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Molecular weight control in ringopening polymerizations.

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MOLECULAR WEIGHT CONTROL
IN
RINGOPENING POLYMERIZATIONS

A MASTERS THESIS

by

DANIEL MARTIN PAUK

Submitted to the Graduate School of the
University of Massachusetts in
partial fulfillment of the requirements for the degree of
MASTERS OF SCIENCE

June 1973

Polymer Science and Engineering

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IN
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Approved as to style and content by

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A C K N O W L E D G E M E N T S

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"A man's life is justified by his efforts, however feeble, towards better understanding. And to understand better is to become more attached. The more I understand, the more I love, for everything that is understood is good."

Jacques Bergier

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N O T A T I O N S

K1	Initiation rate constant	(l/mol min)
K2	Propagation rate constant	(l/mol min)
M	Monomer concentration	(mol/l)
M0	Initial monomer concentration	(mol/l)
I	Initiator concentration	(mol/l)
I0	Initial initiator concentration	(mol/l)
IT	Total initiator added per volume	(mol/l)
IT0T	Total initiator added at 99% conversion per volume	(mol/l)
V0	Reactor volume	(l)
QT and QTT	Initiator addition rate	(mol/min)
TT	Total reaction time to CONV = .99	(min)
CONV	Conversion	(-)
CONADD	Conversion at which the initiator addition is started	(-)
DPN	Number average degree of poly- merization as a function of conversion	(-)
DPN99	DPN at 99% conversion	(-)
DPW	Weight average degree of poly- merization	(-)
ZP	DPW/DPN, polydispersity as a function of conversion	(-)

N O T A T I O N S (Cont.)

ZP99	ZP at 99% conversion	(-)
ZPMAX	Maximum value of ZP for optimal	
CONADD		(-)

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CHAPTER 1

INTRODUCTION

The mechanical properties of polymers are strongly influenced by the molecular weight distribution of the polymer. Allegrezza (1972) in his study of the polymerization of substituted β -lactones sought to modify some of the physical and mechanical properties of polyesters by broadening the Poisson distributed polymer produced in his preparations. His research provided the impetus for this continuing study.

For a living polymerization, it is a simple task to develop a mathematical model of the reaction sequence which upon solution could yield information about conversion and molecular weight distribution.

The work developed in this thesis presents some kinetic data useful in the analysis of β -lactone polymerizations as well as an extensive study of several schemes of initiator addition useful in affording alteration of the molecular weight distribution.

The experiment and analysis presented represent an attempt at accurate determination of kinetic rate constants. The procedure developed suggests better experimental techniques and affords insight into the problem of molecular weight control.

The simulation, using rate constants available in the literature, treats only realistic experimental configurations. In order to make it possible to actually perform such polymerizations in laboratory experiments, only the pulse feed

and the constant rate feed were chosen as elements of the initiator addition control. It is therefore possible to perform these additions with only a syringe and a constant rate pump.

The addition schemes described had to be optimal in such a way that high values of polydispersity could be reached in the shortest possible reaction time, and that the control schemes could be described in terms of as few parameters as possible.

This thesis, however, is presented, integrating the experimental kinetic study with the simulation work, in order to offer the opportunity to compare the requirement of simulation with the uncertainties of kinetic measurements.

C H A P T E R 2

M O L E C U L A R W E I G H T D I S T R I B U T I O N S
I N A N I O N I C P O L Y M E R I Z A T I O N S

2.1 INTRODUCTION

Since the molecular weight distribution (MWD) of a polymer affects its properties, it is often desirable to predict the MWD for a prescribed polymerization mechanism in a given reactor. Amundson & Luss (1968) present a review of methods of computation of MWD. It is pointed out that if little is known about the system kinetics or other parameters, then a statistical approach is appropriate. This approach has some disadvantages, since it requires a great deal of intuition and it can handle only very simple systems.

On the other hand, if polymer structure and kinetics are completely known, then an exact polymer composition can often be calculated. By stating the rate equations that describe a polymerization, one always ends up with an infinite set of differential equations. To convert this infinite set of equations into a finite set one can use Z-transform techniques. An adequate review of the transform application is given by Kilksen (1964).

2.2 CALCULATION OF MWD IN ANIONIC POLYMERIZATION

The initiation of an anionic polymerization is accomplished either by an electron transfer or the reaction of an anion with a monomer. Since in the absence of impurities

no termination takes place, the polymerization proceeds until either all of the available monomer has been consumed or until equilibrium has been achieved. Therefore, anionic polymerization tends to form an essentially monodisperse polymer. In order to tailor the MWD to obtain desired mechanical properties one has to broaden the MWD by specific reaction control. It is generally accepted that control of initiator addition is the best way to affect the MWD and also the MW.

Assuming equal initiation and propagation rate constants, Flory (1940) has shown that one obtains a Poisson-distribution, which is essentially monodisperse for such a polymerization. If the rates are not the same, a modified Poisson distribution results. Gold (1958) and Nanda (1964) show that varying the ratio of the propagation and initiation rate constant k_2/k_1 from 10^{-2} to 10^6 yielded maximum polydispersities of 1.375. All these calculations were made assuming a pulse of initiator feed at $t=0$.

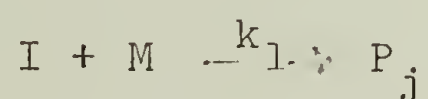
Eisenberg & McQuarrie (1966) first investigated the effect of constant rate and exponentially decreasing rate of initiator addition on the polydispersity Z_p , assuming equal k_2 and k_1 . As a result they plot Z_p vs. the product of the rate constant, the total initiator concentration and a parameter representing the rate of initiator addition.

Bandermann (1971) discusses an optimization method which allows the calculation of optimal initiator addition to produce polymers with required degrees of polymerization and Z_p 's at the condition that kinetics are known. He also finds

that in a continuous reactor periodic initiator addition leads to polymers with narrower MWD than are attainable in a stationary process.

2.3 RATE EQUATIONS AND MOMENTS OF THE MWD

The reaction scheme for an anionic polymerization without transfer and termination is the following:



where I and M are the initiator and monomer concentration, respectively. The rate equations are:

$$2.3.1 \quad \frac{dI}{dt} = -k_1 I M + QT/V_0$$

$$2.3.2 \quad \frac{dM}{dt} = -k_1 I M - k_2 M \sum_{j=1}^{\infty} P_j$$

$$2.3.3 \quad \frac{dP_j}{dt} = k_1 I M \delta(j-1) - k_2 M (P_j - P_{j-1})$$

$$j=1 \quad \delta=1$$

$$j>1 \quad \delta=0$$

$$\text{where } P(z) = \sum_{j=1}^{\infty} P_j z^{-j} \quad |z| \geq 1$$

$$\text{and } P(1) = \lim_{z \rightarrow 1} P(z) = \sum_{j=1}^{\infty} P_j \text{ as defined by Kilksen (1964).}$$

In terms of the Z-transform:

$$2.3.4 \quad \frac{dI}{dt} = -k_1 I M + QT/V_0$$

$$2.3.5 \quad \frac{dM}{dt} = -k_1 I M - k_2 M P(1)$$

$$2.3.6 \quad \frac{dP(z)}{dt} = k_1 I M z^{-1} - k_2 M (1-z^{-1}) P(z)$$

For $z=1$ we obtain:

$$2.3.7 \quad \frac{dP(1)}{dt} = k_1 I M = \frac{d\mu}{dt}_0$$

Defining new variables:

$$x = M/M_0 \quad y = I/I_0 \quad \alpha = k_1/k_2$$

$$r = M_0/I_0 \quad \tau = k_2 M_0 t$$

$$2.3.8 \quad \frac{dy}{d\tau} = -\alpha x y + QT/k_2 M_0 I_0 V_0$$

$$2.3.9 \quad \frac{dx}{d\tau} = -\alpha x y/r - x \mu_0/r$$

$$2.3.10 \quad \frac{dP(z)}{d\tau} = -x P(z) (1-z^{-1}) + \alpha x y z^{-1}$$

$$2.3.11 \quad \frac{dP(1)}{d\tau} = \alpha x y = \frac{d\mu}{d\tau}_0 \quad P(1) = \mu_0$$

The moments are defined as: Kilkson (1964)

$$\mu_k = \lim_{z \rightarrow 1} \frac{\delta^k P(z)}{\delta (\ln z^{-1})^k}$$

$$2.3.12 \quad \frac{d\mu_1}{d\tau} = \lim_{z \rightarrow 1} \{-x(P'(z)(1-z^{-1}) - P(z)z^{-1}) + \alpha_{xy}z^{-1}\}$$

$$2.3.13 \quad \frac{d\mu_1}{d\tau} = x \mu_0 + \frac{d\mu_0}{d\tau}$$

$$2.3.14 \quad \frac{d\mu_2}{d\tau} = \lim_{z \rightarrow 1} -x\{P''(z)(1-z^{-1}) - P'(z)z^{-1} - P'(z)z^{-1} - P(z)\} + \alpha_{xy}z^{-1}$$

$$2.3.15 \quad \frac{d\mu_2}{d\tau} = (2\mu_1 + \mu_0)x + \frac{d\mu_0}{d\tau}$$

Finally, the number average degree of polymerization:

$$2.3.16 \quad \text{DPN} = \frac{\mu_1}{\mu_0}$$

The weight average degree of polymerization:

$$2.3.17 \quad \text{DPW} = \frac{\mu_2}{\mu_1}$$

The polydispersity:

$$2.3.18 \quad \text{ZP} = \text{DPW}/\text{DPN}$$

We now have a mathematical model describing the 3 moments of the MWD of a living polymerization. The parameters needed are the initiator rate constant K_1 and the propagation rate

constant K_2 , and the initial monomer and initiator concentration, M_0 and I_0 , respectively, and Q_T . Q_T is a function describing the history of the initiator addition rate.

Our goal was to find very simple functions of Q_T , addition rate history, in order to be able to reproduce them in laboratory polymerizations, using a syringe and a constant rate pump for the initiator addition. Therefore, Q_T has to be set constant during the entire period of the addition. There are still 2 parameters free to choose, namely the starting time of the addition T_{HE} or in other words the conversion at which the addition starts CON_{ADD} and also the time at which the addition stops. Considering now all the possible addition schemes one can think of 3 basic types. The simplest one is a pulse addition which can be reproduced in a laboratory polymerization simply by a fast addition of the initiator. A second one is the linear addition without pulse, reproducible by a constant addition of initiator solution with a syringe pump. The third type consists of two steps, a fast addition at $t=0$ and a constant addition with a pump starting and ending at fixed times. It was now our task to develop a computer program which accepts the initial conditions M_0 and I_0 , and the function of the initiator addition yielding the 3 moments μ_0 , μ_1 , and μ_2 , and therefore the degree of polymerization DPN and the polydispersity ZP as a function of conversion, for several different addition rate histories.

C H A P T E R 3

S O M E K I N E T I C M E A S U R E M E N T S

3.1 INTRODUCTION

In order to make calculations predicting molecular weight in a polymerization, the kinetics of the system should be determined. We were interested in the anionic ringopening polymerization of Methyl-Propyl-Propio-Lactone with Tetraethylaminobenzoate carried out in Tetrahydrofuran as a solvent. Hall (1969) gives a great number of k_1 and k_2 values for α , α -disubstituted β -lactones. The method used was described by Beste & Hall (1964). They derive a mathematical method for calculating the initiation and propagation rate constants for competitive, consecutive second-order polymerizations. The only data required are the initial monomer and initiator concentration and monomer concentrations at various times during the reaction.

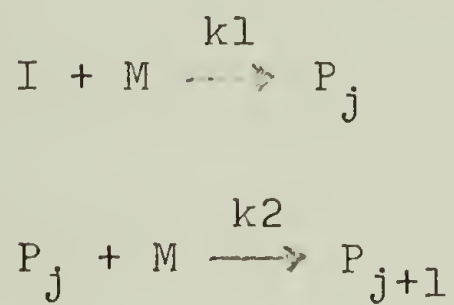
The disadvantage of this method is that the actual concentration I_0 of the reactive initiator species must be known. Therefore, this method cannot be used for systems where only a fraction of the initiator molecules in the reaction mixture are actually able to react with monomer. In our case Tetraethylaminobenzoate (TEABz) is very hygroscopic and reacts with humid air very readily forming the acid, which does not react with monomer. Another way of losing active initiator molecules would be the solvent cage effect.

Therefore, in order to find k_1 and k_2 one has to make the calculations with the true value of I_0 , which is not simply the amount of initiator weighted into the reaction mixture.

The aim of this chapter, therefore, is to describe a method to determine the actual initiator concentration in order to obtain true values for k_1 and k_2 .

3.2. METHODS OF CALCULATION

Assuming an anionic polymerization without transfer and termination, the reaction scheme is the following:



The rate equations are:

$$3.2.1 \quad \frac{dI}{dt} = -k_1 M I$$

$$3.2.2 \quad \frac{dM}{dt} = -k_1 M I - k_2 M (I_0 - I)$$

$$3.2.3 \quad \frac{dP_1}{dt} = -(k_1 - k_2) I M - k_2 M I_0$$

For long reaction times compared to the initiation time:

$$t \rightarrow \infty, \quad I \rightarrow 0 \quad \text{therefore:}$$

$$3.2.4 \quad \frac{d \ln M}{dt} = -k_2 I_0$$

This indicates that if one plots $\ln M$ vs. t one should obtain a straight line with the slope $SL = k_2 I_0$ at long times. Also from the rate equations, using the Eigenzeit transformation (Dostal & Mark, 1935), the time dependent monomer concentration can be written as:

$$3.2.5 \quad M = I_0 \beta \{1 - \exp(-\alpha \tau)\} - I_0 \tau + M_0$$

$$\text{where} \quad \alpha = k_1/k_2 \quad \beta = 1 - \alpha/\alpha$$

$$\tau = \int_0^t k_2 M dt$$

substituting SL/I_0 for k_2 we can express

$$\alpha = k_1 I_0 / SL \text{ and } \tau = \int_0^t M SL / I_0 dt$$

We now have the calculated function $M(t)$ which is only dependent on the parameters I_0 and k_1 , M_0 and SL being constants. Since on the other hand we can obtain an experimental function $M(t)$ from kinetic measurements, these data can be compared with the predicted monomer conversion. By defining a measure of error between the calculated $M(t)$ and the experimental $M(t)$ one can make a two-dimensional search of I_0 and k_1 to minimize the error. Having found the minimal error, I_0 , k_1 and therefore k_2 is obtained.

A second way of determining I_0 which can also serve as check for the previous method is by measuring the molecular weight of the polymer after complete reaction. If the initiation period is short compared to the total reaction time, $M_0/I_0 = \text{DPN}$. Therefore, if we know M_0 and DPN, I_0 can be calculated.

An alternative way of calculating α , the ratio of the rate constants k_1/k_2 , was also developed, starting from equation 3.2.2, rearranging it:

$$\begin{aligned} \frac{dM}{dt} &= -(k_1 - k_2) I M - k_2 M I_0 \\ 3.2.6 \quad \frac{d(\ln M/M_0)}{dt} &= -(k_1 - k_2) I - k_2 I_0 \end{aligned}$$

We now define $\theta = k_2 I_0 t$, $i = I/I_0$ and $m = M/M_0$
 $= SL t$

Therefore:

$$3.2.7 \quad \frac{d(\ln m)}{d\theta} = (1 - \alpha)i - 1$$

$$3.2.8 \quad \frac{d}{d\theta} (\ln m + \theta) = (1 - \alpha)i$$

Equation 3.2.7 indicates that for $I \rightarrow 0$ or $i \rightarrow 1$ the slope of the function $\ln m + \theta$ is $(1-\alpha)$. Therefore, if one has the value of the slope $d \ln m / dt = SL$ for high conversions and data $M(t)$ for low conversions one is able to calculate $\alpha = k_1/k_2$.

3.3 EXPERIMENTS AND RESULTS

The kinetic measurement was carried out in a 100ml flask under slight N_2 -pressure at $50^\circ C$. 4.9926 g of Methylpropylpropiolactone (MPPL) were added to 44 ml Tetrahydrofuran (THF) before 1 ml of initiator solution was injected to initiate the polymerization. From then on every 10 minutes a sample of 1 μ l was taken out of the reactor and injected into a gas chromatograph. Using a APIEZONE N 20% column at $150^\circ C$ (injection port $180^\circ C$, detector $220^\circ C$) one gets two very sharp peaks for THF and MPPL. The percentage of the MPPL peak area was measured with respect to the sum of the THF and MPPL peak area. The calibration was made by injecting a known mixture of THF and MPPL, preferably the reaction mixture immediately after initiation.

From Fig. 3.3.1 it can be seen that for reaction times greater than 40 min., the data plotted as $\ln m$ vs. t follow a straight line. The linear regression of the straight line yields the results:

Correlation factor $r = .9977$

slope $SL = .02300$

With the values of M_0 and SL we now conducted a two-dimensional search for a minimal error between the predicted function $M(t)$ and experimental data. The results are presented in Fig. 3.3.2.

The search procedure yields a optimal value for $K_1 = .264$ but no optimum can be reached for I_0 , the initiator concentration. The error surface assumes the form of a linear

valley, demonstrating the insensitivity of the procedure to values for I_0 . With the alternative mathematical approach (Equation 3.2.8) one was able to obtain a value for $\alpha = .43$ (Table 3.3.2), although only three points of the plot $\ln m + \theta$ vs. θ in Fig. 3.3.3 were used to draw a straight line. All the previous results and also the data from GPC and membrane osmometer measurements are given in Table 3.3.3.

The results of the gas chromatograph measurements are shown in Table 3.3.1.

The following should give some insight of how Table 3.3.3 was obtained and discusses the results by comparing them with the literature. Using the experimental value of I_0 , DPN and K_2 were calculated, the latter being in reasonable agreement with the values for K_2 Hall (1969) gives for polymerizations initiated with Tetramethylammoniumbenzoate and Tetrabutylammoniumbenzoate at 35°C. The value of K_2 obtained indirectly from osmometric data seems to be too low compared to the one from kinetic measurements.

The treatment of kinetic data according to Equation 3.2.4 affords a very simple and accurate method of determining K_2 . In our case the accuracy is proven since the linear regression provides a correlation factor r very close to 1.

The α obtained from Equation 3.2.8 is also in reasonable agreement with values reported by Hall (1969). As mentioned above, the straight line in Fig. 3.2.3 for small values of θ is drawn somewhat arbitrarily due to the small number of experimental points. To overcome this problem it is suggested

that one should measure conversion at very small intervals at the very beginning of the reaction.

Osmometric pressure measurements indicate a degree of polymerization almost three times lower than the expected value. This discrepancy can be explained by considering a possible chain transfer with Benzoic acid forming low molecular weight species which are not detected by the membrane osmometer. Therefore, more emphasis should be given to the purification and dry handling of the initiator of this type before introducing into the reactor. The difference between the expected value of ZP and the value obtained from the GPC measurement seems to support the above explanation, indicating a broader distribution than expected due to chain transfer.

In our case the search method yielded a value for K_2 two orders of magnitude smaller than reported by Hall (1969), whereas it was not possible to obtain any value for I_0 at all. Nevertheless, it is felt that this method represents a way of finding values for K_1 and I_0 if more conversion data for small reaction times were available.

FIGURE 3.3.1

$\ln M/M_0$ as a function of time for the polymerization of MPPL initiated with .000482 mol/l TEABz.

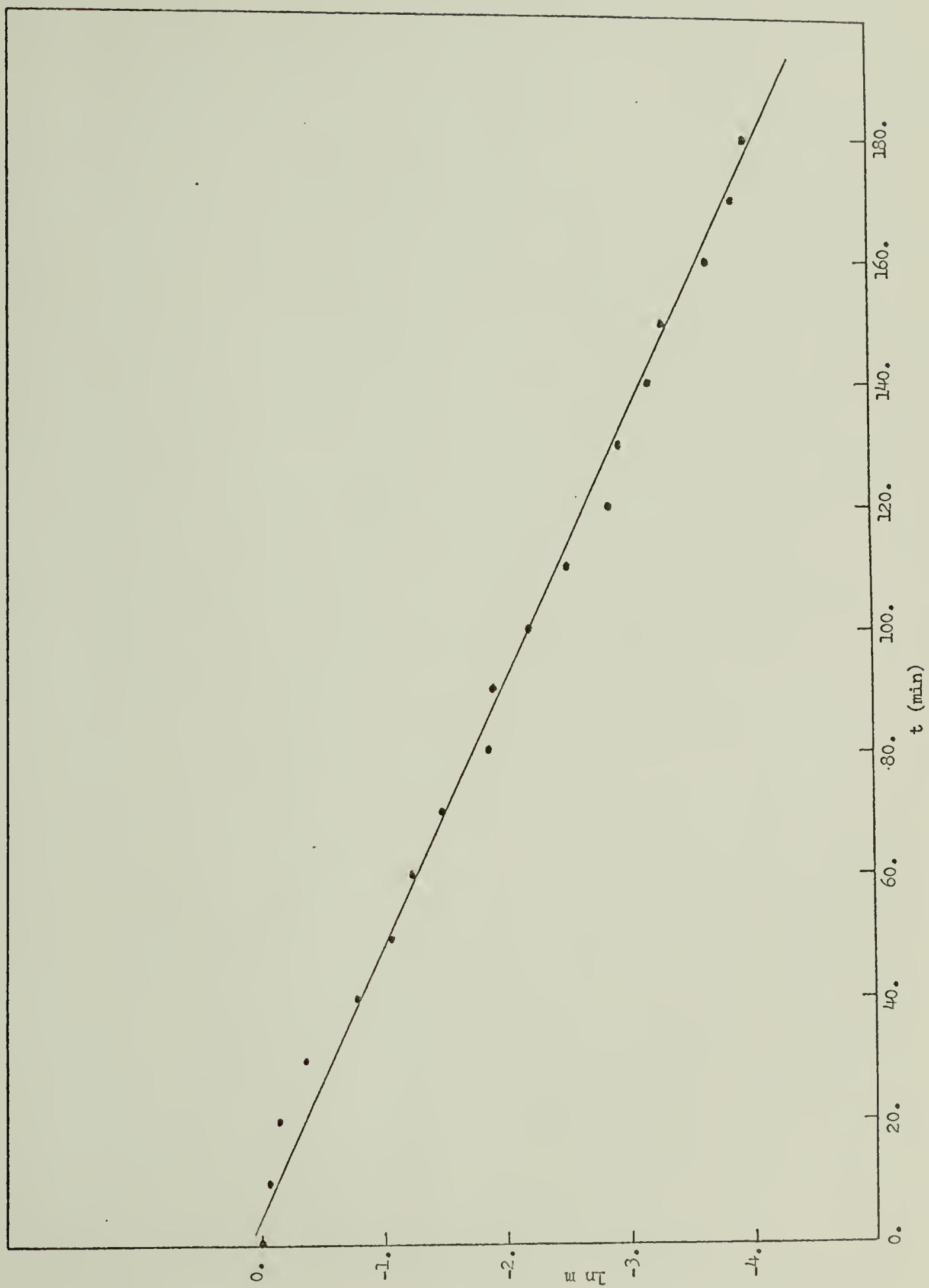


FIGURE 3.3.2

Two-dimensional search for I_0 and K_1 . Heavy lines represent equal sum of percentage error.

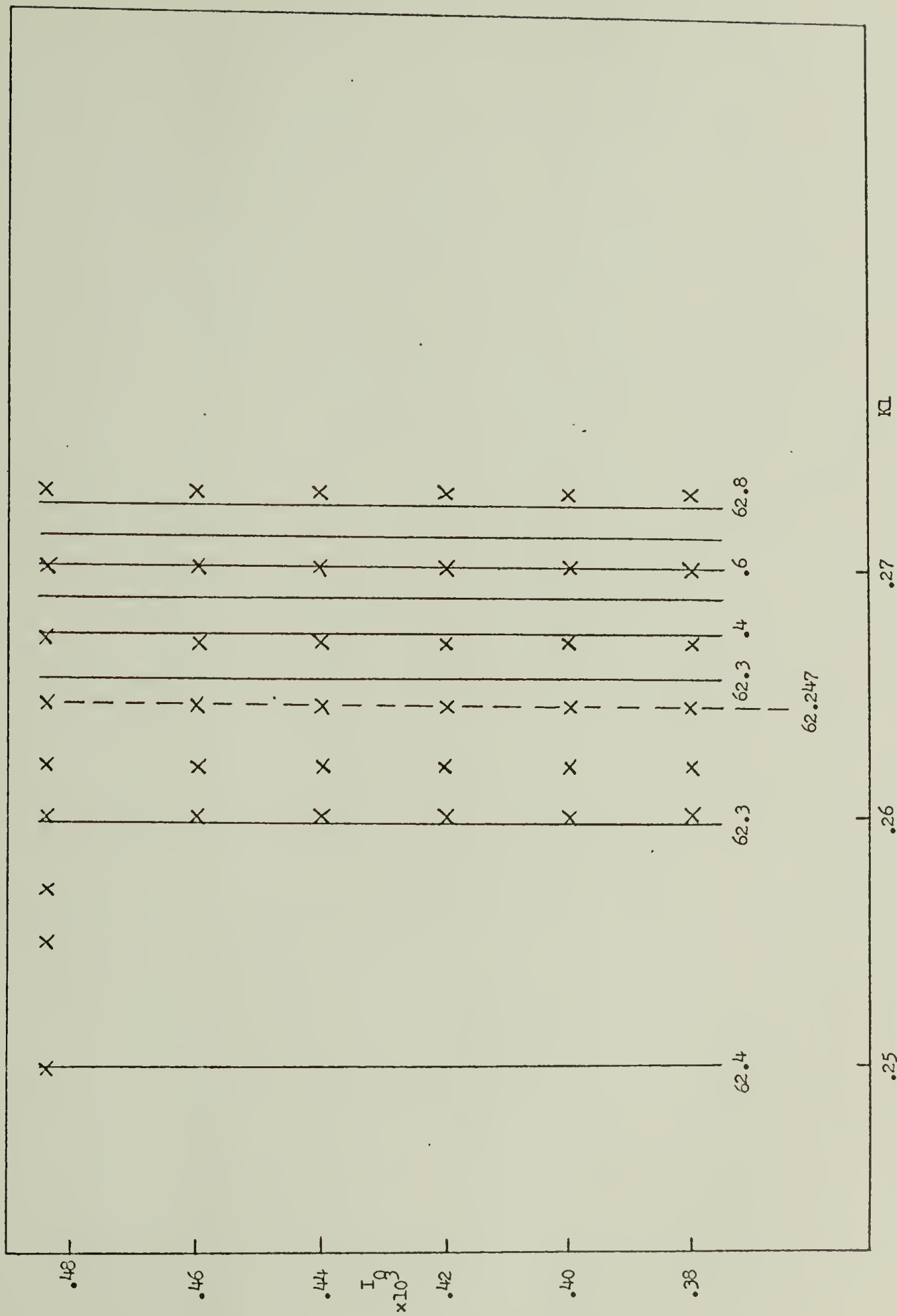


TABLE 3.3.1

Measured conversions M/M_0 as a function of time from kinetic measurements.

K I N E T I C M E A S U R E M E N T S

Initial conditions $I_0 = .000482$ (mol/l)

$M_0 = .709$ (mol/l)

$T = 50^\circ\text{C}$

Time (min.)

$M/M_0 = m$

10	.900
20	.833
30	.586
40	.444
50	.356
60	.289
70	.215
80	.154
90	.148
100	.110
110	.081
120	.065
130	.056
140	.042
150	.038
160	.026
170	.021
180	.019
210	.0085

TABLE 3.3.2

Kinetic data to evaluate α .

E V A L U A T I O N O F α

m	t(min)	θ	$-\ln m$	$\ln m + \theta$
1.00	0.	0.	0.	0.
.900	10	.23	.1056	.1244
.833	20	.46	.183	.2770
.586	30	.69	.372	.3180
.444	40	.69	.813	.1170
.356	50	1.15	1.070	.0800

FIGURE 3.3.3

$\ln m + \theta$ vs. θ . The slope of the curve for small values of θ represent $(1 - \alpha)$.

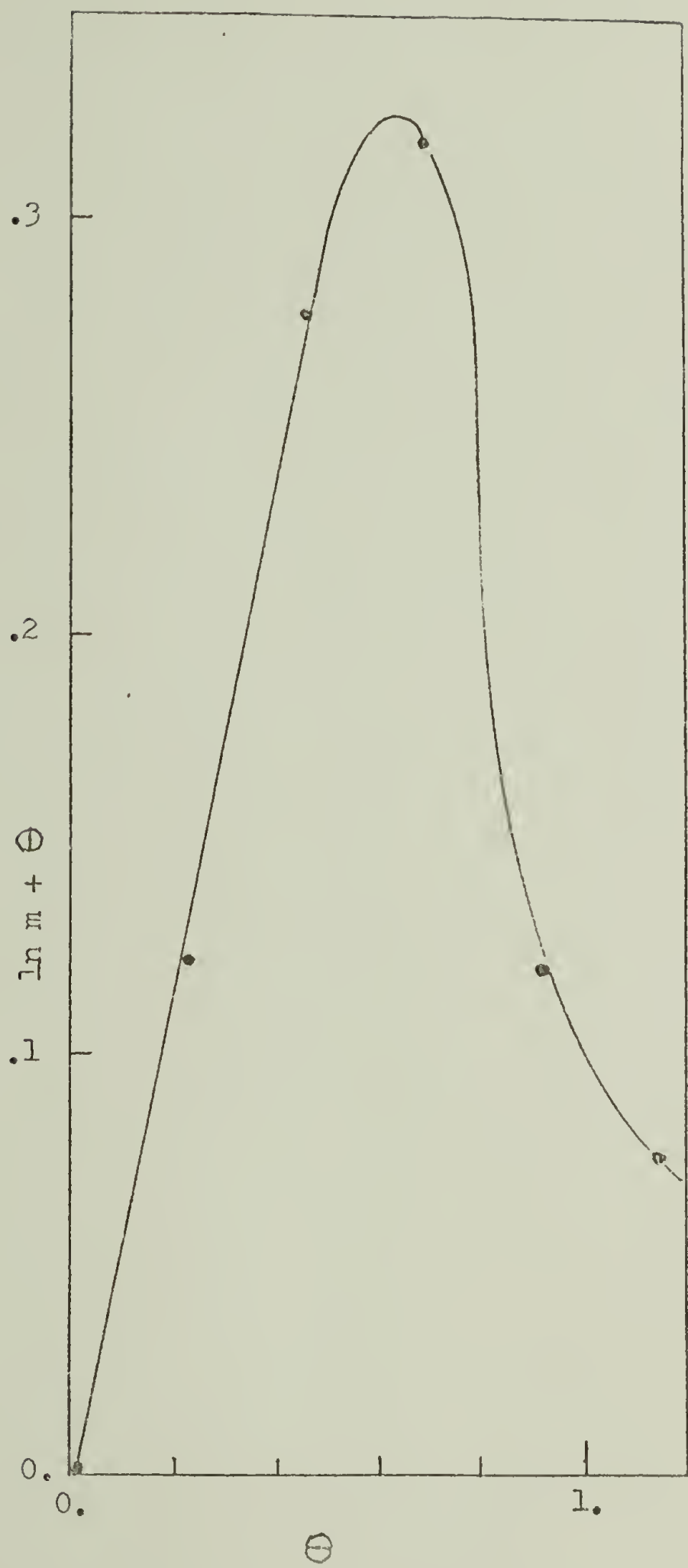


TABLE 3.3.3

Results from experiments, osmometry, GPC and search.

GENERAL RESULTS

<u>Osmometry</u>	<u>Experiment</u>	<u>GPC</u>	<u>$\ln m + \theta$</u>
$M_n = 73,300$	ZP = 1.018	ZP = 1.114	$\alpha = .43$
↓	↑		↓
DPN = 572.	DPN = 1470.		K1 = 20.6**
	↑		
	$I_o = .000482$		
	↓		
	K2 = 47.8*		

*From K2 $I_o = .023$
 **From α , and K2 = 47.8

C H A P T E R 4

T H E C O M P U T E R P R O G R A M

4.1 INTRODUCTION

The 5 equations 2.3.8, 9, 10, 11, 13 and 15 contain the initial monomer and initiator concentration, M_0 and I_0 , respectively, the rate constants K_1 and K_2 and the reactor volume V_0 as parameters. QT , the initiator addition rate, is also a parameter and x , y , μ_0 , μ_1 , and μ_2 are dependent variables. The computer language MIMIC can be used to solve these differential equations in real time if the initial conditions are given. Therefore, the equations had to be rewritten in terms of real time t by substituting τ by $k_2 M_0 t$ in all the equations. In order to set $I_0 = 0$ if necessary one had to substitute y by I/I_0 in equation 2.3.8. We then end up with one differential equation for each, I , x , μ_0 , μ_1 , and μ_2 , which are integrated simultaneously by the Runge-Kutta method. The initial conditions for these five variables are I_0 , 1, 0, 0 and 0, respectively. The integration is interrupted as soon as the conversion reaches 99%. The integration increment DT was set to one minute. An adjustable time increment PT was used to control the binary file storage of the values of DPN , DPW and ZP as a function of the reaction time. The plotter outputs were equated with these stored data. A printed output of the reaction time T , conversion $CONV$, initiator addition rate

QT, totally added initiator IT, monomer and initiator concentrations M and I, the average degrees of polymerization, DPW and DPN, and finally the polydispersity ZP is generated at 99% conversion. T, CONV and IT are also printed out at the beginning of the linear initiator addition.

The calculations were now divided into three types as suggested earlier: the pulse feed allowing only a variation of the initial initiator concentration I_0 , the linear feed allowing only a variation of the total amount of initiator added, ITOT, and finally the linear feed with pulse, which allows a variation of I_0 , IT and the starting time of the initiator addition THE.

4.2 INITIAL PULSE FEED

This type of initiator feed is the same which is used for kinetic measurements and it also corresponds to the case I used by Eisenberg & McQuarrie (1966) (Fig. 4.2.1). The addition rate, QTT, the addition starting time, THE, have to be set zero. The only non-zero parameters for this type of reaction control are M0, K1, K2 and I0, where $I0 = ITOT$.

4.3 LINEAR FEED WITHOUT INITIAL PULSE

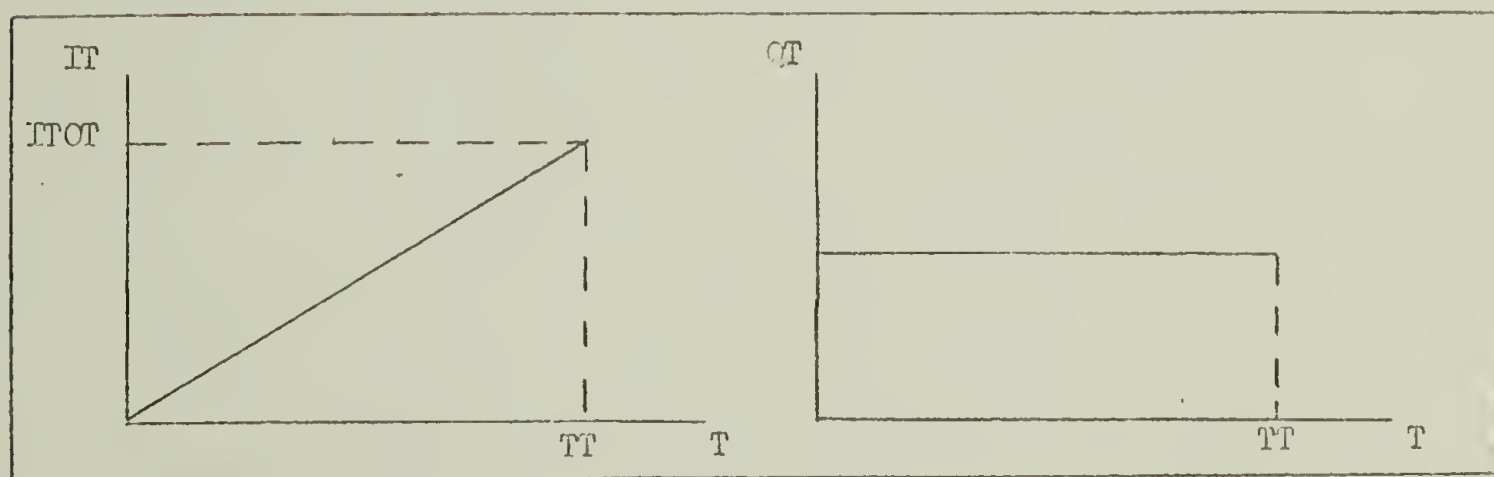
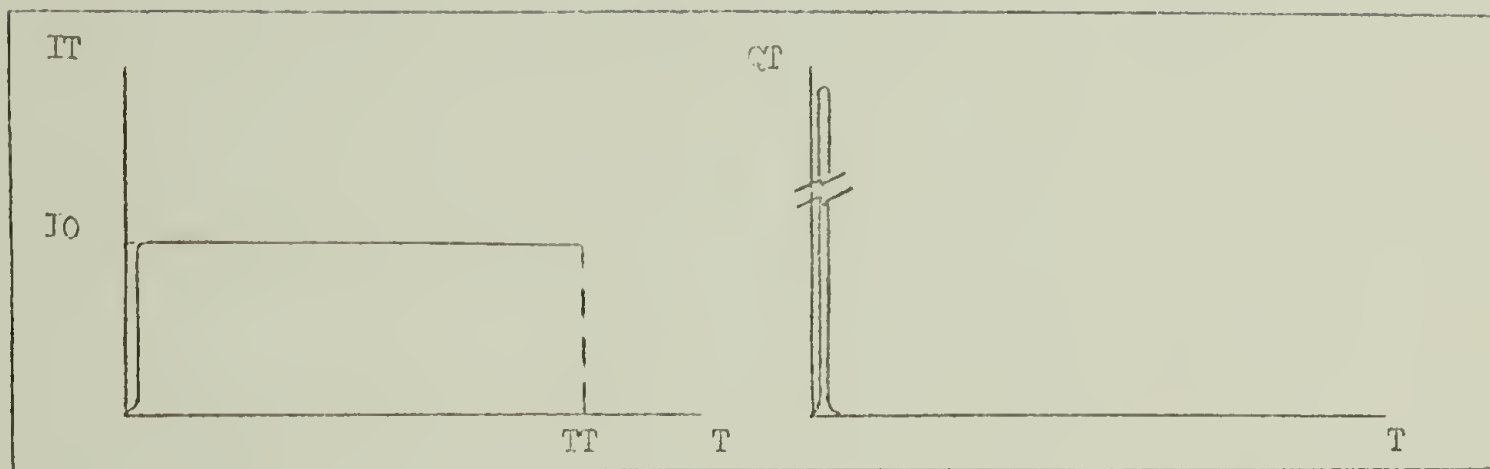
This case corresponds to case II in Eisenberg & McQuarrie (1966) (Fig. 4.3.1). The parameters I0 and THE have to be set zero. To be able to preset the total amount of initiator added, the total amount of initiator in the reactor,

FIGURE 4.2.1

Control scheme for a pulse initiator addition, IT and QT being the total amount of initiator added and the addition rate, respectively.

FIGURE 4.3.1

Control scheme for a linear initiator addition without pulse.



IT, has to approach its desired value ITOT as closely as possible at the end of the reaction. Therefore, to obtain this condition, one has to conduct a search to get the value of QTT which satisfies this condition.

4.4 LINEAR FEED WITH INITIAL PULSE

In this case the reaction is started with a pulse of initiator added. If $THE=0$, a linear feed with the rate QTT is simulated for the very beginning of the reaction (Fig. 4.4.1). If THE is non-zero, a linear initiator feed starts at time THE, (Fig. 4.4.2). In this case also, for every value of THE a search has to be conducted to find QTT for which, at the end of the reaction, $IT=ITOT$.

The case where THE is non-zero is a simplified version of the control Bandermann (1971) obtained at the end of his iteration. It is essentially a two step addition, the first pulse making a narrow distribution of high MW species, the second linear addition broadening the MWD.

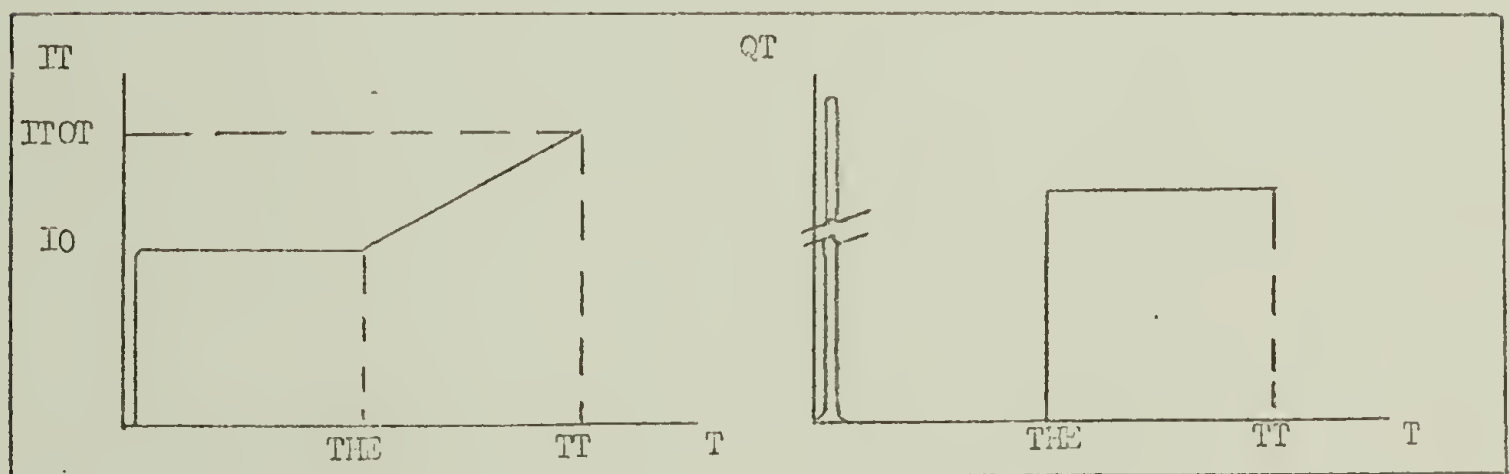
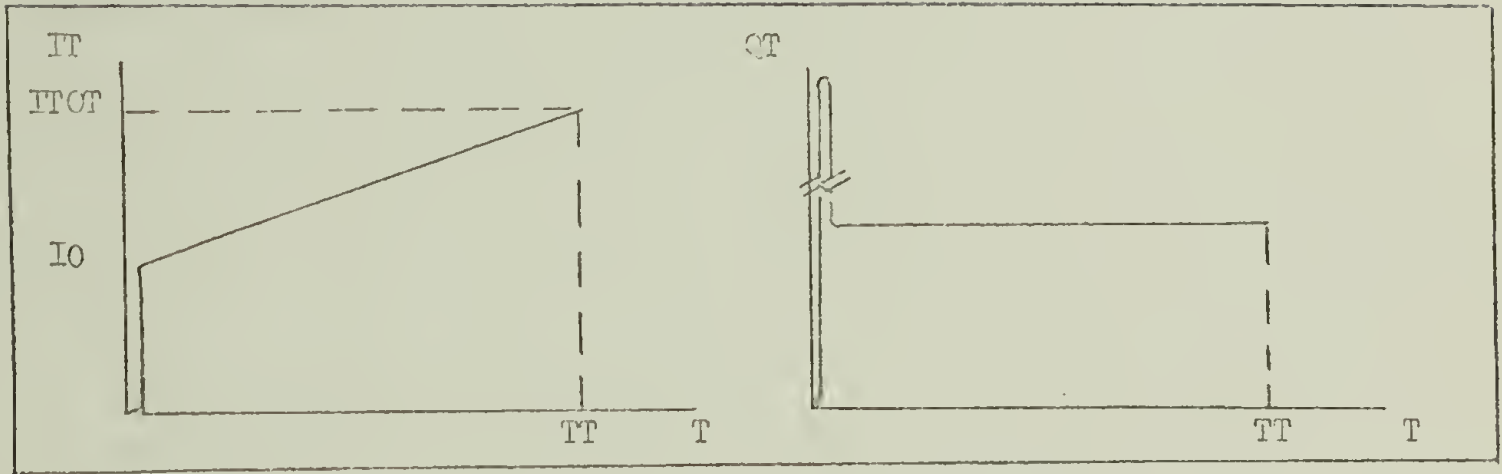
Apparently, four parameters are required to control the reaction: M_0 , I_0 , $ITOT$ and THE . However, it was found that the first three of them can be condensed into more significant ones: $ITOT/I_0$, $ITOT-I_0$ and $M_0/ITOT$. The results were analyzed in terms of conversion at which the linear feed begins (CONADD) rather than with THE .

FIGURE 4.4.1

Control scheme for a linear initiator addition with pulse.

FIGURE 4.4.2

Control scheme for a linear initiator addition with initial pulse and delay ($T_{HE} \neq 0$).



C H A P T E R 5

R E S U L T S O F T H E S I M U L A T I O N

5.1 INITIAL PULSE FEED

This type of reaction control was simulated with $M_0 = .846$. I_0 was varied from .846 to .00025. Fig. 5.1.1 shows that for small values of I_0 ZP is very close to 1. With increasing I_0 , ZP goes through a maximum of 1.328 at $M_0/ITOT = 2.82$, but at the same time DPN decreases very rapidly, as can be seen from Fig. 5.1.2. It also shows how the calculated DPN approaches the theoretical value, which is $M_0/ITOT$. This deviation from the theoretical value of DPN can be understood considering the fact that for low values of $M_0/ITOT$ the total reaction time TT is so small that the time for initiation is comparable to the total reaction time. Fig. 5.1.3 and 5.1.4 show the behavior of DPN , DPW and ZP during the course of the reaction.

In both cases ZP increases very rapidly at the beginning of the reaction and then levels off towards the end. Both DPN and DPW increase linearly with conversion, the slope being proportional to I_0 . Fig. 5.1.5 shows a linear dependence of TT from DPN_{99} for both cases, the pulse and linear feed.

5.2 LINEAR FEED WITHOUT INITIAL PULSE

This reaction control was simulated with $M_0 = .846$.

FIGURE 5.1.1

ZP99 - 1 as a function of $M_o/ITOT$ for a linear and pulse feed initiator addition control.

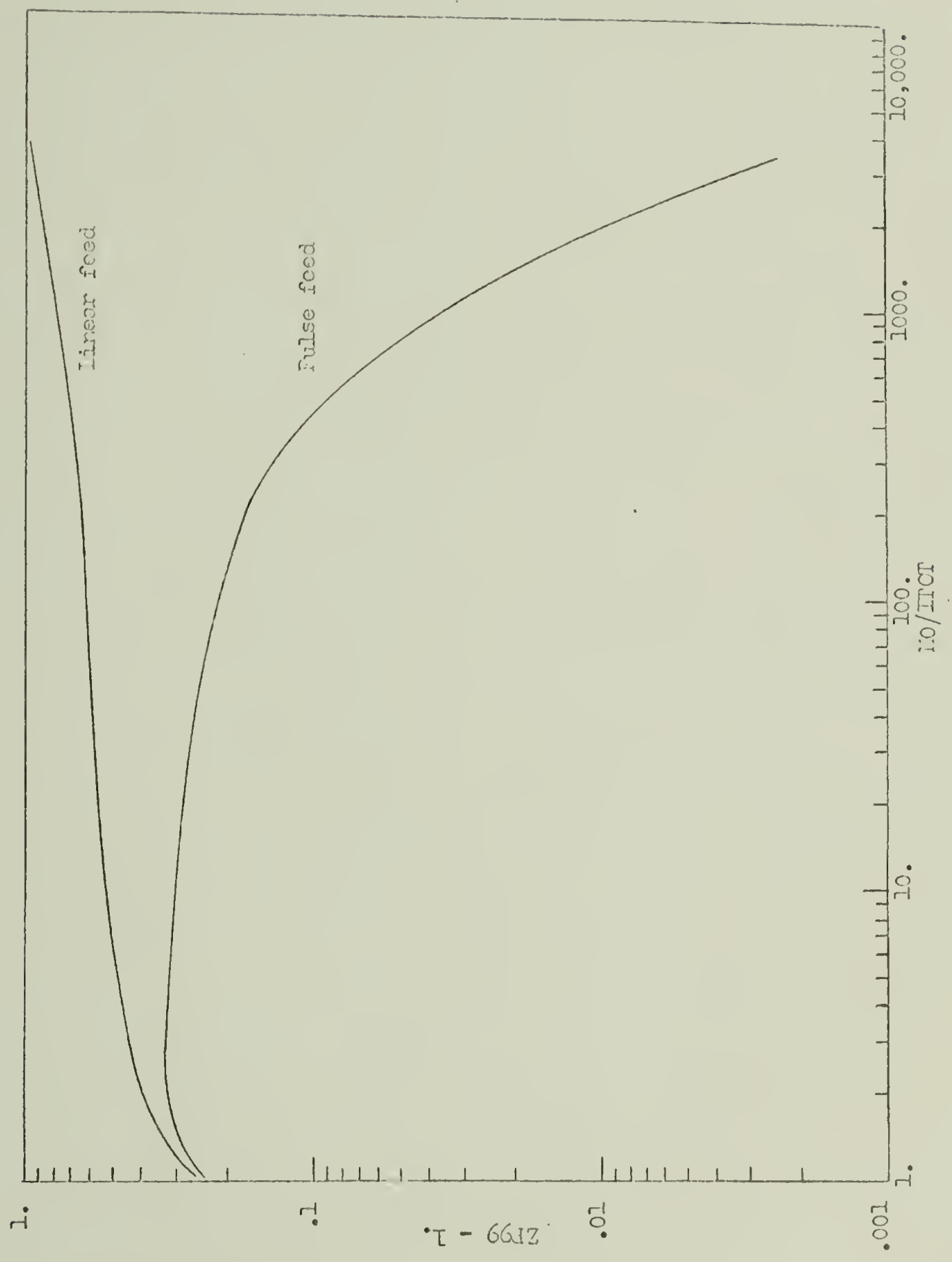


FIGURE 5.1.2

DPN99 as a function of $M_o/ITOT$ for all three different types of initiator control.

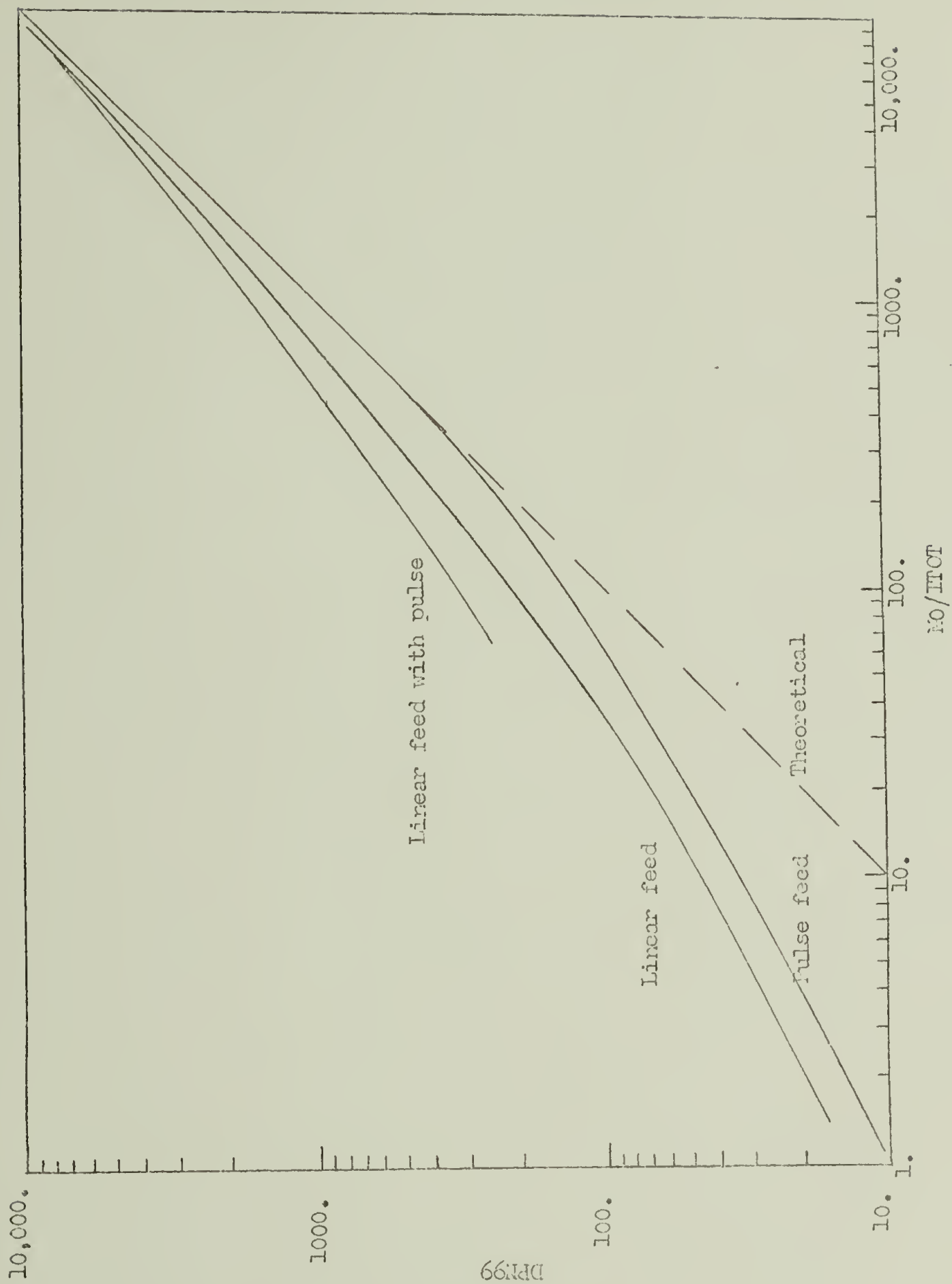


FIGURE 5.1.3

Computer plots of the variables DPN, DPW and ZP as a function of conversion for a pulse feed with $I_0 = .01$.

FIGURE 5.1.4

Computer plots of the variables DPN, DPW and ZP as a function of conversion for a pulse feed with $I_0 = .00025$.

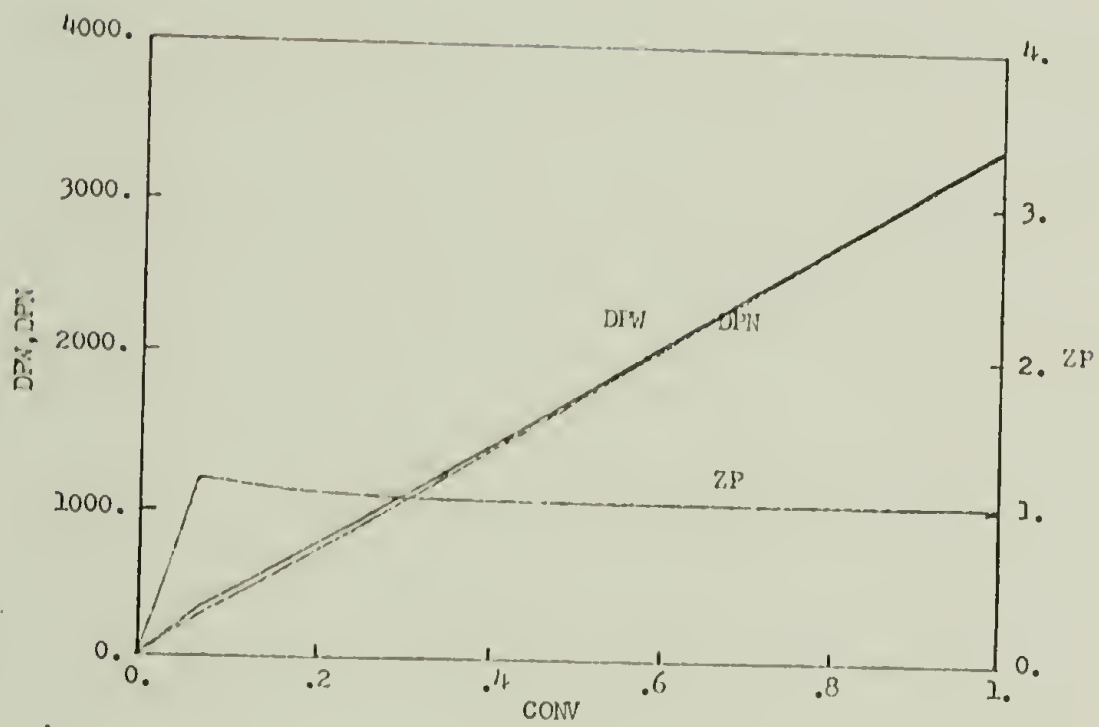
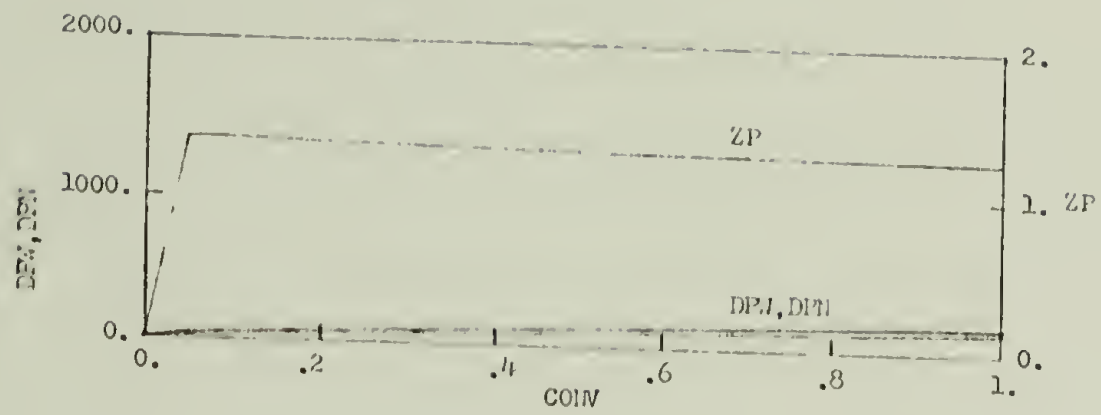


FIGURE 5.1.5

The total reaction times TT as a function of its final DPN99 for pulse and linear feeds.

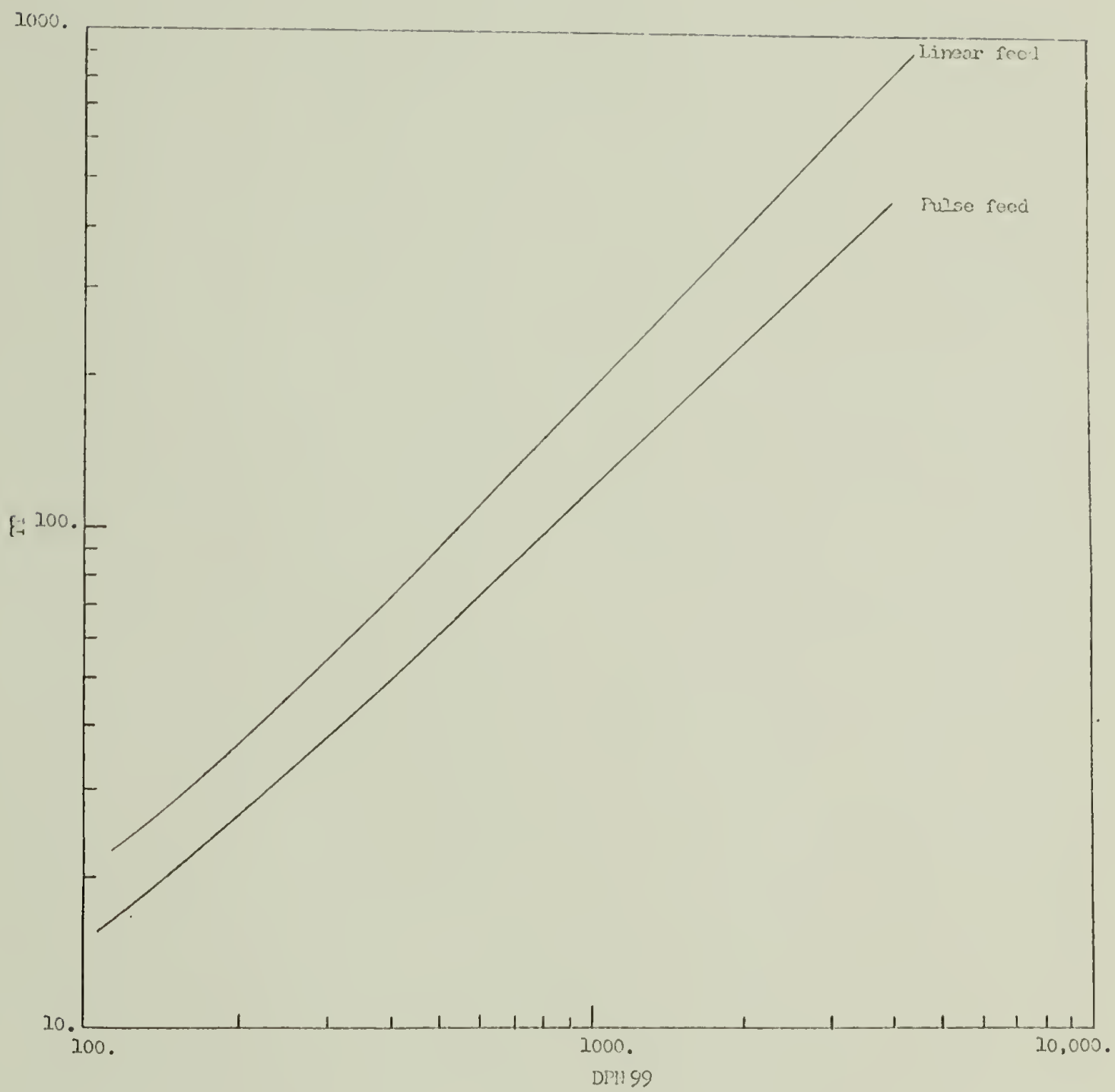


FIGURE 5.2.1

Computer plots of the variables DPN, DPW and ZP as a function of conversion for linear feed without pulse and $IT = .01$.

FIGURE 5.2.2

Computer plots of the variables DPN, DPW and ZP as a function of conversion for linear feed without pulse and $IT = .00025$.

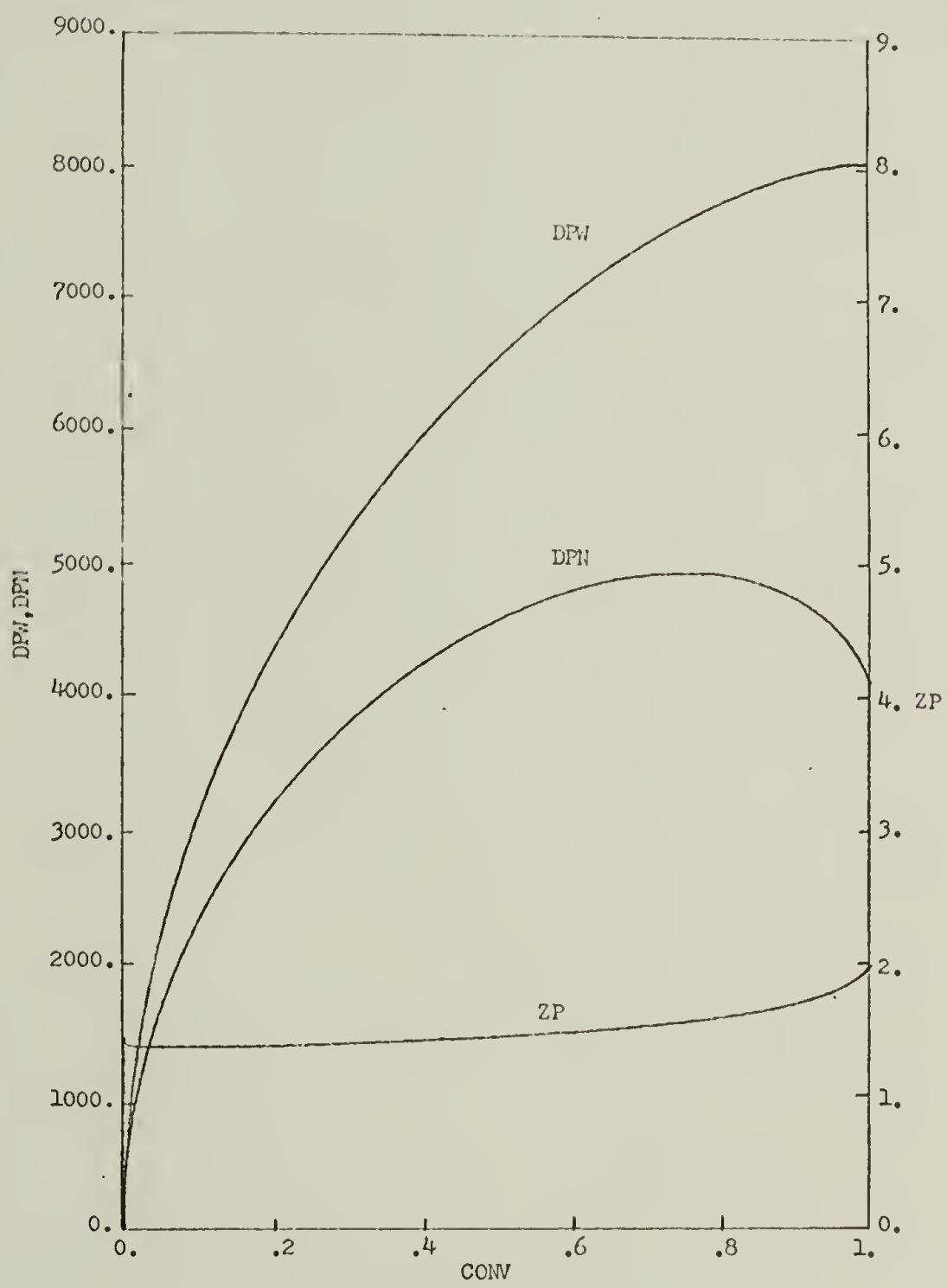
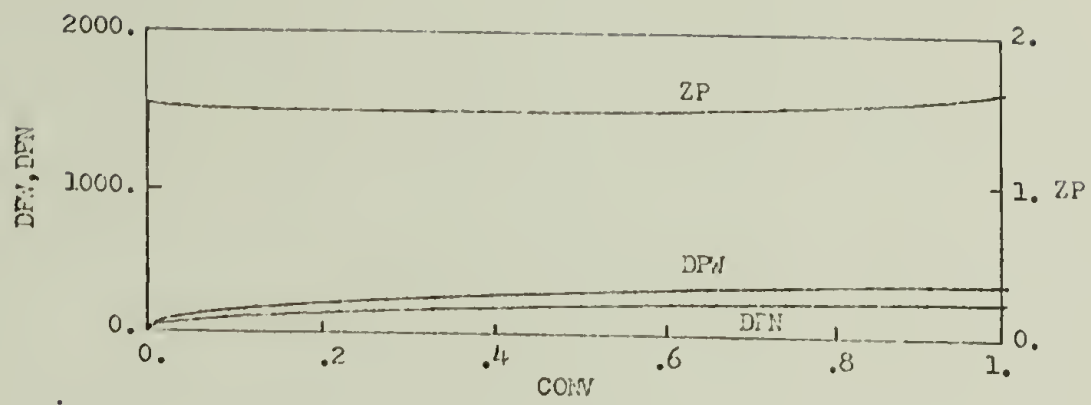


TABLE 5.1.1

Calculated degrees of polymerization DPN, polydispersities ZP and total reaction times TT for various values of $M_0/IT0T$ for an initiator pulse feed.

P U L S E F E E D

$$M0 = .846$$

M0/ITOT	IO	DPN	ZP	TT
.846	1.	9.	1.137	3.
1.21	.7	11.	1.270	2.
1.41	.6	12.	1.295	2.
1.692	.5	14.	1.314	3.
2.115	.4	15.	1.324	3.
2.82	.3	18.	1.328	3.
4.23	.2	22.	1.324	4.
8.46	.1	31.	1.311	5.
12.1	.07	38.	1.303	6.
28.2	.03	61.	1.278	9.
84.6	.01	124.	1.228	18.
169.2	.005	204.	1.181	28.
423	.002	436.	1.100	56.
846.	.001	841.	1.043	102.
1692.	.0005	1675.	1.013	198.
3384.	.00025	3351.	1.003	391.

TABLE 5.2.1

Calculated initiator addition rates Q_T obtained after trial and error, degrees of polymerization DP_n , polydispersities ZP and total reaction times TT for various values of $M_0/ITOT$ for a linear initiator feed.

L I N E A R F E E D

$$M0 = .846$$

M0/ITOT	ITOT	QTT	DPN	ZP	TT
3.38	.25	$.102 \times 10^{-1}$	15.	1.453	6.
8.46	.1	$.1 \times 10^{-2}$	40.	1.524	9.
16.9	.05	$.25 \times 10^{-3}$	67.	1.562	14.
33.84	.025	$.745 \times 10^{-4}$	107.	1.585	21.
84.6	.01	$.152 \times 10^{-4}$	203.	1.608	38.
169.2	.005	$.447 \times 10^{-5}$	339.	1.641	63.
423.	.002	$.847 \times 10^{-6}$	694.	1.719	131.
846.	.001	$.233 \times 10^{-6}$	1226.	1.799	237.
1692.	.0005	$.624 \times 10^{-7}$	2212.	1.886	441.
3384.	.00025	$.104 \times 10^{-7}$	4073.	1.971	838.
8460.	.0001	$.3 \times 10^{-8}$	9023.	2.060	1930.

THE and I0 were set zero and ITOT was varied from .25 to .00025. For each value of ITOT, a QTT had to be found which satisfies the condition $IT=ITOT$ at $CONV=.99$. From Fig. 5.1.1 it can be seen that ZP99, unlike for the case of pulse feed, increases with increasing $M0/ITOT$. Fig. 5.1.2 shows that DPN behaves similar as in the case of pulse feed, but approaches the limiting value more slowly. With this reaction control in general it is possible to obtain higher values of ZP than in the case of pulse feed.

Fig. 5.2.1 and 5.2.2 show the behavior of DPN, DPW and ZP during the reaction for two different values of ITOT. ZP in both cases behaves quite similarly, increasing very rapidly at low conversions, going through a minimum at moderate conversions and increasing again near completion. For high values of ITOT, DPN and DPW increase very slowly in an almost linear fashion. For $ITOT=.00025$, DPN and DPW increase very rapidly at low conversions, then DPN goes through a maximum and drops at high conversions, whereas DPW increases throughout the course of the reaction. Fig. 5.1.5 shows a linear dependence of TT on DPN99, and also that the linear feed gives larger values for TT than the pulse feed.

5.3 LINEAR FEED WITH INITIAL PULSE

For this kind of reaction control three different series were calculated with values for $ITOT/I0$ being 5,

10, and 50, respectively. It has been observed for all three series, as shown in Fig. 5.3.1, that if one plots ZP99 vs. CONADD, ZP99 goes through a maximum. Another feature of these plots is that for the same values of $M_0/ITOT$ one obtains identical curves, whatever the values of $ITOT-I_0$. The relation of those values of CONADD which yield ZPMAX to $M_0/ITOT$ for different values of $ITOT/I_0$ are shown in Fig. 5.3.2.

For the specific case of $ITOT/I_0 = 50$, $M_0/ITOT = 84.6$ and $ITOT-I_0 = .009$ DPN, DPW and ZP were calculated as a function of conversion. Fig. 5.3.3 shows these functions for the parameter $THE=0$, corresponding to $CONADD=0$. Comparing the results with Fig. 5.3.4 shows the three functions for the parameters $THE = 50$ ($CONADD = .33$). In this case the initiator addition was started too early so that DPW was not high enough to yield a high value for ZP99. In the case of $THE = 200$ ($CONADD = .82$) the maximum of ZP99 (ZPMAX) was reached (Fig. 5.3.5). Here DPW had time enough to build up and DPN had time enough after the start of the feed to go to a small value again. It appears that a reasonable condition for maximum ZP99 would be if both DPN and DPW have the same negative slope at the end of the reaction:

$$dDPN/dCONV = dDPW/dCONV$$

In Fig. 5.3.6, where $THE = 350$ ($CONADD = .95$) the negative slope of DPN is greater than the one of DPW, which is the

FIGURE 5.3.1

Example of the behavior of ZP99 (top), TT (middle) and DPN99 (bottom) as a function of the conversion at which the linear feed was started (CONADD). The four curves represent values of $M_0/IT0T$ of 846. (top curves), 423., 169.2 and 84.6 (bottom curves). $M_0 = .846$, $IT0T/I_0 = 10$. The dotted curve represents the location where ZP99 reaches its maximum value.

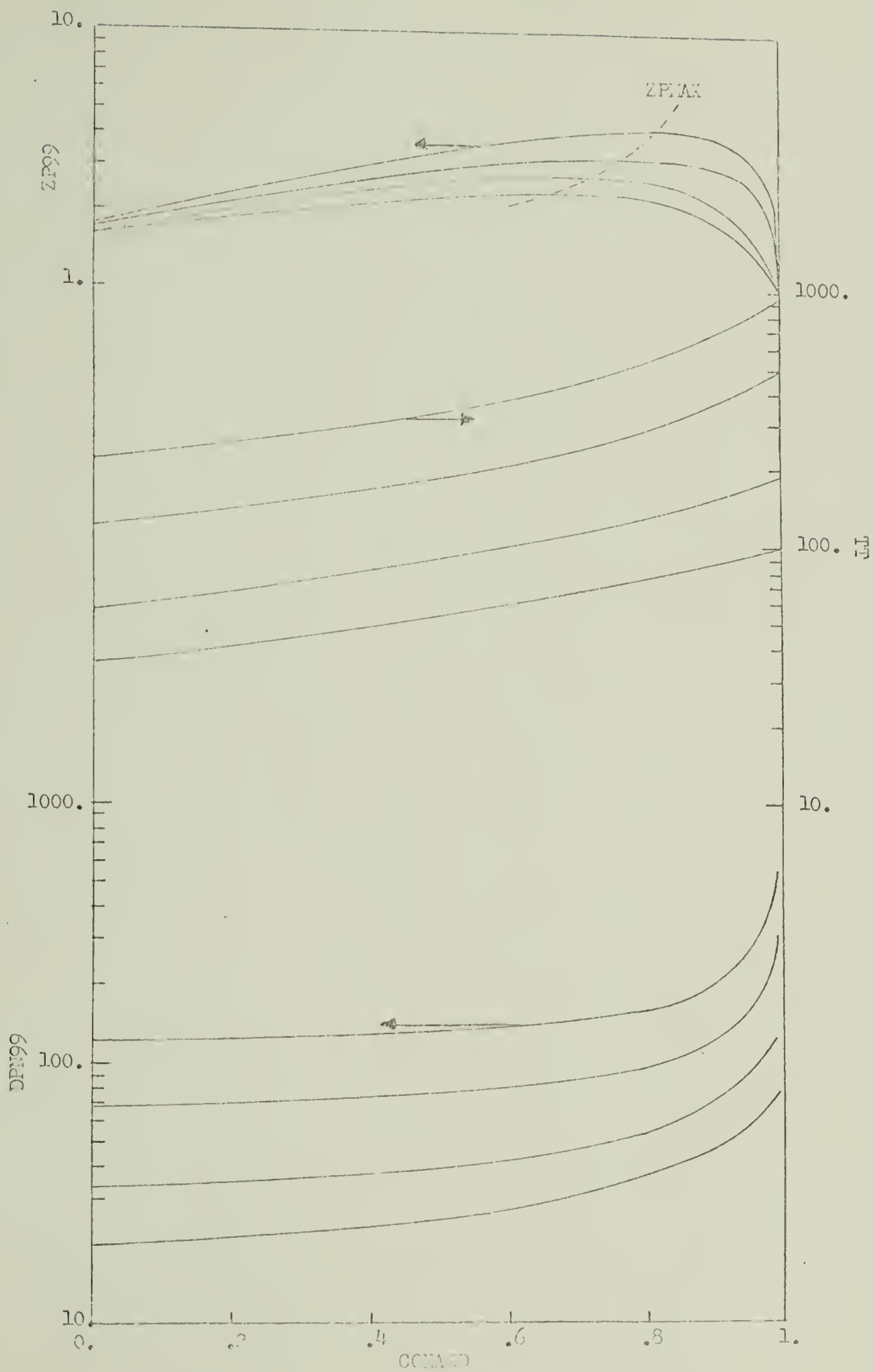


FIGURE 5.3.2

CONADD for which $ZP99 = ZP_{MAX}$ as a function of $M_o/ITOT$
for three different ratios $ITOT/I_o$.

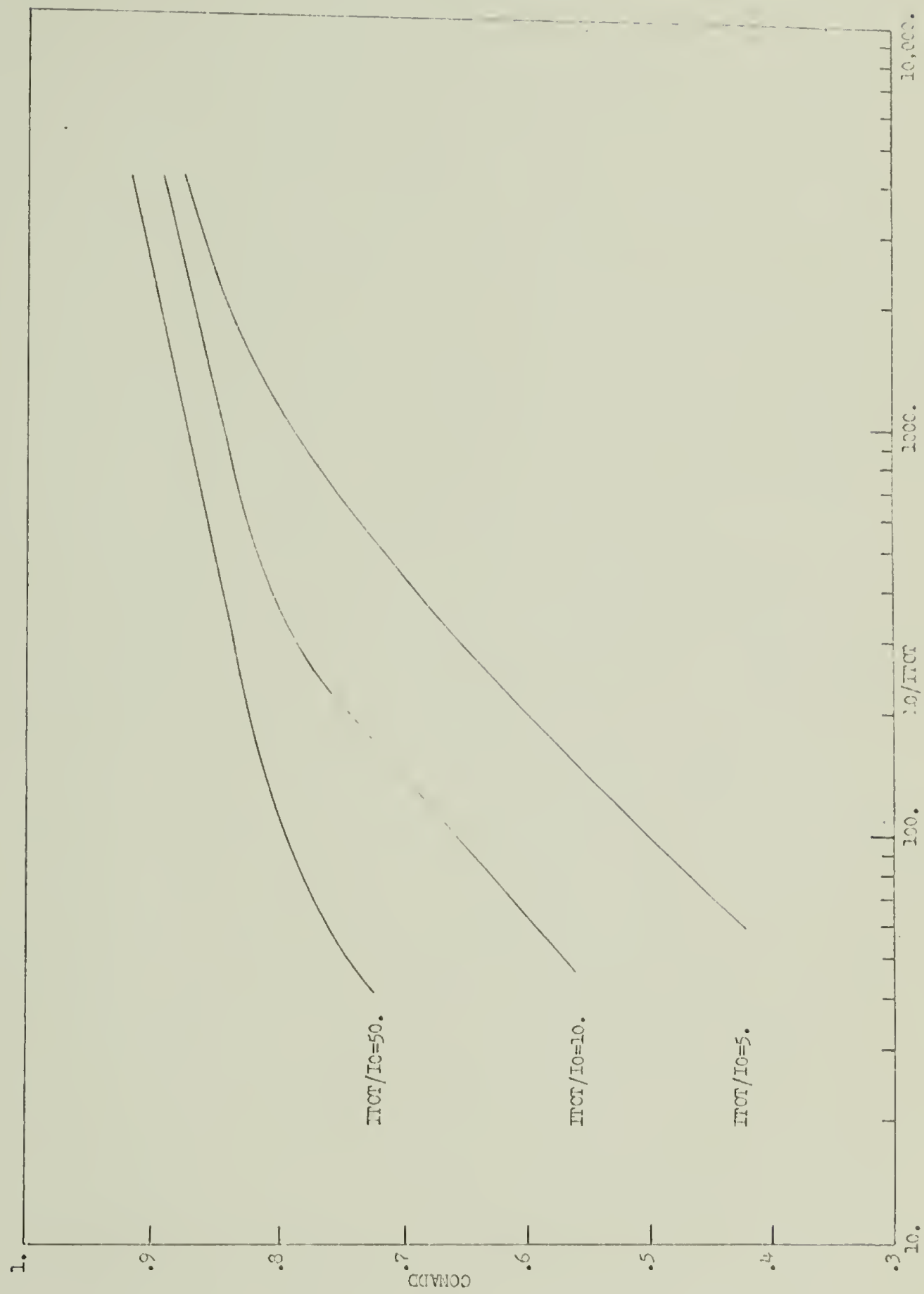


FIGURE 5.3.3

Computer plots of the variables DPN, DPW and ZP as a function of conversion for linear feed with initial pulse and $THE = 0$ ($CONADD = 0$). $M_O = .846$, $ITOT/I_O = 10$.

FIGURE 5.3.4

Computer plots of the variables DPN, DPW and ZP as a function of conversion for linear feed with initial pulse and $THE = 50$ ($CONADD = .33$). $M_O = .846$, $ITOT/I_O = 10$.

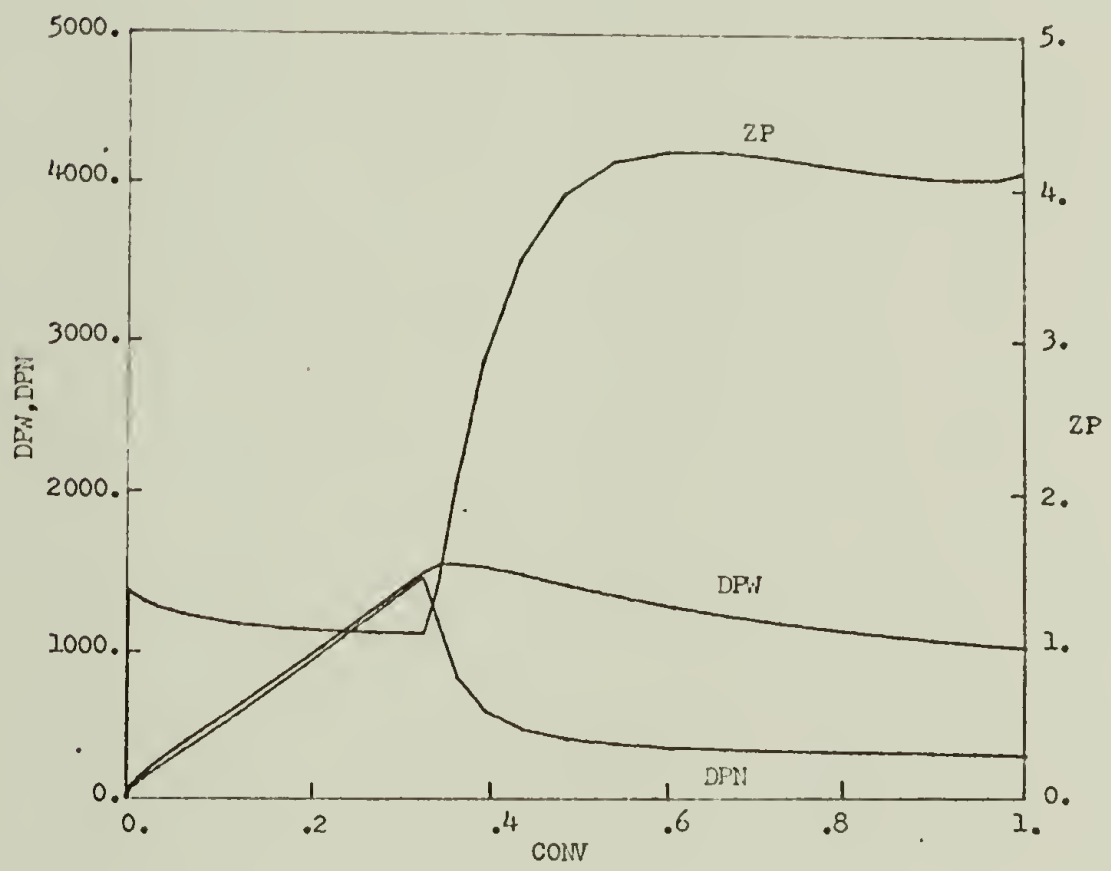
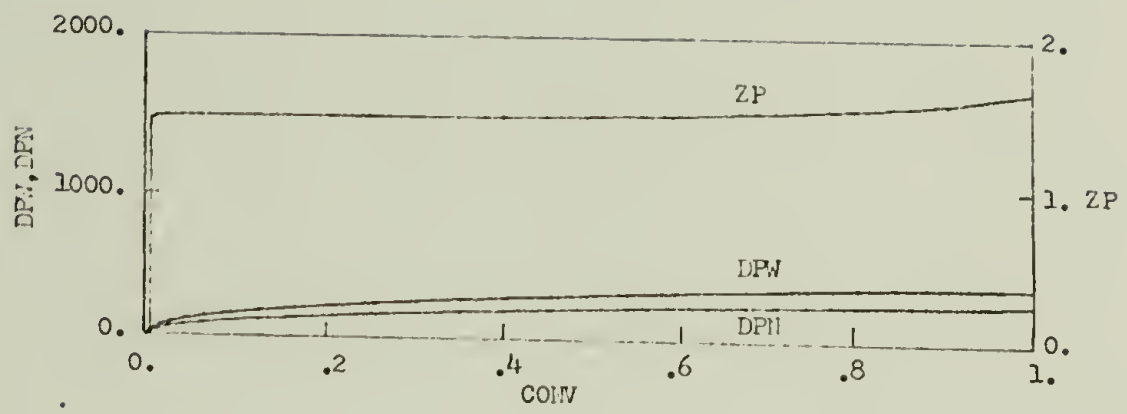


FIGURE 5.3.5

Computer plots of the variables DPN, DPW and ZP as a function of conversion for linear feed with initial pulse and $THE = 200$ ($CONADD = .82$). $M_o = .846$, $ITOT/I_o = 10$.

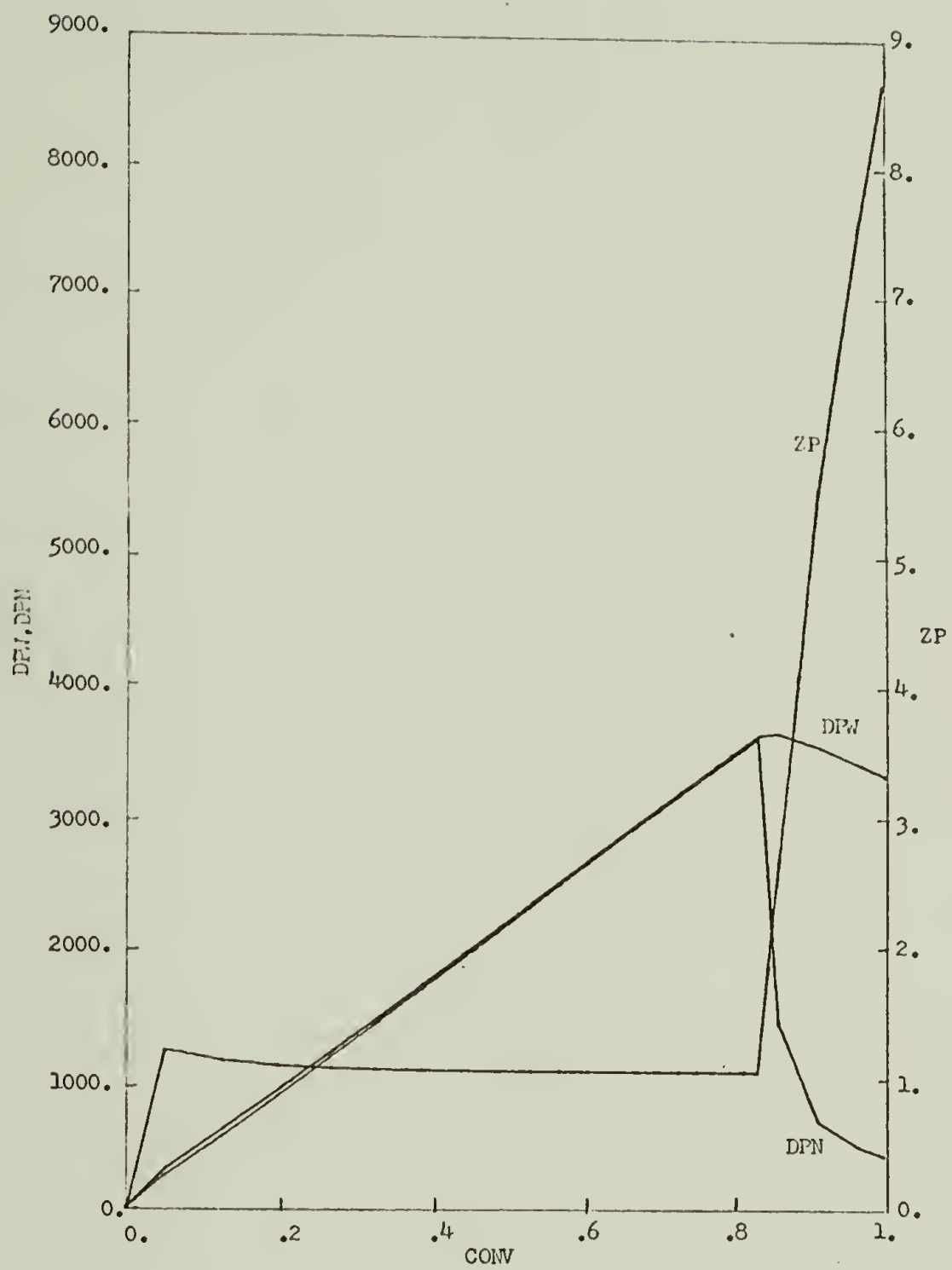


FIGURE 5.3.6

Computer plots of the variables DPN, DPW and ZP as a function of conversion for linear feed with initial pulse and $THE = 350$ ($CONADD = .95$). $M_o = .846$, $ITOT/I_o = 10$.

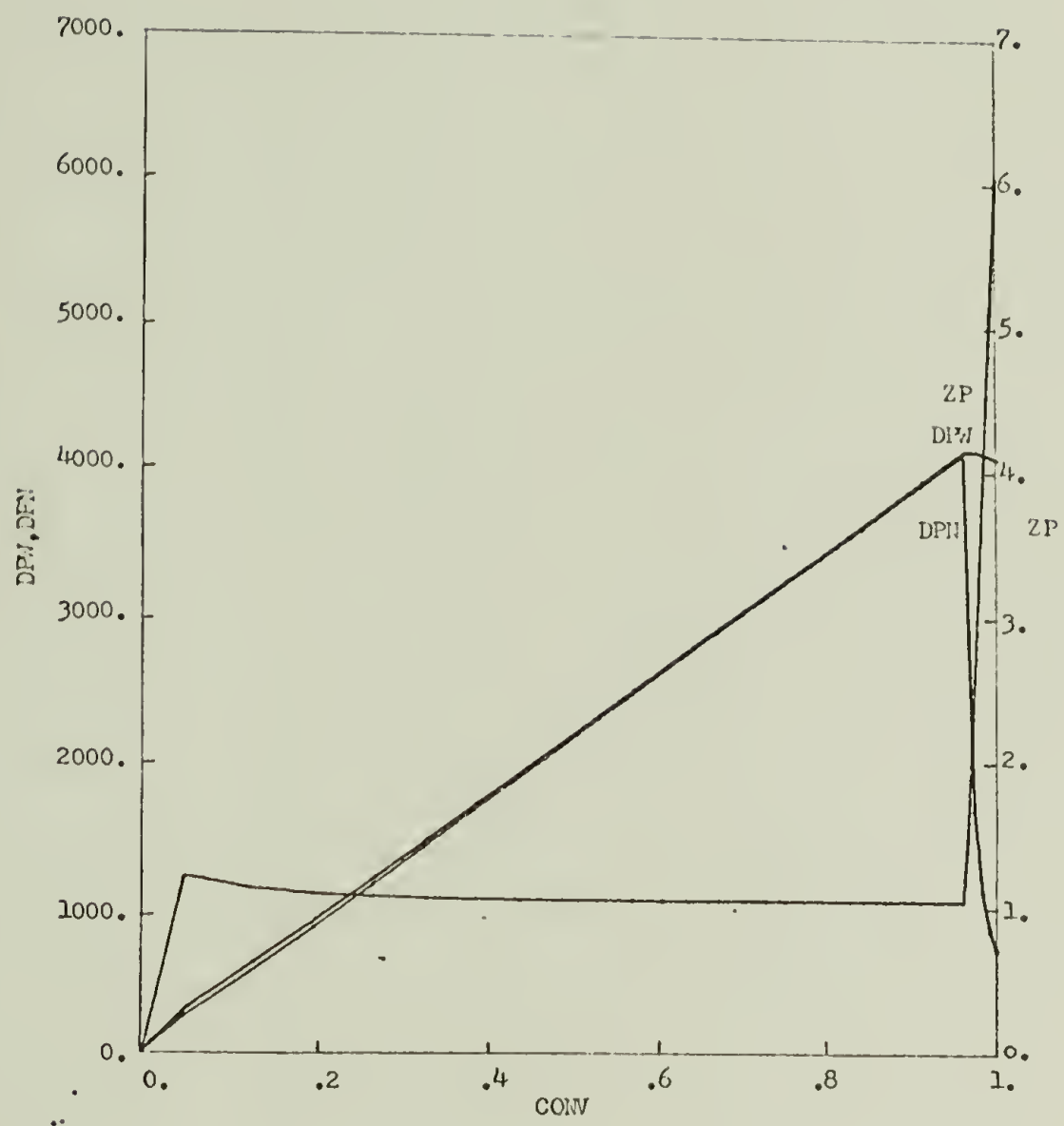


TABLE 5.3.1

Values of optimal polydispersities ZPMAX, degrees of polymerization DPN for the optimal conversion at which initiator addition started (CONADD) and total reaction times TT, calculated for three different values of $ITOT/I_0$ and for various values of $M_0/ITOT$ and $ITOT-I_0$.

L I N E A R F E E D W I T H P U L S E

ITOT/I0 = 5.

MO/ITOT	ITOT-I0	ITOT	I0	M0	DPN	ZPMAX	TT
84.6	.0045	.005625	.001125	.476	240.	1.65	71.
84.6	.009	.01125	.00225	.952	240.	1.67	37.
169.2	.009	.01125	.00225	1.905	420.	1.76	32.
423.	.0045	.005625	.001125	1.506	580.	1.92	62.
846.	.0009	.001125	.000225	.952	1500.	2.42	295.
846.	.0018	.00225	.00045	1.905	1500.	2.42	145.
3384.	.0009	.001125.	.000225	3.810	4800.	3.15	300.

L I N E A R F E E D W I T H P U L S E

ITOT/IO = 10.

MO/ITOT	ITOT-IO	ITOT	IO	MO	DPN	ZPMAX	TT
84.6	.009	.01	.001	.846	290.	2.31	62.
169.2	.0045	.005	.0005	.846	490.	2.77	117.
169.2	.009	.01	.001	1.692	490.	2.77	59.
423.	.0018	.002	.0002	.846	920.	3.30	284.
423.	.0045	.005	.0005	2.115	950.	3.68	120.
846.	.0009	.001	.0001	.846	1600.	4.36	570.
846.	.0018	.002	.0002	1.692	1600.	4.36	278.
846.	.0045	.005	.0005	4.23	1600.	4.32	115.
1692.	.0018	.002	.0002	3.380	2900.	5.10	290.
3384.	.0018	.002	.0002	6.768	4900.	5.98	295.

LINEAR FEED WITH PULSE

ITOT/IO = 50.

MO/ITOT	ITOT-IO	ITOT	IO	MO	DPN	ZPMAX	TT
84.6	.009	.009184	.000184	.777	340.	8.80	230.
169.2	.009	.009184	.000184	1.554	650.	11.8	252.
423.	.009	.009184	.000184	3.88	1000.	15.8	240.
423.	.0045	.004592	.000092	1.941	1000.	15.8	490.
846.	.0045	.004592	.000092	3.882	1700.	19.8	515.
1692.	.0045	.004592	.000092	7.77	2900.	24.0	520.

FIGURE 5.4.1

The behavior of DPN99 (upper part) and ZPMAX (lower part) as a function of the ratio $K1/K2$ for two different sets of initial conditions.

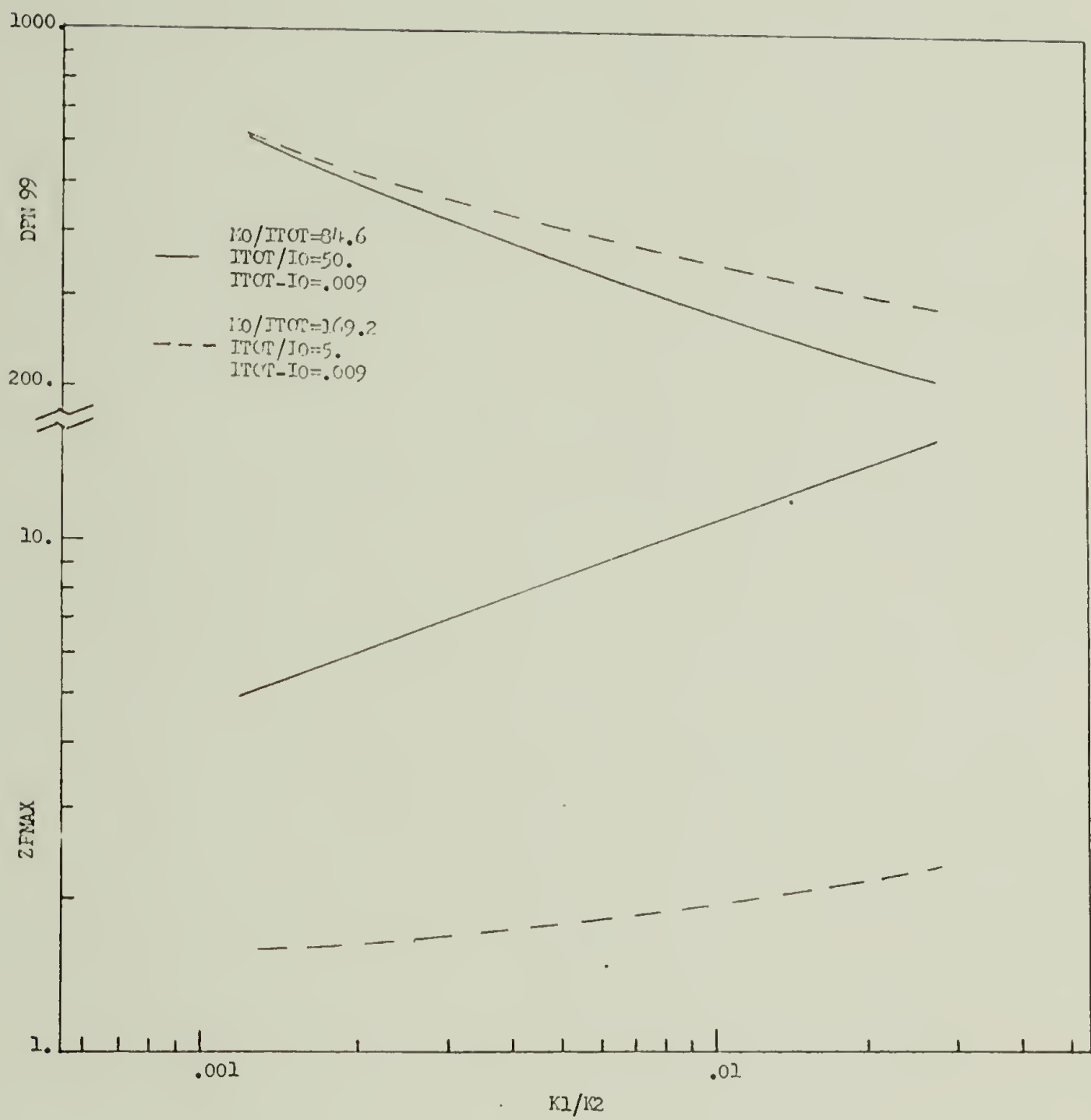


TABLE 5.4.1

Values of optimal polydispersities Z_{PMAX} , degrees of polymerization DPN for optimal conversion at which initiator addition is started ($CONADD$), and total reaction times TT , calculated for a range of $K1/K2$ for two sets of initial conditions.

L I N E A R F E E D W I T H P U L S E

MO/ITOT = 169.2 ITOT/IO = 5. ITOT-IO = .009

K1	K2	α	DPN99	ZPMAX	TT
.26	11.8	.022	300.	2.30	116.
.52	23.9	.022	300.	2.30	58.
.26	23.9	.011	340.	1.97	59.
.52	47.8	.011	350.	1.99	29.
.26	47.8	.00505	410.	1.77	34.
.52	95.6	.00505	410.	1.77	16.
.26	95.6	.00272	495.	1.68	18.
.26	191.2	.00136	600.	1.60	12.

MO/ITOT = 84.6 ITOT/IO = 50. ITOT-IO = .009

K1	K2	α	DPN99	ZPMAX	TT
2.08	95.6	.0217	220.	14.6	119.
1.04	95.6	.0185	268.	11.5	113.
.26	47.8	.00505	340.	8.80	230.
.26	95.6	.00272	460.	6.70	120.
.13	95.6	.00136	580.	5.24	127.

opposite of what Fig. 5.3.4 shows.

Since it was observed that ZPMAX is only a function of $M0/ITOT$ for constant $ITOT/I0$, the values of ZPMAX are plotted in Fig. 5.3.7 vs. $M0/ITOT$ for three different values of $ITOT/I0$. One finds an almost linear increase of ZPMAX with $M0/ITOT$ if logarithmically plotted, yielding higher values of ZPMAX for high values of $ITOT/I0$. Upon inversion of independent variable and parameter one obtains Fig. 5.3.8 where ZPNMAX is plotted logarithmically vs. $ITOT-I0$ with $M0/ITOT$ as a parameter. One can observe that the greater the values for $M0/ITOT$ and $ITOT-I0$ are the more linear the curves. If one plots logarithmically DPN99 vs. $M0/ITOT$ one obtains a curve which is very similar to the one obtained from linear feed without pulse. Fig. 5.1.2 shows how DPN approaches its theoretical value asymptotically for high values of $M0/ITOT$. Fig. 5.3.9 shows a plot of the total reaction time TT vs. $ITOT-I0$. For different parameters $ITOT/I0$ one obtains different straight lines with the same slope.

5.4 INFLUENCE OF THE VARIATION OF $K1/K2$

As mentioned before, all these calculations were made with the rate constants $K1 = .26$ and $K2 = 47.8$. In order to obtain more general results, calculations have been made for various values of $K1/K2$ for two specific examples with $M0/ITOT=84.6$, $ITOT/I0=50$ (case A) and $M0/ITOT=169.2$,

FIGURE 5.3.7

ZPMAX as a function of $M_0/ITOT$ for three different ratios $ITOT/I_0$ for linear feed with pulse.

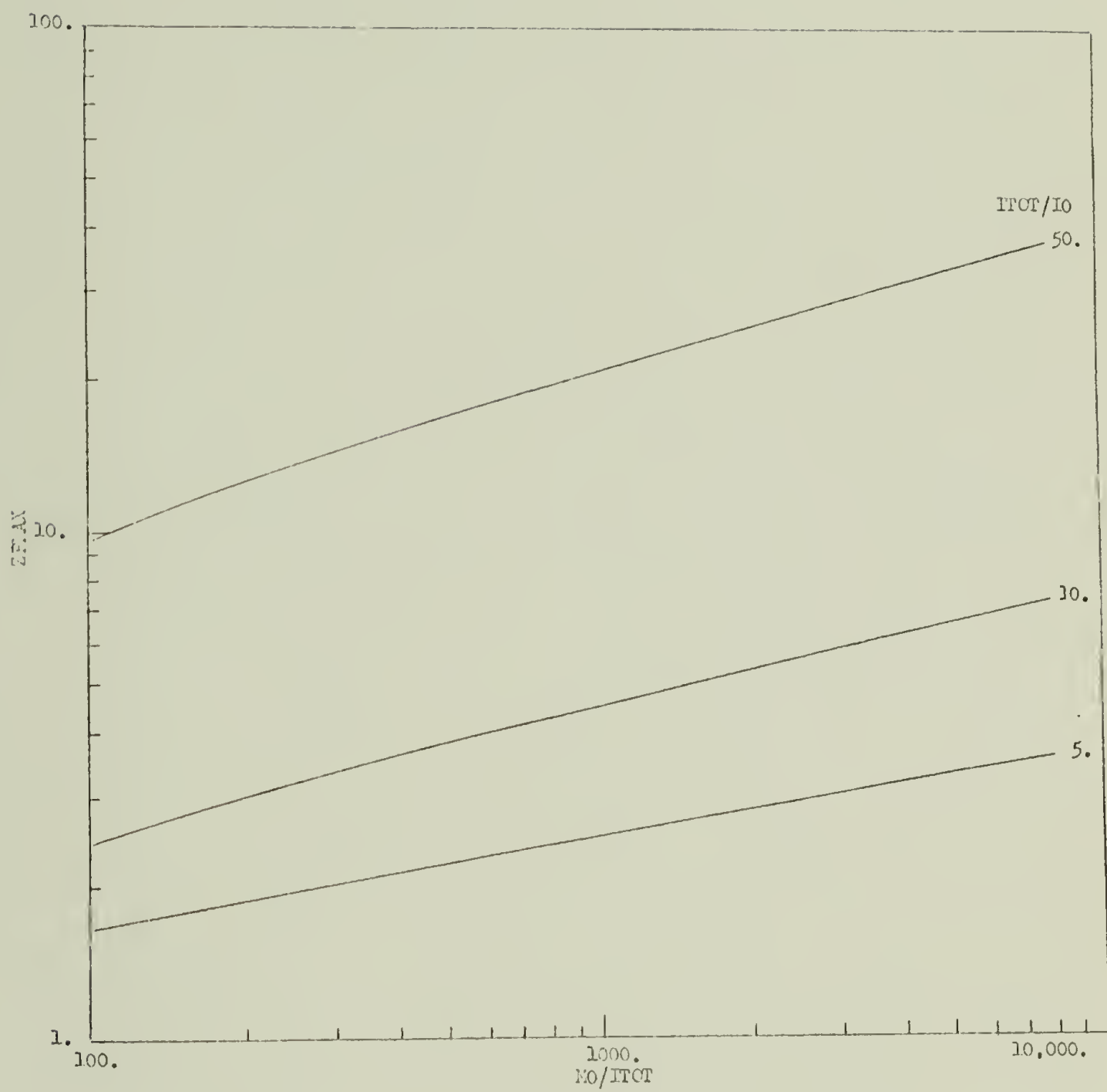


FIGURE 5.3.8

ZPMAX as a function of $ITOT/I_i$ for six different ratios $M_o/ITOT$ for linear feed with pulse.

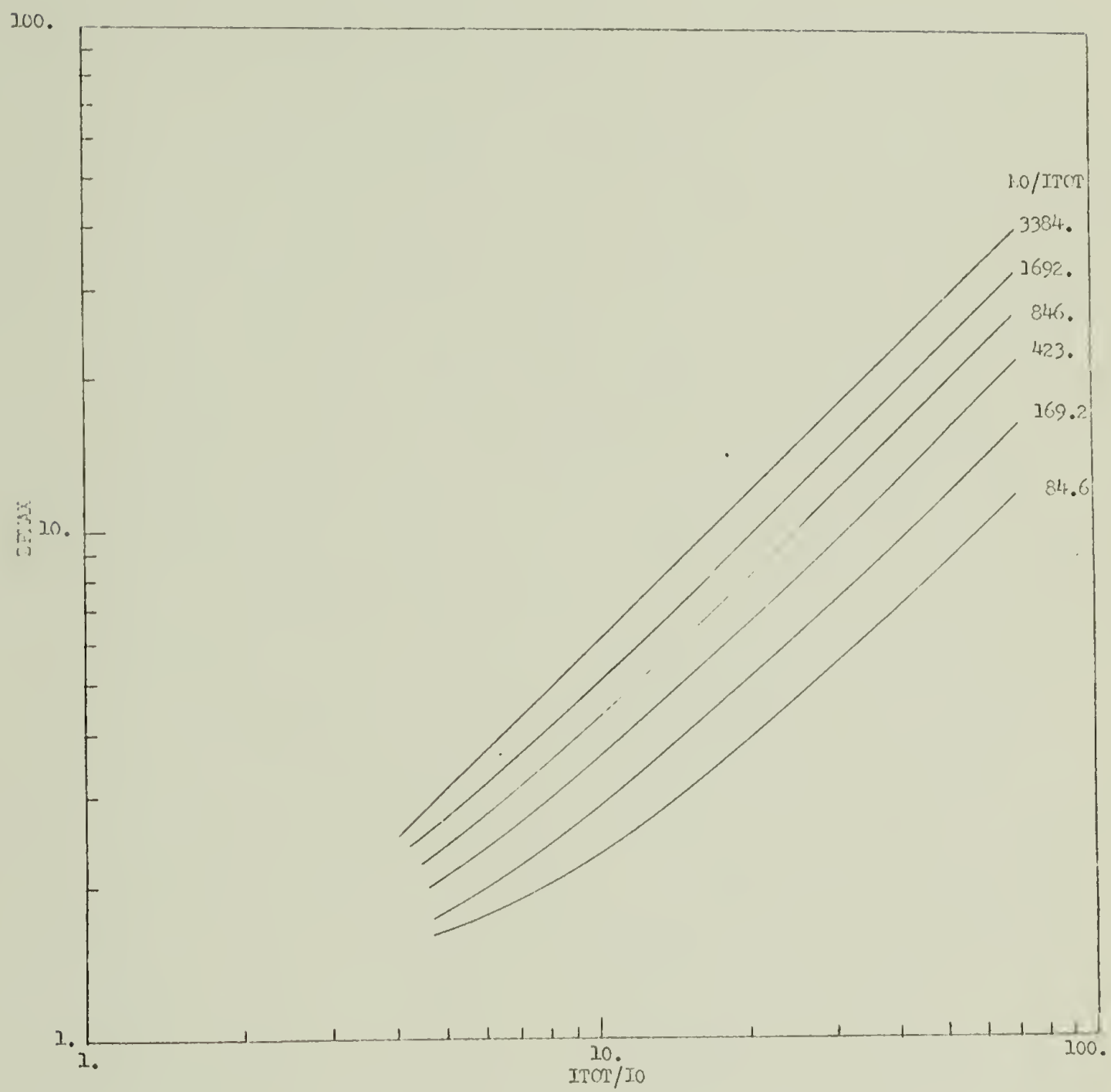
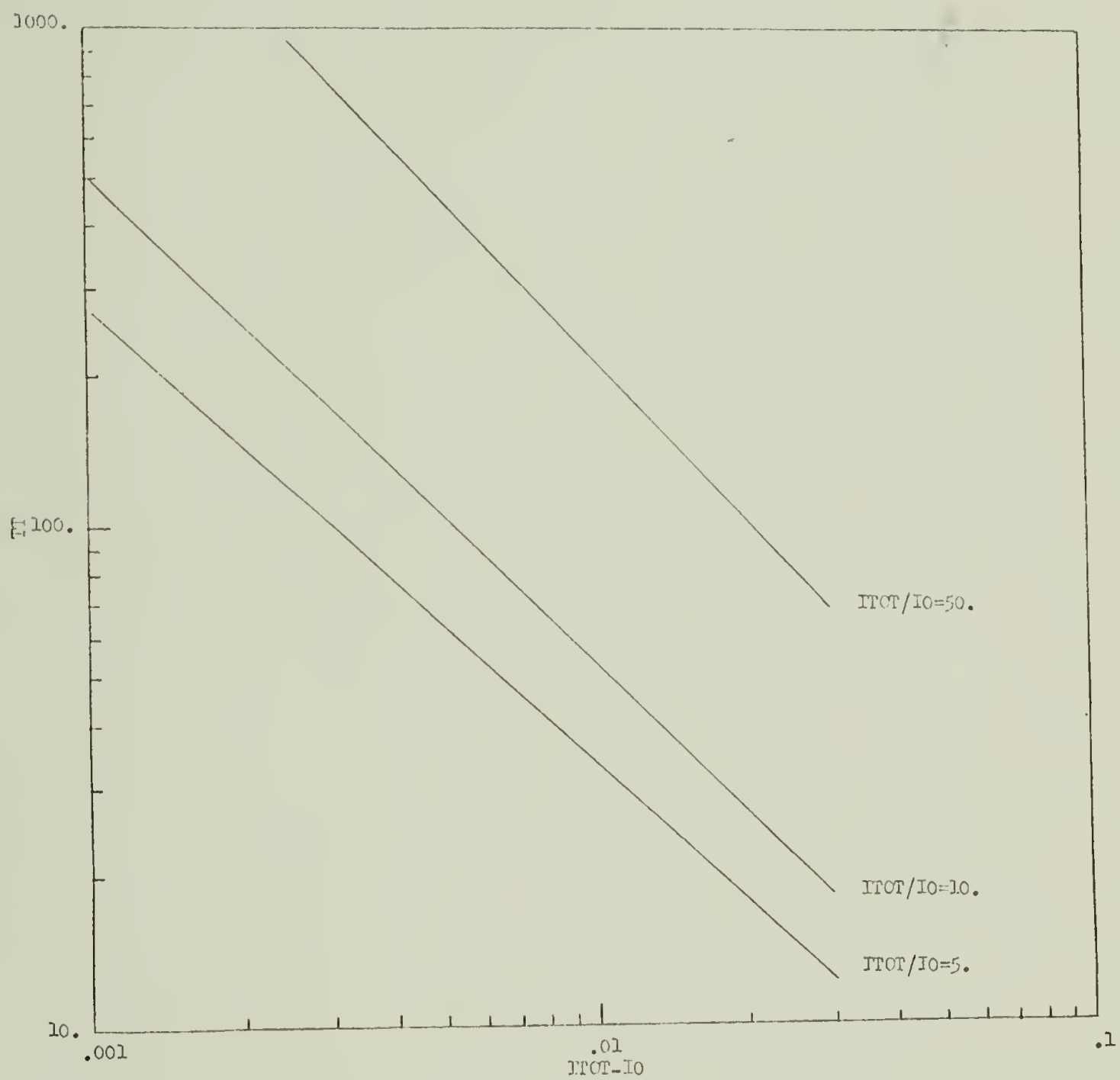


FIGURE 5.3.9

The total reaction times TT as a function of $ITOT-I_0$ for three different ratios $ITOT/I_0$ for linear feed with pulse.



$ITOT/I0=5$ (case B). Fig. 5.4.1 shows that in both cases ZPMAX increases and DP99 decreases with increasing ratio $K1/K2$, but also that in case B these changes are less severe than in case A.

5.5 OPTIMAL REACTION CONTROL

In this section we want to demonstrate a way of choosing initial conditions and reaction control parameters in order to obtain a polymer with the desired properties DPNDES, and ZPDES with a desired total reaction time TTDES.

Assume that the rate constants $K1$ and $K2$ remain the same for different concentrations of monomers and that the initial reactor volume $V0 = .055$ liters. Desired values might be:

$$DPNDES = 1200$$

$$ZPDES = 15$$

$$TTDES = 200 \text{ min.}$$

A first step is to look up the desired reaction parameters $M0/ITOT$, $ITOT/I0$ and $ITOT-I0$. From Fig. 5.1.2 DPNDES leads to $M0/ITOT = 600$. This number together with ZPDES is used in Fig. 5.3.7 to get $ITOT/I0 = 40$, which in turn together with TTDES in Fig. 5.3.9 yields upon interpolation $ITOT-I0 = .01$. Our new parameters now are:

$$M0/ITOT = 600$$

$$I0 = .000256$$

$$ITOT/I0 = 40 \quad \text{which can be solved } ITOT = .010256$$

$$ITOT-I0 = .01$$

$$M0 = 6.154$$

There are still two undetermined parameters remaining, THE (CONADD) and QTT. Both, fulfilling the conditions $IT=ITOT$ and $ZP99=ZP_{MAX}$, can be found by trial and error. In our case CONADD was obtained from Fig. 5.3.2 using the parameters $M0/ITOT$ and $ITOT/I0$, resulting

$$CONADD = .85 \text{ and therefore } QTT = .00013$$

The results of the calculation using these parameters are

$$DPN = 1319 \qquad ZP = 14.3 \qquad TT = 181 \text{ min.}$$

The errors between desired and obtained values can be understood considering the interpolations we made reading out values from the graphs. It has to be pointed out that for this linear feed with pulse control the only way of obtaining any value of ZP with minimal reaction time is by allowing ZP99 to be ZP_{MAX}. Any other condition yields higher reaction times. In case it is desired to minimize TT the only constraint imposed is M0. The highest possible value of M0 is the bulk concentration of monomer. This requires the assumption that K1 and K2 remain unchanged for different values of M0.

CHAPTER 6

CONCLUSIONS

The purpose of this paper was to investigate the possibility of MWD control by pulse and/or constant initiator feed rate for an anionic polymerization. These types of initiator feed programs can be readily applied in real laboratory polymerizations using a syringe pump to inject the initiator solution. For all our calculations we assumed the following values for the rate constants: $K_1 = .26$, $K_2 = 47.8$ and the initial reactor volume $V_0 = .055$ liter, neglecting volume change due to initiation addition.

The first type of calculations dealt with an initial pulse feed. It was found that the highest possible value for ZP99 is 1.328, which is in reasonable agreement with Gold (1958) and Nanda (1964) who predicted a ZP_{MAX} of 1.375, but the corresponding DPN is about 15. This means that for practical values of DPN (50 and higher) ZP will always be lower than 1.30. One disadvantage of this type of reaction control is that ZP and DPN are not independent; or in other words, once $M_0/ITOT$ is chosen, both ZP and DPN are fixed. If one varies M_0 and $ITOT$ keeping $M_0/ITOT$ constant only the total reaction time t_T can be changed.

The second type of initiator feed simulated was the linear feed without pulse. Here too, ZP and DPN are not independent. For the same DPN the total reaction times t_T

are always higher for the linear feed as shown in Fig. 5.1.5. It can also be seen that the difference becomes more significant at higher values of DPN.

In the case of linear feed with pulse control, it was convenient to introduce new variables $M_0/ITOT$, $ITOT/I_0$ and $ITOT-I_0$. Other variables are fixed, because it was found that minimal reaction time was obtained if a trial and error method was used to find THE or CONADD and QTT to meet the conditions $ZP_{99} = ZP_{MAX}$ and $IT = ITOT$, respectively. Because in this case DPN, ZP and TT are independent one is able to detail a procedure to obtain the needed control variables $M_0/ITOT$, $ITOT/I_0$, $ITOT-I_0$, CONADD and QTT for a reaction which yields a polymer with the desired properties DPN_{DES} and ZP_{DES} and a reaction time TT_{DES} .

Compared to the reaction control suggested by Bandermann (1971), the linear feed with pulse control has the advantage that it can be implemented in an actual polymerization, using a simple syringe pump for the linear feed. The actual difference between the two controls is that Bandermann uses QTT (t) only to obtain DPN_{DES} and ZP_{DES} , keeping all the initial concentrations constant, whereas our control scheme also uses initial conditions like M_0 , and I_0 to obtain the desired properties.

Our search for the reaction conditions to get the desired properties needs the mapping of all the variables and parameters and is carried out by trial and error. It is evident that the entire search procedure can be assembled in a

sophisticated computer program in order to yield the desired control variables.

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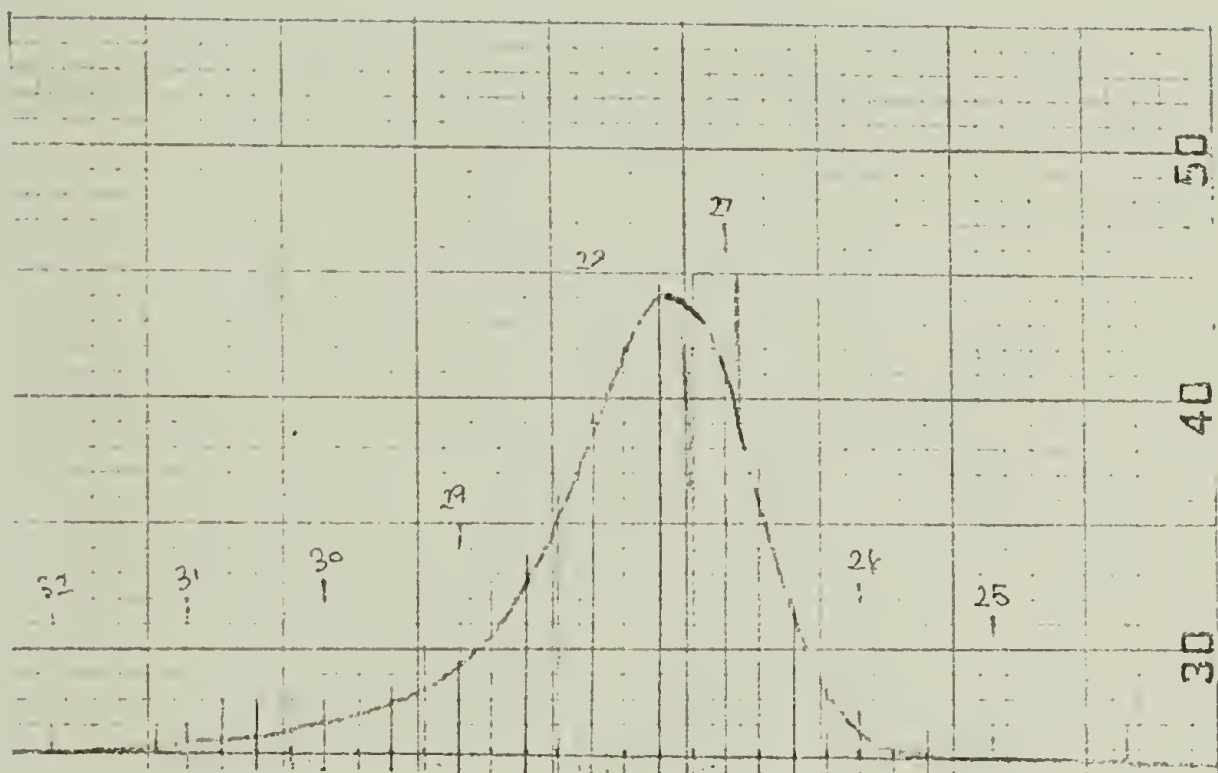
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APPENDIX A-1

Result of the GPC Measurement.



APPENDIX A-2

Computer program for the search.

```

01 CON(SL,M0)
02 ME=CFN(11.,2.)
03 PAR(K1,10)
04 M=10*BETA*(1.-EXP(-ALPHA*TAU))-10*TAU+M0

05 TAU=INI(1DTAU,.0)
06 DT=1.
07 ALPHA=K1*10/SL
08 BETA=(1.-ALPHA)/ALPHA
09 MRD=M/M0
10 FIN(T,110.)
11 1DTAU=M*SL/10
12 PRINT=FSW((T/10.)-FIX(T/10.)-.001,TRUE,FALSE,FALSE)
13 DELTA=(MRD-MEX)*(MRD-MEX)
14 MEX=FUN(ME,T)
15 ERR=100.*ABS(MEX-MRD)/MEX
20 PRINT OUT(T,MRD,ER)
25 END

```

APPENDIX A-3

Computer program simulating the three different initiator addition histories.

```

01*      PROGRAMMED MOLECULAR WEIGHT DISTRIBUTION
02*      M0=INITIAL MONOMER CONC (MOL/L)
03*      K1=INITIATION RATE CONSTANT
04*      K2=PROPAGATION RATE CONSTANT
05*      ITOT=TOTAL INITIATOR CONC (MOL/L)
06*      V0=INITIAL REACTOR VOLUME (L)
07*      QIT=INITIATOR ADDITION RATE (MOL/MIN)
08*      THE=STARTING TIME OF INITIATOR ADDITION (MIN)
09*      I0=INITIAL INITIATOR CONC (MOL/L)
10*      IA=CONC OF ADDED INITIATOR (MOL/L)
12*
13*CONSTANTS  PARAMETERS
14*
15  CON(M0,K1,K2,ITOT,V0)

20  PAR(QIT,THE,I0,IA)
25*
75  A=K1/K2
80  B=(1.-A)/A

85  M=X*M0
90  CONV=1.-X
95  DPN=MU1/MU0
100  DPW=MU2/MU1
105  ZP=DPW/DPN

110*
115*DIFFERENTIAL EQUATIONS
120*
125  1DX=-X*(K1*I+K2*MU0)
126  1DI=-K1*M*I+QIT/V0
135  1DMU0=K2*M0*A*X*I
140  1DMU1=1DMU0+K2*M0*X*MU0
145  1DMU2=1DMU0+K2*M0*X*(2.*MU1+MU0)
155*
160*INTEGRATIONS

165*
170  X=INT(1DX,1.)
175  I=INT(1DI,10)
180  MU0=INT(1DMU0,0.)

185  MU1=INT(1DMU1,0.)
190  MU2=INT(1DMU2,0.)
195  IT=INT(1DIT,10)

```

```

200*
205*CONTROL OF INITIATOR FEED
206*AS SOON AS THE TOTAL INITIATOR CONC REACHES ITOT
207*IT IS SET ZERO

210*
215 CONC=FSW(IT-ITOT,TRUE,TRUE,FALSE)
220 TIME=FSW(1-THE,FALSE,TRUE,TRUE)
225 QRUN=AND(CONC,TIME)
230 QTT=LSF(QRUN,QTT,0.)
235*
240*INTEGRATION CONTROL
245*
250 FIN(CONV,.99)
255 DT=1.
260*
265*OUTPUT EVERY PT MINUTES
266*THE INTERVAL CAN BE CHANGED ACCORDING TO
267*THE TOTAL REACTION TIME BY CHANGING PT
270*
275 LINE=FSW((T/PT)-FIX(T/PT)-.001,TRUE,FALSE,FALSE)
276 PT=10.
290*
291*BINARY FILE OF DATA EVERY PT MINUTES
292*
293 LINE FIL(T,CONV,DPN,DPW,ZP)
294*
295*OUTPUT FOR START OF ADDITION
296*
300 ADD1=FSW(IT-10-QTT*2.,TRUE,FALSE,FALSE)
310 ADD2=FSW(QT,FALSE,FALSE,TRUE)
320 ADD=AND(ADD1,ADD2)
330 ADD OUT(T,CONV,IT)
334*
335*OUTPUT FOR END OF ADDITION
336*
340 ENDE=FSW(CONV-.99,FALSE,TRUE,TRUE)
341 ENDE OUT(T,CONV,QT,IT,M,I)
342 ENDE OUT(DPN,DPW,ZP)
399 END

```

APPENDIX A-4

Computer program generating a plotter output from a binary file.


```

10 PROGRAM PLOT
20 DIMENSION T(102), CONV(102), DPN(102), DPW(102), ZP(102)

30 COMMON X(500)
40 PRINT 50
50 FORMAT(*-FILE NAME AND NO. POINTS *)
60 INPUT, NAME, NUM
61 NUM=ABS(NUM)
70 CALL OPEN(8, NAME)

80 LAST=NUM*5
90 READ(8) (X(I), I=1, LAST)
100 CONTINUE
110 DO 140 J=1, NUM
120 T(J)=X(J*5-4)
122 CONV(J)=X(J*5-3)
124 DPN(J)=X(J*5-2)
126 DPW(J)=X(J*5-1)
128 ZP(J)=X(J*5)
140 CONTINUE
141 IF(NUM .GT. 0) GO TO 150
142 PRINT 143, (J, T(J), CONV(J), DPN(J), DPW(J), ZP(J), J=1, NUM)
143 FORMAT(/(1X, I3, F10.2, F10.4, F10.1, F10.1, F10.5))
150 CALL PLOTS(12., 10.)
160 CALL SCALE(T, 10., NUM, 1)
170 CONV(NUM+1)=0.
172 CONV(NUM+2)=.1
180 DPN(NUM+1)=0.
182 DPN(NUM+2)=1000.
190 DPW(NUM+1)=0.

192 DPW(NUM+2)=1000.
200 ZP(NUM+1)=0.
202 ZP(NUM+2)=1.
210 CALL AXIS(.5, .5, 8HDPN DPW, +8, 9., 90., 0., 1000.)
215 CALL AXIS(.5, .5, 2HZP, -2, 9., 90., 0., 1.)

217 CALL AXIS(1., .5, 10HCONVERSION, -10, 10., 0., 0., .1)
230 CALL PLOT(1., .5, -3)
240 CALL LINE(CONV, DPN, NUM, 1, 0, 0)
241 CALL
      LINE(CONV, DPW, NUM, 1, 0, 0)
242 CALL LINE(CONV, ZP, NUM, 1, 0, 0)
250 CALL PLOT(10., 15., 999)
260 STOP
270 END
280 /USE PLOTHP, C0149, PLOT
290 /USE PLOTTER, C0149, PLOT
300 ENDPROG

```

