{(A_1 t - A_2 t^2)^{j-1-\gamma}}{(j-1-\gamma)! (\gamma+1)} \right\} \]
In the equation, the exponential term in the brace is very small and can be negligible in comparison to unity.

Equations (1)—(5) are integrated numerically for a time step of $10^{-3}$ sec. with the iteration running from $t = 0$ sec. to $t = 2000$ sec.. Table 1 gives the results of the concentrations of several active polymer species for different times with $I_0 = 11.7 \times 10^{-8}$ Einsteins/sec-cm$^2$ by using the thermophysical properties data shown in Table 3 (43). In our system, on the one hand, the step size should be chosen small enough to achieve required accuracy. It must depend on the value of active polymer concentrations. On the other, it should be as large as possible in order to keep rounding error under control and to avoid spending too much time in operation. The numerical method has the disadvantage that the concentration of any particular active polymer may be calculated with calculating all of its precursors.

The active polymer concentrations have also been calculated numerically in thermal polymerization with the initiation rate, $2K_1M^3$, shown in Table 2.

In CSTR

Similarly for a CSTR, a term $\frac{R_i}{\theta}$ ($i=1, 2, 3, \cdots$), has to be subtracted from the right hand side of equations (1)—(4).

\[
\frac{dR_1}{dt} = \Omega_i - K_p MR_1 \cdot - K_t R_1 \cdot \sum_i R_i - \frac{R_1}{\theta}
\]

\[
\frac{dR_2}{dt} = K_p MR_1 \cdot - K_p MR_2 \cdot - K_t R_2 \cdot \sum_i R_i - \frac{R_2}{\theta}
\]
Here, $\theta$ is the reactor residence time. By using the same procedure of generating function used for batch reactor, eq. (9) is also modified for a CSTR by adding $\frac{1}{\theta}$ as shown below

\[
\frac{dR_3}{dt} = K_p M R_2 - K_p M R_3 - K_t R_3 \frac{\Sigma R_i}{\theta} - \frac{R_3}{\theta}
\]

Data Analysis

From the results of numerical calculation with the given kinetic rate constants, the values of $\frac{dR_1}{dt}$, $\omega_1$, $K_p M R_1$, and $K_t R_1 \Sigma R_i$ in equation (1) are the orders of $10^{-13}$, $10^{-6}$, $10^{-6}$, and $10^{-7}$, respectively. $\frac{dR_1}{dt}$ therefore, can be neglected because it is of a very small magnitude as compared to other values in the equation for the photopolymerization process. Similarly, $\frac{dR_2}{dt}$, $\frac{dR_3}{dt}$, etc. can also be set equal to zero. Furthermore, the values of
Table 1

$R_1$, $R_2$, $R_3$, and $\Sigma R_i$ Concentrations vs. Time on Batch UV-Light Photopolymerization

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>$R_1$ (g-mole/l) $(x 10^8)$</th>
<th>$R_2$ (g-mole/l) $(x 10^8)$</th>
<th>$R_3$ (g-mole/l) $(x 10^8)$</th>
<th>$\Sigma R_i$ (g-mole/l) $(x 10^6)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.13904108625813</td>
<td>0.13795610829565</td>
<td>0.13687959675419</td>
<td>0.17700573197387</td>
</tr>
<tr>
<td>400</td>
<td>0.14045031464019</td>
<td>0.13934315516603</td>
<td>0.13824472337207</td>
<td>0.17700535899700</td>
</tr>
<tr>
<td>600</td>
<td>0.141888066204197</td>
<td>0.14075804101094</td>
<td>0.13963701968698</td>
<td>0.17700501088455</td>
</tr>
<tr>
<td>800</td>
<td>0.14334062207170</td>
<td>0.142187266667931</td>
<td>0.14104319150528</td>
<td>0.17700466277142</td>
</tr>
<tr>
<td>1000</td>
<td>0.14480814740148</td>
<td>0.14363097505643</td>
<td>0.14246337219015</td>
<td>0.17700431465760</td>
</tr>
<tr>
<td>1200</td>
<td>0.14629083307410</td>
<td>0.14508935069317</td>
<td>0.14389773607905</td>
<td>0.17700399140844</td>
</tr>
<tr>
<td>1400</td>
<td>0.147788883617386</td>
<td>0.14656254044636</td>
<td>0.14534642008346</td>
<td>0.17700369302408</td>
</tr>
<tr>
<td>1600</td>
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<td>0.14680948112640</td>
<td>0.17700336977378</td>
</tr>
<tr>
<td>1800</td>
<td>0.15082380569465</td>
<td>0.14954646038835</td>
<td>0.14827993310543</td>
<td>0.17700309625384</td>
</tr>
<tr>
<td>2000</td>
<td>0.15236093776075</td>
<td>0.15105734001183</td>
<td>0.1497649585467</td>
<td>0.17700279786797</td>
</tr>
</tbody>
</table>

Conditions: $I_o = 11.7 \times 10^{-8}$ Einsteins/sec-cm$^2$
Temp. = 338°K
$L = 5$ cm
Table 2

R₁, R₂, R₃, and $\sum R_i$ Concentrations vs. Time on Batch Thermal Polymerization

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>R₁ (g-mole/l) (x 10¹²)</th>
<th>R₂ (g-mole/l) (x 10¹²)</th>
<th>R₃ (g-mole/l) (x 10¹²)</th>
<th>$\sum R_i$ (g-mole/l) (x 10⁸)</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td>.30236213308467 (max.)</td>
<td>.30233428895217 (max.)</td>
<td>.30230644738381</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>.30235271969351</td>
<td>.30232487664627</td>
<td>.30229703616304</td>
<td>.20939635716963 (max.)</td>
</tr>
<tr>
<td>60</td>
<td>.3023304282606</td>
<td>.30230520208859</td>
<td>.30227736391487</td>
<td>.20938024116560</td>
</tr>
<tr>
<td>120</td>
<td>.30231336499904</td>
<td>.30228552657150</td>
<td>.30225769070746</td>
<td>.20936899792529</td>
</tr>
<tr>
<td>180</td>
<td>.30229368638226</td>
<td>.30226585026470</td>
<td>.30223801671038</td>
<td>.20935775406368</td>
</tr>
<tr>
<td>240</td>
<td>.30227373474986</td>
<td>.3022459097567</td>
<td>.30221806976446</td>
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</tr>
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<td>300</td>
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<td>.30219812610544</td>
<td>.20933496683385</td>
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<tr>
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<td>.30220591362867</td>
<td>.30217808710628</td>
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<tr>
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<td>.30215814117218</td>
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<tr>
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<td>.30216817238772</td>
<td>.30214035030035</td>
<td>.20930196637413</td>
</tr>
</tbody>
</table>

Conditions: Temp. = 338°K
\( \frac{d}{dt} \sum R_i \), \( \Omega_i \), and \( K_t (\sum R_i)^2 \) in equation (4) are the order of \(-10^{-15}\), \(10^{-6}\), and \(10^{-6}\), respectively. Therefore, the QSSA is valid for values of the kinetic rate constants and can be applied to our photopolymerization system.
CHAPTER 3

EXPERIMENTAL

Experimental investigation of the polymerization of styrene with initiation by photodissociation of sensitizer (benzoin methyl ether) was made in a continuous stirred-tank reactor. Experimental apparatus and procedures are described as follows:

(44)

Experimental Apparatus

The experimental apparatus is shown schematically in Figure 1. The reactor is a stirred baffled stainless steel vessel (7cm ID and 6 cm height). The reactor volume is partially illuminated with a light beam through the bottom of the reactor. The reactor was maintained at a constant temperature by the use of a constant temperature bath which circulated water in the jacket. For the control system, instead of a temperature controller, an UV spectrophotometer was used to monitor the reaction conversion. By providing an upper and lower limits of conversion, shutter mechanism can be opened or closed manually. Agitation speed was measured through the use of a tachometer.

The optical system provides a parallel ultraviolet beam. A 1000 watts Mercury Xenon arc lamp is housed in an air cooled lamp housing and supplied with power by a regulated DC power supply (manufactured by Oriel Optical Co.). The housing contains a mirror which increases the effective intensity of the lamp. A focusing lens mounted in the housing collects the light and produces a collimated beam which passed through a water filter. The filtered beam is reflected upward by a mirror and passes
Figure 1. Arrangement of Experimental Apparatus of Isothermal CSTR
through neutral density filter to improve its cross-sectional uniformity and then through a color glass filter which transmits light with a wavelength of 310-420 nm. An iris diaphragm located under the neutral density filter is used to provide nonuniform irradiation.

The isothermal batch operation was also included in our experimental investigation. The reactor used for the batch systems is the same as the one in isothermal continuous stirred-tank reactor while the inlet and outlet were stopped.

**Experimental Procedure**

(1) Purification of Styrene Monomer

The styrene monomer used for this study is from Aldrich Chemical Co. of 99% purity inhibited with 10-15 ppm of p-tert-butylcatechol. Inhibitor was removed from styrene monomer by slow consecutive dropwise passage through a column (5 cm diameter and 60 cm length) packed with activated alumina. A second column packed with silica gel was connected to the first one and assigned to remove moisture from the monomer. Inhibited monomer was allowed at a flow rate about 1 c.c./min. through these two columns. The purified monomer then flew into a collection flask which was nitrogen blanketed, and nitrogen was bubbled through the monomer to remove oxygen which can react with the monomer. The sensitizer, benzoin methyl ether (manufactured by Aldrich Chemical Co.) is added immediately before the start of run. The experimental investigations involve styrene polymerization by using benzene as solvent.
Purification of benzene (99.9% purity by J.T. Baker Co.) is the same as styrene monomer purifying procedure.

(2) Measurement of Polymer Conversion

Polystyrene is insoluble in methanol while the monomer, dimers, and trimers are soluble. But, as the amounts of dimers, trimers, and impurities from the styrene present in polystyrene are relatively small, the methanol-soluble portion is principally styrene and can be taken as a measured of its presence. Conversion is determined by the gravimetric technique presented by Boundy and Boyer (16) which involves precipitating the polymer in an excess of methanol. About two to three grams of reaction mixture is collected from the reactor. The mixture is then added to 100 c.c. methyl alcohol (99.9% purity, spectrometric grade by Aldrich Chemical Co.) which is vigorously stirred to precipitate the product polymer. For more than 30% of conversion, approximate 5 c.c. of p-dioxane is required to add to the solution before precipitation. The precipitate is filtered with a buchner funnel. The polymer is then dried in a vacuum oven at 70°C for at least 12 hours to remove traces of the monomer and place it in the desiccator to cool. The conversion can thus be determined. The gravimetric method of determining the conversion by ascertaining the methanol-soluble fraction of the product gives satisfactory result, but the time involved is lengthy. An ultraviolet spectrophotometric procedure has been developed for the rapid and accurate determination of monomer in polystyrene. (45) It will reduce the time required for an analysis to approximately 10
minutes is of interest for UV light on-off regulation purposes.
The procedure can be described as follows: The concentration of styrene monomer dissolved in tetrahydrofuran (THF) at the order of 0.001% wt, monomer absorbance at wave length 250 μm varies linearly with concentration. Thus, the fraction of styrene in a mixture is:

\[
g = \frac{\text{absorbance of unknown sample}}{\text{absorbance of pure styrene}}
\]

and the conversion is

\[
x = 1 - g
\]

A Bausch and Lamb spectronic 710 spectrophotometer was used for conversion measurement.

(3) Measurement of Incident Light Intensity

The light intensity of the Mercury Xenon Arc Lamp was measured using the potassium ferrioxalate actiometer developed by Parker (46) and Hatch and Parker (47). The experiment was carried out in a acrylic reactor (3.8 cm diameter and 5 cm height) and all the measurements were made in a dark room. The recommended procedures were as follows:

1. Solution A: Dissolve 0.006 molar of \(\text{K}_3\text{Fe(C_2O_4)_3}\cdot\text{H}_2\text{O}\) (2.947 g) into 100 c.c. of 1 N \(\text{H}_2\text{SO}_4\) and then diluted to 1000 c.c.
2. Solution B: Dissolve 0.1 g of 1,10 phenathroline into 100 c.c. of \(\text{H}_2\text{O}\) (0.1% wt).
3. Solution C: 600 c.c. of 1 N sodium acetate is added to 360 c.c. of 1 N \(\text{H}_2\text{SO}_4\) and then diluted to 1000 c.c.
4. 25 c.c. of A is added into the reactor and under exposure of ultraviolet light. In this experiment, exposing time
ranges from 3 sec. to 20 sec. for each run.

5. 1 c.c. of solution A from the reactor is then transferred to a 25 c.c. calibrated flask. Two c.c. of solution B is added followed by a volume of 0.5 c.c. of buffer solution C, and then diluted to 25 c.c.

6. After making up and mixing, the liquid was allowed to stand for one hour for complete reaction and then it was measured at 5100 Å and 9°C with a spectrophotometer.

The incident light intensity can be varied by changing the number of neutral density filters or the opening of the iris diaphragm. Experimental results of incident light intensity is summarized in Table 3a. A plot of I₀ versus time is given in Figure 2.

(4) Determination of MWD

The molecular weight distribution of product polymer was measured via gel permeation chromatography (GPC) manufactured by Water Associates model 6000Å. In the GPC process, the molecules are separated based on some measure of molecular size; the large molecules penetrate into the gel the least and hence are eluted first. The chromatograph was equipped with five µstyrgeal columns. The columns were packed in series having permeability limits of $10^6$, $10^5$, $10^4$, $10^3$ and 500 Å's. If it is deemed necessary to obtain numerical data, attention must be paid to: Sample preparation, sample injection, column selection, calibration method, baseline determination, and computation.
<table>
<thead>
<tr>
<th>Run</th>
<th>No. of N.D. Filters</th>
<th>Reactant Volume (c.c.)</th>
<th>Time (sec)</th>
<th>Absorbance</th>
<th>$I_0 \times 10^{-8}$ (Eins/sec-cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>25</td>
<td>3</td>
<td>0.135</td>
<td>15.75</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>24</td>
<td>6</td>
<td>0.278</td>
<td>15.57</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>23</td>
<td>9</td>
<td>0.415</td>
<td>14.85</td>
</tr>
<tr>
<td>4</td>
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<td>12</td>
<td>0.563</td>
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</tr>
<tr>
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<td>15</td>
<td>0.712</td>
<td>13.96</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>25</td>
<td>3</td>
<td>0.100</td>
<td>11.67</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>24</td>
<td>6</td>
<td>0.212</td>
<td>11.87</td>
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<tr>
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<td>1</td>
<td>23</td>
<td>9</td>
<td>0.339</td>
<td>12.13</td>
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<tr>
<td>9</td>
<td>1</td>
<td>22</td>
<td>12</td>
<td>0.441</td>
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<td>20</td>
<td>18</td>
<td>0.738</td>
<td>11.48</td>
</tr>
<tr>
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<td>2</td>
<td>25</td>
<td>5</td>
<td>0.103</td>
<td>7.24</td>
</tr>
<tr>
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<td>2</td>
<td>24</td>
<td>10</td>
<td>0.207</td>
<td>6.99</td>
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<td>0.284</td>
<td>6.12</td>
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<td>0.403</td>
<td>6.23</td>
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<td>10</td>
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<td>23</td>
<td>15</td>
<td>0.234</td>
<td>4.83</td>
</tr>
<tr>
<td>18</td>
<td>3</td>
<td>22</td>
<td>20</td>
<td>0.331</td>
<td>4.89</td>
</tr>
</tbody>
</table>
Figure 2. Experimental Measurements of Incident Light Intensity
The columns were calibrated by using six standard polystyrene samples (supplied by Water Associates) with molecular weights of $4 \times 10^3$, $9 \times 10^3$, $5 \times 10^4$, $2.4 \times 10^5$, $4.7 \times 10^5$ and $2.7 \times 10^6$. Calibrations were made monthly and the calibration curve was typical and over the range of interest, which is expressible as a semi-logarithmic relation of molecular weight with elution volume. A typical calibration curve is given in the Figure 3. A least-squares regression was employed to calibrate the standard curve of a quadratic equation. The polymer sample was prepared at a concentration of 0.025% wt dissolved in toluene (Aldrich-spectrophotometric grade) to minimize the possibility of viscous fingering caused by high concentrations of polymer, particularly high molecular weight polymers. Before the sample was dissolved, the solvent was filtered to remove any material likely to clog the columns. The solution was injected at a flow rate of 2.5 c.c./min. through the 30.5 cm long and 0.3 cm diameter stainless steel columns. From the GPC elution curves, marked the retention volumes for the start ($V_i$) and finish ($V_f$) of the polymer chromatogram. Drew a linear baseline from before $V_i$ to after $V_f$. Once the baseline has been determined, measure peak heights to three significant figures for about 30 equally spaced points along the GPC curve. Tabulate these data under the headings shown below.

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retention Volume or Counts</td>
<td>Height (cm)</td>
<td>Chain Length</td>
<td>Column 2 / Column 3</td>
<td>Column 2 * Column 3</td>
</tr>
</tbody>
</table>

* Column 3
Figure 3. Molecular Weight vs. Elution Volume for GPC Calibration
After calibrating, list chain lengths in column 3 and determine chain length averages by the following equations:

\[ \bar{X}_n \text{ (Number Average Chain Length)} = \frac{\sum \text{column 2}}{\sum \text{column 4}} \]
\[ \bar{X}_w \text{ (Weight Average Chain Length)} = \frac{\sum \text{column 5}}{\sum \text{column 2}} \]

Polydispersity then is the ratio, \( \frac{\bar{X}_w}{\bar{X}_n} \).
CHAPTER 4

PERIODIC OPERATION OF A PHOTOPOLYMERIZATION IN A CONTINUOUS STIRRED-TANK REACTOR

Most polymerization processes are carried out either steady state or batchwise. In this chapter a more general class of processes, the periodic process, is considered. This class exhibits some properties which may be of great practical value. The theory of periodic processes includes the theory of steady-state and batch processes, since these two types can be regarded as special cases of periodic processes. The dynamic behavior of many chemical systems can be represented by a set of differential equations:

\[ \frac{d x_i}{dt} = f_i(x_1, x_2, \ldots, x_n; y_1, y_2, \ldots, y_r) \]

\( i = 1, 2, \ldots, n \)

where the \( x \)'s denote state and the \( y \)'s denote control variables. If the control variables are given function time, and if the initial values \( x_i(0) \) of the state variables are known, the state of the system can be calculated as a function of time by integrating differential equations.

Another mode of operation is to use periodic control function \( y(t) \) - that is, functions satisfying the relations:

\[ y_j(t+\tau) = y_j(t) \]

for any \( t \)

\( j = 1, 2, \ldots, r \)

where \( \tau \) is the period for the cyclic operation.
In our photopolymerization system there are five state variables \( n=5 \) and one control variable \( r=1 \). Here, we control either the UV light intensity incident upon the reactor or flow rate to the reactor. The UV light intensity in the process is described as

\[
I_o(t) = \begin{cases} 
0 & t \in (0, r) \quad \text{i.e., UV light is off} \\
I_o & t \in (r, \tau) \quad \text{i.e., UV light is on}
\end{cases}
\]

where \( r \) is a parameter restricted by

\[
0 < r < 1
\]

and \( I_o(t) = I_o(t+\tau) \)

Owing to a course of the polymerization reactors, a typical product has a distribution of polymers with vastly varying chain length. Therefore two subjects will be presented in this study: polydispersity, which is often used as a measure of breadth of the molecular weight distribution, and molecular weight distribution itself.

**Polydispersity of Periodic Operation**

In the polymerization there are in principle an infinite number of reactions taking place and one could write an infinite set of differential equations representing them. Fortunately, the properties of a molecular weight distribution can usually be characterized by the polymer moments and the equations for these are quite simple. The reaction occurs in a continuous stirred-tank reactor, as shown schematically in Figure 4. The procedure is accompanied by three assumptions for a bulk
Figure 4. Schematic Diagram of Reaction Vessel
photopolymerization carried out in a CSTR:
(1) The reactor is perfectly mixed, isothermal and operated
under stationary state conditions.
(2) The kinetic constants of the various reaction steps are
independent from the chain length at low steady state;
i.e., no gel effect occurs.
(3) No density variation occurs in the reactor; i.e., the
reaction volume is constant.

**Mathematical Equations for Polymer Moments**

The material balance equations for the reactor are:
For total active polymer:

\[
\frac{d\bar{R}_i}{dt} = \Omega_i - K_t (\bar{R}_i)^2 - \bar{R}_i
\]

(1)

For monomer:

\[
\frac{dM}{dt} = \frac{M_0}{\theta} - \Omega_i - K_p M \bar{R}_i - \frac{M}{\theta}
\]

(2)

where $\theta$ is the residence time of reactor.

The $i$th moment of the distribution, $Q_i$, is defined as

\[
Q_n = \sum_{i=1}^{\infty} i^n \bar{P}_i
\]

The number and weight average chain length, $X_n$ and $X_w$, are
experimentally measurable and are related to the leading moments:

\[
X_n = \frac{Q_1}{Q_0} = \frac{\sum iP_i}{\sum P_i}
\]

\[
X_w = \frac{Q_2}{Q_1} = \frac{\sum i^2P_i}{\sum iP_i}
\]
The distribution of chain sizes is described in terms of polydispersity, PD, which is defined as

\[ PD = \frac{\langle X_w \rangle}{\langle X_n \rangle} \]

The \( \langle P_i \rangle \), \( \langle iP_i \rangle \), and \( \langle i^2P_i \rangle \) are, respectively, the zeroth, first, and second moments of the dead polymer size distribution in the outlet stream, and can be expressed as (33)

\[ \frac{d\langle P_i \rangle}{dt} = \frac{1}{2}\Omega_i - \frac{\langle P_i \rangle}{\theta} \]  
(3)

\[ \frac{d\langle iP_i \rangle}{dt} = M(\frac{K}{K_{1/2}^t})\Omega_i - \frac{\langle iP_i \rangle}{\theta} \]  
(4)

\[ \frac{d\langle i^2P_i \rangle}{dt} = 3M^2\frac{K^2}{K_{t}} + 5M\frac{K}{K_{1/2}^t}\Omega_i + 2\Omega_i - \frac{\langle i^2P_i \rangle}{\theta} \]  
(5)

For a steady operation of reactor by continuous irradiation at a fixed dose rate \( I_o \), total radical concentration \( \Sigma R_{i,s} \), monomer concentration \( M_s \), and moments of the dead polymer size distribution \( \Sigma P_{i,s} \), \( \Sigma iP_{i,s} \), and \( \Sigma i^2P_{i,s} \) are calculated by setting the derivatives equal to zero in equations (1)—(5).

**UV Light Off**

After several hours of steady operation, the UV light is shut off by closing the shutter while maintaining other operating conditions at its previously set value. At this time, the thermal initiation may only occur in this system, thus \( \Omega_i = 2K_{i}M^3 \) (43). Neglecting the first and third terms relative to the second term on the right of equation (1), the equation is then written as...
\[ \frac{d\Sigma R_i}{dt} = -K_t (\Sigma R_i)^2 \]

instead of the more exact expression.

With the initial condition

\[ \Sigma R_i(0) = \Sigma R_{is} \]

then the differential equation is easily integrated:

\[ \Sigma R_i(t) = \frac{\Sigma R_{is}}{1 + K_t t \Sigma R_{is}} \]

\[ = \frac{1}{K_t t} \quad (K_t t \Sigma R_{is} \gg 1) \quad (6) \]

The monomer concentration can be solved by substituting eq. (6) into eq. (2). Also the thermal initiation rate is negligible in comparison to other terms on the right of eq. (2). The following expression is obtained

\[ \frac{dM}{dt} = \frac{M \circ}{\theta} - \left(\frac{1}{\theta} + \frac{K_d}{K_t t}\right)M \]

with the initial condition

\[ M(0) = M_s \]

Since \( t \rightarrow 1 \), the approximate solution for \( M(t) \) is

\[ M(t) = C_1 + C_2 e^{-t/\theta} \quad (7) \]

where

\[ C_1 = M_\circ \]

\[ C_2 = M_s - M_\circ \]
Substitute equation (7) into equations (3)—(5). The three initial conditions appropriate for this system are

\[ \sum P_i(0) = \sum P_{is} \]
\[ \sum iP_i(0) = \sum iP_{is} \]
\[ \sum i^2P_i(0) = \sum i^2P_{is} \]

By solving equations, we obtain

\[ \sum P_i(t) = K_i (C_1^3 \theta + 3C_1^2C_2^{t/\theta} - 3C_1^2 \theta - \frac{C_3^3}{2} - \frac{3t/\theta}{2}) \]
\[ + \left( \sum P_{is} - K_i \theta (C_1^3 - 3C_1^2C_2^{t/\theta} - \frac{C_3^3}{2}) e^{t/\theta} \right) \]

(8)

\[ \sum iP_i(t) = \sqrt{2} K_p \sqrt{K_i/K_t} C_1^{\theta} e^{5/2}(t/\theta) \left\{ \sum_{n=0}^{\infty} (2.5) \frac{C_2}{n} \frac{1}{1-n} e^{(1-n) t/\theta} \right\} + \]
\[ + 2.5 \frac{C_2}{C_1^{\theta}} e^{t/\theta} + \left( \sum P_{is} - \sqrt{2} K_p \sqrt{K_i/K_t} C_1^{\theta} e^{5/2}(t/\theta) \left\{ \sum_{n=0}^{\infty} (2.5) \frac{C_2}{n} \frac{1}{1-n} e^{(1-n) t/\theta} \right\} \right) \]

(9)

\[ \sum i^2P_i(t) = \frac{K^2}{K_t} (C_1^3 \theta + 2C_1^2C_2^{t/\theta} - C_2^{t/\theta}) \]
\[ + 5\sqrt{2} K_p \sqrt{K_i/K_t} C_1^{2\theta} e^{5/2}(t/\theta) \left\{ \sum_{n=0}^{\infty} (2.5) \frac{C_2}{n} \frac{1}{1-n} e^{(1-n) t/\theta} \right\} + 2.5 \frac{C_2}{C_1^{\theta}} e^{t/\theta} \]
\[ + \left( \sum i^2P_{is} - \frac{K^2}{K_t} (C_1^3 - C_2^{2\theta}) - 5\sqrt{2} K_p \sqrt{K_i/K_t} C_1^{2\theta} e^{5/2}(t/\theta) \left\{ \sum_{n=0}^{\infty} (2.5) \frac{C_2}{n} \frac{1}{1-n} e^{(1-n) t/\theta} \right\} \right) \]
\[ \times e^{-t/\theta} \]

(10)
Replacing t by \( r\tau \) in eqs. (6)—(10), we can obtain the state values at the end of light-off period, \( \sum R_{ir\tau}, M_{ir\tau}, \sum P_{ir\tau}, \sum iP_{ir\tau} \) and \( \sum i^2P_{ir\tau} \).

**UV Light On**

After the light-off period, the UV light is turned on by opening the shutter. Similarly, mass balances for total active polymer, monomer, and moments of dead polymer in this period are expressed as equations (1)—(5) with the initiation rate, \( \Omega_i = 2\phi_1 I_{as} \). The five boundary conditions in this period are

\[
\begin{align*}
\sum R_i(r\tau) &= R_{ir\tau} \\
M(r\tau) &= M_{r\tau} \\
\sum P_i(r\tau) &= P_{ir\tau} \\
\sum iP_i(r\tau) &= iP_{ir\tau} \\
\sum i^2P_i(r\tau) &= i^2P_{ir\tau}
\end{align*}
\]

Thus, the final solutions for equations (1)—(5) are

\[
\sum R_i(t) = \frac{\sqrt{\Omega_i/K_t}}{1 + \frac{2\sqrt{\Omega_i K_t (t-r\tau)}}{(Ce \sqrt{\Omega_i K_t (t-r\tau)} \gg 1)}}
\]

\[
M(t) = \frac{C_3}{C_4} \left[1 - e^{-C_4(t-r\tau)}\right] + M_{r\tau} e^{-C_4(t-r\tau)} = C_5 - C_6 e^{-C_4(t-r\tau)}
\]
Similarly replacing $t$ by $\tau$ in equations (11)--(15), we can obtain the state values.

It is very often difficult to calculate and to measure the differential molecular weight distribution of a polymer but relatively easy to determine the moments of the molecular weight distribution. Therefore, these moments are often used to characterize the polymer.
Relations Among Cycles

Once the solutions of monomer concentration and polymer moments as a function of reaction time for the first cycle have been obtained analytically, an attempt to set up the cycle-variant for above properties in periodic operation is made.

For Cycle 1, where \( 0 \leq t \leq r \tau \)

\[
I_0(t) = 0 \quad \text{and} \quad M(0) = M_s
\]

Thus integration of equation (2) yield,

\[
M|_{n=1} = C_1 + C_2 e^{-t/\theta}
\]

\[
I_0(t)=0
\]

and

\[
M|_{n=1} = A + BM_s
\]

\[
t=r \tau
\]

where

\[
A = \frac{M_0 (1 - e^{-r \tau/\theta})}{-r \tau/\theta}
\]

\[
B = e^{-r \tau/\theta}
\]

Similarly, for cycle 1, where \( r \tau \leq t \leq \tau \)

\[
I_0(t) = I_0 \quad \text{and} \quad M_{r \tau} = M|_{n=1}
\]

Thus integration of equation (2) for the new limits yields,

\[
M|_{n=1} = C_5 - C_6 e^{-C_4(t-r \tau)}
\]

\[
I_0(t)=I_0
\]

and

\[
M|_{n=1} = D + EM_{r \tau}
\]

\[
t=r \tau
\]

\[
= G + HM_s
\]
where
\[ D = \frac{C_3}{C_4} \left(1 - e^{-C_4 \tau (1-r)}\right) \]
\[ E = e^{-C_4 \tau (1-r)} \]
\[ G = D + EA \]
\[ H = BE \]

After repeating the above procedure for a number of cycles, the following relationships can be found.

\[ M_{n=n}^{l=n-2} = P \sum_{k=0}^{l=n-1} H^l + H^{n-1}(A + BM_s) \quad (16) \]

and

\[ M_{n=n}^{l=n-1} = G \sum_{k=0}^{l=n-1} H^l + H^n M_s \quad (17) \]

where \( n = \) cycle number; 2, 3, \( \cdots \), \( \infty \)

and

\[ P = A + BD \]

Since \( H = BE < 1 \), so that

\[ \sum_{k=0}^{n-1} H^k = \frac{1-H^n}{1-H} \]

which can be substituted into equations (16) and (17).

Expressions for the moments of dead polymer are similarly derived from the equations (8)—(10) and (13)—(15).

For cycle 1, where \( 0 \leq t \leq r \tau \)

\[ \sum_{i=1}^{n=1} P_i |_{t=r \tau} = S_1 + S_2 \sum_{i} P_{is} \]

\[ \sum_{i=1}^{n=1} P_i |_{t=t} = S_3 + S_4 \sum_{i} P_{ir \tau} \]
\[ \sum_{i=1}^{n} P_{i} |_{n=1} = P_{1} + P_{2} \sum_{i}^{n} P_{is} \]
\[ \sum_{i=1}^{n} P_{i} |_{n=1} = P_{3} + P_{4} \sum_{i}^{n} P_{i} r_{n} \]
\[ \sum_{i=1}^{n} i P_{i} |_{n=1} = X_{1} + X_{2} \sum_{i}^{n} i P_{is} \]
\[ \sum_{i=1}^{n} i^{2} P_{i} |_{n=1} = X_{3} + X_{4} \sum_{i}^{n} i^{2} P_{i} r_{n} \]

and for cycle \( n \)

\[ \sum_{i=1}^{n} P_{i} |_{n=n} = R_{3} \sum_{\ell=0}^{n-2} R_{2}^{\ell} + R_{2}^{n-1} (S_{1} + S_{2} \sum_{i}^{n} P_{is}) \]
\[ \sum_{i=1}^{n} P_{i} |_{n=n} = R_{3} \sum_{\ell=0}^{n-1} R_{2}^{\ell} + R_{2}^{n} \sum_{i}^{n} P_{is} \]
\[ \sum_{i=1}^{n} i P_{i} |_{n=n} = T_{3} \sum_{\ell=0}^{n-2} T_{2}^{\ell} + T_{2}^{n-1} (P_{1} + P_{2} \sum_{i}^{n} i P_{is}) \]
\[ \sum_{i=1}^{n} i P_{i} |_{n=n} = T_{3} \sum_{\ell=0}^{n-1} T_{2}^{\ell} + T_{2}^{n} \sum_{i}^{n} P_{is} \]
\[ \sum_{i=1}^{n} i^{2} P_{i} |_{n=n} = Y_{3} \sum_{\ell=0}^{n-2} Y_{2}^{\ell} + Y_{2}^{n-1} (X_{1} + X_{2} \sum_{i}^{n} i^{2} P_{is}) \]
\[ \sum_{i=1}^{n} i^{2} P_{i} |_{n=n} = Y_{3} \sum_{\ell=0}^{n-1} Y_{2}^{\ell} + Y_{2}^{n} \sum_{i}^{n} i^{2} P_{is} \]

where \( n = \) cycle number; \( 2, 3, \ldots, \infty \)

and

\[ R_{1} = S_{3} + S_{1} S_{4} \]
\[ R_{2} = S_{2} S_{4} \]
\[ R_{3} = S_{1} + S_{2} S_{3} \]
\[ T_{1} = P_{3} + P_{1} P_{4} \]
\[ T_{2} = P_{2} P_{4} \]
\[ T_{3} = P_{1} + P_{2} P_{3} \]
\[ Y_{1} = X_{3} + X_{1} X_{4} \]
\[ Y_{2} = X_{2} X_{4} \]
\[ Y_{3} = X_{1} + X_{2} X_{3} \]
Periodic Operation Experiment

Isothermal experiments were carried out at four temperatures namely, 338\(^0\)K, 358\(^0\)K, 373\(^0\)K and 393\(^0\)K. Temperatures were maintained by circulating oil through a constant temperature bath and the jacket around reactor. A tubing pump was used to maintain the feed flow into the reactor. The flow from the pump was calibrated occasionally using time flow technique. The product leaving the reactor as overflow from an opening at the top. The reaction volume, therefore can be considered to be constant irrespective of the fact that volume changes during polymerization. Three flow rates namely, 1.5, 2 and 4 c.c./min. were maintained during the experiment. UV light on/off control was carried out by manually operating a shutter in the UV path. On/off control by actually turning the UV lamp on and off was not feasible because the mercury vapor used in these experiments takes about 15-20 minutes to cool once it is turned off and can not be turned on again unless it is cooled to ambient temperature.

Reactor temperature was maintained at required level by circulating oil through its jacket. Reactants at room temperature were then fed into the reactor. When the light was turned on, the reactor temperature started to rise and the required temperature was maintained by constant temperature bath. When steady state is reached, the reaction was continued for at least one residence time in order to make sure that conversion, number average and weight average chain lengths also reach the steady state. UV on/off control was then used to continue the reaction beyond the
lower steady state. The values of conversion and polydispersity at steady states are then used to compare the changes with UV on/off operation.

Results

The variation in the transient concentration of monomer and polydispersity of polymer in different cycles is shown in Figure 5. As may be seen, the cycle-invariant condition is eventually achieved where the initial and final state are equal. Analytical results of the transient behavior are shown in Figs. 6 through 9. The polydispersity becomes higher as the light is off. Because $X_n$ does not increase as rapidly as $X_w$. From Figure 7 it is seen that the isothermal, unsteady state simulation is performed at conditions of several experimental runs. Good agreement is obtained between the analytical and numerical solution. The experimental results are shown in Figs. 10 through 20. The objective of the analytical and numerical solutions is to obtain a qualitative understanding of the experimental results. Experimental increases in polydispersity are less than those predictedly model. In our study, it is shown that the polydispersity increases with the value of $\tau_{off}/\tau$. Hence, wider molecular weight distribution comes from a wider range of free radical concentration existing inside the reactor with a larger value of $\tau_{off}/\tau$ under unsteady state operation.

In our photopolymerization case the steady state polydispersity
Figure 5. Time Profile of Reactor Behavior

\[ I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2 \]

\[ S_0 = 0.015 \text{ g-moles/l} \]

\[ \theta = 6000 \text{ sec.} \]

\[ T = 358^\circ \text{K} \]
Figure 6. Transient Response to Perturbation from Stable Polydispersity at $\tau_{off}/\tau = 0.1$

$I_o = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$

$S_o = 0.015 \text{ g-moles/l}$

$\theta = 6000 \text{ sec.}$

$T = 358^\circ \text{K}$

$\tau_{off}/\tau = 0.1$
Figure 7. Transient Response to Perturbation from Stable Polydispersity at $\tau_{\text{off}}/\tau = 0.333$
Figure 8. Transient Response to Perturbation from Stable Polydispersity at $\tau_{off}/\tau = 0.5$

$I_0 = 11.7 \times 10^{-8}$ Eins/sec-cm$^2$

$S_0 = 0.015$ g-moles/l

$\theta = 6000$ sec.

$T = 358^\circ$K

$\tau_{off}/\tau = 0.5$
Figure 9. Transient Response to Perturbation from Stable Polydispersity at $\tau_{off}/\tau = 0.8$

$I_o = 11.7 \times 10^{-8}$ Eins/sec-cm$^2$

$S_o = 0.015$ g-moles/l

$\theta = 6000$ sec.

$T = 358^\circ K$

$\tau_{off}/\tau = 0.8$
$I_0 = 11.7 \times 10^{-8}$ Eins/sec-cm$^2$

$S_0 = 0.015$ g-moles/l

$\theta = 9000$ sec.

$T = 373^\circ K$

$(\tau_{off}/\tau)_{av.} = 0.25$

EXP

Figure 10. Experimental Data of Transient Response to Perturbation at $(\tau_{off}/\tau)_{av.} = 0.25$, $\theta = 9000$ sec and $T = 373^\circ K$
Figure 11. Experimental Data of Transient Response to Perturbation at $(\tau_{\text{off}}/\tau)_{\text{avg.}} = 0.28$, $\theta = 9000 \text{ sec}$ and $T = 373^\circ \text{K}$

$I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$
$S_0 = 0.015 \text{ g-mole/l}$
$\theta = 9000 \text{ sec}$
$T = 373^\circ \text{K}$
Figure 12. Experimental Data of Transient Response to Perturbation at $\tau_{\text{off}}/\tau = 0.1$, $\theta = 6000 \text{ sec}$ and $T = 358^\circ \text{K}$

$I_o = 11.7 \times 10^{-8} \text{Ein}\text{s/}\text{sec-cm}^2$

$S_o = 0.015 \text{ g-moles/l}$

$\theta = 6000 \text{ sec}$

$T = 358^\circ \text{K}$
Figure 13. Experimental Data of Transient Response
to Perturbation at $\frac{\tau_{off}}{\tau} = 0.333$,
$\theta = 6000$ sec and $T = 358^\circ K$

$I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$
$S_0 = 0.015 \text{ g-moles/l}$
$\theta = 6000 \text{ sec}$
$T = 358^\circ K$

$\frac{PD}{PD_{ss}}$
Figure 14. Experimental Data of Transient Response to Perturbation at $\tau_{\text{off}}/\tau = 0.5$,
$\theta = 6000$ sec and $T = 358^\circ$K

$I_o = 11.7 \times 10^{-8}$ Eins/sec-cm$^2$
$S_o = 0.015$ g-moles/l
$\theta = 6000$ sec.
$T = 358^\circ$K

$\frac{PD}{PD_{ss}}$

Time (hr)
Figure 15. Experimental Data of Transient Response to Perturbation at $\tau_{off}/\tau = 0.5$, $\theta = 3200$ sec and $T = 393^\circ K$

$I_0 = 11.7 \times 10^{-8}$ Eins/sec-cm$^2$
$S_0 = 0.015$ g-moles/l
$\theta = 3200$ sec.
$T = 393^\circ K$
\[ I_o = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2 \]

\[ S_o = 0.015 \text{ g-moles/l} \]

\[ \theta = 3000 \text{ sec.} \]

\[ T = 393^\circ \text{K} \]

\[ \frac{\tau_{off}}{\tau} = 0.2 \]

Figure 16. Experimental Data of Transient Response to Perturbation at \( \frac{\tau_{off}}{\tau} = 0.2 \), \( \theta = 3000 \text{ sec} \) and \( T = 393^\circ \text{K} \)
Figure 17. Experimental Data of Transient Response to Perturbation at $\tau_{off}/\tau = 0.5$, $\theta = 6000$ sec and $T = 358^\circ K$
Figure 18. Experimental Data of Transient Response to Perturbation at $\tau_{\text{off}}/\tau = 0.5$, $\theta = 6000$ sec and $T = 338^\circ$K.
Figure 19. Experimental Data of Transient Response to Perturbation at $\tau_{\text{off}}/\tau = 0.333$, $\theta = 6000$ sec and $T = 338^\circ K$

$I_0 = 11.7 \times 10^{-8}$ Eins/sec-cm$^2$

$S_0 = 0.015$ g-moles/l

$\theta = 6000$ sec.

$T = 338^\circ K$
Figure 20. Experimental Data of Transient Response to Perturbation at $\tau_{\text{off}}/\tau = 0.8$, $\theta = 6000$ sec and $T = 358^\circ K$

$I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$

$S_0 = 0.015$ g-moles/l

$\theta = 6000$ sec.

$T = 358^\circ K$

$\tau_{\text{off}}/\tau = 0.8$

- EXP
will always be about 1.5 analytically as shown in Appendix A. Thus, there is no possibility of molecular weight distribution width flexibility in the steady state. As to the experimental result, the polydispersity is about 3.0 and a broader molecular weight distribution is obtained at steady state. The disagreements show that the model does not describe the experimental results well. An attempt will be made on development of a mathematical model to correlate the effects of mixing on photosensitized polymerizations due to nonuniform distribution of the absorbed light intensity. The effect of temperature on polydispersity is summarized by Figure 21. The model prediction is the increase of polydispersity with decreasing temperature at a given value of $\tau_{\text{off}}/\tau$.

**Molecular Weight Distribution**

The distribution of molecular weights in a polymeric material may be represented as a differential distribution. A smooth curve results from the numerous points on the graph, although there are no values of $P_i$ except for integer values of $i$. The weight distribution function $W_i$ is defined by

$$W_i = \frac{\text{weight of dead polymer of length } i}{\text{total weight of dead polymer}}$$

The solution of a reactor model consisting of a very large number of non-linear algebraic equations will owing to the calculation tediousness and difficulty be possible only with the help of computers. Such a big number of equations to be solved requires theoretically an excessive need of mass storage and large computing time. In practical work however this demand
Figure 21. Effect of Temperature on the Transient Response of Polydispersity
is not particularly restrictive, because in our technical photopolymerizations usually appears of polymerization up to \( 4 \times 10^3 \). A problem of up to which degree of polymerization should the distribution be accounted for depends on the parameter \( \tau_{\text{off}} / \tau \), the ratio of light-off period to light on-off period, used in our system. Of course, a suitable termination criterion should be oriented on the sum of the individual weight fraction \( W_i \). This sum must be equal to 1.0 theoretically, when all the polymers are taken into consideration. For a physical standpoint it seems more reasonable to terminate the calculation for \( i=i^* \) where

\[
1 - \sum_{i=1}^{i^*} W_i \leq 0.005
\]

in our system. More computation time will be needed for a strong tailing of distribution to meet the criterion.

**Mathematical Equations for MWD**

Material balances for dead polymers are

\[
\begin{align*}
\frac{dP_2}{dt} &= \frac{1}{2} K_t R_1^2 R_1 - \frac{P_2}{6} \\
\frac{dP_3}{dt} &= K_t R_1 R_2 - \frac{P_3}{6} \\
\frac{dP_4}{dt} &= K_t (R_1 R_3 + \frac{1}{2} R_2 R_2) - \frac{P_4}{6} \\
\frac{dP_5}{dt} &= K_t (R_1 R_4 + R_2 R_3) - \frac{P_5}{6} \\
\frac{dP_6}{dt} &= K_t (R_1 R_5 + R_2 R_4 + \frac{1}{2} R_3 R_3) - \frac{P_6}{6}
\end{align*}
\]

...
The generalized expression will be

\[
\frac{dP_i}{dt} = \frac{1}{2} K_t \sum_{j=1}^{i-1} R_j R_{i-j} - \frac{P_i}{\theta} \tag{18}
\]

\[i = 2, 3, \cdots \infty\]

For the periodic process, the rate equation (18) is solved and the effects of the system parameter on the molecular weight distribution are examined. After solving the differential equation (18), it is possible to obtain the concentration of each of a large number of polymer species during the course of polymerization. The reactor is to be operated isothermally and the volumetric change will be neglected. The rate constants are assumed to be independent of molecular size.

UV Light Off

A QSSA with respect to the concentration of free radicals for each chain length can be assumed

\[
R_1 = \frac{2K_i M^3}{K_p M + K_t \Sigma R_i} \tag{19}
\]

\[
R_i = \left( \frac{K_i M}{K_p M + K_t \Sigma R_i} \right)^{i-1} R_1 \tag{20}
\]

\[i = 2, 3, \cdots \infty\]

By the substitution of equations (6), (19)-(20) into equation (18), one obtains

\[
\frac{dP_i}{dt} = 2(i-1)K_t K_i^2 M^{i-2} (K_p M + \frac{1}{t})^{-i} - \frac{P_i}{\theta} \tag{21}
\]
Since $K_pM >> \frac{1}{t}$ in our system, equation (21) reduces to

$$\frac{dP_i}{dt} = 2(i-1)K_tK_pK_r^{-2}M^4$$

(22)

Substituting equation (7) in equation (22), and using the initial condition that

$$P_i(0) = P_{\text{is}}$$

then the solution for the period, $0 \leq t \leq r\tau$, is given by

$$P_i(t) = A_1(C_1^i + 4C_1^3C_2^2e^{-t/\theta} - 6C_1^2C_2^2e^{-2t/\theta} - 2C_1C_2^3e^{-3t/\theta} - \frac{1}{3}C_2^4e^{-3t/\theta})$$

$$+ \left(P_{\text{is}} - A_1(C_1^i - 6C_1^2C_2^2 - 2C_1C_2^3 - \frac{1}{3}C_2^4)e^{-t/\theta}\right)$$

(23)

$$i = 2, 3, \cdots, \infty$$

where $P_{\text{is}}$ is the concentration of dead polymer species at steady state, and

$$A_1 = 2(i-1)K_tK_p^2K_r^{-2}\theta$$

Replacing $t$ by $r\tau$ in equation (23), we can obtain the concentration of dead polymer at the end of light-off period, $P_{i\tau\tau}$.

**UV Light On**

Similarly, application of the QSSA for the free radicals yields

$$R_1 = \frac{Q_i}{K_pM + K_t^{\tau}R_i}$$

(24)

By substituting equations (11), (20) and (24) into equation (18), the rate of formation of dead polymer of chain length $i$ is
where

\[ D_1 = \sqrt{\Omega_i t} \]

and

\[ D_2 = \frac{1}{2}(i-1)K_1^2 t_i - 2n_i^2 \]

and \( D_2 < K_1 M \) is reasonable for our system.

Substituting equation (12) into equation (25), then it can be integrated

\[
P_i(t) = D_1 K_i^{-i} e^{-t/\theta} \sum_{n=0}^{\infty} \left( -\frac{D_2}{K_1} \right)^n \int_{-t/\theta}^{t/\theta} \left( \frac{1}{C_5 - C_6 e^{-C_4(t-r\tau)}} \right)^{n+2} \frac{1}{C_5 - C_6 e^{-C_4(t-r\tau)}} \, dt + ce \]

Letting

\[ x = C_5 - C_6 e^{-C_4(t-r\tau)} \]

and

\[ D_3 = \frac{1}{C_4 \theta} \]

then the concentration of dead polymer of chain length \( i \) in eq. (26) is given by

\[
P_i(t) = \frac{-D_1 K_i^{-i} (-C_6)^3 e^{-(t-r\tau)/\theta}}{C_4} \sum_{n=0}^{\infty} \left( -\frac{D_2}{K_1} \right)^n \int_{x^{n+2} (x-C_5)^{D_3+1}}^{\infty} \frac{dx}{x^{n+2} (x-C_5)^{D_3+1}} \frac{1}{x^{n+2} (x-C_5)^{D_3+1}} + ce \]

The integral in equation (27) is evaluated by

\[
\int \frac{dx}{x^{n+2} (x-C_5)^{D_3+1}} = \frac{1}{x^{n+2} (x-C_5)^{D_3+1}} \sum_{\beta=0}^{(n+1+\beta)! (D_3-\beta-1)! x-C_5^\beta \beta = 0} \frac{x}{(n+1)! D_3!} (-1)^{\beta+1} \]

(28)
Substituting equation (28) into equation (27) and rearranging, then the solution for the concentration of dead polymer of chain length \( i \), subject to the boundary condition \( P_i (r \tau) = P_{ir \tau} \) for the period, \( r \tau \leq t \leq \tau \), is

\[
P_i(t) = \frac{-D_1 K^{-i} (-C_6)^3 e^{-(t-r \tau)/\theta} \binom{i}{n}^{\frac{1}{K_p}} \left(\frac{1}{-C_4 (t-r \tau)}\right)^n}{\binom{C_5-C_6}{C_4 (t-r \tau)}}
\]

\[
\sum_{\beta=0}^{\infty} (-1)^{\beta+1} \binom{n+1+\beta}{n+1} ! (D_3-\beta-1)! \frac{-C_6 e^{-(t-r \tau)/(n+1)!D_3!}}{C_5-C_6 e^{-(t-r \tau)}} \binom{D_3}{-C_4 (t-r \tau)}^{\beta} \binom{1}{-C_6 e^{-(t-r \tau)}}^{n}
\]

\[
\left(\frac{1}{C_5-C_6 e^{-(t-r \tau)}}\right)^2 \left[\left(\frac{-C_6 e^{-(t-r \tau)}}{C_5-C_6}ight)^D_3\right]^2
\]

\[
+ \left( P_{ir \tau} + \frac{D_1 K^{-i} (-C_6)^3 e^{-(t-r \tau)/\theta} \binom{i}{n}^{\frac{1}{K_p}} \left(\frac{1}{C_5-C_6} \right)^n}{\binom{C_5-C_6}{C_4 (t-r \tau)}} \right)
\]

\[
\sum_{\beta=0}^{\infty} (-1)^{\beta+1} \binom{n+1+\beta}{n+1} ! (D_3-\beta-1)! \frac{-C_6 e^{-(t-r \tau)/(n+1)!D_3!}}{C_5-C_6 e^{-(t-r \tau)}} \binom{D_3}{-C_4 (t-r \tau)}^{\beta} \binom{1}{-C_6 e^{-(t-r \tau)}}^{n}
\]

\[
\left(\frac{1}{C_5-C_6 e^{-(t-r \tau)}}\right)^2 \left[\left(\frac{-C_6 e^{-(t-r \tau)}}{C_5-C_6}ight)^D_3\right]^2
\]

\[
- (t-r \tau)/\theta \binom{D_3}{-C_4 (t-r \tau)}^{\beta} \binom{1}{-C_6 e^{-(t-r \tau)}}^{n}
\]

\[(29)\]

Once the concentration of dead polymer of chain length \( i \) as a function of time, \( P_i(t) \) and the state value at the end of light-off period, \( P_{ir \tau} \) are obtained, an expression for the \( P_i \) as a function of cycle number can be derived from the equations (23) and (29). By the same procedure as we described in the case of polydispersity, the following relationships can be found:
and for cycle $n$

$$P_i |_{n=1} = W_1 + W_2 P_{is}$$
$$t=r\tau$$

$$P_i |_{n=1} = W_3 + W_4 P_{ir\tau}$$
$$t=\tau$$

and for cycle $n$

$$P_i |_{n=n} = Q_3 \sum_{\lambda=0}^{\lambda=n-2} Q_2^\lambda + Q_2^{n-1}(W_1 + W_2 P_{is})$$
$$t=(r+n-1)\tau$$

$$P_i |_{n=n} = Q_1 \sum_{\lambda=0}^{\lambda=n-1} Q_2^\lambda + Q_2^n P_{is}$$
$$t=n\tau$$

where $n = \text{cycle number}; 2, 3, \cdots, \infty$

and

$$Q_1 = W_3 + W_1 W_4$$
$$Q_2 = W_2 W_4$$
$$Q_3 = W_1 + W_2 W_3$$

**Discussion of MWD**

Some advantages and disadvantages against other methods concerning the precision and expenditure, should be mentioned. The molecular weight distribution curves, which derived from the theoretical kinetics, can be obtained analytically for any location of any cycle as a function of time during the process. But if the numerical calculations are employed, the solutions should be obtained from the beginning and then continuing, and too many reaction rate equations may be needed to complete the distribution curves. Most of the molecular weight distribution is derived from the empirical formula or methodical techniques.
Here the theoretical method is introduced, which is more precise because it does not need any approximation in the calculation procedure. In contrary, the theoretical method demands more computation of the molecular weight distribution to obtain precise distribution curves. Also, it enables one to reduce an infinite number of equations to a finite number, in which a degree of polymerization step of 25 may be involved.

An outstanding effect of the parameter $\tau_{\text{off}}/\tau$, ratio of light-off period to forced period, on the molecular weight distribution is shown together with the distribution curve at a real steady state in Figures 22 through 24 at different temperatures. Broadening distribution with longer tailing is formed at controlled steady state.

Representative chromatograms are presented in Figures 25 through 28. These are the plots of the molecular weight distribution at a steady state against that of a UV light-off period perturbation about the steady state. In each case, the molecular weight distribution from the steady state and the cyclic operation are essentially not the same and the distribution from the cyclic operation gets broader.
Figure 22. MWD Broadening after Periodic Operation

\[ I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2 \]
\[ S_0 = 0.015 \text{ g-moles/l} \]
\[ \theta = 6000 \text{ sec} \]
\[ T = 338^\circ \text{K} \]
\[ \tau_{\text{off}} / \tau = 0.5 \]

---

real S.S.
--- S.S. after cyclic operation

Figure 22. MWD Broadening after Periodic Operation
at \( \tau_{\text{off}} / \tau = 0.5 \), \( \theta = 6000 \) sec and \( T = 338^\circ \text{K} \)
Figure 23. MWD Broadening after Periodic Operation at

\[ \tau_{\text{off}} / \tau = 0.5, \theta = 6000 \text{ sec and } T = 393^\circ \text{K} \]

\[ I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2 \]
\[ S_0 = 0.015 \text{ g-moles/l} \]
\[ \theta = 6000 \text{ sec} \]
\[ T = 393^\circ \text{K} \]
Figure 24. Effect of $\tau_{\text{off}}/\tau$ on MWD Broadening
$I_o = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$

$S_o = 0.015 \text{ g-moles/l}$

$\theta = 9000 \text{ sec.}$

$T = 373^\circ K$

$\tau_{off}/\tau = 0.28$

A: real S.S.

B: S.S. after cyclic operation

Figure 25. GPC Curves Attainable by Steady State and Periodic Operation at $\tau_{off}/\tau = 0.28,$ $\theta = 9000 \text{ sec and } T = 373^\circ K$
Figure 26. GPC Curves Attainable by Steady State and Periodic Operation at $\tau_{\text{off}}/\tau = 0.5$,
$\theta = 3200$ sec and $T = 393^\circ K$

$I_0 = 11.7 \times 10^{-8}$ Eins/sec-cm$^2$
$S_0 = 0.015$ g-moles/l
$\theta = 3200$ sec.
$T = 393^\circ K$

$A : \text{real S.S.}$
$B : \text{S.S. after cyclic operation}$

Baseline, Elution Count

GPC conditions:

solvent: toluene
temp.: room temp.
flow : 2.5 c.c./min.
detector: RI @ 8X
chart speed:1 cm/min.
$I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$
$S_0 = 0.015 \text{ g-moles/l}$
$\theta = 6000 \text{ sec.}$
$T = 338^\circ \text{K}$

$\tau_{\text{off}}/\tau = 0.333$

A : real S.S.
B : S.S. after cyclic operation

Figure 27. GPC Curves Attainable by Steady State and Periodic Operation at $\tau_{\text{off}}/\tau = 0.333$, $\theta = 6000 \text{ sec and } T = 338^\circ \text{K}$
Figure 28. GPC Curves Attainable by Steady State and Periodic Operation at $\tau_{\text{off}}/\tau = 0.8$, $\theta = 6000 \text{ sec}$ and $T = 358^\circ \text{K}$.
CHAPTER 5

AN ANALYTICAL STUDY OF A NONUNIFORMLY INITIATED PHOTOPOLYMERIZATION

In this study, the analysis is based on the irradiation of chemical species circulating in a continuous stirred-tank reactor having a high dose rate region and a very low dose rate region. A schematic diagram of the reactor used is shown in Figure 29.

A volume $V_L$ (Region I) is illuminated with a parallel, effectively uniform beam of absorbed radiation. For these conditions, and with negligible reflection, the total rate of light absorption is averaged over the path length of the light within the lighted volume. The remaining volume of the reactor, $V_D$ (Region II), is irradiated with a very low dose rate. A stirred provides mixing between and within these two regions.

The model consists of measuring the monomer concentration, sensitizer concentration, and three moments of the dead polymer in the reactor as a function of time with three certain parameters such as the size of the lighted volume, the volumetric pumping rate between regions, and the absorbed intensity in region II. The absorbed intensity profile along the axial direction of the reactor is shown in Figure 30 at different values of sensitizer concentration and can be expressed by

$$I_{as} = I_o \epsilon_s \epsilon_{se} \left( \epsilon_s S + \epsilon_m \right) x$$
Figure 29. Schematic Flow Pattern in Reactor
Figure 30. Rate of Absorbed Light Intensity Distribution in the Reactor

\[ I_o = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2 \]

1. \[ S = 0.015 \text{ g-moles/l} \]
2. \[ S = 0.025 \text{ g-moles/l} \]

Distance (cm)

\[ I_{as}, \text{ Eins/sec-cm}^3 \times 10^7 \]
Due to the light attenuation of axial nonuniformities and the existence of agitator, the volume of the region I and the rate of light absorption in region II will be found. Mixing phenomena are important in determining the observed reaction rate and molecular weight distribution in optically dense photo-reaction mixtures in our study. The accurate prediction of mixing effects requires a detailed knowledge of the mechanism of the reaction of interest, the physics of the radiation used, and the mixing processes themselves. The mixing process in a stirred vessel has been studied by Marr et al. (48). They found volumetric pumping rate to be dependent upon the agitator speed N, and impeller diameter D according to the equation

$$q = fND^3$$

where f is the coefficient of impeller discharge.

Since q value can not be measured experimentally, an empirical correlation will be used.

In photochemical reactions, nonuniform initiation results from radiation attenuation or from partial illumination of the reaction volume. In either case large initiation rates are found in certain regions of the reaction volume, and small rates in others. The rate of mass transfer in the direction of initiation rate variation will then be a factor determining average reactant concentration and hence the observed reaction rate.

**Model Development**

In region I, mass balances on the growing radicals, monomer
and three moments of dead polymer in CSTR are expressed by the following equations: (44)

\[
\frac{dS_I}{dt} = \frac{QS_0}{(V_I + V_{II})} + \left(\frac{1 + \epsilon X_{II}}{\theta_I}\right)S_{II} - \left(\frac{1 + \epsilon X_I}{\theta_I}\right)S_I - \frac{Q_{S_I}}{(V_I + V_{II})} - \frac{\phi_s I_{as I}}{(V_I + V_{II})}
\]

(1)

\[
\frac{dM_I}{dt} = \frac{QM_0}{(V_I + V_{II})} + \left(\frac{1 + \epsilon X_{II}}{\theta_I}\right)M_{II} - \left(\frac{1 + \epsilon X_I}{\theta_I}\right)M_I - \frac{Q_{M_I} R_{II}}{(V_I + V_{II})} - \frac{K_{p_I} M_I R_{II}}{(V_I + V_{II})}
\]

(2)

\[
\frac{d\sum P_{iII}}{dt} = K_{fmi} M_I \sum R_{II} + \frac{1}{2} K_{tII} \sum R_{II}^2 + \left(\frac{1 + \epsilon X_{II}}{\theta_I}\right)\sum P_{iII} - \left(\frac{1 + \epsilon X_I}{\theta_I}\right)\sum P_{iII} - \frac{Q_{\sum P_{iII}}}{(V_I + V_{II})}
\]

(3)

\[
\frac{d\sum iP_{iII}}{dt} = K_{tII} \sum R_{II} \sum iR_{II} + K_{fmi} M_I \sum iR_{II} + \left(\frac{1 + \epsilon X_{II}}{\theta_I}\right)\sum iP_{iII} - \left(\frac{1 + \epsilon X_I}{\theta_I}\right)\sum iP_{iII} - \frac{Q_{\sum iP_{iII}}}{(V_I + V_{II})}
\]

(4)

\[
\frac{d\sum i^2 P_{iII}}{dt} = K_{tII} \sum R_{II} \sum i^2 R_{II} + K_{tII} \sum iR_{II}^2 + K_{fmi} M_I \sum i^2 R_{II} + \left(\frac{1 + \epsilon X_{II}}{\theta_I}\right)\sum i^2 P_{iII} - \left(\frac{1 + \epsilon X_I}{\theta_I}\right)\sum i^2 P_{iII} - \frac{Q_{\sum i^2 P_{iII}}}{(V_I + V_{II})}
\]

(5)

and in region II

\[
\frac{dS_{II}}{dt} = \frac{QS_0}{(V_I + V_{II})} + \left(\frac{1 + \epsilon X_{II}}{\theta_{II}}\right)S_{II} - \left(\frac{1 + \epsilon X_I}{\theta_{II}}\right)S_{II} - \frac{\phi_s I_{as II}}{(V_I + V_{II})} - \frac{Q_{S_{II}}(1 + \epsilon X)}{(V_I + V_{II})}
\]

(6)
For a batch reactor, the \( Q \) from the equations (1) through (10) should be set equal to zero. In order to obtain the zeroth, first and second moments of active polymer, the following equations apply:

\[
\frac{dM_{II}}{dt} = \frac{QM_{II}}{(V_I + V_{II})} + \frac{(1 + \varepsilon X_I)M_I - (1 + \varepsilon X_{II})M_{II}}{\theta_{II}} - K_p M_{II}R_{III}
\]

\[
\frac{d\Sigma P_{III}}{dt} = K_{fm_{III}} M_{III} \Sigma R_{III} + \frac{1}{2} K_{t_{III}} \Sigma R_{III}^2
\]

\[
+ \frac{(1 + \varepsilon X_I) \Sigma P_{II} - (1 + \varepsilon X_{II}) \Sigma P_{III}}{\theta_{II}} - \frac{Q^\Sigma P_{III}(1 + \varepsilon X_I)}{(V_I + V_{II})}
\]

\[
\frac{d\Sigma i_{III}}{dt} = K_{t_{III}} R_{III} \Sigma i_{R_{III}} + K_{fm_{III}} M_{III} \Sigma i_{R_{III}}
\]

\[
+ \frac{(1 + \varepsilon X_I) \Sigma i_{P_{II}} - (1 + \varepsilon X_{II}) \Sigma i_{P_{III}}}{\theta_{II}} - \frac{Q^\Sigma i_{P_{III}}(1 + \varepsilon X_I)}{(V_I + V_{II})}
\]

\[
\frac{d\Sigma i^2_{P_{III}}}{dt} = K_{t_{III}} R_{III} \Sigma i^2_{R_{III}} + K_{t_{III}} \Sigma i^2_{R_{III}} + K_{fm_{III}} M_{III} \Sigma i^2_{R_{III}}
\]

\[
+ \frac{(1 + \varepsilon X_I) \Sigma i^2_{P_{II}} - (1 + \varepsilon X_{II}) \Sigma i^2_{P_{III}}}{\theta_{II}} - \frac{Q^\Sigma i^2_{P_{III}}(1 + \varepsilon X_I)}{(V_I + V_{II})}
\]

where \( \varepsilon \) and conversion \( X \), are defined as

\[
\varepsilon = \frac{V_{x=1} - V_{x=0}}{V_{x=0}}
\]

\[
X = \frac{M_o - M}{M_o + M}
\]

and

\[
\bar{X} = \frac{V_{I}X_{I} + V_{II}X_{II}}{(V_I + V_{II})}
\]

For a batch reactor, the \( Q \) from the equations (1) through (10) should be set equal to zero. In order to obtain the zeroth, first and second moments of active polymer, the following
material balances will be expressed as

\[ \frac{dS_{i}}{dt} = \frac{(1+\varepsilon_{\text{II}})S_{\text{II}} - (1+\varepsilon_{\text{I}})S_{\text{I}}}{\theta_{\text{I}}} + 2\phi_{s\text{asI}} - K_{d_{\text{I}}}S_{\text{I}}M_{\text{I}} - \frac{QS_{\text{I}}}{(V_{\text{I}}+V_{\text{II}})} \]  

(11)

\[ \frac{dS_{\text{II}}}{dt} = \frac{(1+\varepsilon_{\text{II}})S_{\text{II}} - (1+\varepsilon_{\text{I}})S_{\text{I}}}{\theta_{\text{II}}} + 2\phi_{s\text{asII}} - K_{d_{\text{II}}}S_{\text{II}}M_{\text{II}} - \frac{Q(1+\varepsilon_{\text{II}})S_{\text{II}}}{(V_{\text{I}}+V_{\text{II}})} \]  

(12)

\[ \frac{dR_{\text{II}}}{dt} = \frac{(1+\varepsilon_{\text{II}})R_{\text{II}} - (1+\varepsilon_{\text{I}})R_{\text{I}}}{\theta_{\text{I}}} + \Omega_{\text{II}} - K_{t_{\text{I}}}R_{\text{II}}^{2} - \frac{QR_{\text{II}}}{(V_{\text{I}}+V_{\text{II}})} \]  

(13)

\[ \frac{dR_{\text{III}}}{dt} = \frac{(1+\varepsilon_{\text{II}})R_{\text{III}} - (1+\varepsilon_{\text{I}})R_{\text{I}}}{\theta_{\text{II}}} + \Omega_{\text{III}} - K_{t_{\text{II}}}R_{\text{III}}^{2} - \frac{Q(1+\varepsilon_{\text{II}})R_{\text{III}}}{(V_{\text{I}}+V_{\text{II}})} \]  

(14)

where

\[ \Omega_{\text{II}} = 2K_{i_{\text{I}}}M_{\text{I}}^{3} + K_{p}S_{\text{I}}M_{\text{I}} \]

\[ \Omega_{\text{III}} = 2K_{i_{\text{II}}}M_{\text{II}}^{3} + K_{p}S_{\text{II}}M_{\text{II}} \]

If QSSA is applied, and let \( K_{d} = K_{p} \), the solutions of equations (11) and (12) will be

\[ S_{\text{I}} = \frac{(C_{2}/C_{7} + C_{5}/C_{3})}{(C_{6}/C_{3} - C_{1}/C_{7})} \]  

(15)

\[ S_{\text{II}} = \frac{(C_{2}/C_{1} + C_{5}/C_{6})}{(C_{7}/C_{1} - C_{3}/C_{6})} \]  

(16)

By substituting equations (15) and (16) into equations (13) and (14), we obtain
The first and second moments of active polymer in both regions are obtained by applying the same procedure described above:

\[ \tilde{\Sigma}_{R_{II}} = \frac{-C_8 + \sqrt{C_8^2 + 4C_4 K_{tI} (\theta_{I} \Omega_{I} + C_9 \Sigma_{R_{III}})}}{2C_4 K_{tI}} \]

\[ \tilde{\Sigma}_{R_{III}} = \frac{-C_9 + \sqrt{C_9^2 + 4C_9 K_{tII} (\theta_{II} \Omega_{III} + C_8 \Sigma_{R_{II}})}}{2C_9 K_{tII}} \]

where

\[ C_1 = (1 + \epsilon x_I) + \theta_I (K_{pI} + \frac{Q}{V_I + V_{II}}) \]

\[ C_2 = 2 \theta_I \phi_s \text{ as I} \]

\[ C_3 = (1 + \epsilon x_{II}) + \theta_{II} (K_{pII} + \frac{(1 + \epsilon x)Q}{V_I + V_{II}}) \]

\[ C_4 = 2 \theta_{II} \phi_s \text{ as II} \]

\[ C_5 = 1 + \epsilon x_I \]

\[ C_6 = 1 + \epsilon x_{II} \]

\[ C_7 = 1 + \epsilon x_I \]

\[ C_8 = C_6 + \frac{\theta_I Q}{V_I + V_{II}} \]

\[ C_9 = C_7 + \frac{\theta_{II} (1 + \epsilon x)Q}{V_I + V_{II}} \]

The first and second moments of active polymer in both regions are obtained by applying the same procedure described above:

\[ \sum_{i R_{II}} = \frac{C_9 \sum_{i R_{III}} + K_{pI} \sum_{i R_{III}} + \Omega_{I}}{\frac{C_8}{\theta_I} + K_{tI} \sum_{i R_{II}}} \]

\[ \sum_{i R_{III}} = \frac{C_8 \sum_{i R_{II}} + K_{pII} \sum_{i R_{II}} + \Omega_{III}}{\frac{C_9}{\theta_{II}} + K_{tII} \sum_{i R_{III}}} \]
From numerical analysis, the concentration of active sensitizer, zeroth, first, and second moments of active polymer calculated in batch reactor are approximately the same as those calculated in CSTR. Here, the rate constants of termination in both regions, $K_{tI}$ and $K_{tII}$, are assumed to be equal and are independent of the chain length.

OPTIMIZATION OF BATCH POLYMERIZATION REACTOR

Now that we have a method for efficiently computing the conversion and polydispersity, then we might obtain the parameters, $V_I$, $q$ (i.e., $\theta_I$ and $\theta_{II}$), and $I_{asII}$. The objective of optimization is to obtain the polydispersity $\frac{X_w^*}{X_n^*}$ and conversion of the polymerization, $X$, as close as possible to the experimental data of batch reactor, $\frac{X_w^*}{X_n^*}$ and $X^*$, respectively, by solving the nonlinear simultaneous equations (1) through (10) of batch reactor (i.e., $Q = 0$), and with the appropriate parameters. The objective function to be minimized can be generally written as

$$f = \frac{C_g \sum_i^2 R_{iII} + 2K_{P_{II}} \sum_i R_{iII} + \Omega_{II} + K_{P_{II}} \sum_i R_{iII}}{C_g \sum_i^2 R_{iII} + K_{tI} \sum_i R_{iII} + K_{fm} M_{I}}$$

$$f = \frac{C_g \sum_i^2 R_{iIII} + 2K_{P_{III}} \sum_i R_{iIII} + \Omega_{III} + K_{P_{III}} \sum_i R_{iIII}}{C_g \sum_i^2 R_{iIII} + K_{tIII} \sum_i R_{iIII} + K_{fm} M_{II}}$$
where \( n \) is the number of data points. Now the optimization problem becomes one of minimizing the objective function \( F(t) \) defined by equation (17) subject to the following inequality constraints:

\[
L \leq X_k \leq U \quad k = 1, 2, 3
\]

where \( X_k \), \( L \), and \( U \) are the parameters, the lower and upper limits of parameter, respectively.

Method

The algorithm (49) explained is based upon the automatic method proposed by Rosenbrock (50). This method is a sequential search technique to produce new constrained parameters. The procedure is then to vary the available parameters until the objective function is a minimum. The algorithm requires a starting point that satisfies the constraints and does not lie in the boundary zones which are defined as follows:

Lower Zone: \( G_k \leq X_k \leq (G_k + (H_k - G_k) \times 10^{-4}) \)

Upper Zone: \( H_k \leq X_k \leq (H_k - (H_k - G_k) \times 10^{-4}) \)

The algorithm proceeds as follows:

(1) Define by \( F^0 \) the current best objective function value for a point where the constraints are satisfied, and \( F^* \) the current best objective function value for a point where the constraints are satisfied and in addition the boundary zones are not violated.
$F^0$ and $F^*$ are initially set equal to the objective function value at the starting point.

(2) If the current point objective function evaluation, $F$, is worse than $F^0$ or if the constraints are violated, the trial is a failure and the unconstrained procedure is continued.

(3) If the current point lies within a boundary zone, the objective function is modified as follows:

$$F(\text{new}) = F(\text{old}) - (F(\text{old}) - F^*)(3\lambda - 4\lambda^2 + 2\lambda^3)$$

where

$$\lambda = \frac{\text{distance into boundary zone}}{\text{width of boundary zone}}$$

$$= \frac{G_k + (H_k - G_k) \times 10^{-4} - X_k}{(H_k - G_k) \times 10^{-4}} \quad \text{(lower zone)}$$

$$= \frac{X_k - (H_k - (H_k - G_k) \times 10^{-4})}{(H_k - G_k) \times 10^{-4}} \quad \text{(upper zone)}$$

At the inner edge of the boundary zone, $\lambda = 0$, i.e., the function is unaltered ($F(\text{new}) = F(\text{old})$). At the constraint, $\lambda = 1$, and thus $F(\text{new}) = F^*$. Thus the function value is replaced by the best current function value in the feasible region and not in a boundary zone. For a function which improves as the constraint is approached, the modified function has an optimum in the boundary zone.

(4) If an improvement in the objective function has been obtained without violating the boundary zones or constraints, $F^*$ is set equal to $F^0$ and the procedure continued.

(5) The search procedure is terminated when the convergence criteria is satisfied.
There are three difficulties which have to be met in developing a practical method for dealing with the problem: (1) Determining Length of Step: The principle adopted was to try a step of arbitrary length \( e \). If \( e \) was initially so small that it made no change in objective function, it would be increased on the next attempt. (2) Determining Direction of Step: The next problem is to decide when and how to change the directions in which the steps \( e \) are taken. It was decided to work throughout with \( n \) orthogonal directions rather than choose a single direction in which to progress at each stage. (3) Inserting Limits.

**Results and Analysis**

The experimental results obtained from isothermal batch reactor were compared and analyzed with the numerical calculation from the procedure described above. These three parameters can be evaluated by this search technique. Figure 31 shows the experimental data of batch reactor and numerical calculation by using the searched parameters. Good agreement is obtained between solution and experiments after fitting parameters.

The result without the parameter \( I_{asII} \) (i.e., by setting \( I_{asII} = 0 \)) is shown in Fig. 32 in which the polydispersity increases with the reaction time. The disagreement with the experimental data indicates that the light intensity absorption in low dose rate region cannot be neglected when the model predicted. As \( I_{asII} \) is \( 5 \times 10^{-10} \text{Eins/sec-cm}^3 \), the polydispersity appears to be obtained within a certain range which is shown in Figure 33. Explanation
Figure 31. Polydispersity vs. Time by Batch Data and Prediction of Parameters fitting

\[ I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2 \]
\[ I_{asI} = 2.25 \times 10^{-7} \text{Eins/sec-cm}^3 \]
\[ T = 338^\circ \text{K} \]

(1) \( S_0 = 0.015 \text{ g-moles/l} \)
- - - EXP
--- Model

(2) \( S_0 = 0.025 \text{ g-moles/l} \)
- - - EXP
--- Model

\[ V_I = 0.02 \text{ l} \]
\[ q = 3 \times 10^{-5} \text{ l/sec} \]
\[ I_{asII} = 2 \times 10^{-9} \text{ Eins/sec-cm}^3 \]
Figure 32. Effect of Initiation Without $I_{asII}$ on Polydispersity in Two-Region Model

$I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$
$S_0 = 0.015 \text{ g-moles/l}$
$T = 338^\circ \text{K}$

$V_I = 0.02 \text{ liters}$
$q = 3 \times 10^{-5} \text{ l/sec}$
$I_{asII} = 0$
Figure 33. Effect of Small $I_{asII}$ on Polydispersity in Two-Region Model

$I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$

$S_0 = 0.015 \text{ g-moles/l}$

$T = 338^\circ \text{K}$

$V_I = 0.02 \text{ liters}$

$q = 3 \times 10^{-5} \text{ l/sec}$

$I_{asII} = 5 \times 10^{-10} \text{ Eins/sec-cm}^3$
for this behavior is that the difference in radical concentration between two regions decreases with the small but significant initiation rate in low dose rate region. Figure 34 shows that the higher initiation rate in low dose rate region would produce a nearly uniform polydispersity. Also, Figure 35 shows uniform polydispersity can be produced by having a small volume of high dose rate region. Figure 36 shows that the similar result is achieved by increasing the speed of agitation, since the radical life time is very short and a marked difference in the initiation rates exists in these two regions. By applying the parameters to the proposed two-region model for a CSTR under UV light on-off regulation, the results show some agreements as shown in Figures 37 through 41, and the polydispersity of steady state can be increased from about 1.5 (perfect mixing) to about the range of 2.8-3.2.
Figure 34. Effect of Large $I_{asII}$ on Polydispersity in Two-Region Model.

$I_o = 11.7 \times 10^{-8}$ Eins/sec-cm$^2$

$S_o = 0.015$ g-moles/l

$T = 338^\circ K$

$V_I = 0.03$ liters

$q = 3 \times 10^{-5}$ l/sec

$I_{asII} = 2 \times 10^{-9}$ Eins/sec-cm$^3$
Figure 35. Effect of Lighted Volume on Polydispersity in Two-Region Model

$I_o = 11.7 \times 10^{-8}$ Eins/sec-cm$^2$
$S_o = 0.015$ g-moles/l
$T = 338^\circ K$
$q = 3 \times 10^{-5}$ l/sec
$I_{asII} = 5 \times 10^{-10}$ Eins/sec-cm$^3$

---

$V_I = 0.04$ liters
$V_I = 0.01$ liters
Figure 36. Effect of Volumetric Pumping Rate on Polydispersity in Two-Region Model

$I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$
$S_0 = 0.015 \text{ g-moles/l}$
$T = 338^\circ \text{K}$

$V_I = 0.02 \text{ liters}$
$I_{asII} = 5 \times 10^{-10} \text{Eins/sec-cm}^3$

$q = 1 \times 10^{-5} \text{ l/sec}$
$q = 4 \times 10^{-5} \text{ l/sec}$
Figure 37. Experimental PD vs. Time Data and Prediction of Two-Region Model at $(\tau_{\text{off}}/\tau)_{\text{avg}} = 0.28$, $\theta = 9000$ sec and $T = 373^\circ K$

$I_0 = 11.7 \times 10^{-8}$ Eins/sec-cm$^2$

$S_0 = 0.015$ g-moles/l

$\theta = 9000$ sec.

$T = 373^\circ K$
Figure 38. Experimental PD vs. Time Data and Prediction of Two-Region Model at $\tau_{\text{off}}/\tau = 0.1$, $\theta = 6000$ sec and $T = 358^\circ K$
$I_o = 11.7 \times 10^{-8} \text{Ein} \text{s/sec-cm}^2$

$S_o = 0.015 \text{g-moles/l}$

$\theta = 6000 \text{ sec}$

$T = 338^\circ \text{K}$

$\tau_{\text{Off}}/\tau = 0.333$

**EXP**  
Model

---

**Figure 39.** Experimental PD vs. Time Data and Prediction of Two-Region Model at $\tau_{\text{Off}}/\tau = 0.333$, $\theta = 6000 \text{ sec}$ and $T = 338^\circ \text{K}$
\[ I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2 \]
\[ S_0 = 0.015 \text{ g-moles/l} \]
\[ \theta = 3200 \text{ sec.} \]
\[ T = 393^\circ \text{K} \]
\[ \tau_{off}/\tau = 0.5 \]

Figure 40. Experimental PD vs. Time Data and Prediction of Two-Region Model at \( \tau_{off}/\tau = 0.5 \), \( \theta = 3200 \text{ sec and } T = 393^\circ \text{K} \)
Figure 41. Experimental PD vs. Time Data and Prediction of Two-Region Model at $\tau_{off}/\tau = 0.8$

$\theta = 6000$ sec and $T = 358^\circ K$
CHAPTER 6

REACTOR MULTIPLICITY, STABILITY AND CONTROLLABILITY
FOR PHOTOPOLYMERIZATION IN A CSTR

A study of steady state and dynamic behavior of an isothermal CSTR has been carried out numerically. It is mathematically demonstrated that there is a clear possibility of the existence of multiple steady states induced by viscosity effects in isothermal CSTR. In solutions of high viscosity, that mass consumption rate of free-radical polymerization increases with conversion, reaching a peak at very high viscosity, then falling off rapidly. Given this sort of behavior, it is demonstrated mathematically that steady-state mass balance solutions are possible at three levels of conversion. The lower and higher steady states are stable while the metastable steady-state is shown to be necessarily unstable. This multiple steady-state problem is discussed in relation to reactor stability and control. A broader molecular weight distribution being achieved by regulating UV light on-off around the metastable steady state is investigated.

Reactor Performance Characteristics

Mass balance equations for a perfectly mixed isothermal CSTR are expressed the same as the equations (1) through (5) in Chapter 4. In which, \( \frac{K_p}{K_t^{1/2}} \) is allowed to vary with conversion as follows: (43)

\[
\frac{K_p}{K_t^{1/2}} = \left( \frac{K_p}{K_t^{1/2}} \right)_0 e^{(A_1 X + A_2 X^2 + A_3 X^3)}
\]
The subscript 0 means value at zero conversion, and $A_1$, $A_2$, and $A_3$ and $(\frac{DP_{K_{1/2}}}{K_t})_0$ are independent of conversion $X$ for any temperature. In bulk radical polymerization, the viscosity of the medium increases as polymerization progresses. Such an increase decreases termination rate, which is diffusion controlled, and therefore it accelerates the polymerization rate markedly. The abnormal increases in the rate of conversion, the degree of polymerization, and the mean lifetime of polymer radicals have been inclusively recognized as the gel effect, or the Trommsdorff effect. The general solution is to separate equation (2) in Chapter 2 into two terms, Mass Supply Rate (MSR) and Mass Consumption Rate (MCR):

$$MSR = \frac{M_o - M(1+\varepsilon X)}{\theta} = \frac{M_o X}{\theta}$$

$$MCR = \Omega \frac{1/2}{1+\varepsilon X} \left( \frac{K_{1/2}}{K_t} \right) \exp(A_1 X + A_2 X^2 + A_3 X^3)$$

A volume change denoted by $\varepsilon$ is also involved in the equations. Figure 42 shows typical solutions obtained for styrene polymerization. At steady state MSR should be equal to MCR. The Msr is a linear function of $X$ with a slope of $M_o/\theta$. The existence of the two steady states shown in the figure requires the supply and consumption curves be tangent at one point, a physically unlikely situation. More likely is the occurrence of one or three steady states. When three steady states are found, the central one is metastable. At this state, a decrease in $X$ results in less mass consumption, and the monomer concentration $M$ increases (or $X$ decreases) until it reaches the lower steady state.
Figure 42. MSR & MCR vs. $X$ at Different $I_\circ$'s and Flow Rates
On the other hand, if the X is increased (or M is decreased) from the metastable steady state value, MCR > MSR, and the mass continues to fall (or X continues to increase) until the upper steady state is reached.

Metastable Steady State

Conversions of metastable states have been obtained by observing the effect of perturbation from stable conversions. Figure 43 shows a typical reactor conversion history for metastable steady state determination. The conversion is raised above the predicted low stable steady state by means of the batch operation and $I_0 = 1.5 \times 10^{-8} \text{Eins/cm}^2\text{-sec}$. The reactor is then operated continuously with flow rate $G = 2.9 \times 10^{-5} \text{l/sec}$, and reaction is permitted to find its real metastable state. The conversion is then raised to the predicted metastable state by means of the batch operation. A decrease in conversion following the continuous operation indicates undershoot below the metastable point and the conversion is raised by the batch operation. Similarly, an increase in conversion indicates overshoot beyond the metastable point and the shutter is closed to lower the conversion. By means of this step-wise procedure, the metastable point is reached.

Numerical calculation has been carried on the reactor control by on-off regulation of the light intensity. The on-off operation is obtained through a shutter mechanism. This is deemed most suitable for a UV lamp which for a proper operation must be maintained at constant output. Conversion is readily controlled
Figure 43. Light ON/OFF Regulation at Metastable S.S. with $\tau_{on}/\tau_{off} = 2.5$
with 0.025 below or above the metastable steady state. If $X \geq X_{\text{meta}} + 0.025$, the shutter is closed manually and vice versa ($I_0 = 3 \times 10^{-8} \text{Eins/sec-cm}^2$). From the figure, the polymer formed at the controller metastable steady state has a higher polydispersity than that obtained at the real metastable steady state.

Figure 44 illustrates the effect on the polydispersity with the same conversion range as in Figure 43 at different UV light on-off period and upper light intensity. It shows that when light on-off ratio is increased from 2.5 to 10, the upper light intensity should be decreased from $3 \times 10^{-8}$ to $1.8 \times 10^{-8} \text{Eins/sec-cm}^2$ in order to keep the same conversion range. In addition, the produced polydispersity decreases from 2.2 to 1.7, due to the increased number average chain length and the decreased weight average chain length.

The Control Analysis

Figure 45 shows the calculated results representing the reactor performance characteristics in terms of conversion, $X$ and number average chain length, $X_n$. Note that there are three regions in Figure 45: the curve a-b (Region I, low stable), curve b-c (Region II, metastable) and curve c-d (Region III, high stable). Operation in region III may be discounted for the bulk polymerization because of high viscosity (In order to reach higher conversion, the experiments of solution photopolymerization were carried out and shown in Appendix B). With regard to Region I and II, the obvious advantage of operation in the metastable region is the significantly higher conversion and molecular weight
Figure 44. Light ON/OFF Regulation at Metastable S.S. with $\tau_{on}/\tau_{off} = 10$
Figure 45. Reactor Performance Characteristics-
Calculated Results

\[ T = 338^\circ K \]

\[
\frac{I_o}{Eins/sec \cdot cm^2}
\]

1. \(2 \times 10^{-8}\)
2. \(1 \times 10^{-8}\)
attainable for the same residence time. While the reactor is operated in Region I, an increase in \( \theta \) (residence time) or a decrease in \( G \) (flow rate) at a fixed \( I_o \) results in an increase in \( X \) and \( X_n \). Also, an increase in \( I_o \) would shift the characteristics curve to lower residence time (or higher flow rate). The converse is true for Region II. The striped bands shown in Figures 46 through 48 are the range of \( X, X_n \), and \( X_w \) by on-off regulation of the light intensity on the three regions. As the light-off period is small, the bands are narrow in comparison to Figures 49—51 for which \( \tau_{on}/\tau_{off} \) is 4 and the band in metastable region combines with the low stable region. Having established the characteristics of operation in the metastable region, it is necessary to determine the conditions required to control a CSTR within this region. This was accomplished by means of a fourth order Runge-Kutta integration of the transient reactor equations (1)—(5) in Chapter 4. The responses obtained are to a step-change in set-point conversion \( X \) and are shown in Figures 52—55 in terms of conversion \( X \), number average chain length \( X_n \), weight average chain length \( X_w \) and controlled variable, flow rate, as a function of time.

The response is shown in Figure 52 with the control parameter in terms of the flow rate \( G \). The initial point is reached over the metastable state before a step-change takes place. For this application \( K_c \) represents the change in flow rate per unit conversion. For \( K_c = 0.000001 \) l/sec the response is deemed only marginally stable on the basis that after 30000 seconds the conversion continues to increase slowly and eventually reaction
Figure 46. $X$ vs. $\theta$ at Three Steady States Regions

with $\tau_{\text{off}}/\tau = 0.1$
Figure 47. $X_n$ vs. $\theta$ at Three Steady States Regions with $\tau_{off}/\tau = 0.1$
Figure 48. $X_w$ vs. $\theta$ at Three Steady States Regions

with $\tau_{off}/\tau = 0.1$
Figure 49. $X$ vs. $\theta$ at Three Steady States Regions with $\tau_{\text{off}}/\tau = 0.2$

$I_0 = 1.5 \times 10^{-8} \text{Ein/s cm}^2$

$S_0 = 0.25 \text{ g-moles/l}$

$T = 338^\circ \text{K}$

$\tau_{\text{on}} : \tau_{\text{off}} = 4 : 1$
Figure 50. $X_n$ vs. $\theta$ at Three Steady States Regions
with $\tau_{off}/\tau = 0.2$
Figure 51. $X_w$ vs. $\theta$ at Three Steady States Regions with $r_{off}/\tau = 0.2$
Figure 52. Proportional Control of the Flow Rate Based on Conversion at Metastable State—Initial Point Above the Steady State
Figure 53. Control on $X_n$ and $X_w$—Initial Point Above the Steady State
becomes runaway. For \( K_c = 0.0001 \) l/sec the response is stable. In Figure 54, conversely, the initial point is reached below the metastable state before a step-change takes place. For \( K_c = 0.00001 \) l/sec the response continues to creep slowly downward. The control parameter has the same effect on \( X_n \) and \( X_w \) as that on the conversion in both cases.

It is also shown in Figures 56—58 that the polydispersity is independent of flow rate with a fixed \( I_0 \). It means that the higher polydispersity can not be obtained by the regulation of reactor flow rate in any steady state.

Polymerization reactor characteristics for the no mixing state can also be represented in Appendix C.

**Optimal Policies**

A series of optimal light intensity policies are shown in Figure 59 with lines connecting points of constant conversion, and finally with lines connecting points of constant number average chain length. The intersection of the desired number average chain length and conversion curves determines the optimal light intensity policy. This leads to a novel development in the presentation of graphical solution for all problems, i.e., for any given conversion and number average chain length, one can locate the starting light intensity and flow rate to reach the steady state of a CSTR. If the point is at the higher steady state, the batch reactor should be started and pass the metastable region, and then the reactor will be changed to CSTR.
Figure 54. Proportional Control of the Flow Rate Based on Conversion at Metastable State—Initial Point Below the Steady State

\[ t \leq 20500 \quad G = 0 \]
\[ t > 20500 \quad G = K_C (X - 0.67) + 2.9 \times 10^{-5} \]

1. \( K_C = 0.00001 \text{ l/sec} \)
2. \( K_C = 0.0001 \text{ l/sec} \)
Figure 55. Control on $X_n$ and $X_w$—Initial Point Below the Steady State
\[ I_0 = 3 \times 10^{-8} \text{Eins/sec-cm}^2 \]
\[ S_0 = 0.25 \text{ g-moles/l} \]
\[ T = 338^\circ \text{K} \]

Figure 56. Flow Rate Regulation at Low Steady State
Figure 57. Flow Rate Regulation at Metastable Steady State

$I_0 = 1.5 \times 10^{-8} \text{Eins/sec-cm}^2$

$S_0 = 0.25 \text{ g-moles/l}$

$T = 338^\circ \text{K}$
$I_0 = 3 \times 10^{-8} \text{Eins/sec-cm}^2$

$S_0 = 0.25 \text{ g-mole/l}$

$T = 393^\circ \text{K}$

Figure 58. Flow Rate Regulation at High Steady State
Figure 59. Reactor Performance Characteristics at Different Levels of Light Intensity
When the point is at metastable state, UV light on-off regulation should be employed. If the point is at the low stable state, the reaction can be started by using a CSTR.

In a CSTR, approximate optimization of light intensity or flow rate control to attain not only the reaction conversion but also the desired number average chain length. Figure 60 shows that the conversion, $X$ and number average chain length, $X_n$ with respect to reactor residence time (flow rate) for different levels of light intensity.

Note that the start-up policy of a CSTR to determine the molecular weight distribution by varying the light intensity and/or the inlet flow rate is numerically studied and shown in Appendix D.
Figure 60. Model Simulation of Optimal Light Intensity and Residence Time Profiles

$S_0 = 0.015$ g-moles/l

$T = 338^\circ$K

(1) High S.S.

(2) Low & Meta S.S.
Based on the results of this study, the following conclusions are made:

The concentration of active polymer as a function of time for addition photopolymerization has been evaluated analytically. It is verified that the quasi-stationary state approximation used for active polymers is valid for photopolymerization reactions.

It is shown that it is possible to modify appreciably the breadth of the molecular weight distribution and to increase the polydispersity by up to 80% theoretically and numerically for a free radical photopolymerization in a periodically operated in a CSTR. The broadening depends on the parameter $\tau_{\text{off}}/\tau$, the ratio of light-off period to light on/off period, when compared with steady-state operation and the conversion and number average chain length appear to be little affected by the periodic operation.

Both perfect and imperfect mixing models have been studied for free-radical polymerization reactors. It appears that the two-region model is likely to be more realistic for photopolymerization process, as it agrees well with experimental results. Disagreement between perfect mixing model and experimental data suggests the possibility of fluid elements circulating in a CSTR.
The polydispersity of molecular weight distribution of the polymer formed in batch reactor is shown to depend markedly on dose rate, fractional volume of high dose rate and rate of mass transfer between the two regions. In the process where the polydispersity is maintained within a certain range the light absorption in low dose region is small but significant and cannot be set equal to zero.

The stabilization of the metastable state in an isothermal CSTR has been examined. The photochemical reactor exhibits precise control of conversion and molecular weight for a simple on-off regulation of light intensity. As a result, it is shown that the polydispersity at the controlled steady state is higher than that at real metastable state.

On-off regulation of flow rate at low stable state and metastable state also have been investigated. The results show that no noticeable increase in polydispersity occurs at these steady states. The number average chain length changes proportionally with an increase or decrease in weight average chain length. The reason is, the flow rate regulation cannot produce wide range difference in active polymer concentration which may be achieved by using light on-off regulation in photopolymerization process.

The feasibility of controlling a CSTR when operating at a metastable point is studied theoretically for the photopolymerization reaction. Stable operation of the system is dependent upon the magnitude of the proportionality constant. In the
examples shown here, stability is obtained only for values of $K_c$ approaching on-off control. For the starting point above or below the real metastable state, the smaller $K_c$ values will cause the reaction system runaway.

The rate of initiation by ultraviolet light may be changed very rapidly and may lead to greater reactor stability and ease of reactor control. Better reactor performance is obtained as compared with other periodic polymerization reactors.

The method is described for deriving equations for the three moments and the degree of polymerization directly from the polymerization kinetics for photopolymerization in CSTRs. The determination of these moments leads to expressions for number average chain length, weight average chain length, polydispersity, and molecular weight distribution of a polymer as a function of the parameter, ratio of light-off period to the light on-off period. These results are exact, and no simplifying assumptions need to be made in their derivation.

For further study, the following recommendation is made: It is indispensable for representing $I_o$, $\bar{R}_1$ and $M$ with discontinuities, particularly periodic phenomena, by employing the Fourier series. The Fourier coefficients can often be computed efficiently by the method of Fast Fourier transformation, which results in a considerable savings of computation time. The moments of dead polymer may be calculated by the integration of equations and lead to the expression of MWD. Emphasis is placed on the reaction time, instead of cycle number in the unsteady state process.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_o$</td>
<td>Incident light intensity, Eins/sec-cm$^2$</td>
</tr>
<tr>
<td>$I_{as}$</td>
<td>Absorbed light intensity, Eins/sec-cm$^3$</td>
</tr>
<tr>
<td>$i,j$</td>
<td>Number of monomer units</td>
</tr>
<tr>
<td>$K_c$</td>
<td>Controller proportional constant</td>
</tr>
<tr>
<td>$K_d$</td>
<td>Rate constant for reaction of sensitizer radical with monomer, cc/g-mole-sec</td>
</tr>
<tr>
<td>$K_i$</td>
<td>Rate constant for initiation 3rd order in monomer, cc$^2$/g-mole$^2$-sec</td>
</tr>
<tr>
<td>$K_f$</td>
<td>Rate constant for chain transfer to monomer, cc/g-mole-sec</td>
</tr>
<tr>
<td>$K_p$</td>
<td>Propagation rate constant, cc/g-mole-sec</td>
</tr>
<tr>
<td>$K_{tc}$</td>
<td>Rate constant for termination by combination, cc/g-mole-sec</td>
</tr>
<tr>
<td>$K_{td}$</td>
<td>Rate constant for termination by disproportionation, cc/g-mole-sec</td>
</tr>
<tr>
<td>$K_t$</td>
<td>$K_{tc} + K_{td}$</td>
</tr>
<tr>
<td>$L$</td>
<td>Reactor length, cm</td>
</tr>
<tr>
<td>$M_o$</td>
<td>Monomer concentration in feed, g-moles/cc</td>
</tr>
<tr>
<td>$M$</td>
<td>Monomer concentration in reactor, g-moles/cc</td>
</tr>
<tr>
<td>$P_i$</td>
<td>Concentration of dead polymer of chain length $i$ monomer units, g-mole/cc</td>
</tr>
<tr>
<td>$\sum P_i$</td>
<td>Zeroth moment of dead polymer, g-moles/cc</td>
</tr>
<tr>
<td>$\sum_i P_i$</td>
<td>First moment of dead polymer, g-moles/cc</td>
</tr>
<tr>
<td>$\sum_i^2 P_i$</td>
<td>Second moment of dead polymer, g-moles/cc</td>
</tr>
<tr>
<td>PD</td>
<td>Polydispersity, dimensionless</td>
</tr>
<tr>
<td>$Q$</td>
<td>Volumetric flow rate, cc/sec</td>
</tr>
<tr>
<td>$q$</td>
<td>Volumetric flow rate between two regions, cc/sec</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------------------</td>
</tr>
<tr>
<td>$R_i$</td>
<td>Concentration of free radical of chain length i monomer units, g-moles/cc</td>
</tr>
<tr>
<td>$\Sigma R_i$</td>
<td>Total active polymer or zeroth moment of active polymer, g-moles/cc</td>
</tr>
<tr>
<td>$\Sigma_i R_i$</td>
<td>First moment of active polymer, g-moles/cc</td>
</tr>
<tr>
<td>$\Sigma_i^2 R_i$</td>
<td>Second moment of active polymer, g-moles/cc</td>
</tr>
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<td>$S_o$</td>
<td>Sensitizer concentration in feed, g-moles/cc</td>
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<tr>
<td>$S$</td>
<td>Sensitizer concentration in reactor, g-moles/cc</td>
</tr>
<tr>
<td>$t$</td>
<td>Time, sec</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature in reactor, °K</td>
</tr>
<tr>
<td>$V$</td>
<td>Reactor volume, cc</td>
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<tr>
<td>$W_i$</td>
<td>Weight fraction of polymer of chain length i monomer units, dimensionless</td>
</tr>
<tr>
<td>$x$</td>
<td>Distance, cm</td>
</tr>
<tr>
<td>$X$</td>
<td>Fractional conversion, dimensionless</td>
</tr>
<tr>
<td>$X_n$</td>
<td>Number average chain length, dimensionless</td>
</tr>
<tr>
<td>$X_w$</td>
<td>Weight average chain length, dimensionless</td>
</tr>
<tr>
<td>$Z$</td>
<td>Distance, cm</td>
</tr>
<tr>
<td>Greek Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>( \Omega_i )</td>
<td>Total initiation rate, g-moles/cc-sec</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>Fractional change in volume between zero and complete conversion, dimensionless</td>
</tr>
<tr>
<td>( \epsilon_m )</td>
<td>Molar absorptivity of monomer, cm(^2)/g-moles</td>
</tr>
<tr>
<td>( \epsilon_{p_i} )</td>
<td>Molar absorptivity of dead polymer of chain length of i monomer units, cm(^2)/g-moles</td>
</tr>
<tr>
<td>( \epsilon_s )</td>
<td>Molar absorptivity of sensitizer, cm(^2)/g-moles</td>
</tr>
<tr>
<td>( \phi_s )</td>
<td>Quantum yield from sensitizer, g-moles/Eins</td>
</tr>
<tr>
<td>( \tau_{off} )</td>
<td>UV light-off period, sec</td>
</tr>
<tr>
<td>( \tau )</td>
<td>Forced period, UV light on/off period, sec</td>
</tr>
<tr>
<td>( \phi )</td>
<td>Generating function</td>
</tr>
<tr>
<td>( \theta )</td>
<td>Reactor residence time, sec</td>
</tr>
</tbody>
</table>
Table 3

Summary of Kinetic Model Parameters and Thermophysical Properties Data

\[
\begin{align*}
(K_p)_o &= 1.051 \times 10^7 \exp\left(-\frac{3557}{T}\right) \text{ liter/g-mole-sec} \\
(K_t)_o &= 1.255 \times 10^9 \exp\left(-\frac{844}{T}\right) \text{ liter/g-mole-sec} \\
(K_f)_o &= 2.31 \times 10^6 \exp\left(-\frac{6377}{T}\right) \text{ liter/g-mole-sec} \\
K_i &= 2.19 \times 10^5 \exp\left(-\frac{13810}{T}\right) \text{ liter}^2/\text{g-mole}^2\text{-sec} \\
A_1 &= 2.57 - 5.05 \times 10^{-3}T \\
A_2 &= 9.56 - 1.76 \times 10^{-2}T \\
A_3 &= -3.03 + 7.85 \times 10^{-3}T \\
\epsilon_m &= 0.0155 \text{ liter/g-mole-cm} \\
\epsilon_s &= 88.5 \text{ liter/g-mole-cm} \\
\epsilon_{Pi} &= 76.2 \text{ liter/g-mole-cm} \\
\phi_s &= 0.072 \text{ g-mole/Eins} \\
\rho_m &= 924 - 0.918 \times (T-273.1) \text{ g/liter} \\
\rho_p &= 1084.8 - 0.605 \times (T-273.1) \text{ g/liter}
\end{align*}
\]
APPENDIX A

CALCULATION OF MWD AT STEADY STATE IN CSTR
For addition polymers produced in continuous stirred-tank reactors, a method is described for deriving equations for the degree of polymerization directly from the equations for the polymerization kinetics. Several investigators (51) (52) have solved the kinetic equations for free radical polymerization in CSTR to obtain expressions for the polymerization size distribution as a function of reactor operating conditions. The purpose of this study is to present relationships from which the moments, number average chain length $X_n$, and weight average chain length $X_w$ may be calculated and to illustrate the derivation of these quantities from the photopolymerization system.

Mass-balance equations of monomer and free radical from the reaction mechanism expressed in Chapter 2

\[
\frac{dM}{dt} = \frac{M}{\theta} - \Omega_i - \frac{M}{\theta} \quad \Omega_i = K_p M_i^c R_i + K_d (S^\cdot)M
\]

\[
\frac{dS^\cdot}{dt} = 2\phi S^\cdot \alpha_s - K_d (S^\cdot)M - \frac{S^\cdot}{\theta}
\]

\[
\frac{dR_1}{dt} = K_d (S^\cdot)M - K_p M R_1 - K_t R_1 \sum R_i - \frac{R_1}{\theta}
\]

\[
\frac{dR_2}{dt} = K_p M R_1 - K_p M R_2 - K_t R_2 \sum R_i - \frac{R_2}{\theta}
\]

\[\vdots\]

\[
\frac{dR_j}{dt} = K_p M R_{j-1} - K_p M R_j - K_t R_j \sum R_i - \frac{R_j}{\theta}
\]

Similarly for the dead polymers the mass-balance is given by

\[
\frac{dP_j}{dt} = \frac{1}{2} K_t R \sum R_i - \frac{P_j}{\theta}
\]  \hspace{1cm} (1)
\[
\frac{dP_3}{dt} = K_t R_1 R_2 - \frac{P_3}{\theta} \quad (2)
\]

\[
\frac{dP_4}{dt} = K_t (R_1 R_3 + \frac{1}{2} R_2 R_2) - \frac{P_4}{\theta} \quad (3)
\]

\[
\frac{dP_5}{dt} = K_t (R_1 R_4 + R_2 R_3) - \frac{P_5}{\theta} \quad (4)
\]

\[
\frac{dP_6}{dt} = K_t (R_1 R_5 + R_2 R_4 + \frac{1}{2} R_3 R_3) - \frac{P_6}{\theta} \quad (5)
\]

\[
\ldots
\]

\[
\frac{dP_i}{dt} = \frac{1}{2} K_t \sum_{i=1}^{j-1} R_i R_{j-i} - \frac{P_j}{\theta} \quad (6)
\]

At steady state, all the derivatives are set equal to zero. Therefore

\[
S. = \frac{2\phi_s I_{as}}{\frac{1}{\theta} + K_d M}
\]

\[
M = \frac{M_o}{1 + K_p \sum R_i + K_d S.}
\]

\[
= \frac{M_o - (2\phi_s I_{as})}{1 + K_p \sum R_i}
\]

\[
R_1 = \frac{K_p M}{K_p M + K_t \sum R_i + \frac{1}{\theta}} \frac{2\phi_s I_{as}}{\frac{1}{\theta} + K_d M}
\]
\[ R_2 = \frac{K_P M R_1}{K_P M + K_t \Sigma R_i + \frac{1}{\theta}} \]
\[ = \frac{K_d K_P M^2}{(K_P M + K_t \Sigma R_i + \frac{1}{\theta})^2} \frac{2 \phi_s I_{as}}{\frac{1}{\theta} + K_d M} \]

\[ R_j = \frac{K_d K_j^{-1} M^j}{(K_P M + K_t \Sigma R_i + \frac{1}{\theta})^j} \frac{2 \phi_s I_{as}}{\frac{1}{\theta} + K_d M} \]

The sum of equations of active polymer to infinity gives

\[ \sum_{i=1}^{\infty} R_i = K_d \frac{2 \phi_s I_{as}}{\frac{1}{\theta} + K_d M} \sum_{i=1}^{\infty} \left( \frac{K_P}{K_P M + K_t \Sigma R_i + \frac{1}{\theta}} \right)^i \]
\[ = K_d \frac{2 \phi_s I_{as}}{\frac{1}{\theta} + K_d M} \sum_{i=1}^{\infty} \left( \frac{K_P}{K_P M + K_t \Sigma R_i + \frac{1}{\theta}} \right)^i \]

(7)

Since

\[ \frac{K_P M}{K_P M + K_t \Sigma R_i + \frac{1}{\theta}} < 1 \]

and

\[ K_d M >> \frac{1}{\theta} \]

also it can be assumed that

\[ K_d = K_P \]

then equation (7) reduces to

\[ \sum_{i=1}^{\infty} R_i = \frac{2 \phi_s I_{as}}{\frac{1}{\theta} + K_d M} \left( \frac{K_P M}{K_t \Sigma R_i} \right) \]
\[ = \frac{2 \phi_s I_{as}}{K_t \Sigma R_i} \]
So that the total active polymer can be expressed as

$$\sum R_i = \left( \frac{2\phi s_{as}}{K_t} \right)^{1/2}$$

Substituting the solved concentrations of active polymers, total polymer and monomer into the equations (1) through (6), finally one obtains

$$P_j = \theta K_t \left( \frac{2\phi s_{as}}{K_p} \right)^2 \left( \frac{1}{2} \right)^j \left( \frac{K_M}{K_p + K_t \sum R_i} \right)^j$$

$$= A \left( \frac{1}{2} \right)^j B \quad (8)$$

where

$$A = \theta K_t \left( \frac{2\phi s_{as}}{K_p} \right)^2$$

$$B = \frac{K_M}{K_p + K_t \sum R_i}$$

and use of equation (8) to obtain expressions for the moments gives

$$\sum P_j = \frac{1}{2} AB^2 (1 + 2B + 3B^2 + 4B^3 + \cdots)$$

$$= \frac{1}{2} AB^2 \frac{1}{(1-B)^2}$$

$$\sum j P_j = AB^2 (1 + 3B + 6B^2 + 10B^3 + 15B^4 + 21B^5 + \cdots)$$

$$= AB^2 \frac{1}{(1-B)^3}$$

$$\sum j^2 P_j = AB^2 (3 + 12B + 30B^2 + 60B^3 + 105B^4 + \cdots)$$

$$-AB^2 (1 + 3B + 6B^2 + 10B^3 + 15B^4 + \cdots)$$

$$= AB^2 \left( \frac{3}{(1-B)^4} \right) - \frac{1}{(1-B)^3}$$
Finally, the number average and weight average chain length can be obtained

\[ X_w = \frac{\sum j^2 p_j}{\sum j p_j} \]
\[ = \frac{3}{1-B} - 1 \]
\[ X_n = \frac{\sum j p_j}{\sum p_j} \]
\[ = \frac{2}{1-B} \]

Since \( B = 1 \), \( X_w \approx \frac{3}{1-B} \), and the ratio, polydispersity, is

\[ \frac{X_w}{X_n} = 1.5 \]

Thus a sequence of steady state concentrations of monomer and the molecular weight distribution of polymer from reactor can be calculated.

Also

\[ K_p = f_1(\text{temp.}) \]
\[ K_t = f_2(\text{temp.}) \]
\[ \sum R_i = f_3(I_o, \text{temp.}) \]
\[ M = f_4(I_o, \text{temp.}) \]

so that

\[ B = \frac{K_p M}{K_p M + K_t \sum R_i} \]
\[ = f_5(I_o, \text{temp.}) \]

where \( f_i \) is a function.

Since \( X_n \) and \( X_w \) are very strongly dependent upon the value of \( B \) which is very close to unity, the values of \( X_n \) and \( X_w \) will depend upon the \( I_o \) and temperature. The effects of \( I_o \) and/or
temperatures on $X_n$, $X_w$ and molecular weight distribution are shown in Figures 61 through 64. The distribution curve may shift to the higher molecular weight once the temperature increases at a given $I_o$. The $X_n$ increases proportionally with $X_w$ due to the term, $1-B$. Also, the same effect is observed in the decrease of $I_o$ at a given temperature. Figure 65 shows that the polydispersity and $X_n$ behavior have been calculated numerically by UV light on and off using the equations (1)—(5) in Chapter 4. It is verified that the polydispersity, although sharply rising, can be reached steady state again and $X_n$ can be reached to a higher location which is the steady state of thermal polymerization.
Figure 61. MWD at Steady State

$I_0 = 5.85 \times 10^{-8} \text{Ein}/\text{sec-cm}^2$
$S_0 = 0.015 \text{ g-moles/l}$
$\theta = 6000 \text{ sec}$
$T = 338^\circ \text{K}$
$S_0 = 0.015 \text{ g-moles/l}$

$\theta = 6000 \text{ sec.}$

$T = 358^\circ \text{K}$

$I_0 (\text{Eins/sec-cm}^2)$

$1 \quad 11.7 \times 10^{-8}$

$2 \quad 5.85 \times 10^{-8}$

Figure 62. Effect of $I_0$ on MWD at Steady State with $T = 358^\circ \text{K}$
Figure 63. Effect of $I_o$ on MWD at Steady State with $T = 393^\circ K$

$S_o = 0.015$ g-moles/l
$\theta = 3000$ sec.
$T = 393^\circ K$

$I_o (\text{Eins/sec-cm}^2)$

1. $11.7 \times 10^{-8}$
2. $9.36 \times 10^{-8}$
Figure 64. Effect of $I_0$ on MWD at Steady State with $T = 393^\circ K$
Figure 65. Transient Response of Polydispersity by the UV Light ON and OFF

\[ I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2 \]
\[ S_0 = 0.015 \text{ g-moles/l} \]
\[ \theta = 9200 \text{ sec} \]
\[ T = 373^\circ \text{K} \]
APPENDIX B

SOLUTION PHOTO-POLYMERIZATION OF BATCH REACTOR
In solution polymerization the viscosity of the reaction mass is much lower than in bulk polymerization, and heat transfer is thereby improved. The choice of solvent is important as it may affect both the properties of the polymer and the rate of reaction (53). Here, the experimental investigation of the solution polymerization of styrene with initiation by photo-dissociation of sensitizer was made in batch reactor. Also, the comparison between bulk and solution photopolymerization will be made.

Figure 66 shows experimental results obtained at four different sensitizer concentrations and three different solvent concentrations. For the two runs at 50% of benzene (0.1 l benzene and 0.1 l styrene), the results show that if a higher sensitizer concentration is used, a longer reaction time is needed to consume all the sensitizer, and the conversion will increase. For the runs at 30% benzene (0.06 l benzene and 0.14 l styrene) and 25% benzene (0.05 l benzene and 0.15 l styrene), the results show that higher conversions (75% and 90% respectively) are reached when more concentrated solutions of styrene and sensitizer are used. Figure 66 also shows that the $X_n$ values are approximately 75 and do not vary appreciably for all the runs. The measured $X_w$ values are slightly higher than the low $S_o$ runs and are about 200.

As compared to the result of Figure 67, the reaction rate is lower in solution polymerization, and the molecular weight is lower than that obtained by bulk polymerization. This means
Figure 66. Experimental Data of Photopolymerization at Different Concentrations of Sensitizer and Solvent
Figure 67. Experimental Data of Bulk Polymerization

$I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$
$S_0 = 0.1 \text{ g-moles/l}$
$T = 338^\circ \text{K}$
the lower polydispersity will be obtained with the batch process of solution polymerization.
APPENDIX C

EFFECT OF NO MIXING ON REACTOR PERFORMANCE
The perfect mixing (PM) state with respect to chain centers, which are uniformly mixed throughout the reactor, has been considered in Chapter 6. The mean chain lifetime is long compared with the mixing time in the reactor, and the effective initiation rate is the average rate. For the opposite extreme mixing state, the no mixing (NM) state, the chain centers are born and die at the same location, subject to the local initiation rate. The mean chain lifetime is short compared with the mixing time. (33) In our study, the mass consumption rate and reactor performance characteristics in a CSTR at no mixing will be investigated and compared with perfect mixing state.

For sensitized initiation and thermal decomposition of monomer, the local initiation rate in the absence of mixing is given by

$$\Omega_i(Z) = 2K_i M^3 + 2\phi_s I_{as} - (\epsilon_s S + \epsilon_m M_o)Z$$

$$= 2K_i M^3 + 2\phi_s I_o \epsilon_s S - CZ$$

$$= A + Be$$

where

$$A = 2K_i M^3$$

$$B = 2\phi_s I_o \epsilon_s S$$

$$C = \epsilon_s S + \epsilon_m M_o$$

The sensitizer and monomer are assumed to be perfectly mixed. Thus the concentrations of the sensitizer and the monomer are uniform throughout the reactor and are independent of distance, Z.
The averaged square root of initiation rate is integrated over the reactor length

\[
\bar{\Omega}_{1/2} = \frac{1}{L} \int_0^L (A + Be^{-CZ})^{1/2} \, dZ
\]

\[
= -\frac{1}{CL} \int_1^D \frac{(A + Bx)^{1/2}}{x} \, dx
\]

Equation (1) can be integrated, and becomes

\[
\bar{\Omega}_{1/2} = -\frac{1}{CL} \left\{ 2(E-F) + \sqrt{A} \xi_n \frac{(E-\sqrt{A})(F+\sqrt{A})}{(E+\sqrt{A})(F-\sqrt{A})} \right\}
\]

where

\[
E = \sqrt{A+BD}
\]

\[
F = \sqrt{A+BE}
\]

The resulting equation of \( \bar{\Omega}_{1/2} \) are used in the calculation of mass consumption rate in CSTR

\[
MCR = \bar{\Omega}_{1/2} M \frac{K_D}{K_{t1/2} e} (A_1X + A_2X^2 + A_3X^3)
\]

Therefore the MCR of no mixing is strongly dependent upon the light absorption compared with that of perfect mixing. The effect of sensitizer concentration on the MCR for both no mixing and perfect mixing states is shown in Figure 68. It shows that the sensitizer concentration, \( S_0 \) has appreciable effect on the
MCR of no mixing state. Also, the MCR curves of different temperatures are presented in Figure 69. It is verified that both perfect mixing and no mixing have the same effect on MCR at temperatures 85 °C and 100 °C. Figure 70 shows the calculated results representing the reactor performance characteristics in terms of fractional conversion X. An increase in θ at a fixed $I_o$ results in the transition from the perfect mixing state to no mixing state.
Figure 68. Effect of Sensitizer Concentration on MCR of Perfect and No Mixing

$I_0 = 1.5 \times 10^{-8}$ Eins/sec-cm$^2$
$T = 338^\circ$K
$I_0 = 1.5 \times 10^{-8}$ Eins/sec-cm$^2$

$S_0 = 0.015$ g-moles/l

**Temperature**

1. $358^\circ K$
2. $373^\circ K$

**Figure 69. Effect of Temperature on MCR of Perfect and No Mixing**
Figure 70. Effect of No Mixing on Reactor Performance Characteristics

$I_0 = 1.5 \times 10^{-8} \text{Eins/sec-cm}^2$
$S_0 = 0.25 \text{ g-moles/l}$
$T = 338^\circ K$
APPENDIX D

START-UP AND DYNAMIC BEHAVIOR OF A CSTR
This study is concerned with the dynamics of CSTR during the start-up period. Predictions of dynamic behavior are realistic only when allowance is made for changes which occur in either the light intensity incident upon the reactor or the flow rate to the reactor.

The objective function to be reduced to zero as the process reaches to the steady state might be

\[ F = \left( \frac{X_n}{X_{ns}} - 1 \right)^2 + \left( \frac{P}{P_s} - 1 \right)^2 + \left( \frac{X}{X_s} - 1 \right)^2 \]

where \( X_{ns}, P_s \) and \( X_s \) are the values of number average chain length, polydispersity and conversion, respectively at steady state. Material balances for a CSTR are described as in Appendix 1. The properties of \( X, X_n, X_w/X_n \) and \( F \) can be found as a function of time by numerical treatment of the differential equations. The form of the solutions depends on the start-up procedures which determine the initial values. A fourth-order Runge-Kutta method is used in this work. If the reactor \( I_o \) is linearly increased from 0 to \( 1.5\times10^{-8}\) Eins/sec-cm\(^2\) and then kept constant, the changes in conversion \( X \), number average chain length \( X_n \), polydispersity \( X_w/X_n \) and objective function \( F \) with time are shown by curve A in Figure 71. Sharp decline in \( X_n \) and \( F \) soon after start-up would, in this particular process, be accompanied by catastrophic events and this region would not be attained. The behavior of a real reactor is not as violent as this. If the flow is not started until the \( I_o \) reaches the predicted steady-state value the changes in \( X, X_n, X_w/X_n \) and \( F \) are altered. This is shown by curve B. Also, the curve C shows that \( I_o \) is linearly
S₀ = 0.25 moles/1
θ = 10000 sec.
T = 338°K

Figure 71. X, Xₙ and PD Changes with Different I₀ Paths
decreased from $3.0 \times 10^{-8}$ to $1.5 \times 10^{-8}$ $\text{Ein} / \text{sec-cm}^2$ and then kept constant, the changes in $X, \frac{X_n}{X_n}, \frac{X_w}{X_n}$ and $F$ are approximately the same as those in curve B. The location of the steady state is not affected by the variations of $I_o$ and the flow rate with $X, \frac{X_n}{X_n}, \frac{X_w}{X_n}$ and $F$ whereas the approach to the steady state is affected greatly. The approach to the steady state depends on start-up procedure.

Figure 72 shows the changes in $X, \frac{X_n}{X_n}, \frac{X_w}{X_n}$ and $F$ that occur when the flow rates are stepwise increased from zero to $3.0 \times 10^{-5}$ $\ell / \text{sec}$, then maintained at $3.0 \times 10^{-5}$ $\ell / \text{sec}$ and stepwise decreased from $6.0 \times 10^{-5}$ $\ell / \text{sec}$ to $3.0 \times 10^{-5}$ $\ell / \text{sec}$. It is shown that such variations, although small, can be expected to have a noticeable effect on reactor performance.
Figure 72. $X$, $X_n$ and PD Changes with Different Flow Rate Paths

$I_0 = 1.5 \times 10^{-8} \text{Eins/sec-cm}^2$
$S_0 = 0.25 \text{ g-moles/l}$
$T = 338^\circ \text{K}$
APPENDIX E

SUMMARY OF EXPERIMENTAL RESULTS—

PERIODIC OPERATION IN A CSTR
TABLE 4

PERIODIC OPERATION EXPERIMENT 1

$I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$

$S_0 = 0.015 \text{ g-moles/l}$

$\theta = 9000 \text{ sec.}$

$T = 373^\circ \text{K}$

$(\tau_{off}/\tau_{av.}) = 0.25$

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<th>$X_w$</th>
<th>PD</th>
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* steady state reached, periodic operation started
TABLE 5
PERIODIC OPERATION EXPERIMENT 2

$I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$

$S_0 = 0.015 \text{ g-moles/l}$

$\theta = 9000 \text{ sec.}$

$T = 373^\circ \text{K}$

$(\tau_{off}/\tau)_{av} = 0.28$

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* steady state reached, periodic operation started
TABLE 6
PERIODIC OPERATION EXPERIMENT 3

$I_o = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$

$S_o = 0.015 \text{ g-moles/l}$

$\theta = 6000 \text{ sec.}$

$T = 358^\circ \text{K}$

$\tau_{off}/\tau = 0.1$

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* staedy state reached, periodic operation started
### TABLE 7

**PERIODIC OPERATION EXPERIMENT 4**

\[ I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2 \]

\[ S_0 = 0.015 \text{g-moles/l} \]

\[ \theta = 6000 \text{ sec.} \]

\[ T = 358^\circ \text{K} \]

\[ \tau_{off}/\tau = 0.333 \]

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<td>191</td>
<td>562</td>
<td>2.95</td>
</tr>
<tr>
<td>14</td>
<td>0.203</td>
<td>184</td>
<td>561</td>
<td>3.05</td>
</tr>
<tr>
<td>15</td>
<td>0.224</td>
<td>180</td>
<td>543</td>
<td>3.01</td>
</tr>
</tbody>
</table>

* steady state reached, periodic operation started
**TABLE 8**

**PERIODIC OPERATION EXPERIMENT 5**

$I_0 = 11.7 \times 10^{-8}\text{Eins/sec-cm}^2$

$S_0 = 0.015 \text{ g-moles/l}$

$\theta = 6000 \text{ sec.}$

$T = 358^\circ\text{K}$

$\tau_{\text{off}}/\tau = 0.5$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$X$</th>
<th>$X_n$</th>
<th>$X_w$</th>
<th>PD</th>
</tr>
</thead>
<tbody>
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<td>581</td>
<td>2.91</td>
</tr>
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<td>0.222</td>
<td>196</td>
<td>584</td>
<td>2.97</td>
</tr>
<tr>
<td>3</td>
<td>0.229</td>
<td>200</td>
<td>578</td>
<td>2.88</td>
</tr>
<tr>
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<td>0.161</td>
<td>198</td>
<td>588</td>
<td>2.98</td>
</tr>
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<td>0.195</td>
<td>207</td>
<td>605</td>
<td>2.93</td>
</tr>
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<td>0.184</td>
<td>185</td>
<td>578</td>
<td>3.13</td>
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<td>9</td>
<td>0.179</td>
<td>193</td>
<td>618</td>
<td>3.20</td>
</tr>
<tr>
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<td>0.129</td>
<td>182</td>
<td>641</td>
<td>3.52</td>
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<td>11</td>
<td>0.181</td>
<td>184</td>
<td>613</td>
<td>3.32</td>
</tr>
</tbody>
</table>

* steady state reached, periodic operation started
TABLE 9

PERIODIC OPERATION EXPERIMENT 6

\[ I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2 \]
\[ S_0 = 0.015 \text{ g-moles/l} \]
\[ \theta = 3200 \text{ sec.} \]
\[ T = 393^\circ \text{K} \]
\[ \tau_{off}/\tau = 0.5 \]

<table>
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<tr>
<th>Sample</th>
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<th>[X_w]</th>
<th>PD</th>
</tr>
</thead>
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<td>1027</td>
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</tr>
<tr>
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<td>0.396</td>
<td>335</td>
<td>914</td>
<td>2.73</td>
</tr>
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<td>259</td>
<td>725</td>
<td>2.80</td>
</tr>
<tr>
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<td>283</td>
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<td>3.09</td>
</tr>
<tr>
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<td>0.343</td>
<td>334</td>
<td>930</td>
<td>2.79</td>
</tr>
<tr>
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<td>0.263</td>
<td>376</td>
<td>1181</td>
<td>3.14</td>
</tr>
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<td>7</td>
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<td>1073</td>
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<td>341</td>
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<td>0.321</td>
<td>317</td>
<td>1046</td>
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<tr>
<td>10</td>
<td>0.234</td>
<td>358</td>
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<tr>
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<td>0.227</td>
<td>320</td>
<td>1084</td>
<td>3.39</td>
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</tbody>
</table>

* steady state reached, periodic operation started
TABLE 10

PERIODIC OPERATION EXPERIMENT 7

\[ I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2 \]
\[ S_0 = 0.015 \text{ g-moles/l} \]
\[ \theta = 3000 \text{ sec.} \]
\[ T = 393^\circ\text{K} \]
\[ \tau_{off}/\tau = 0.2 \]

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<th>X_n</th>
<th>X_w</th>
<th>PD</th>
</tr>
</thead>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
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<td>360</td>
<td>1219</td>
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<tr>
<td>6</td>
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<td>375</td>
<td>1142</td>
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</tr>
<tr>
<td>7</td>
<td>0.283</td>
<td>374</td>
<td>1152</td>
<td>3.08</td>
</tr>
<tr>
<td>8</td>
<td>0.262</td>
<td>371</td>
<td>1122</td>
<td>3.03</td>
</tr>
<tr>
<td>9</td>
<td>0.284</td>
<td>365</td>
<td>1122</td>
<td>3.07</td>
</tr>
<tr>
<td>10</td>
<td>0.251</td>
<td>309</td>
<td>1123</td>
<td>3.63</td>
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<td>317</td>
<td>1033</td>
<td>3.25</td>
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<tr>
<td>12</td>
<td>0.259</td>
<td>376</td>
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</table>

* steady state reached, periodic operation started
TABLE 11
PERIODIC OPERATION EXPERIMENT 8

\[ I_o = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2 \]
\[ S_o = 0.015 \text{ g-moles/l} \]
\[ \theta = 6000 \text{ sec.} \]
\[ T = 358^\circ \text{K} \]
\[ \tau_{off}/\tau = 0.5 \quad (\text{the same condition as in exp. 5}) \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>X</th>
<th>X_n</th>
<th>X_w</th>
<th>PD</th>
</tr>
</thead>
<tbody>
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<td>371</td>
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</tr>
<tr>
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<td>-</td>
<td>128</td>
<td>380</td>
<td>2.97</td>
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<td>3</td>
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<td>149</td>
<td>426</td>
<td>3.19  *</td>
</tr>
<tr>
<td>4</td>
<td>0.158</td>
<td>176</td>
<td>514</td>
<td>2.92</td>
</tr>
<tr>
<td>5</td>
<td>0.185</td>
<td>160</td>
<td>485</td>
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<td>0.134</td>
<td>157</td>
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<td>3.20</td>
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<td>0.174</td>
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<td>511</td>
<td>3.22</td>
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<td>0.129</td>
<td>157</td>
<td>573</td>
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<td>0.136</td>
<td>151</td>
<td>528</td>
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<tr>
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<td>3.29</td>
</tr>
<tr>
<td>12</td>
<td>0.123</td>
<td>155</td>
<td>536</td>
<td>3.45</td>
</tr>
<tr>
<td>13</td>
<td>0.169</td>
<td>154</td>
<td>512</td>
<td>3.32</td>
</tr>
<tr>
<td>14</td>
<td>0.123</td>
<td>152</td>
<td>526</td>
<td>3.45</td>
</tr>
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<td>15</td>
<td>0.155</td>
<td>165</td>
<td>590</td>
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<td>170</td>
<td>637</td>
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<tr>
<td>17</td>
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<td>155</td>
<td>550</td>
<td>3.58</td>
</tr>
</tbody>
</table>

* steady state reached, periodic operation started
TABLE 12

PERIODIC OPERATION EXPERIMENT 9

$I_0 = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$

$S_0 = 0.015 \text{ g-moles/l}$

$\theta = 6000 \text{ sec.}$

$T = 338°K$

$\tau_{off}/\tau = 0.5$

<table>
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<th>$X_w$</th>
<th>PD</th>
</tr>
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<td>363</td>
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<td>102</td>
<td>297</td>
<td>2.92*</td>
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<td>5</td>
<td>0.106</td>
<td>111</td>
<td>321</td>
<td>2.88</td>
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<td>94</td>
<td>282</td>
<td>2.99</td>
</tr>
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<td>109</td>
<td>316</td>
<td>2.89</td>
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<td>106</td>
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<td>100</td>
<td>295</td>
<td>2.96</td>
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<td>0.098</td>
<td>86</td>
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<td>3.13</td>
</tr>
<tr>
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<td>0.065</td>
<td>91</td>
<td>284</td>
<td>3.13</td>
</tr>
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<td>0.095</td>
<td>85</td>
<td>276</td>
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<td>84</td>
<td>265</td>
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<td>281</td>
<td>3.29</td>
</tr>
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<td>266</td>
<td>3.20</td>
</tr>
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<td>276</td>
<td>3.20</td>
</tr>
</tbody>
</table>

* steady state reached, periodic operation started
TABLE 13
PERIODIC OPERATION EXPERIMENT 10

I_o = 11.7x10^{-8} Eins/sec-cm^2
S_o = 0.015 g-moles/l
θ = 6000 sec.
T = 338°K
τ_{off}/τ = 0.333

<table>
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<th>X_n</th>
<th>X_w</th>
<th>PD</th>
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</thead>
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<td>2.75</td>
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<td>117</td>
<td>398</td>
<td>3.41</td>
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<td>113</td>
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<td>3.45</td>
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<td>116</td>
<td>390</td>
<td>3.36</td>
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<td>3.56</td>
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<td>3.73</td>
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<td>377</td>
<td>3.51</td>
</tr>
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</table>

* steady state reached, periodic operation started
TABLE 14
PERIODIC OPERATION EXPERIMENT 11

$I_o = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$

$S_o = 0.015 \text{ g-mole/l}$

$\theta = 6000 \text{ sec.}$

$T = 358^\circ \text{K}$

$\tau_{off}/\tau = 0.8$

<table>
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<tr>
<th>Sample</th>
<th>$X$</th>
<th>$X_n$</th>
<th>$X_w$</th>
<th>PD</th>
</tr>
</thead>
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<td>143</td>
<td>516</td>
<td>3.60</td>
</tr>
<tr>
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<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0.252</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
| 6      | 0.251| 290   | 953   | 3.28| *
| 7      | 0.097| 301   | 1515  | 5.03|
| 8      | 0.119| 307   | 1399  | 4.55|
| 9      | 0.095| 244   | 1248  | 5.13|
| 10     | 0.110| 212   | 1128  | 5.33|
| 11     | 0.096| 222   | 1350  | 6.08|
| 12     | 0.089| 160   | 895   | 5.58|
| 13     | 0.110| 193   | 1123  | 5.83|
| 14     | 0.094| 219   | 1119  | 5.11|
| 15     | 0.086| 253   | 1460  | 5.77|
| 16     | 0.112| 177   | 985   | 5.57|

* steady state reached, periodic operation started
APPENDIX F

SUMMARY OF EXPERIMENTAL RESULTS—
SOLUTION POLYMERIZATION OF BATCH REACTOR
TABLE 15

SOLUTION POLYMERIZATION EXPERIMENT 1

$I_o = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$

$T = 338^\circ \text{K}$

$S_o = 0.19 \text{ g-moles/l}$

Solution: 25% benzene

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (min)</th>
<th>X</th>
<th>$X_n$</th>
<th>$X_w$</th>
<th>PD</th>
</tr>
</thead>
<tbody>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>0.227</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>420</td>
<td>0.311</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>660</td>
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<td>0.807</td>
<td>-</td>
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<td>-</td>
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<tr>
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<td>1500</td>
<td>0.868</td>
<td>70</td>
<td>204</td>
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<td>-</td>
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<td>1620</td>
<td>0.879</td>
<td>-</td>
<td>-</td>
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<td>72</td>
<td>216</td>
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<td>1725</td>
<td>0.863</td>
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<td>0.877</td>
<td>-</td>
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<td>2055</td>
<td>0.898</td>
<td>73</td>
<td>211</td>
<td>2.89</td>
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</tbody>
</table>
TABLE 16
SOLUTION POLYMERIZATION EXPERIMENT 2

$I_o = 11.7 \times 10^{-8} \text{Eins/sec-cm}^2$

$T = 338^\circ\text{K}$

$S_o = 0.25 \text{ g-moles/l}$

Solution: 30% benzene

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (min)</th>
<th>$X$</th>
<th>$X_n$</th>
<th>$X_w$</th>
<th>PD</th>
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</tr>
<tr>
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<td>0.250</td>
<td>111</td>
<td>322</td>
<td>2.90</td>
</tr>
<tr>
<td>3</td>
<td>540</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>720</td>
<td>0.378</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
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<td>241</td>
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<td>-</td>
<td>-</td>
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<td>0.581</td>
<td>57</td>
<td>176</td>
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<td>0.760</td>
<td>47</td>
<td>163</td>
<td>3.46</td>
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</tbody>
</table>
TABLE 17

SOLUTION POLYMERIZATION EXPERIMENT 3

$I_0 = 11.7 \times 10^{-8} \text{ Eins/sec-cm}^2$

$T = 338^\circ K$

$S_0 = 0.125 \text{ g-moles/l}$

Solution: 50% benzene

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (min)</th>
<th>X</th>
<th>$X_n$</th>
<th>$X_w$</th>
<th>PD</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>343</td>
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<td>280</td>
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</tr>
</tbody>
</table>
TABLE 18

SOLUTION POLYMERIZATION EXPERIMENT 4

$I_0 = 11.7 \times 10^{-8}$ Einst/sec-cm²

$T = 338^\circ K$

$S_o = 0.05$ g-moles/l

Solution: 50% benzene

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (min)</th>
<th>X</th>
<th>$X_n$</th>
<th>$X_w$</th>
<th>PD</th>
</tr>
</thead>
<tbody>
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</tr>
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</tr>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>-</td>
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</tr>
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</table>
APPENDIX G

COMPUTER PROGRAM FOR CALCULATIONS
PROGRAM #1
FREE RADICAL CONCENTRATIONS CALCULATION
OF BATCH PHOTOPOLYMERIZATION

COMMON KP,KT,KI,XR1,XR2,XR3,XR4,XR5,XSR
REAL KI,KP,KT,KF,I1,IT

DOUBLE PRECISION PM,XM0,XM,XR1,XR2,XR3,XR4,XR5,XSR,
CR1,R2,R3,R4,R5,SR,F1,F2,F3,F4,F5,FSR,F0,D1F0,D1F1,D1F2,
D1F3,D1F4,D1F5,D1FSR,D2F0,D2F1,D2F2,D2F3,D2F4,D2F5,D2FSR,
D3F0,D3F1,D3F2,D3F3,D3F4,D3F5,D3FSR,D4F0,D4F1,D4F2,D4F3,
D4F4,D4F5,D4FSR,D5F0,D5F1,D5F2,D5F3,D5F4,D5FSR

DATA R1,R2,R3,R4,R5,SR/6*0.0/K=-1
H=0.01
IT=338.
KI=2.19E5*EXP(-13810/IT)
KP=1.051E7*EXP(-3557/IT)
KT=1.255E9*EXP(-844/IT)
RF=2.31E6*EXP(-6377/IT)
PM=924-.918*(IT-273.1)
PP=1084.8-.605*(IT-273.1)
E=PM/PP-1
XMO=PM-ZXMW
T=0
XM=XMO
XC=(XMO-XM)/(XMO+E*XM)
WRITE(6,80)
80 FORMAT('0','BATCH POLYMERIZATION WITH UV LIGHT'
WRITE(6,85)
85 FORMAT('0','THE CONC. OF R1,R2,R3,R4,R5 AND SUM OF R')

99 XK=XM
XR1=R1
XR2=R2
XR3=R3
XR4=R4
XR5=R5
XSR=SR
D1F0=H*F0(DUMMY)
D1F1=H*F1(DUMMY)
D1F2=H*F2(DUMMY)
D1F3=H*F3(DUMMY)
D1F4=H*F4(DUMMY)
D1F5=H*F5(DUMMY)
D1FSR=H*FSR(DUMMY)
XR=XM-D1F0/2
XR1=R1+D1F1/2
XR2=R2+D1F2/2
XR3=R3+D1F3/2
XR4=R4+D1F4/2
XR5=R5+D1F5/2
XSR=SR+D1FSR/2
D2F0=H*F0(DUMMY)
D2F1=H*F1(DUMMY)
D2F2=H*F2(DUMMY)
D2F3=H*F3(DUMMY)
D2F4=H*F4(DUMMY)
D2F5=H*F5(DUMMY)
D2FSR=N*FSR(DUMMY)
XR=XM+D2F0/2
XR1=R1+D2F1/2
XR2=R2+D2F2/2
XR3=R3+D2F3/2
XR4=R4+D2F4/2
XR5=R5+D2F5/2
XSR=SR+D2FSR/2
D3F0=H*F0(DUMMY)
D3F1=H*F1(DUMMY)
D3F2=H*F2(DUMMY)
D3F3=H*F3(DUMMY)
D3F4=H*F4(DUMMY)
D3F5=H*F5(DUMMY)
D3FSR=H*FSR(DUMMY)
XR=XM+D3F0
XR1=R1+D3F1
XR2=R2+D3F2
XR3=R3+D3F3
XR4=R4+D3F4
XR5=R5+D3F5
XSR=SR+D3FSR
D4F0=H*F0(DUMMY)
D4F1=H*F1(DUMMY)
D4F2=H*F2(DUMMY)
D4F3=H*F3(DUMMY)
D4F4=H*F4(DUMMY)
D4F5=H*F5(DUMMY)
D4FSR=H*FSR(DUMMY)
DF0=(D1F0+2*D2F0+2*D3F0+D4F0)/6
DF1=(D1F1+2*D2F1+2*D3F1+D4F1)/6
DF2=(D1F2+2*D2F2+2*D3F2+D4F2)/6
DF3=(D1F3+2*D2F3+2*D3F3+D4F3)/6
DF4=(D1F4+2*D2F4+2*D3F4+D4F4)/6
DF5=(D1F5+2*D2F5+2*D3F5+D4F5)/6
DFSR=(D1FSR+2*D2FSR+2*D3FSR+D4FSR)/6
XM=XM+DF0
R1=R1+DF1
R2=R2+DF2
R3=R3+DF3
R4=R4+DF4
R5=R5+DF5
SR=SR+DFSR
T=T+H
K=K+1
IF(T.GT.2000) GO TO 200
IF(K.R/1000*1000 .EQ. 0) GO TO 100
GO TO 99
100 WRITE(6,110) T,XM
110 FORMAT('0', 'TIME =', F5.1, 'X1 =', F11.8)
WRITE(6,120) R1,R2,R3,R4,R5,SR
120 FORMAT(' ', 6(D20.14, 1X))
GO TO 99
200 STOP
END

C
FUNCTION F0(DUMMY)
COMMON KP,KT,KT,XK,XSR,XR1,XR2,XR3,XR4,XR5,KF
REAL KI,KP,KT,KF
DOUBLE PRECISION XR1,XR2,XR3,XR4,XR5,XSR,F0,I1,XK
I1=2*KI*XK**3+2*0.072*0.000117/5.2*(1-EXP(-88.5*0.015*5.2))
F0=-I1-KP*XK*XSR
RETURN
END

C
FUNCTION F1(DUMMY)
COMMON KP,KT,KT,XK,XSR,XR1,XR2,XR3,XR4,XR5,KF
REAL KI,KP,KT,KF
DOUBLE PRECISION XR1,XR2,XR3,XR4,XR5,XSR,F1,I1,XK
I1=2*KI*XK**3+2*0.072*0.000117/5.2*(1-EXP(-88.5*0.015*5.2))
F1=I1-KF*XK*XSR-KT*XR1*XSR
RETURN
END

C
FUNCTION F2(DUMMY)
COMMON KP,KT,KT,XK,XSR,XR1,XR2,XR3,XR4,XR5,KF
REAL KI,KP,KT,KF
DOUBLE PRECISION XR1,XR2,XR3,XR4,XR5,XSR,F2,XK
F2=KP*XK*XK**2-KT*XR2*XSR
RETURN
END

C
FUNCTION F3(DUMMY)
COMMON KP,KT,KT,XK,XSR,XR1,XR2,XR3,XR4,XR5,KF
REAL KI,KP,KT,KF
DOUBLE PRECISION XR1,XR2,XR3,XR4,XR5,XSR,F3,XK
F3=KP*XK*XK*XK**3-KT*XR3*XSR
RETURN
END

C
FUNCTION F4(DUMMY)
COMMON KP,KT,KT,XK,XSR,XR1,XR2,XR3,XR4,XR5,KF
REAL KI,KP,KT,KF
DOUBLE PRECISION XR1,XR2,XR3,XR4,XR5,XSR,F4,XK
F4=KP*XK*XK*XK**4-KT*XR4*XSR
RETURN
END

C
FUNCTION F5(DUMMY)
COMMON KP,KT,KT,XK,XSR,XR1,XR2,XR3,XR4,XR5,KF
REAL KI,KP,KT,KF
DOUBLE PRECISION XR1,XR2,XR3,XR4,XR5,XSR,F5,XK
F5=KP*XK*XK*XK**5-KT*XR5*XSR
RETURN
END
FUNCTION FSR(DUMMY)
COMMON KP,KI,XK,XSR,XR1,XR2,XR3,XR4,XR5,KF
REAL KI,KP,KT,KF
DOUBLE PRECISION XR1,XR2,XR3,XR4,XR5,XSR,FSR,I1,XK
I1=2*KI*XK**3+2*.072*.000117/5.2*(1-EXP(-88.5*.015*5.2))
FSR=I1-KT*XSR**2
RETURN
END
PROGRAM 42
POLYDISPERSITY CALCULATION
UV LIGHT ON/OFF REGULATION AT LOW STEADY STATE

DIMENSION S(2000)
READ,SO,XIO,TEMP,SITA,R,V1
TAU=SITA

PM=924-.918*(TEMP-273.1)
XMW=104
XM0=PM/XMW
XKP=1.051E7*EXP(-3557/TEMP)
XKT=1.255E9*EXP(-844/TEMP)
XI=2.19E5*EXP(-13810/TEMP)

V=0.2
DV=V1/V
AS=0.072
ES=88.5
XL=5.2
XL1=XL/DV
XC1=SITA*AS*XIO/XL1
S(1)=S0
DO 10 I=1,2000
FS=S(I)-S0+XC1*(1-EXP(-ES*S(I)*XL1))
DFS=1+XC1*ES*XL1*EXP(-ES*S(I)*XL1)
XS1=S(I)-FS/DFS
IF(ABS((S(I)-XS1)/S(I)) .LE. 0.01) GO TO 20
N=I+1
S(N)=XS1
10 CONTINUE
20 XIAS=XI0*(1-EXP(-ES*XS1*XL1))*DV/XL1
AI=2*AS*XIAS
SR=SQRT(AI/XKT)
XM=(XMO-SITA*AI)/(1+SITA*XKP*SR)
XS=XKP*XM/(XKP*XM+XKT*SR+1/SITA)
WRITE(2,24)
24 FORMAT('0','POLYDISPERSITY CALCULATION')
WRITE(2,26)
26 FORMAT('0','UV LIGHT ON/OFF REGULATION AT LOW S. S.')
WRITE(2,32) TEMP
32 FORMAT('0','TEMPERATURE=',F5.1, 1 K')
WRITE(2,34) MO
34 FORMAT('0','UV INTENSITY=',F8.6)
WRITE(2,36) SITA
36 FORMAT('0','RESIDENT TIME=',F7.1)
WRITE(2,38) SO
38 FORMAT('0','INLET MONOMER CONC.,=',F5.3)
WRITE(2,39) R
39 FORMAT( '0','THE RATIO OF (OFF/(ON+OFF)) TIME=',F5.3)
WRITE(2,42)
42 FORMAT( '0')
WRITE(2,44)
44 FORMAT( '0','AT LOW STEADY STATE :')
WRITE(2,45)
45 FORMAT( '0',----------------------------------')
WRITE(2,46) SR
46 FORMAT( '0','SUM OF THE FREE RADICAL CONC.=',F15.13)
WRITE(2,48) XM
48 FORMAT( '0','OUTLET MONOMER CONC.=',F6.4)
WRITE(2,50) XS1
50 FORMAT( '0','OUTLET SENSITIZER CONC.=',E10.4)
SUM=0.0
SP=0.0
SIP=0.0
SIIP=0.0
DO 100 I=2,10000
PI=((I-1)/2.)*XS**I*AI**2*XKT*SITA/(XRP*XM)**2
SP=SP+PI
SIP=SIP+I*PISIIP=SIIP+I**2*PI
XMW=I*PI/(XMO-XM)
SUM=SUM+XMW
IF(SUM .LT. 0.995) 100 T0 200
100 CONTINUE
200 XN=SIP/SP
XW=SIIP/SIP
PD=XW/XN
WRITE(2,220) SP,SIP,SITP
220 FORMAT( '0',SP=',F10.7,5X,SIP=',F10.8,5X,SIIP=',F10.5)
WRITE(2,230) PD
230 FORMAT( '0',PD =',F7.4)
C
RT=R*TAU
C1=XMO
C2=XM-XMO
C3=XMO/SITA-AI
C4=1/SITA+XKP*SQRT(AI/XKT)
C5=C3/C4
D=EXP(-C4*(1-R)*TAU)
C=C5-C3*D/C4
B=EXP(-RT/SITA)
A=XMO*(1-B)
C6=C3/C4-(A+B*XM)
G=C+D*A
H=B*D
P=A+C*B
C
D1=SITA*C1**3
D2=3*RT*C2*C1**2*EXP(-RT/SITA)
D3=3*C1*SITA*C2**2*EXP(-2*RT/SITA)
D4=SITA/2*C2**3*EXP(-3*RT/SITA)
D5=(D1-3*C1*SITA*C2**2-SITA/2*C2**3)*EXP(-RT/SITA)
S1 = XKI * (D1 + D2 - D3 - D4 - D5)
S2 = EXP(-RT/SITA)
S3 = 5 * SITA * AI * (1 - EXP(-(1-R) * TAU/SITA))
S4 = EXP(-(1-R) * TAU/SITA)
R1 = S3 + S1 * S4
R2 = S2 * S4
R3 = S1 + S2 * S3

C
E1 = XKP * C1 * 2.5 * SQR(T(2*XKI/XKT))
E5 = SITA * C5 - SITA * C6 / (1 - SITA * C4) * EXP(-C4 * (1-R) * TAU)
E6 = SITA * C5 - SITA * C6 / (1 - SITA * C4) * EXP(-(1-R) * TAU/SITA)
SUM1 = EXP(RT/SITA)
SUM2 = 1.
V1 = -15/8 * (C2/C1) * 2 * EXP(-RT/SITA)
V2 = -15/8 * (C2/C1) * 2
SUM1 = SUM1 + V1
SUM2 = SUM2 + V2
DO 235 N = 2, 20
CALL BINOM(V1, V2, N, C1, C2, RT, SITA)
SUM1 = SUM1 + V1
SUM2 = SUM2 + V2
235 CONTINUE
XSUM = E1 * SITA * (SUM1 - SUM2) + E1 * 2.5 * C2 * RT / C1
F1 = EXP(-RT/SITA) * XSUM
F2 = EXP(-RT/SITA)
F3 = XKP * SQR(T(AI/XKT) * (E5 - E6))
F4 = EXP(-(1-R) * TAU/SITA)
T1 = F3 + F1 * F4
T2 = F2 * F4
T3 = F1 + F2 * F3

C
F1 = SITA * C1 * 2 + 2 * C1 * C2 * RT * EXP(-RT/SITA)
F2 = SITA * C2 * 2 * EXP(-2 * RT/SITA)
F3 = SITA * (C1 * 2 - C2 * 2) * EXP(-RT/SITA)
X1 = 3 * XKP * 2 / XKT * F1 * F2 * F3 + 5 * XSUM
X2 = EXP(-RT/SITA)
C8 = 3 * (XKP * C5) ** 2 / XKT + 5 * XKP * C5 * SQR(T(AI/XKT)) + 2 * AI
C9 = 6 * C5 * C6 * XKP * 2 / XKT + 5 * XKP * C6 * SQR(T(AI/XKT))
C10 = 3 * (XKP * C6) ** 2 / XKT
F4 = SITA * C9
F5 = SITA * C9 * EXP(-C4 * (1-R) * TAU) / (1 - SITA * C4)
F6 = SITA * C10 * EXP(-2 * C4 * (1-R) * TAU) / (1 - 2 * SITA * C4)
F7 = SITA * (-C8 + C9) / (1 - SITA * C4) - C10 / (1 - 2 * SITA * C4) * EXP(-(1-R) * TAU/SITA)
X3 = F4 - F5 + F6 + F7
X4 = EXP(-(1-R) * TAU/SITA)
Y1 = X3 + X1 * X4
Y2 = X2 * X4
Y3 = X1 + X2 * X3

C
XMOT = XM
XMRT = A + B * XM
XCOT = (XM0 - XMRT) / XM0
XCRT = (XM0 - XMRT) / XM0
SPOT = SP
SPRT=S1+S2*SP
SIP0T=SIP
SIPRT=P1+P2*SIP
SIIP0T=X1+X2*SIIP
PD1T=SPRT*SIIPRT/SIPRT**2
WRITE(2, 240)
240 FORMAT(’0’, ’+++++++++++++++++++++++++++++++++++++++’)  
WRITE(2, 245)
245 FORMAT(’0’)  
WRITE(2, 250) XM0T, XMRT
250 FORMAT(’0’, ’XM0T=’, F7.5, 5X, ’XMRT=’, F7.5)
WRITE(2, 260) XCO T, XCRT
260 FORMAT(’0’, ’XCO T=’, F7.5, 5X, ’XCRT=’, F7.5)
WRITE(2, 270) SP0T, SPRT
270 FORMAT(’0’, ’SP0T=’, F10.7, 5X, ’SPRT=’, F10.7)
WRITE(2, 280) SIP0T, SIPRT
280 FORMAT(’0’, ’SIP0T=’, F10.8, 5X, ’SIPRT=’, F10.8)
WRITE(2, 290) SIIP0T, SIIPRT
290 FORMAT(’0’, ’SIIP0T=’, F10.5, 5X, ’SIIPRT=’, F10.5)
WRITE(2, 295) PD1T
295 FORMAT(’0’, ’PD1T=’, F10.5)
DO 500 N=1,20
Q=(1-H**N)/(1-H)
XM T=G*Q+XM*H**N
XM1 T=P*Q+(A+B*XM)*H**N
XCRT=(XMO-XMT)/XMO
XC1 T=(XMO-XM1T)/XMO
XR=(1-R2**N)/(1-R2)
SPRT=R1*XR+SP*H**N
SP1 T=R3*XR+(S1+S2*SP)*H**N
XT=(1-T2**N)/(1-T2)
SIPT=T1*XT+SIP*T2**N
SIIP1 T=T3*XT+(P1+P2*SIP)*T2**N
XY=(1-Y2**N)/(1-Y2)
SIIP0T=Y1*XY+SIIP*Y2**N
SIIPP1 T=Y3*XY4+(X1+X2*SIIP)*Y2**N
XNT=SIPT/SPT
XN1 T=SIPT1/SP1 T
XWT=SIIP0T/SIPT
XW1 T=SIIP1 T/SIPT1
PD1T=XWT/XNT
PD1 T=XW1T/XN1T
C
WRITE(2, 307) N
307 FORMAT(’0’, ’N=’, I2)
WRITE(2, 310) XMT, XM1 T
310 FORMAT(’0’, ’XMT=’, F7.5, 5X, ’XM1 T=’, F7.5)
WRITE(2, 315) XCT, XC1 T
315 FORMAT(’0’, ’XCT=’, F7.5, 5X, ’XC1 T=’, F7.5)
WRITE(2, 370) PD1T, PD1 T
370 FORMAT(’0’, ’PD1 T=’, F9.6, 5X, ’PD1 T=’, F9.6)
WRITE(2, 410)
410 FORMAT(’0’)

C

C

C
SUBROUTINE BINOM(V1, V2, N, C1, C2, RT, SITA)
V1 = V1 * (N - 1) / (N + 1) * (2.5 - N) * (C2 / C1) * EXP(-RT / SITA)
V2 = V2 * (N - 1) / (N + 1) * (2.5 - N) * (C2 / C1)
RETURN
END
PROGRAM #3
NUMERICAL CALCULATION FOR POLYDISPERSITY
UV LIGHT ON/OFF REGULATION AT LOW STATIONARY STATE

DIMENSION PEI(100)
REAL KT,KP,KI,IO,I1,IAS,IT
READ,TIMESS,,TSTOP,G,IT,XSO,IO,V1
READ,NI
READ,(PEI(I),I=1,NI)

XLH=5.2
EM=.0155
ES=88.5
AS=.072
H=500
V=.2
DV=V1/V
SITA=V/G
KI=2.19E5*EXP(-13810/IT)
KP=1.051E7*EXP(-3557/IT)
KT=1.255E9*EXP(-844/IT)
A1=2.57-.00505*IT
A2=9.56-.0176*IT
A3=-3.03+.00785*IT
PM=924-.918*(IT-273.1)
PP=1084-.8-.605*(IT-273.1)
XMW=104
XMO=PM/XMW
VO=V*PM/PP
E=(VO-V)/V
TIME=0
XM=XMO
XS=XSO
SP=0
SIP=0
SIIP=0
SITA=V/G
WRITE(2,50) IO
50 FORMAT(,’-’,’THE UV INTENSITY =’,F8.6)
WRITE(2,60) IT
60 FORMAT(,’-’,’TEMPERATURE =’,F4.0,’ K’)
WRITE(2,70) SITA
70 FORMAT(,’-’,’RESIDENT TIME =’,F7.1,’ SEC.’)
99 ESS=ES*XS
EMM=EM*XM
ESM=ESS+EMM
XC=(XMO-XM)/(XMO+EXM)
IAS=IO*(ESS/ESM)*(1-EXP(-ESS*XLH*DV))/XLH
GE=1,
GE1=(KP/KT**.5)*GE
XIS=2*AS*IAS
XIM=2*KI*IAS**3
THERMO=XIM
UV=XIS+XIM
IF(TIME .EQ. TIMESS) GO TO 120
100 I1=UV
N1=NI-1
DO 102 I=1,N1,2
IF(TIME.GE.PEI(I) ,.AND. TIME.LT.PEI(I+1)) GO TO 105
IF(TIME.GE.PEI(I+1) ,.AND. TIME.LT.PEI(I+2)) GO TO 107
102 CONTINUE
GO TO 109
105 I1=THERMO
GO TO 109
107 I1=UV
109 D1F1=H*F1(XM,XS,I1,GE1,XMO,V,G,E)
D1F2=H*F2(XM,XS,V,G,AS,IAS,XSO,XC,E)
XK=XM+D1F1/2
XL=XS+D1F2/2
D2F1=H*F1(XK,XL,I1,GE1,XMO,V,G,E)
D2F2=H*F2(XK,XL,V,G,AS,IAS,XSO,XC,E)
XM=XM+D2F1/2
XL=XS+D2F2/2
D3F1=H*F1(XK,XL,I1,GE1,XMO,V,G,E)
D3F2=H*F2(XK,XL,V,G,AS,IAS,XSO,XC,E)
XK=XM+D3F1
XL=XS+D3F2
D4F1=H*F1(XK,XL,I1,GE1,XMO,V,G,E)
D4F2=H*F2(XK,XL,V,G,AS,IAS,XSO,XC,E)
DF1=(D1F1+2*D2F1+2*D3F1+D4F1)/6
DF2=(D1F2+2*D2F2+2*D3F2+D4F2)/6
XM=XM+DF1
XS=XS+DE2BR=I1+GE1*XM*SQRT(I1)
BK=KT*SQRT(I1/KT)
B=2*GE1*XM*BR/SQRT(I1)
SR=SQRT(I1/KT)
SIR=BR/BK
SIIR=(BR+B)/BK
C1F3=H*F3(SP,SR,KT,V,G,E,XC)
C1F4=H*F4(SIP,SR,SIR,V,G,KT,E,XC)
C1F5=H*F5(SIIP,SR,SIR,SIIR,KT,V,G,E,XC)
XSP=SP+C1F3/2
XSIP=SIP+C1F4/2
XSIIP=SIIP+C1F5/2
C2F3=H*F3(XSP,SR,KT,V,G,E,XC)
C2F4=H*F4(XSIP,SR,SIR,V,G,KT,E,XC)
C2F5=H*F5(XSIIP,SR,SIR,SIIR,KT,V,G,E,XC)
XSP=SP+C2F3/2
XSIP=SIP+C2F4/2
XSIIP=SIIP+C2F5/2
C3F3=H*F3(XSP,SR,KT,V,G,E,XC)
C3F4=H*F4(XSIP,SR,SIR,V,G,KT,E,XC)
C3F5=H*F5(XSIIP,SR,SIR,SIIR,KT,V,G,E,XC)
XSP=SP+C3F3
XSIP=SIP+C3F4
XSIIP=SIIP+C3F5
C4F3 = H*F3(XSP,SR,KT,V,G,E,XC)
C4F4 = H*F4(XSIP,SR,SIR,V,G,KT,E,XC)
C4F5 = H*F5(XSIIP,SR,SIR,SIIR,KTO,G,E,XC)
CF3 = (C1F3 + 2*C2F3 + 2*C3F3 + C4F3)/6
CF4 = (C1F4 + 2*C2F4 + 2*C3F4 + C4F4)/6
CF5 = (C1F5 + 2*C2F5 + 2*C3F5 + C4F5)/6
SP = SP + CF3
SIP = SIP + CF4
SIIP = SIIP + CF5
U1 = SIP/SP
U2 = SIIP/SIP
F = U2/U1
XC = (XMO - XM)/(XMO + E*XM)
TIME = TIME + H
WRITE(2,110) TIME, XC, XM, XS, P
110 FORMAT(' ', F7.0, 1X, F6.4, 1X, F4.2, 1X, CF6.4, 1X, F6, 3)
IF(TIME .GE. TSTOP) GO TO 160
IF(TIME .GT. TIMES) GO TO 130
GO TO 99
120 XCS = XC
U1S = U1
U2S = U2
FS = P
GO TO 100
130 RXC = XC/XCS
RP = F/FS
WRITE(2,150) RXC, RP
150 FORMAT(' ', 'RXC=', F5.3, 2X, 'RP=', F5.3)
GO TO 97.
160 STOP
END

FUNCTION F1(XM, XS, I1, GE1, XMO, V, G, E)
REAL KT, KP, KI, IO, IAS, I1
XC = (XMO - XM)/(XMO + E*XM)
F1 = (XMO - XM*(1 + E*XC))*G/V - I1**.5*XM*GE1
RETURN
END

FUNCTION F2(XM, XS, V, G, AS, IAS, XSO, XC, E)
REAL KT, KP, KI, IO, I1, IAS
F2 = (XSO - XS*(1 + E*XC))*G/V - AS*IAS
RETURN
END

FUNCTION F3(SP, SR, KT, V, G, E, XC)
REAL KT, KP, KI, IO, I1, IAS
F3 = -SP*(1 + E*XC)*G/V + 5*KT*SR**2
RETURN
END
FUNCTION F4(SIP, SR, SIR, V, G, KT, E, XC)
REAL KT, KP, KI, IO, I1, IAS
F4 = -SIP*(1+E*XC)*G/V + KT*SR*SIR
RETURN
END

C
C
FUNCTION F5(SIIP, SR, SIR, SIIR, KT, V, G, E, XC)
REAL KT, KP, KI, IO, I1, IAS
F5 = -SIIP*(1+E*XC)*G/V + KT*(SR*SIIR + SIR**2)
RETURN
END
PROGRAM MOLECULAR WEIGHT DISTRIBUTION
UV LIGHT ON-OFF REGULATION AT LOW STEADY STATE

DOUBLE PRECISION R1, R2, R3, V1, V3, SUM1, SUM2, FINAL1, FINAL2,
CTOTAL1, TOTAl2, C1, C2, C3, C4, C5, C6, D1, D2, D3, XP, XKP, XK1, XKT, XKI, AI,
CXMT, XMRT, U1, U2, W3, W4, Q1, Q2, Q3, XQ, PI0, P1T, PIRT, XMWT, XMWRT,
CX, B1, B2, B3, R4, R5, B6, B7, B8, B9, B10, PM, XMO,
CAY, CQ, Q1, 0, Q2, R1, XSP, SITA, XM, TOL1, TOL2, XM0
DIMENSION S(2000), TOL1(1000), TOL2(1000)
READ, SO, XTO, TEMP, SITA, NP, XNi, V1
TAU=SITA

PM=924-.918*(TEMP-273.1)
XMW=104
XMO=PM/XMW
XKP=1.051E7*EXP(-3557/TEMP)
XKT=1.255E9*EXP(-844/TEMP)
XKI=2.19E5*EXP(-13810/TEMP)

V=0.2
DV=V1/V
AS=0.072
ES=88.5
XL=5.2
XL1=XL*XM
XC1=SITA*AS*XI0/XL1
S(I)=S0
DO 10 I=1,2000
FS=S(I)-SO+XC1*(1-EXP(-ES*S(I)*XL1))
DFS=1+XC1*ES*XL1*EXP(-ES*S(I)*XL1)
XS1=S(I)-FS/DFS
IF(ABS((S(I)-XS1)/S(I)) .LE. 0.01) GO TO 20
N=I+I
S(N)=XS1
10 CONTINUE
XIAS=XI0*(1-EXP(-ES*XS1*XL1))*DV/XL1
AI=2*AS*XI0
SR=(AI/XKT)**.5
XM=(XMO-SITA*AI)/(1+SITA*XKP*SR)
XS=XKP*XM/(XKP*XM+XKT*SR+1/SITA)
WRITE(6,24)
24 FORMAT('MOLECULAR WEIGHT DISTRIBUTION')
WRITE(6,26)
26 FORMAT('UV LIGHT ON-OFF CONTROL AT LOW S. S.')
WRITE(6,28)
28 FORMAT('######################################')
WRITE(6,29) XKP, XKT
29 FORMAT('KP=', F6.1, 'KT=', E10.3)
WRITE(6,32) TEMP
32 FORMAT('TEMPERATURE=', F5.1, 'K')
WRITE(6,34) XIO
34 FORMAT('UV INTENSITY=', F8.6)
WRITE(6,36) SITA
36 FORMAT('0', 'RESIDENT TIME=', F7.1)
WRITE(6, 37) XMO
37 FORMAT('0', 'INLET MONOMER CONC.=', F5.3)
WRITE(6, 38) SO
38 FORMAT('0', 'INLET SENSITIZER CONC.=', F5.3)
WRITE(6, 42)
42 FORMAT('0')
44 FORMAT('0', 'AT LOW STEADY STATE :')
WRITE(6, 45)
45 FORMAT('0', '---------------')
WRITE(6, 46) SR
46 FORMAT('0', 'SUM OF THE FREE RADICAL CONC.=', F15.13)
WRITE(6, 48) XM
48 FORMAT('0', 'OUTLET MONOMER CONC.,=', F6.4)
WRITE(6, 50) XS1
50 FORMAT('0', 'OUTLET SENSITIZER CONC.=', E10.4)

C
SIP0=0.
DO 500 1=1,12000
PI0=((I-1)/2.)*XS*I*AT**2*XKT*SITA/(XKP*XM)**2
SIP0=SIP0+I*PI0
500 CONTINUE
WRITE(6, 55) SIP0
55 FORMAT('0', 'SIP0 =', F10.7)

C
DO 1000 LR=1,NP
R=XNI*LR
WRITE(6, 60) R
60 FORMAT('1', 'THE RATIO OF TIME LENGTH (OFF/(ON+OFF)) =', CF5.3)
WRITE(6, 65)
65 FORMAT('0', '---------------')
RT=R*TAU
C1=XMO
C2=XM-XMO
C3=XMO/SITA-AI
C4=1/SITA+XKP*(AI/XKT)**4.5
C5=C3/C4
D=EXP(-C4*(1-R)*TAU)
C=C5*(1-D)
B=EXP(-RT/SITA)
A=XMO*(1-B)
C6=C3/C4-(A+B*XM)
G=C+D*A
H=B*D
F=A+C*B

C
D2=(AI*XKT)**.5
D3=1/(C4*SITA)
XMRT=A+B*XM
XMRT=G+H*XM
B1=SITA*C1**4
B2=4*C2*C1**3
B3 = 6*SITA*C1*C2**2
B4 = 2*SITA*C1*C2**3
B5 = SITA*C2**4/3
B6 = EXP(-RT/SITA)
B7 = EXP(-2*RT/SITA)
B8 = EXP(-3*RT/SITA)
B9 = EXP(-4*RT/SITA)
B10 = B1 + B2*RT*B6 - B3*D7 - B4*B8 - B5*B9

XP1 = SQRT(2*XKI/XKT)*C1**2.5*XKP
XP2 = 2.5*C2/C1*RT
XP3 = 15.*B6/(C2/C1)**2*SITA
XP4 = SITA*XP2*B6 - XP3*B7
XP6 = XKP*SQRT(AI/XKT)
XP7 = SITA*C5
XP8 = SITA*C6/(1-C4*SITA)
XP9 = EXP(-(1-R)*TAU/SITA)
P1 = XP1*(XP4-XP5)
P2 = B6
P3 = XP6*(XP7-XP8*B6)-XP6*(XP7-XP8)*XP9
P4 = XP9

T1 = P1*F4+P3
T2 = P2*P4
T3 = P1+F2*P3

C
DO 980 I = 25, 4000, 25
P10 = ((I-1)/2.)*X5**I*A1**2*XKT*SITA/(XKP*XK)**2
X1 = 2*XKT*(I-1)*(XKI/XKP)**2
P1RT = X8*B10/(P10-XB*(B1-B3-B4-B5))*B6

C
R1 = C5-C6*EXP(-C4*(1-R)*TAU)
R2 = -C6*EXP(-C4*(1-R)*TAU)
R3 = C5-C6
XP = -.5*XKT*(I-1)*(AI/XKP)**2*(-C6)**2*(-D3)/C4

C
N = 0
V1 = 1
V3 = 1
SUM1 = 1/((-D3)*R1**2*R2**D3)
SUM2 = 1/((-D3)*R3**2*(-C6)**2*(-D3)/C4
TOTAL1 = SUM1
TOTAL2 = SUM2

C
DO 600 K = 1, 60
SUM1 = SUM1*(K+1)*R2/((K-D3)*R1)
SUM2 = SUM2*(K+1)*(-C6)/((K-D3)*R3)
TOTAL1 = TOTAL1 + SUM1
TOTAL2 = TOTAL2 + SUM2
600 CONTINUE

C
DO 900 N = 1, 200
CALL BINOM(N, I, R1, R3, XKP, D2, V1, V3)
SUM1 = 1/((-D3)*R1**2*R2**D3)
SUM2 = 1/((-D3)*R3**2*(-C6)**D3)
FINAL1 = SUM1
FINAL2 = SUM2

DO 800 L = 1, 60
SUM1 = SUM1 * (N + L + 1) * R2 / ((L - D3) * R1)
SUM2 = SUM2 * (N + L + 1) * (-C6) / ((L - D3) * R3)
FIN1 = FIN1 + SUM1
FIN2 = FIN2 + SUM2
800 CONTINUE

TOTAL1 = TOTAL1 + V1 * FIN1
TOTAL2 = TOTAL2 + V3 * FIN2
900 CONTINUE

PIT = EXP(-(-1-R)*TAU/SITA)*(XP*TOTAL1+PIRT-XP*TOTAL2)
KK = I/25
TOL1(KK) = TOTAL1
TOL2(KK) = TOTAL2
SIPRT = P1+F2*SIP0
SIPT = P3+F4*SIPRT
XM0 = I*PI0/SIP0
XMRT = I*PIRT/SIPRT
XM = 1*PIT/SIPT
WRITE(6,902) I, PI0, XM0, PIRT, XMRT
902 FORMAT('0', 'I=', I5, 3X, 'PI0=', D20.4, 3X, 'XM0=', D20.14)
980 CONTINUE

DO 990 NC = 1, 15
WRITE(6,987)
987 FORMAT('0')
985 CONTINUE

PI0 = (((I-1)/2.)*XS**I*AI**2*XKT*SITA/(XKP*XM)**2
XP = -S*KKT*(I-1)*(AI/XKP)**2*(-C6)**D3/C4
XB = 2*KKT*(I-1)*(XKI/XKP)**2
Q = (1-H**NC)/(1-H)
XM0 = G*Q+XM*H**NC
XMRT = P*Q+(A+B*X)*H**NC

NN = I/25
W1 = XB*B10-XB*(B1-B3-B4-B5)*B6
W2 = B6
W3 = EXP(-(X*(1-R)*TAU/SITA))*XP*(TOL1(NN)-TOL2(NN))
W4 = EXP(-(X*(1-R)*TAU/SITA))
Q1 = W3+W1*W4
Q2 = W2*W4
Q3 = W1+W2*W3
Q4 = 1-Q2**NC/(1-Q2)
Q1 = Q1*Q4
Q2 = W2*Q4
Q1 = W1+W2*Q4
Q2 = W2*W4
Q3 = W1+W2*W3
XQ = (1-Q2**NC)/(1-Q2)
PIT = Q1*XQ
PIRT = Q3*XQ*(W1+W2*PI0)*Q2**NC
XT = (1-T2**NC)/(1-T2)
SIPRT = T1*X+T2**NC
SIPRT = T3*X+P1+F2*SIP0*T2**NC
STRT = (AI + XKP * XMT * SR) / (XRT * SR)
XMWT = I * PIT / SIPT
XMWRT = I * PIR T / SIPRT
WRITE (6, 940) NC, I, XMWT, XMWRT
940 FORMAT (' ', 'NC=', I2, 3X, 'I=', I5, 3X, 'XMWT=', D20.14, 3X,
C 'XMWRT=', D20.14)
985 CONTINUE
C
990 CONTINUE
1000 CONTINUE
STOP
END

SUBROUTINE BINOM(N, I, R1, R3, XKP, D2, V1, V3)
DOUBLE PRECISION R1, R2, R3, V1, V3, D2, XKP
V1 = -V1 * (I + N - 1) * (D2 / (XKP * R1)) / N
V3 = -V3 * (I + N - 1) * (D2 / (XKP * R3)) / N
RETURN
END
PROGRAM #5
ROSENBRICK'S SEARCHING TECHNIQUE

DIMENSION X(3),XE(3),XV(3,3),SA(3),D(3),G(3),H(3),AL(3),
PH(3),A(3,3),D(3,3),DX(3),DA(1),VV(3,3),EINT(3),VM(3)
DIMENSION XSR1(1000),XSIR1(1000),XSIIR1(1000)
COMMON KOUNT,KT,KT1,KT2,KP,AS,E,XC1,XC2,XL1,XL2,XX1,XX2,
CSR1,SR2,SR1,SIR1,SIR2,SIIR1,SIIR2,SP1,SP2,SP1,SP2,
CS1,SP1,SP2,SDA1,SDA2,IAS1,IAS2,V1,V2,XM0,I11,I12,
CG1,CE2
INTEGER P,PR,R,C
REAL LC, IT
M=-1
P=3
L=3
LOOPY=100
PR=1
ND=0
NDATA=0
NSTEP=0

READ,X
READ,XE
READ,TIME1,TIME2,TIME3
READ,UEXP1,UEXP2,UEXP3
READ,PEXP1,PEXP2,PEXP3
READ,XEXP1,XEXP2,XEXP3

IF(ND-1) 30,20,30
20 DA(1)=1
30 LOOP=PR-1
ISW=0
INIT=0
KOUNT=0
TERM=0
DELY=1.0E-6
F9=0.0
NPAR=NDATA
N=L
DO 40 K=1,L
40 AL(K)=(CH(X,DA,N,NPAR,K)-CG(X,DA,N,NPAR,K))*.0001
DO 60 I=1,P
DO 60 J=1,P
XV(I,J)=0.0
60 CONTINUE
IF(I-J) 61,61,60
61 XV(I,J)=1.0
60 CONTINUE
DO 65 KK=1,P
EINT(KK)=XE(KK)
65 CONTINUE
1000 DO 70 J=1,P
   IF(NSTEE.EQ.0) XE(J)=EINT(J)
   SA(J)=2.0
70   D(J)=0.0
   FBEST=F9
80   I=1
   IF(INIT.EQ.0) GO TO 120
90   DO 110 K=1,P
110  X(K)=X(K)+XE(I)*XV(I,K)
   DO 50 K=1,L
50   H(K)=F0

C
C 120 F9=F(X,DA,N,NPAR)
   F9=M*F9
   IF(ISW.EQ.0) F0=F9
   ISW=1
   IF(ABS(F9)-DELY) 122,122,125
122 TERM=1.0
   GO TO 450
125 CONTINUE
C
C 130 XXC=CX(X,DA,N,NPAR,J)
   LC=CG(X,DA,N,NPAR,J)
   UC=CH(X,DA,N,NPAR,J)
   IF(XXC.LE.LC) GO TO 420
   IF(XXC,GE,UC) GO TO 420
   IF(F9,LT,F0) GO TO 420
   IF(XXC .LT. LC .OR. UC .LE. XXC) GO TO 150
   IF(LC .LT. XXC .AND. XXC .LT. LC+BW) GO TO 160
   IF(UC—BW .LT. XXC .AND. XXC .LT. UC) GO TO 170
   H(J)=F0
   GO TO 210
C
C 140 CONTINUE
C
   BW=AL(J)
   IF(XXC .LE. LC .OR. UC .LE. XXC) GO TO 150
   IF(LC .LT. XXC .AND. XXC .LT. LC+BW) GO TO 160
   IF(UC-BW .LT. XXC .AND. XXC .LT. UC) GO TO 170
   PH(J)=1.0
   GO TO 210
C
C 150 PH(J)=0.0
   GO TO 190
160 PW=(LC+BW-XXC)/BW
   GO TO 180
170 PW=(XXC-UC+BW)/BW
180 PH(J)=1.0-3.0*PW4.0*PW**2-2.0*PW**3
C
190 F9=H(J)+(F9-H(J))*PH(J)
210 CONTINUE
  IF(J.EQ.L) GO TO 220
  J=J+1
  GO TO 130

220 INIT=1
  IF(F9.LT.F0) GO TO 420
  D(I)=D(I)+X(I)
  XE(I)=3.0*X(I)
  F0=F9
  IF(SA(I).GE.1.5) SA(I)=1.0

230 DO 240 J,J=1,P
  IF(SA(J).GE.0.5) GO TO 440
  240 CONTINUE

250 VV(C,R)=0.0
  DO 260 R=1,P
    KR=R
    DO 260 C=1,P
      DO 265 K=KR,P
        VV(R,C)=D(K)*XV(K,C)+VV(R,C)
        265 VV(R,C)=B(K)*XV(K,C)+VV(R,C)
    260 B(R,C)=VV(R,C)
    BMAG=0.0
    DO 280 C=1,P
      BMAG=BMAG+B(C,C)
    280 CONTINUE
    BMAG=SQRT(BMAG)
    BX(1)=BMAG
    DO 310 C=1,P
      XV(1,C)=B(1,C)/BMAG

310 DO 390 R=2,P
  IR=R-1
  DO 390 C=1,P
    SUMV=0.0
    DO 330 K=IR,K
      SUMAV=0.0
      DO 330 K=IR,K
        SUMAV=SUMAV+VV(R,KJ)*XV(KK,KJ)
      320 SUMVM=SUMAV*XV(KK,C)+SUMVM
      390 B(R,C)=VV(R,C)-SUMVM
    DO 340 R=2,P
      BBMAG=0.0
      DO 350 K=1,P
        BBMAG=BBMAG+B(R,K)*B(R,K)
      350 XY(R,C)=B(R,C)/BBMAG

340 LOOP=LOOP+1
LAF=LAP+1
IF(LAP,EQ,PR) GO TO 450
GO TO 1000
C
420 IF(INIT,EQ,0) GO TO 450
DO 430 IX=1,P
430 X(IX)=X(IX)-XE(I)*XV(I,IX)
XE(I)=-.5*XE(I)
IF(SA(I).LT.1.5) SA(I)=0.0
GO TO 230
C
440 CONTINUE
IF(I.EQ.P) GO TO 80
I=I+1
GO TO 90
C
450 WRITE(2,455)
455 FORMAT('-')
WRITE(2,460) (X(JM),JM=1,P)
460 FORMAT(3(F12.8,3X))
C
LAP=0
IF(TERM,EQ,1.0) GO TO 480
IF(LOOP.GE,LOOPY) GO TO 480
GO TO 1000
C
480 CONTINUE
STOP
END
C
FUNCTION F (X,DA,N,NPAR)
DIMENSION X(N),DA(NPAR)
DIMENSION XSR1(1000),XSIR1(1000),XSIIR1(1000)
COMMON KOUNT,KT,KT1,KT2,KP,AS,E,XC1,XC2,XL1,XL2,XK1,XK2,
CSR1,SR2,SIR1,SIR2,SIIR1,SIIR2,XSP1,XSP2,XSIP1,XSIP2,
CSOiIP1,XSIP2,SIDAI,SIDA2,IAS1,IAS2,V1,V2,XM0,I11,I12,
CGE1,GE2
REAL KT,KT1,KT2,KP,KI,IO,I11,I12,IT,IAS1,IAS2
EM=.0155
ES=88.5
V=.2
XSO=.015
IT=338.
XL=5.2*X(1)/.2
V1=X(1)
V2=.2-V1
SIDAI=V1/X(2)
SIDA2=V2/X(2)
AS=.072
H=500
KI=2.19E5*EXP(-13810/IT)
KP=1.051E7*EXP(-3557/IT)
KT=1.255E9*EXP(-844/IT)
PM=924-.918*(IT-273.1)
PP=1084.8-.605*(IT-273.1)
XMW = 1.04
XM0 = FM / XMW
V0 = VP / FM
E = (V0 - V) / V
T = 0
XM1 = XM0
XM2 = XM0
XS1 = XS0
XS2 = XS0
SF1 = 0
SF2 = 0
SI1P1 = 0
SI1P2 = 0
XC1 = (XMO - XM1) / (XM0 + E*XM1)
XC2 = (XMO - XM2) / (XM0 + E*XM2)
EMM1 = EM * XM1
ESS1 = ES * XS1
ESM1 = ESS1 + EMM1
XK1 = XM1
XK2 = XM2
XL1 = XS1
XL2 = XS2
XSP1 = SF1
XSP2 = SF2
XSIP1 = SI1P1
XSIP2 = SI1P2
C6 = 1 + E*XC1
C7 = 1 + E*XC2
ID = .000117
IAS1 = ID * (ESS1 / ESM1) * (1 - EX**(-ESM1*XL)) / XL
IAS2 = X(3)
Y3 = 2.57 - .00505*IIT
Y4 = 9.56 - .0176*IIT
Y5 = -3.03 + .00785*IIT
GE1 = EX**((Y3*XC1 + Y4*XC1**2 + Y5*XC1**3))
GE2 = EX**((Y3*XC2 + Y4*XC2**2 + Y5*XC2**3))
KT1 = KT / GE1**2
KT2 = KT / GE2**2
XIS1 = 2*AS*IAS1
XIS2 = 2*AS*IAS2
XIM1 = 2*KI*XM1**3
XIM2 = 2*KI*XM2**3
II1 = XIS1 + XIM1
II2 = XIS2 + XIM2
SR1 = (II1 / KT)**.5
SR2 = (II2 / KT)**.5
XSIR1(1) = 0
DO 301 K = 1, 1000
W2 = (C6*XSIR1(K) / SIDA2 + KP*XM2*SR2*GE2 + I12) / C(C7/ SIDA2 + KT*SR2)
SIR1 = (C7*W2 / SIDA1 + KP*XM1*SR1*GE1 + I11) / (C6 / SIDA1 + KT*SR1)
YY=ABS(SIR1-XSIR1(K))/SIR1
IF(YY.LE.,001) GO TO 302
L=K+1
XSIR1(L)=SIR1
301 CONTINUE
302 SIR2=(C6*SIR1/SIDA2+KT*XM2*SIR2*GE2+I12)/(C7/SIDA2+KT*SR2)
XSIR1(1)=0
DO 401 K=1,1000
W3=(C6*XSIR1(K)/SIDA2+2*KP*XM2*SIR2*GE2)/(C7/SIDA2+KT*SR2)
XSIR1=(C7*W3/SIDA1+2*KP*SM1*SIR1*GE1)/(C6/SIDA1+KT*SR1)
YW=ABS(XSIR1-XSIR1(K))/XSIR1
IF(YW.LE.,001) GO TO 402
L=K+1
XSIR1(L)=XSIR1
401 CONTINUE
402 SIR2=(C6*XSIR1/SIDA2+2*KP*XM2*SIR2*GE2)/(C7/SIDA2+KT*SR2)
D1F11=H*F11(DUMMY)
D1F12=H*F12(DUMMY)
D1F21=H*F21(DUMMY)
D1F22=H*F22(DUMMY)
XK1=XM1+D1F11/2
XK2=XM2+D1F12/2
XL1=XS1+D1F21/2
XL2=XS2+D1F22/2
D2F11=H*F11(DUMMY)
D2F12=H*F12(DUMMY)
D2F21=H*F21(DUMMY)
D2F22=H*F22(DUMMY)
XK1=XM1+D2F11/2
XK2=XM2+D2F12/2
XL1=XS1+D2F21/2
XL2=XS2+D2F22/2
D3F11=H*F11(DUMMY)
D3F12=H*F12(DUMMY)
D3F21=H*F21(DUMMY)
D3F22=H*F22(DUMMY)
XK1=XM1+D3F11
XK2=XM2+D3F12
XL1=XS1+D3F21
XL2=XS2+D3F22
D4F11=H*F11(DUMMY)
D4F12=H*F12(DUMMY)
D4F21=H*F21(DUMMY)
D4F22=H*F22(DUMMY)
DF11=(D1F11+2*D2F11+2*D3F11+D4F11)/6
DF12=(D1F12+2*D2F12+2*D3F12+D4F12)/6
DF21=(D1F21+2*D2F21+2*D3F21+D4F21)/6
DF22=(D1F22+2*D2F22+2*D3F22+D4F22)/6
C1F31=H*F31(DUMMY)
C1F32=H*F32(DUMMY)
C1F41=H*F41(DUMMY)
C1F42=H*F42(DUMMY)
C1F51=H*F51(DUMMY)
U21 = SIIP1 / SIP1
U22 = SIIP2 / SIP2
P1 = U21 / U11
P2 = U22 / U12
XC1 = (XM0 - XM1) / (XM0 + E * XM1)
XC2 = (XM0 - XM2) / (XM0 + E * XM2)
T = T + H
XLADA = 10
IF (T . EQ. TIME1) GO TO 104
IF (T . EQ. TIME2) GO TO 106
IF (T . GE. TIME3) GO TO 106
GO TO 99
104 FA = ((U11 - UEXP1) / UEXP1)**2 + ((P1 - PEXP1) / PEXP1)**2
+ XLADA * (XC1 - XEXP1)**2
PRINT, U11, P1, XC1
GO TO 99
106 FB = ((U11 - UEXP2) / UEXP2)**2 + ((P1 - PEXP2) / PEXP2)**2
+ XLADA * (XC1 - XEXP2)**2
PRINT, U11, P1, XC1
GO TO 99
108 FC = ((U11 - UEXP3) / UEXP3)**2 + ((P1 - PEXP3) / PEXP3)**2
+ XLADA * (XC1 - XEXP3)**2
PRINT, U11, P1, XC1
F = FA + FB + FC
GO TO 99
WRITE (2, 105) (X(JM), JM = 1, 3)
105 FORMAT (3(F12.8, 3X))
KOUNT = KOUNT + 1
RETURN
END

FUNCTION F11(DUMMY)
COMMUN KOUNT, KT, KT1, KT2, KP, AS, E, XC1, XC2, XL1, XL2, XK1, XK2,
CSR1, SR2, SIR1, SIR2, SIIR1, SIIR2, XSP1, XSP2, XSIP1, XSIP2,
CXSIIP1, CXSIIP2, SIDA1, SIDA2, IAS1, IAS2, V1, V2, XM0, I11, I12,
CGE1, GE2
REAL KT, KT1, KT2, KP, I11, I12
F11 = -KP*XK1*SR1*GE1 + ((1+E*XC2)*XK2-(1+E*XC1)*XK1)/SIDA1
RETURN
END

FUNCTION F12(DUMMY)
COMMUN KOUNT, KT, KT1, KT2, KP, AS, E, XC1, XC2, XL1, XL2, XK1, XK2,
CSR1, SR2, SIR1, SIR2, SIIR1, SIIR2, XSP1, XSP2, XSIP1, XSIP2,
CXSIIP1, CXSIIP2, SIDA1, SIDA2, IAS1, IAS2, V1, V2, XM0, I11, I12,
CGE1, GE2
REAL KT, KT1, KT2, KP, I11, I12
F12 = -KP*XK2*SR2*GE2 + ((1+E*XC1)*XK1-(1+E*XC2)*XK2)/SIDA2
-C-XK2*FV(DUMMY)/V2
RETURN
END
FUNCTION F21(DUMMY)
COMMON KOUNT,KT,KT1,KT2,KP,AS,E, XC1, XC2, XL1, XL2, XK1, XK2,
CSR1,SR1,SIR1,SIR2,SIIR1,SIIR2,XSP1,XSP2,XSIP1,XSIP2,
CXSIIP1,XSIIP2,SIDA1,SIDA2,IAS1,IAS2,V1,V2,XMO,I11,I12,
CGE1,GE2
REAL KT,KT1,KT2,KP,I11,I12,IAS1
F21=-AS*IAS14((1+E*XC2)*XL2-(1+E*X1)*XL1)/SIDA1
RETURN
END

FUNCTION F22(DUMMY)
COMMON KOUNT,KT,KT1,KT2,KP,AS,E, XC1, XC2, XL1, XL2, XK1, XK2,
CSR1,SR1,SIR1,SIR2,SIIR1,SIIR2,XSP1,XSP2,XSIP1,XSIP2,
CXSIIP1,XSIIP2,SIDA1,SIDA2,IAS1,IAS2,V1,V2,XMO,I11,I12,
CGE1,GE2
REAL KT,KT1,KT2,KP,I11,I12,IAS2
F22=-AS*IAS24((1+E*XC1)*XL1-(1+E*X2)*XL2)/SIDA2
C-XL2*FV(DUMMY)/V2
RETURN
END

FUNCTION F31(DUMMY)
COMMON KOUNT,KT,KT1,KT2,KP,AS,E, XC1, XC2, XL1, XL2, XK1, XK2,
CSR1,SR1,SIR1,SIR2,SIIR1,SIIR2,XSP1,XSP2,XSIP1,XSIP2,
CXSIIP1,XSIIP2,SIDA1,SIDA2,IAS1,IAS2,V1,V2,XMO,I11,I12,
CGE1,GE2
REAL KT,KT1,KT2,KP,I11,I12
F31=.5*KT*SR1**2+(1+E*XC2)*XSP2-(1+E*XC1)*XSP1)/SIDA1
RETURN
END

FUNCTION F32(DUMMY)
COMMON KOUNT,KT,KT1,KT2,KP,AS,E, XC1, XC2, XL1, XL2, XK1, XK2,
CSR1,SR1,SIR1,SIR2,SIIR1,SIIR2,XSP1,XSP2,XSIP1,XSIP2,
CXSIIP1,XSIIP2,SIDA1,SIDA2,IAS1,IAS2,V1,V2,XMO,I11,I12,
CGE1,GE2
REAL KT,KT1,KT2,KP,I11,I12
F32=.5*KT*SR2**2+(1+E*XC1)*XSP1-(1+E*XC2)*XSP2)/SIDA2
C-XSP2*FV(DUMMY)/V2
RETURN
END
FUNCTION F41(DUMMY)  
COMMON KOUNT, KT1, KT2, KP, AS, E, XC1, XC2, XL1, XL2, XK1, XK2,  
CSR1, SR2, SIR1, SIR2, SIIR1, SIIR2, XSP1, XSP2, XSIP1, XSIP2,  
CXSIIP1, XSSIP2, SIDA1, SIDA2, IAS1, IAS2, V1, V2, XMO, I11, I12,  
CGE1, GE2  
REAL KT1, KT2, KP, I11, I12  
F41 = KT1 * SR1 * SIR1 + ((1 + E * XC2) * XSIP2 - (1 + E * XC1) * XSIP1) / SIDA1  
RETURN  
END  

FUNCTION F42(DUMMY)  
COMMON KOUNT, KT1, KT2, KP, AS, E, XC1, XC2, XL1, XL2, XK1, XK2,  
CSR1, SR2, SIR1, SIR2, SIIR1, SIIR2, XSP1, XSP2, XSIP1, XSIP2,  
CXSIIP1, XSSIP2, SIDA1, SIDA2, IAS1, IAS2, V1, V2, XMO, I11, I12,  
CGE1, GE2  
REAL KT1, KT2, KP, I11, I12  
F42 = KT2 * SR2 * SIR2 + ((1 + E * XC1) * XSIP1 - (1 + E * XC2) * XSIP2) / SIDA2  
C - XSIP2 * FV(DUMMY) / V2  
RETURN  
END  

FUNCTION F51(DUMMY)  
COMMON KOUNT, KT1, KT2, KP, AS, E, XC1, XC2, XL1, XL2, XK1, XK2,  
CSR1, SR2, SIR1, SIR2, SIIR1, SIIR2, XSP1, XSP2, XSIP1, XSIP2,  
CXSIIP1, XSSIP2, SIDA1, SIDA2, IAS1, IAS2, V1, V2, XMO, I11, I12,  
CGE1, GE2  
REAL KT1, KT2, KP, I11, I12  
F51 = KT1 * SR1 * SIIR1 + KT * SIR1**2 + ((1 + E * XC2) * XSSIP2  
C - (1 + E * XC1) * XSSIP1) / SIDA1  
RETURN  
END  

FUNCTION F52(DUMMY)  
COMMON KOUNT, KT1, KT2, KP, AS, E, XC1, XC2, XL1, XL2, XK1, XK2,  
CSR1, SR2, SIR1, SIR2, SIIR1, SIIR2, XSP1, XSP2, XSIP1, XSIP2,  
CXSIIP1, XSSIP2, SIDA1, SIDA2, IAS1, IAS2, V1, V2, XMO, I11, I12,  
CGE1, GE2  
REAL KT1, KT2, KP, I11, I12  
F52 = KT2 * SR2 * SIIR2 + KT * SIR2**2 + ((1 + E * XC1) * XSSIP1  
C - (1 + E * XC2) * XSSIP2) / SIDA2 - XSSIP2 * FV(DUMMY) / V2  
RETURN  
END
FUNCTION FV(DUMMY)
COMMON KOUNT,KT,KT1,KT2,KP,AS,E,XC1,XC2,XL1,XL2,XK1,XK2,
CSR1,SR2,SIR1,SIR2,SII1,SII2,XSP1,XSP2,XSI1,XSI2,
REAL KT,KT1,KT2,KP,I11,I12
ALPHA=KP*XK1*SR1*GE1+(1+E*XC2)*XK2-(1+E*XC1)*XK1)/SIDA1
BETA=-KP*XK2*SR2*GE2+(1+E*XC1)*XK1-(1+E*XC2)*XK2)/SIDA2
GAMMA=-E*V2*V2*(XMO+E*XK2)
THETA=-E*V1*ALPHA/(XMO+E*XK2)
FV=(GAMMA+THETA)*(1+E*XK2/XMO)
RETURN
END

FUNCTION CX(X,DA,N,NPAR,K)
DIMENSION X(N),DA(NPAR)
CX=X(K)
RETURN
END

FUNCTION CG(X,DA,N,NPAR,K)
DIMENSION X(N),DA(NPAR)
GO TO (1,2,3),K
1 CG=0.0
   GO TO 10
2 CG=0.0
   GO TO 10
3 CG=0.0
10 RETURN
END

FUNCTION CH(X,DA,N,NPAR,K)
DIMENSION X(N),DA(NPAR)
GO TO (1,2,3),K
1 CH=.05
   GO TO 10
2 CH=.0002
   GO TO 10
3 CH=.00001
10 RETURN
END
PROGRAM #6
TO CALCULATE REACTOR PERFORMANCE OF CSTR
AT LOW STEADY STATE

DIMENSION XSIR1(1000),XSIIR1(1000)
COMMON KOUNT,KT,KT1,KT2,KP,AS,E,XC1,XC2,XL1,XL2,XK1,XK2,
CSR1,SR2,SIR1,SIR2,SIIR1,SIIR2,XSP1,XSP2,XSIP1,XSIP2,XC,G,
CXSIIP1,XSIIP2,SIDA1,SIDA2,IAS1,IAS2,V1,V2,XM0,I11,I12,
CGE1,GE2,V,XSO
REAL KT,KT1,KT2,KP,KI,IO,I11,I12,IT,IAS1,IAS2
READ,TSO,X3,X4,IAS2
READ,G,XSO,IT,IO
V=.2
SITA=V/G
0=X4
V1=X3
V2=V-V1
SIDA1=V1/Q
SIDA2=V2/Q
EM=.0155
ES=85.5
GE1=1.
GE2=1.
AS=.072
WRITE(2,20) SITA
20 FORMAT(1X,'RESIDENT TIME=',F7.1,' SEC')
WRITE(2,30) IT
30 FORMAT(1X,'TEMPERATURE =',F5.0,1X,' K')
WRITE(2,40) XIAS2
40 FORMAT(1X,'LIGHT INTENSITY IN DARK REG. =',F10.8)
WRITE(2,45)
45 FORMAT(1X,'-')
WRITE(2,50) V1
50 FORMAT(1X,'VOLUME IN LIGHT REGION =',F5.3)
WRITE(2,60) Q
60 FORMAT(1X,'FLOW RATE BETW. TWO REGIONS =',F9.7)
WRITE(2,70) SIDA1
70 FORMAT(1X,'RESIDENT TIME IN LIGHT REGION =',F7.1)
WRITE(2,80) SIDA2
80 FORMAT(1X,'RESIDENT TIME IN DARK REGION =',F7.1)
WRITE(2,90)
90 FORMAT(1X)
XL=5.2*V1/V
H=500
KI=2.19E5*EXP(-13810/IT)
KP=1.051E7*EXP(-3557/IT)
KT=1.255E9*EXP(-844/IT)
PM=924-.918*(IT-273.1)
PP=1084.8-.605*(IT-273.1)
XMW=104
XM0=PM/XMW
V0=V*PM/PP
E=(V0-V)/V
T=0
XM1=XM0
XM2=XM0
XS1=XS0
XS2=XS0
SP1=0
SP2=0
SIP1=0
SIP2=0
SIIP1=0
SIIP2=0
XC1=(XM0-XM1)/(XM0+E*XM1)
XC2=(XM0-XM2)/(XM0+E*XM2)
XC=(V1*XC1+V2*XC2)/V
EM1=EM*XM1
ESS1=FeS*XS1
ESM1=ESS1+EM1
XK1=XM1
XK2=XM2
XL1=XS1
XL2=XS2
XSP1=SP1
XSP2=SP2
XSIP1=SIP1
XSIP2=SIP2
XSIIP1=SIIP1
XSIIP2=SIIP2
C6=1+E*XC1
C7=1+E*XC2
IAS1=I0*(ESS1/ESM1)*(1-EXP(-ESM1*XL))/XL
Y3=2.57-.00505*IT
Y4=9.56-.0176*IT
Y5=-3.03+.00785*IT
KT1=KT/GE1**2
KT2=KT/GE2**2
XIS1=2*AS*IAS1
XIS2=2*AS*IAS2
XIM1=2*KI*XM1**3
XIM2=2*KI*XM2**3
II1=XIS1+XIM1
II2=XIS2+XIM2
SR1=(II1/1T)**.5
SR2=(II2/1T)**.5
XSI1R1(1)=0
DO 301 K=1,1000
W2=(C6*XSI1R(K)/SIDA2+KP*XMR1*SR1*SR2*GE2+II2)/
C(C7/2SIDA2+KT*SR2)
S1R1=(C7W2/2SIDA1+KPXM1SR1*GE1+II1)/C7/S1DA1+KT*SR1
YY=ABS(S1R1-XSI1R(K))/S1R1
IF(YY.LE.,001) GO TO 302
L=K+1
XSI1R(L)=S1R1
301 CONTINUE
302 S1R2=(C6*XSI1R/2SIDA2+KP*XMR1*SR1*SR2*GE2+II2)/C7/SID1A2+KT*SR2
XSI1R1(1)=0
DO 401 K=1,1000
W3=(C6*XSII1(K)/SIDA2+2*KP*XM2*SIR2*GE2)/
C(C7/SIDA2+KT*SR2)
XSII1=(C7*W3/SIDA1+2*KP*XM1*SIR1*GE1)/(C6/SIDA1+KT*SR1)
YW=ABS(XSII1-XSII1(K))/XSII1
IF(YW.LE.,001) GO TO 402
L=K+1
XSII1(L)=XSII1
401 CONTINUE
402 SITR2=(C6*XSII1/SIDA2+2*KP*XM2*SIR2*GE2)/
C(C7/SIDA2+KT*SR2)
D1F11=H*F11(DUMMY)
D1F12=H*F12(DUMMY)
D1F21=H*F21(DUMMY)
D1F22=H*F22(DUMMY)
XK1=XM1+D1F11/2
XK2=XM1+D1F12/2
XL1=XS1+D1F21/2
XL2=XS2+D1F22/2
D2F11=H*F11(DUMMY)
D2F12=H*F12(DUMMY)
D2F21=H*F21(DUMMY)
D2F22=H*F22(DUMMY)
XK1=XM1+D2F11/2
XK2=XM1+D2F12/2
XL1=XS1+D2F21/2
XL2=XS2+D2F22/2
D3F11=H*F11(DUMMY)
D3F12=H*F12(DUMMY)
D3F21=H*F21(DUMMY)
D3F22=H*F22(DUMMY)
XK1=XM1+D3F11
XK2=XM2+D3F12
XL1=XS1+D3F21
XL2=XS2+D3F22
D4F11=H*F11(DUMMY)
D4F12=H*F12(DUMMY)
D4F21=H*F21(DUMMY)
D4F22=H*F22(DUMMY)
DF11=(D1F11+2*D2F11+2*D3F11+D4F11)/6
DF12=(D1F12+2*D2F12+2*D3F12+D4F12)/6
DF21=(D1F21+2*D2F21+2*D3F21+D4F21)/6
DF22=(D1F22+2*D2F22+2*D3F22+D4F22)/6
C1F31=H*F31(DUMMY)
C1F32=H*F32(DUMMY)
C1F41=H*F41(DUMMY)
C1F42=H*F42(DUMMY)
C1F51=H*F51(DUMMY)
C1F52=H*F52(DUMMY)
XSP1=SP1+C1F31/2
XSP2=SP2+C1F32/2
XSIP1=SIP1+C1F41/2
XSIP2=SIP2+C1F42/2
XSII1P1=SIIP1+C1F51/2
XSII1P2=SIIP2+C1F52/2
C2F31=H*F31(DUMMY)
C2F32=H*F32(DUMMY)
C2F41=H*F41(DUMMY)
C2F42=H*F42(DUMMY)
C2F51=H*F51(DUMMY)
C2F52=H*F52(DUMMY)
XSP1=SP1+C2F31/2
XSP2=SP2+C2F32/2
XSIP1=SIP1+C2F41/2
XSIP2=SIP2+C2F42/2
XSIIP1=SIIP1+C2F51/2
XSIIP2=SIIP2+C2F52/2
C3F31=H*F31(DUMMY)
C3F32=H*F32(DUMMY)
C3F41=H*F41(DUMMY)
C3F42=H*F42(DUMMY)
C3F51=H*F51(DUMMY)
C3F52=H*F52(DUMMY)
XSP1=SP1+C3F31
XSP2=SP2+C3F32
XSIP1=SIP1+C3F41
XSIP2=SIP2+C3F42
XSIIP1=SIIP1+C3F51
XSIIP2=SIIP2+C3F52
C4F31=H*F31(DUMMY)
C4F32=H*F32(DUMMY)
C4F41=H*F41(DUMMY)
C4F42=H*F42(DUMMY)
C4F51=H*F51(DUMMY)
C4F52=H*F52(DUMMY)
CF31=(C1F31+2*C2F31+2*C3F31+C4F31)/6
CF32=(C1F32+2*C2F32+2*C3F32+C4F32)/6
CF41=(C1F41+2*C2F41+2*C3F41+C4F41)/6
CF42=(C1F42+2*C2F42+2*C3F42+C4F42)/6
CF51=(C1F51+2*C2F51+2*C3F51+C4F51)/6
CF52=(C1F52+2*C2F52+2*C3F52+C4F52)/6
SP1=SP1+CF31
SP2=SP2+CF32
SP1=SP1+CF41
SP2=SP2+CF42
SIIP1=SIIP1+CF51
SIIP2=SIIP2+CF52
XM1=XM1+DF11
XM2=XM2+DF12
XS1=XS1+DF21
XS2=XS2+DF22
U11=SIP1/SP1
U12=SIP2/SP2
U21=SIIP1/SIP1
U22=SIIP2/SIP2
F1=U21/U11
F2=U22/U12
XC1=(XMO-XM1)/(XMO+E*XM1)
XC2=(XMO-XM2)/(XMO+E*XM2)
XC=(V1*XC1+V2*XC2)/V
T=T+H
WRITE(2,103) T,XC1,XC2,U11,U12,U21,U22,P1,P2
103 FORMAT(2,F6.0,2X,2(F7.4,2X),4(F7.2,1X),2(F5.2,2X))
    IF(T,GE,TSTOP) GO TO 104
    GO TO 99
104 STOP

FUNCTION F11(DUMMY)
    COMMON KOUNT,KT,KT1,KT2,KP,AS,E,XC1,XC2,XL1,XL2,XK1,XK2,
     CSR1,SR1,SIR1,SIR2,SIIR1,SIIR2,XSP1,XSP2,XSIP1,XSIP2,XC,G,
     CXSIIP1,XSIIP2,SIDA1,SIDA2,IAS1,IAS2,V1,V2,XMO,I11,I12,
     CGE1,GE2,V,XSO
    REAL KT,KT1,KT2,KP,I11,I12,IAS1,IAS2
    F11=XMO*G/V-KP*XK1*SR1*GE1+((1+E*XC2)*XK2-(1+E*XC1)*XK1)
        /SIDA1-XK1*(1+E*XC)*G/V
    RETURN
END

FUNCTION F12(DUMMY)
    COMMON KOUNT,KT,KT1,KT2,KP,AS,E,XC1,XC2,XL1,XL2,XK1,XK2,
     CSR1,SR1,SIR1,SIR2,SIIR1,SIIR2,XSP1,XSP2,XSIP1,XSIP2,XC,G,
     CXSIIP1,XSIIP2,SIDA1,SIDA2,IAS1,IAS2,V1,V2,XMO,I11,I12,
     CGE1,GE2,V,XSO
    REAL KT,KT1,KT2,KP,I11,I12,IAS1,IAS2
    F12=XMO*G/V-KP*XK2*SR2*GE2+((1+E*XC1)*XK1-(1+E*XC2)*XK2)
        /SIDA2-XK2*(1+E*XC)*G/V
    RETURN
END

FUNCTION F21(DUMMY)
    COMMON KOUNT,KT,KT1,KT2,KP,AS,E,XC1,XC2,XL1,XL2,XK1,XK2,
     CSR1,SR2,SIR1,SIR2,SIIR1,SIIR2,XSP1,XSP2,XSIP1,XSIP2,XC,G,
     CXSIIP1,XSIIP2,SIDA1,SIDA2,IAS1,IAS2,V1,V2,XMO,I11,I12,
     CGE1,GE2,V,XSO
    REAL KT,KT1,KT2,KP,I11,I12,IAS1,IAS2
    F21=XSO*G/V-AS*IAS1+((1+E*XC2)*XL2-(1+E*XC1)*XL1)/SIDA1
        -XL1*(1+E*XC)*G/V
    RETURN
END

FUNCTION F22(DUMMY)
    COMMON KOUNT,KT,KT1,KT2,KP,AS,E,XC1,XC2,XL1,XL2,XK1,XK2,
     CSR1,SR2,SIR1,SIR2,SIIR1,SIIR2,XSP1,XSP2,XSIP1,XSIP2,XC,G,
     CXSIIP1,XSIIP2,SIDA1,SIDA2,IAS1,IAS2,V1,V2,XMO,I11,I12,
     CGE1,GE2,V,XSO
    REAL KT,KT1,KT2,KP,I11,I12,IAS1,IAS2
    F22=XSO*G/V-AS*IAS2+((1+E*XC1)*XL1-(1+E*XC2)*XL2)/SIDA2
        -XL2*(1+E*XC)*G/V
    RETURN
END
FUNCTION F31(DUMMY)
COMMON KOUNT, KT, KT1, KT2, KP, AS, E, XC1, XC2, X1, X2, XK1, XK2,
CSR1, SR2, SIR1, SIR2, SIIR1, SIIR2, XSP1, XSP2, XSIP1, XSIIP2, XG,
CXSIIP1, XSIIP2, SIDA1, SIDA2, IAS1, IAS2, V1, V2, XMO, I11, I12,
CGE1, GE2, V, XS0
REAL KT, KT1, KT2, KP, I11, I12, IAS1, IAS2
F31=.5*KT*KR1**2+(1+E*XC2)*XSP2-(1+E*XC1)*XSP1)/SIDA1
C-XSP1*(1+E*XC)*G/V
RETURN
END

FUNCTION F32(DUMMY)
COMMON KOUNT, KT, KT1, KT2, KP, AS, E, XC1, XC2, X1, X2, XK1, XK2,
CSR1, SR2, SIR1, SIR2, SIIR1, SIIR2, XSP1, XSP2, XSIP1, XSIIP2, XG,
CXSIIP1, XSIIP2, SIDA1, SIDA2, IAS1, IAS2, V1, V2, XMO, I11, I12,
CGE1, GE2, V, XS0
REAL KT, KT1, KT2, KP, I11, I12, IAS1, IAS2
F32=KT*SR2**2+(1+E*XC1)*XSP1-(1+E*XC2)*XSP2)/SIDA2
C-XSP2*(1+E*XC)*G/V
RETURN
END

FUNCTION F41(DUMMY)
COMMON KOUNT, KT, KT1, KT2, KP, AS, E, XC1, XC2, X1, X2, XK1, XK2,
CSR1, SR2, SIR1, SIR2, SIIR1, SIIR2, XSP1, XSP2, XSIP1, XSIIP2, XG,
CXSIIP1, XSIIP2, SIDA1, SIDA2, IAS1, IAS2, V1, V2, XMO, I11, I12,
CGE1, GE2, V, XS0
REAL KT, KT1, KT2, KP, I11, I12, IAS1, IAS2
F41=KT*SR1**2+(1+E*XC2)*XSIIP2-(1+E*XC1)*XSIIP1)/SIDA1
C-XSIIP1*(1+E*XC)*G/V
RETURN
END

FUNCTION F42(DUMMY)
COMMON KOUNT, KT, KT1, KT2, KP, AS, E, XC1, XC2, X1, X2, XK1, XK2,
CSR1, SR2, SIR1, SIR2, SIIR1, SIIR2, XSP1, XSP2, XSIP1, XSIIP2, XG,
CXSIIP1, XSIIP2, SIDA1, SIDA2, IAS1, IAS2, V1, V2, XMO, I11, I12,
CGE1, GE2, V, XS0
REAL KT, KT1, KT2, KP, I11, I12, IAS1, IAS2
F42=KT*SR2**2+(1+E*XC1)*XSIIP1-(1+E*XC2)*XSIIP2)/SIDA2
C-XSIIP2*(1+E*XC)*G/V
RETURN
END

FUNCTION F51(DUMMY)
COMMON KOUNT, KT, KT1, KT2, KP, AS, E, XC1, XC2, X1, X2, XK1, XK2,
CSR1, SR2, SIR1, SIR2, SIIR1, SIIR2, XSP1, XSP2, XSIP1, XSIIP2, XG,
CXSIIP1, XSIIP2, SIDA1, SIDA2, IAS1, IAS2, V1, V2, XMO, I11, I12,
CGE1, GE2, V, XS0
REAL KT, KT1, KT2, KP, I11, I12, IAS1, IAS2
F51=KT*SR1**2+(1+E*XC2)*XSIIP2
C-(1+E*XC1)*XSIIP1)/SIDA1-XSIIP1*(1+E*XC)*G/V
RETURN
END
FUNCTION F52(DUMMY)
COMMON KOUNT,KT,KT1,KT2,KP,AS,E,XC1,XC2,XL1,XL2,XK1,XK2,
CSR1,SR2,SIR1,SIR2,SII1R1,SIIR2,XSP1,XSP2,XSIP1,XSIP2,XC,G,
CXSIIIP1,XSIIIP2,SIIA1,SIIA2,IAS1,IAS2,V1,V2,XMO,I11,I12,
CGE1,GE2,V,XSO
REAL KT,KT1,KT2,KP,I11,I12,IAS1,IAS2
F52=KT*SR2*SII2+KT*SIR2*S2+(1+E*XG1)*XSII1P1
C-(1+E*XG2)*XSII2P2/SIIA2-XSII2P2/(1+E*XG)*G/V
RETURN
END
References


34. Muller, A.C., Eichacker, J.C., and Hill, F.B., BNL-16455 (1971)


