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Effect of mixing on polymerizations in batch reactors

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EFFECT OF MIXING ON POLYMERIZATIONS

IN BATCH REACTORS

BY

JOHN GUY STEENROD

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EFFECT OF MIXING ON POLYMERIZATIONS

IN BATCH REACTORS

BY

JOHN GUY STEENROD

FOR

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FACULTY COMMITTEE

APPROVED: _____

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NEWARK, NEW JERSEY

SEPTEMBER, 1974

ABSTRACT

The effects of mixing on polymerizations in batch reactors are examined theoretically for initiations by thermal decomposition of catalyst and by absorption of ionizing radiation. Mathematical expressions for predicting the first three moments of the dead polymer size distribution are presented. Two extreme mixing states, perfect and no mixing, are considered. It is shown that in batch reactors mixing in any direction in which nonuniform initiations exist increases the polymerization reaction rate and the number average molecular weight, and decreases the weight average and the polydispersity.

Experimentally, the effects of mixing were studied in a solution polymerization system, in a batch reactor. Two states of mixing were studied, perfect and no mixing for a catalyst initiated polymerization.

The experimental work verified that the polymerization rate for the perfect mixing state is greater than for the no mixing state at zero hours reaction time, for a total reactor volume/volume of catalyst solution (τ) = 35.7. It was also shown that for a total reactor volume/volume of catalyst solution (τ) = 1, that no or negligible mixing effects exist.

ACKNOWLEDGEMENTS

I would like to express my great appreciation to my advisor Dr. H. T. Chen, for all his time and invaluable advice in developing this thesis.

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INTRODUCTION

Addition polymerizations are usually initiated through the use of catalyst. Alternate means of initiation are available including initiation by absorption of ionizing radiation. Both catalyst decomposition and radiation absorption lead to the production of free radical species which initiate the polymerization reaction.

The observed rate of polymerization, when carried out with an initiation rate which is constant throughout the reaction volume, depends in general on the specific rate of initiation and on the concentration of the monomer. When the initiation rate varies over the reaction volume, the observed rate will usually depend also on the rate of diffusion or mixing. For radiation polymerizations, nonuniform initiation follows from radiation attenuation, and the nonuniformity in polymerization initiated by the decomposition of catalyst results from a nonuniform distribution of catalyst. In this paper we present mathematical expressions to show the influence of mixing on an addition polymerization. Emphasis is placed on the comparison between catalytic and ionizing radiation initiations.

REACTOR EQUATIONS

The reaction mechanism to be considered is that of addition polymerization in bulk. We will treat the following initiation modes:

Initiation by absorption of ionizing radiation by monomer

$$M_1 \xrightarrow{G_R I_a} R_1 \cdot$$
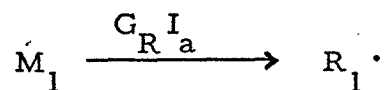
Initiation by thermal decomposition of catalyst

$$S \xrightarrow{k_i} S \cdot$$

$$S \cdot + M_1 \xrightarrow{k_d} R_1 \cdot$$
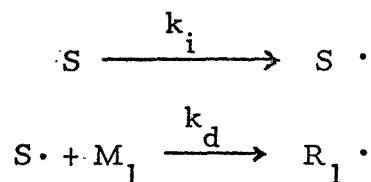
The remaining steps in the mechanism are

Propagation

$$R_j \cdot + M_1 \xrightarrow{k_p} R_{j+1} \cdot$$

Termination

$$R_i \cdot + R_j \cdot \xrightarrow{k_{tc}} P_{i+j}$$

$$R_i \cdot + R_j \cdot \xrightarrow{k_{td}} P_i + P_j$$
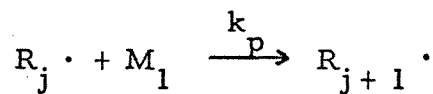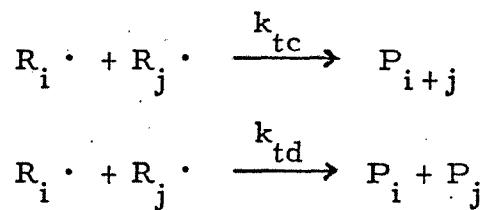
The following assumptions will be made:

1. The rate constants are independent of chain length.

2. Conversions are small (i.e., monomer concentration is constant and equal to the initial concentration).

3. The lifetime of the monomer is long compared with the mixing time (i.e., monomer concentration is uniform throughout the reactor).

4. The chain length is great.

5. The stationary state approximation applies.

In addition, two mixing states will be considered. In one, which will be referred to as the perfect mixing (PM) state, the centers are uniformly mixed throughout the reactor. 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 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.

Perfect Mixing (PM)

The mass balances for monomer, chain centers and dead polymers are

$$- \frac{dm}{dt} = k_p \, m \, \Sigma \gamma_i(t) \qquad (1)$$

$$\frac{d\gamma_1(t)}{dt} = \overline{\Omega}(t) - k_p \, \gamma_1(t) m - (k_{tc} + k_{td}) \, \gamma_1(t) \, \Sigma \gamma_i(t) \qquad (2)$$
$$= 0$$

$$\frac{d\gamma_j(t)}{dt} = k_p \, \gamma_{j-1}(t) m - k_p \, \gamma_j(t) m - (k_{tc} + k_{td}) \, \gamma_j(t) \, \Sigma \gamma_i(t)$$
$$= 0 \qquad (3)$$

where

$$j = 2, 3, \text{----} \infty$$

$$\frac{d\Sigma\gamma_i(t)}{dt} = \bar{\Omega}(t) - (k_{tc} + k_{td})\,[\Sigma\gamma_i(t)]^2 = 0 \tag{4}$$

$$\frac{dp_j(t)}{dt} = k_{td}\,\gamma_j(t)\,\Sigma\gamma_i(t) + \frac{1}{2}k_{tc}\sum_{i=1}^{j-1}\gamma_i(t)\,\gamma_{j-i}(t) \tag{5}$$

where

$$j = 1, 2, ---- \infty$$

where $\Sigma\gamma_i$ is the total polymer radical concentration, and $\bar{\Omega}$ represents the effective initiation rate given by

$$\bar{\Omega}(t) = \frac{1}{V_c}\iiint_{V_c}\Omega(\underline{v}, t)\,dV \tag{6}$$

where the vector $\underline{v}$ specifies position in the reactor, and

$$\Omega(\underline{v}, t) = \Omega(\underline{v}) = G_R I_a(\underline{v}) \tag{7}$$

for ionizing radiation initiation and

$$\Omega(\underline{v}, t) = k_i\,s(\underline{v}, t) = k_i\,s_o(\underline{v})\,e^{-k_i t} \tag{8}$$

for catalytic initiation.

The number and weight average for the dead polymer formed during the reaction are defined as,

$$X_n(t) = \frac{\Sigma i\,p_i(t)}{\Sigma p_i(t)} \tag{9}$$

$$X_w(t) = \frac{\Sigma i^2 p_i(t)}{\Sigma i\,p_i(t)} \tag{10}$$

where Σp_i, $\Sigma i p_i$ and $\Sigma i^2 p_i$ are respectively, the zero-th, first and second moments of dead polymer size distribution. From Eqs. (1) to (5), it may be shown that

$$\Sigma p_i(t) = [(k_{td} + 0.5 k_{tc})/k_t] \int_0^t \bar{\Omega}(t)\, dt \tag{11}$$

$$\Sigma i p_i(t) = (k_p m/k_t^{0.5}) \int_0^t [\bar{\Omega}(t)]^{1/2}\, dt \tag{12}$$

$$\Sigma i^2 p_i(t) = (k_p^2/k_t)(2 + k_{tc}/k_t)\, m^2\, t \tag{13}$$

Note that Eqs. (11) to (13) are obtained with the aid of the following summation identities [1],

$$\sum_{j=1}^{\infty} j \sum_{i=1}^{j-1} \gamma_i\, \gamma_{j-i} = 2 \left(\sum_{j=1}^{\infty} \gamma_j \right) \left(\sum_{j=1}^{\infty} j\, \gamma_j \right) \tag{14}$$

$$\sum_{j=1}^{\infty} j^2 \sum_{i=1}^{j-1} \gamma_i\, \gamma_{j-i} = 2 \left(\sum_{i=1}^{\infty} \gamma_i \right) \left(\sum_{i=1}^{\infty} i^2\, \gamma_i \right) + 2 \left(\sum_{i=1}^{\infty} i\, \gamma_i \right)^2 \tag{15}$$

No Mixing (NM)

The rate of polymerization at any given time is,

$$-\frac{dm}{dt} = k_p m\, \overline{\Sigma \gamma_i(\underline{v}, t)} \tag{16}$$

and the first three moments of the dead polymer size distribution are

$$\Sigma p_i(t) = (k_{td} + 0.5\, k_{tc}) \int_0^t \overline{[\Sigma \gamma_i(\underline{v},\, t)]^2}\ dt \qquad (17)$$

$$\Sigma i\, p_i(t) = k_t \int_0^t \overline{\Sigma \gamma_i(\underline{v},\, t)\, \Sigma i\, \gamma_i(\underline{v},\, t)}\ dt \qquad (18)$$

$$\Sigma i^2 p_i(t) = k_t \int_0^t \overline{\Sigma \gamma_i(\underline{v},\, t)\, \Sigma i^2 \gamma_i(\underline{v},\, t)}\ dt\ +$$

$$k_{tc} \int_0^t \overline{[\Sigma i\, \gamma_i(\underline{v},\, t)]^2}\ dt \qquad (19)$$

where an overlined quantity is the volume-averaged value of the quantity over the reactor volume, and

$$\Sigma \gamma_i(\underline{v},\, t) = \left[\frac{\Omega(\underline{v},\, t)}{k_t} \right]^{1/2} \qquad (20)$$

$$k_t\, \Sigma \gamma_i(\underline{v},\, t)\, \Sigma i\, \gamma_i(\underline{v},\, t) = k_p\, m \Sigma \gamma_i(\underline{v},\, t) \qquad (21)$$

$$k_t\, \Sigma \gamma_i(\underline{v},\, t)\, \Sigma i^2 \gamma_i(\underline{v},\, t) = 2\, k_p\, m\, \Sigma i\, \gamma_i(\underline{v},\, t) + k_p\, m\, \Sigma \gamma_i(\underline{v},\, t) \qquad (22)$$

By combining Eqs. (16) to (22) one may obtain the following expression,

$$-\frac{dm}{dt} = \left[(k_p\, m)/(k_t^{0.5}\, V_c) \right] \iiint_{V_c} [\Omega(\underline{v},\, t)]^{1/2}\, dV \qquad (23)$$

$$\Sigma\, p_i(t) \;=\; \left[(k_{td} + 0.5\, k_{tc})/k_t V_c\right] \int_o^t \left[\;\iiint\limits_{V_c} \Omega\,(\underline{v}\,,\, t)\, dV\,\right]\; dt \qquad (24)$$

$$\Sigma_i\, p_i(t) \;=\; \left[(k_p\, m)/(k_t^{0.5}\, V_c)\right] \int_o^t \left\{\;\iiint\limits_{V_c} [\Omega\,(\underline{v},\, t)]^{1/2}\, dV\right\}\; dt \qquad (25)$$

$$\Sigma\, i^2\, p_i(t) \;=\; (k_p^2 / k_t)(2 + k_{tc}/k_t)\, m^2 t \qquad (26)$$

INFLUENCE OF MIXING

A basic analytical tool used in determination of the influence of mixing is the Schwarz inequality [2, 3],

$$\frac{1}{V_c}\iiint\limits_{V_c}\left[\Omega(\underline{v}, t)\right]^{1/2} dV \leq \left[\frac{1}{V_c}\iiint\limits_{V_c}\Omega(\underline{v}, t)\, dV\right]^{1/2} = \left[\bar{\Omega}(t)\right]^{1/2}$$

(27)

By comparing Eq. (27) with Eqs. (1), (6), (11), (12), (13) and (23) to (26), one may show that

$$\left(-\frac{dm}{dt}\right)_{PM} \geq \left(-\frac{dm}{dt}\right)_{NM}$$

(28)

$$\left[\Sigma p_i(t)\right]_{PM} = \left[\Sigma p_i(t)\right]_{NM}$$

(29)

$$\left[\Sigma i\, p_i(t)\right]_{PM} \geq \left[\Sigma i\, p_i(t)\right]_{NM}$$

(30)

$$\left[\Sigma i^2\, p_i(t)\right]_{PM} = \left[\Sigma i\, p_i(t)\right]_{NM}$$

(31)

and

$$\left[X_n(t)\right]_{PM} \geq \left[X_n(t)\right]_{NM}$$

(32)

$$\left[X_w(t)\right]_{PM} \leq \left[X_w(t)\right]_{NM}$$

(33)

We have now shown that in the presence of spatially nonuniform initiation, the introduction of mixing will result in an increase in both the rate of polymerization $(-\frac{dm}{dt})$ and the number average molecular weight, and a decrease of the weight average. Thus, the polydispersity (X_n/X_w), an index of broadness of molecular weight distribution, decreases with mixing. Note that the findings are consistent with the solutions previously developed for radiation-induced polymerizations in continuous stirred-tank reactors [1,4].

CONCLUDING REMARKS

We have presented mathematical expressions for predicting the first three moments of the dead polymer size distribution. Solutions are given for two extreme mixing states, that is PM and NM. The analysis is based on an addition polymerization in batch reactors. Initiations considered are the thermal decomposition of catalyst and the absorption of ionizing radiation by monomer. It is shown that in either initiation mode the transition from the NM to the PM state results in increased polymerization rate, increased X_n, decreased X_w and decreased polydispersity.

The **rate** of initiation by radiation (Eq. 7) is essentially independent of temperature, and because of the physical separation of radiation source and the reaction medium, the initiation rate may be changed very rapidly. By contrast the rate of initiation with chemical initiators (Eq. 8) are usually strongly temperature dependent, and because the chemical initiator is in solution in the reaction medium, the initiation rate can not be changed very quickly. Because of these facts radiation initiation may lead to greater reactor stability and greater ease of reactor control. A detailed discussion will be given in the subsequent papers.

EXPERIMENTAL

Introduction

Previous experimental work on the effects of mixing for nonuniformly initiated polymerizations have dealt primarily with photo or radiation initiated reactions (1-7), around which theoretical equations have been developed. Little, if any, experimental work however, has been done with catalyst initiated polymerizations. Hill and Felder (3) predicted that their equations for no mixing (NM) and perfect mixing (PM) cases apply for photo or radiation initiated polymerizations as well as catalyst initiated polymerizations.

This thesis's experimental work will determine the effect of mixing on reaction rate for a catalyst initiated styrene polymerization in solution. The results will be fitted to modified equations of Hill and Felder's (3), for a catalyst initiated reaction, which are in terms of catalyst concentration instead of radiation intensity and catalyst volume (τ = total reactor volume/catalyst volume) instead of optical thickness (τ = total reactor volume/irradiated volume).

Use Of A Solution Polymerization

A dilute solution polymerization reaction system was chosen for the following reasons:

1. Simpler mathematical model with a dilute monomer concentration (assume monomer concentration constant)

2. Ease in maintaining an isothermal reaction.

3. Uniform temperature distribution, no high viscosity problems, as encountered with bulk polymerizations.

Solvent - Catalyst Selection

A benzene - Vazo-64 (2,2' azobisisobutyronitrile) solvent - catalyst system was chosen for the following reasons:

1. A high purity catalyst was needed with a reasonable half-life at the reaction temperature. Thus Vazo-64, with a half-life of about one hour at $83^{o}C$ was chosen. In addition to its half-life, Vazo-64 undergoes a clean decomposition reaction with few side products to complicate the reaction kinetics. Vazo-64 also undergoes negligible chain transfer to polymer reactions ([8]), also simplifing kinetics.

2. A solvent was needed that boiled at a temperature that would result in a catalyst half-life of reasonable length, about one hour. The solvent also had to solvate the catalyst, monomer, and all reaction products at the temperature of operation, to keep the reaction kinetics simple. Finally, the solvent had to be a poor chain transfer to polymer agent, thus simplifing the kinetic expressions as well as resulting in a fairly high molecular weight polymer, making polymer recovery from reaction mix easier.

    Therefore benzene, with a boiling point at atmospheric pressure of about $80^{o}C$, a very good feed and product solvent, and a poor chain transfer agent ([9],[10]) was selected.

Stopping The Reaction And Recovering The Polymer

A solvent - non-solvent system was needed in which the catalyst, monomer, and reaction solvent would be soluble and yet the polymer would be very insoluble, and would precipitate from the solution when a small amount of non-solvent was added. The non-solvent would also have to have a reasonably high boiling point, preferrably about $50^{o}C$, so that when added to the hot reaction mixture to stop the reaction, the material would not flash away before it could be condensed back into the system. The non-solvent had to be a very good chain transfer agent to terminate all the intermediate polymer chains and thus completely stop the reaction.

Thus methanol was chosen, with a boiling point over $50^{o}C$ at atmospheric pressure and a traditionally used non-solvent for stopping styrene solution polymerizations inorder to follow the polymerization reaction (9). Methanol is an excellent chain transfer agent and non-solvent for polystyrene (8-10). The styrene monomer, Vazo-64 catalyst, and reaction solvent benzene, however are very soluble in methanol over a wide temperature range (8-10).

Chemistry Of Styrene Polymerization

The following reactions are from a text by Bamford, Barb, Jenkins and Onyon (8), and follow their simplifing assumptions:

Reaction Initiation

$$\text{catalyst} \quad CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CH3}{|}}{C}}-N=N-C-CH_3 \quad \xrightarrow{\text{heat}} \quad 2\ CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CH3}{|}}{C}}\cdot \ +\ N_2$$

monomer   2 CH$_2$=CH$\emptyset$ $\xrightarrow{\text{heat}}$ $\overset{\bullet}{C}$H$\emptyset$-CH$_2$-CH$_2$-$\overset{\bullet}{C}$H$\emptyset$
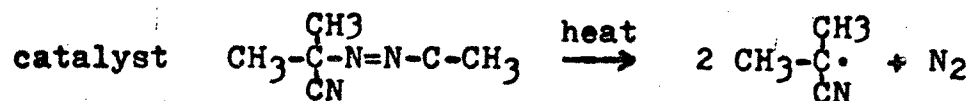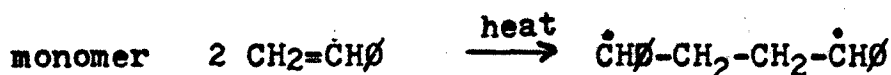
The catalyst reaction is first order to over 90% of completion;
in benzene solution over the temperature range 40°C to 112°C
the rate constant fits the following equation (8):

$$K_d = 1.0 \times 10^{15} e^{-30450/RT} \text{ (seconds)}^{-1}$$

Chain Initiation

hydrogen transfer   CH$_3$-$\overset{\overset{\displaystyle CH3}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}$$\bullet$ + CH$_2$=CH$\emptyset$ $\longrightarrow$ CH$_3$-$\overset{\overset{\displaystyle Ch3}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}$H + CH$_2$=$\overset{\bullet}{C}$$\emptyset$
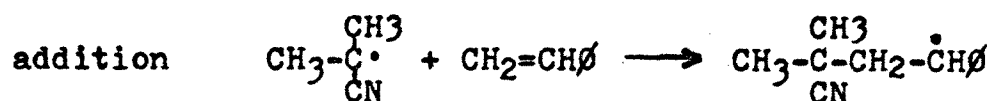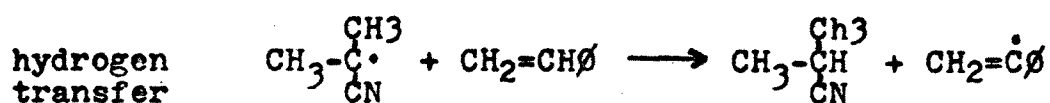
addition   CH$_3$-$\overset{\overset{\displaystyle CH3}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}$$\bullet$ + CH$_2$=CH$\emptyset$ $\longrightarrow$ CH$_3$-$\overset{\overset{\displaystyle CH3}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}$-CH$_2$-$\overset{\bullet}{C}H\emptyset$

Chain Reinitiation By Transfer Radicals

monomer   CH$_3$-$\overset{\bullet}{C}$H$\emptyset$ + CH$_2$=CH$\emptyset$ $\longrightarrow$ CH$_3$-CH$\emptyset$-CH$_2$-$\overset{\bullet}{C}$H$\emptyset$

solvent $\emptyset$$\overset{\bullet}{\cdot}$ + CH$_2$=CH$\emptyset$ $\longrightarrow$ $\emptyset$CH$_2$-$\overset{\bullet}{C}$H$\emptyset$

Propagation

R$\bullet$ + CH$_2$=CH$\emptyset$ $\longrightarrow$ RCH$_2$-$\overset{\bullet}{C}$H$\emptyset$

Chain Transfer

to monomer   RCH$_2$-$\overset{\bullet}{C}$H$\emptyset$ + CH$_2$=CH$\emptyset$ $\longrightarrow$ RCH=CH$\emptyset$ + CH$_3$-$\overset{\bullet}{C}$H$\emptyset$

or

RCH$_2$-CH$_2$$\emptyset$ + CH$_2$=$\overset{\bullet}{C}$$\emptyset$
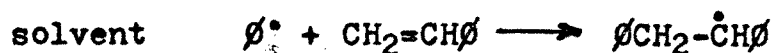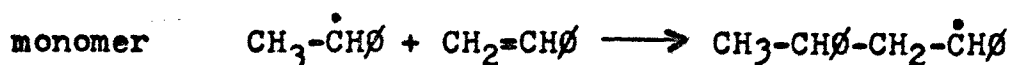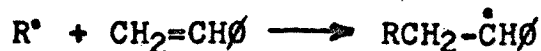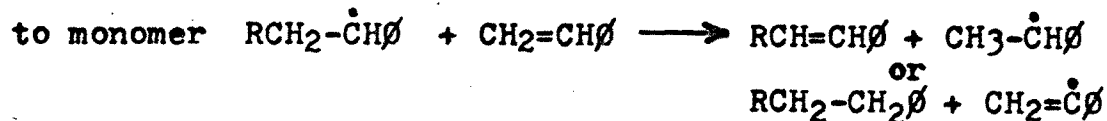
to polymer Assumed negligible for this reaction.

Termination

coupling   R$_1^{\bullet}$ + R$_2^{\bullet}$ $\longrightarrow$ R$_1$-R$_2$

disproportionation   R$_1^{\bullet}$ + R$_2^{\bullet}$ $\longrightarrow$ R$_1$ + R$_2$
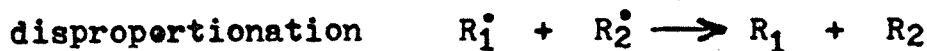
It should be noted that $\phi\dot{\,}$, $CH_2=\dot{C}\phi$, or $CH_3-\dot{C}H\phi$ do not participate to any extent in termination reactions, therefore any reactions of the type:

coupling $\quad\quad X^\bullet + R_r^\bullet \longrightarrow P_r$

disproportionation $X^\bullet + X^\bullet \longrightarrow 2\ X$
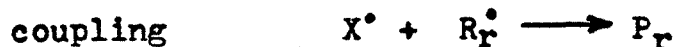
$\quad\quad\quad$ where $X = \phi^\bullet$, $CH_2=\dot{C}\phi$, or $CH_3-\dot{C}H\phi$

$\quad\quad\quad\quad\quad P_r$ = terminated polymer chain

are negligible $(8,10)$.

Experimental Procedures

$\quad$ Reagents. Benzene: Reagent grade, 99% pure, thiophene

$\quad\quad\quad\quad\quad\quad\quad$ free;

$\quad\quad\quad\quad\quad\quad\quad$ Supplier: Aldrich Chemical Company,

$\quad\quad\quad\quad\quad\quad\quad$ Parsippany, New Jersey.

$\quad\quad\quad$ Methanol: Reagent grade, 99% pure;

$\quad\quad\quad\quad\quad\quad\quad$ Supplier: Aldrich Chemical Company.

$\quad\quad\quad$ Styrene: 99% pure, 15-20 ppm t-catechol as a

$\quad\quad\quad\quad\quad\quad\quad$ stabilizer;

$\quad\quad\quad\quad\quad\quad\quad$ Supplier: Aldrich Chemical Company.

$\quad\quad$ Vazo-64 (2,2'azobisisobutyronitrile): 99% pure;

$\quad\quad\quad\quad\quad\quad\quad$ Supplier: E. I. Dupont, Industrial

$\quad\quad\quad\quad\quad\quad\quad$ Chemicals Division, Wilmington, Delaware.

$\quad$ Description of apparatus. The polymerization reactor is a two liter batch reactor with variable speed agitator and reflux condenser, see Figure 1. Catalyst may be injected via a syringe with its needle extending half-way into the reaction mix. The reactor is heated with a heating mantle
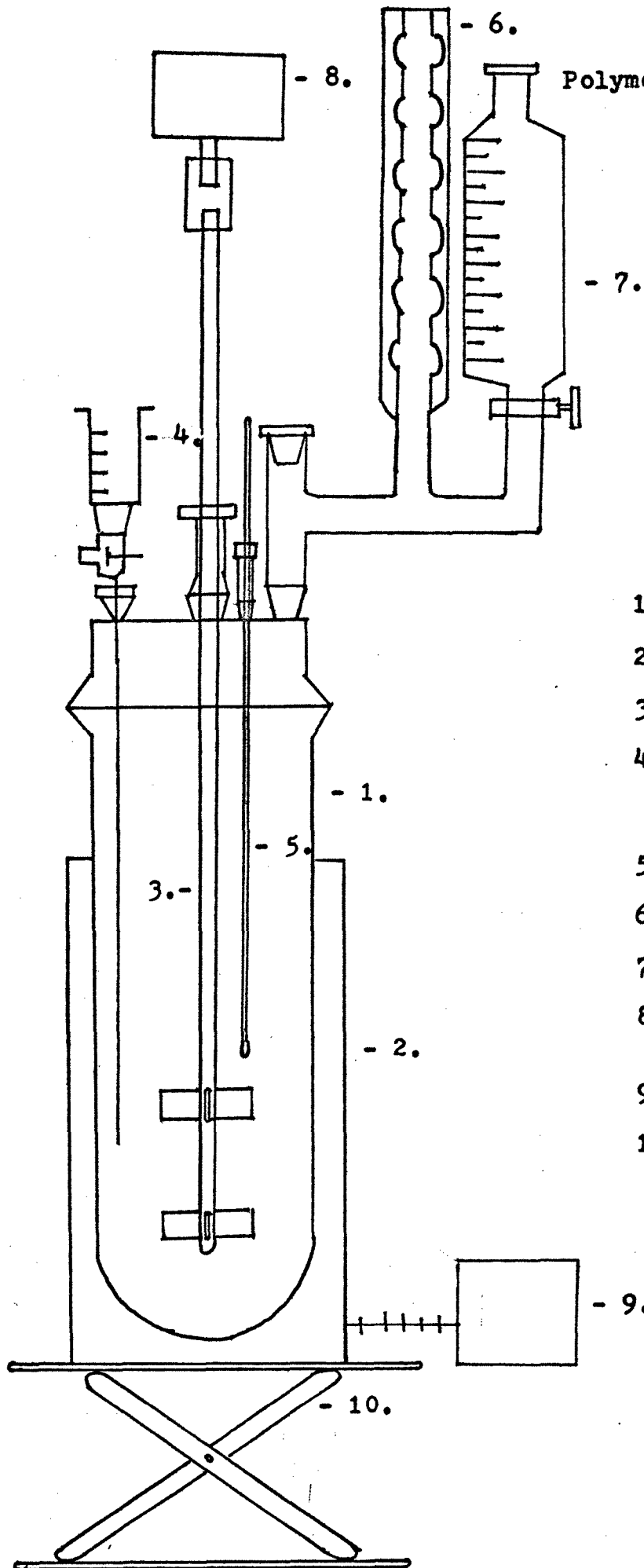
Figure 1
Polymerization Reactor

1. 2 Liter Pyrex Resin Flask

2. Heating Mantle

3. Glass Agitator

4. 5 Cubic Centimeter Syringe With 14 Inch Needle

5. 0 to 150 $^{\circ}$C Thermometer

6. Reflux Condenser

7. 1 Liter Buret

8. Agitator Motor And Controller

9. 110 Volt Autotransformer

10. Laboratory Jack

controlled via an autotransformer. Reaction temperatures are monitored with the thermometer shown in Figure 1. Agitator speed is determined via a hand held tachometer and varied with a motor controller. The reaction is terminated by addition of methanol via the 1000 cubic centimeter buret shown in Figure 1.

One portion of the study , case II, required that the catalyst be added over the reaction period to the reactor, while maintaining the same thermal history as the reaction mass. This was accomplished with the catalyst vessel shown in Figure 2. The vessel is a 500 cubic centimeter three neck round bottomed flask, equipped with reflux condenser, thermometer, and septum sampling port. The flask is heated with a heating mantle which is regulated with an autotransformer. Catalyst samples are withdrawn through the septum with a syringe and transferred to the reactor.

Once the reaction in the polymerization reactor is completed and the reaction has been stopped, the reaction mix is combined with methanol, a portion at a time, in a four liter beaker. The beaker is then placed in a dry ice bath, until cooled. The polymer which has now all precipitated from the solution is then filtered with a vacuum filter flask and buchner funnel with filter paper, see Figure 3.

Reaction procedure. The reactions are carried-out as follows:

Figure 2

Catalyst Vessel
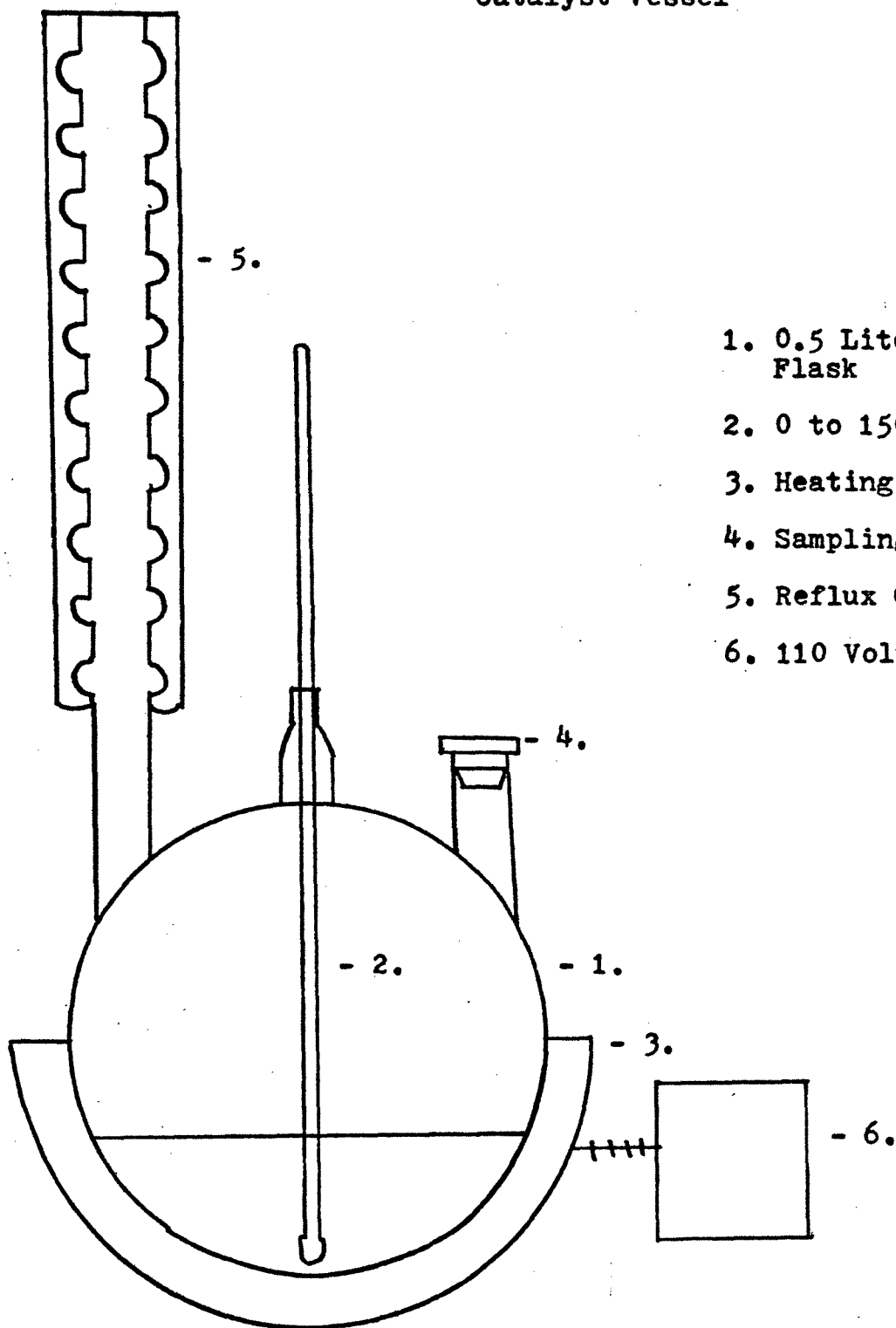
1. 0.5 Liter Round Bottom Flask

2. 0 to 150 °C Thermometer

3. Heating Mantle

4. Sampling Septum Port

5. Reflux Condenser

6. 110 Volt Autotransformer

Figure 3

Precipitation and Filtration Apparatus

VACUUM

- 2.
- 3.
- 5.
- 4.
- 1.
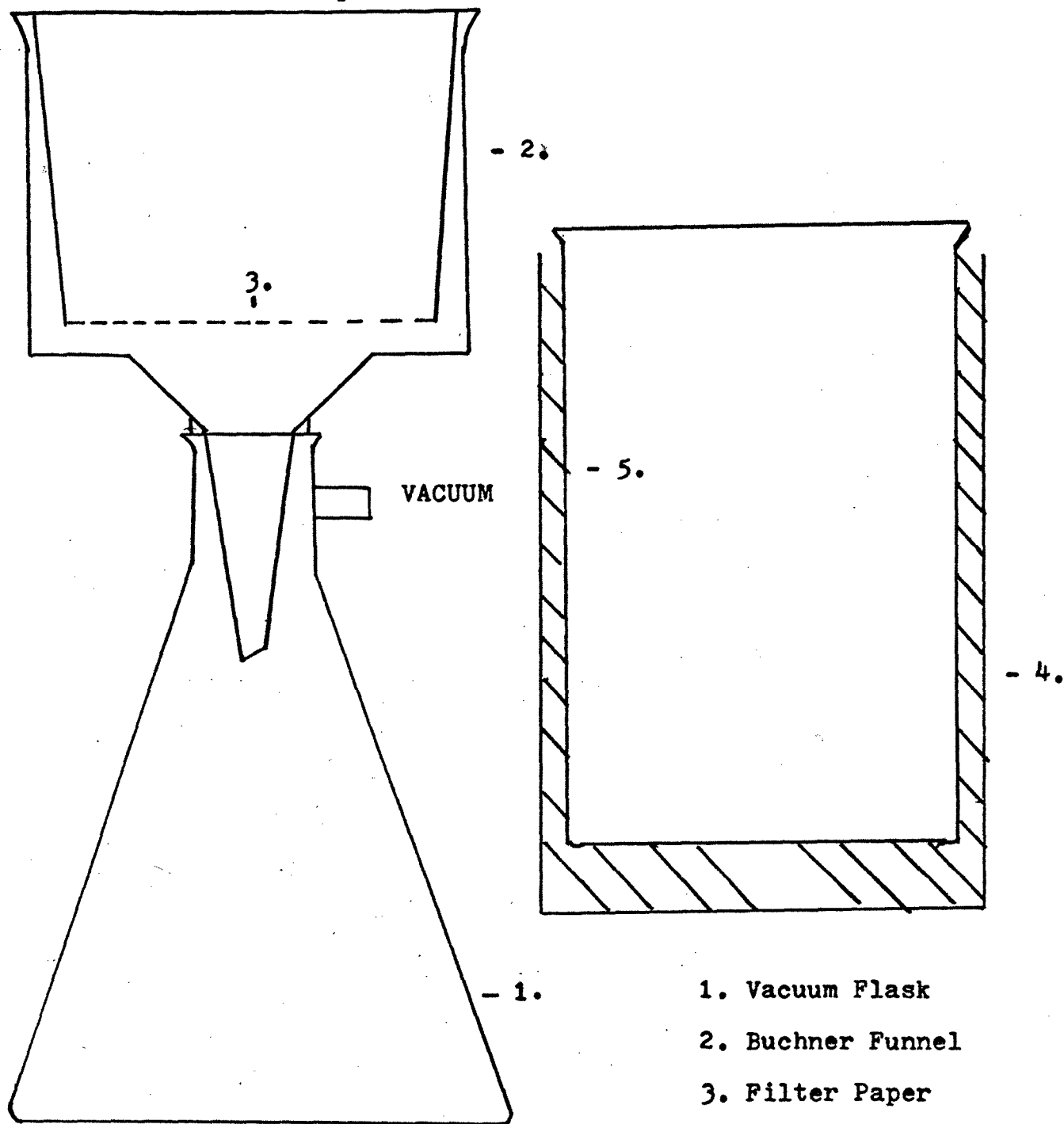
1. Vacuum Flask
2. Buchner Funnel
3. Filter Paper
4. Dry Ice Bath
5. 4 Liter Beaker

Overall Reactant Feed Concentrations

styrene 7.93×10^{-4} (gram-mole/cc)

benzene 1.025×10^{-2} (gram-mole/cc)

Vazo-64 2-20% (gram Vazo-64/gram monomer x 100) or

1.14×10^{-5} to 11.4×10^{-5} (gram-mole/cc)

In case I of the experiment, all catalyst, monomer, and solvent were added to the reactor at the start of the run. The procedure was as follows:

1. Add designated amount of catalyst to reactor.

2. Add 1000 cubic centimeters of benzene to reactor and agitate briefly.

3. Heat benzene-catalyst solution in reactor to $50^{\circ}C$, about twenty minutes required.

4. At $50^{\circ}C$ add all styrene to reactor, mix throughly.

5. Heat entire reactor mix to $83^{\circ}C$, thirty minutes required.

6. Turn on agitator and adjust to proper speed (700 revolutions/minute) or do not agitate, depending on run's requirement.

7. Record temperature of reaction mix and agitator speed, every five minutes throughout run.

8. Stop run by adding 500 cubic centimeters of methanol to reaction mix agitate the mix while adding methanol, five minutes required.

9. Allow reaction mix to cool to room temperature.

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Product work-up procedure. The product work-up was done
as follows:

1. Place 4000 cubic centimeter beaker in dry ice bath.

2. Add 500 cubic centimeters of reaction mix to 4000
   cubic centimeter beaker, fill remainder with methanol.

3. Allow beaker contents to cool to below- 5°C.

4. Filter methanol-reaction mix with a buchner funnel
   and filter paper, pulling a vacuum on the mixture in
   the funnel, see Figure 3.

5. Continue filtering and refiltering filtrate until clear.

6. Repeat steps 1-5 until all product work-up is completed.

7. Vacuum dry recovered polymer until weight is constant,
   and record final weight.

Discussion Of Results

Case I. Case I closely simulates a fully radiated photo
or radiation initiated reactor where the optical thickness (τ)
would equal one by definition (1-3,6-7). Since for case I,
all the catalyst is added to the reaction mix at the beginning
of the run, the catalyst volume equals the reaction volume or
the simulated optical thickness would equal one.

The first set of runs in this case were to determine the
affect, if any, of catalyst percentage (grams catalyst/gram
monomer x 100) upon product rate at agitator speeds of 0 and
700 revolutions/minute. The 0 and 700 revolutions/minute
agitator speeds were the lower and upper limits, respectively,
of the equipment, and were intended to approximate no mix (NM)
and perfect mix (PM) states . The runs in the first set of

runs were for a one hour reaction time, where the catalyst level
was varied from 2.0 to 20.0 percent catalyst. The results
from these runs, see Table I, were plotted, product(grams)
versus percent catalyst, see Figure 4. Due to the unexplainable
decrease in grams of product from 5 to 20 percent catalyst
and the somewhat erratic data over this range for the 0 revolutions/
minute plot, a catalyst level of 5 percent catalyst was
chosen for the other runs in this study.

The second set of runs in this case were for two hour
reaction times at 5 percent catalyst levels for both 0 and 700
revolutions/minute agitator speed, see Table I.

The sets of data in this case at 5 percent catalyst level
and one and two hour reaction times were then plotted, product
(grams) versus reaction time(hours), see Figure 5. Since
the reactor system is a batch reactor, the product rates (-dM/dt)
for the 0 and 700 revolutions/minute agitator speed states
are determined by taking the slopes of both curves from Figure 5,
at various reaction times. The product rate (-dM/dt) is then
plotted versus reaction time, see Figure 6.

From Figure 6, it can be seen that when extrapolated to
zero reaction time, the product rate (-dM/dt) at 0 revolutions/
minute equals the product rate (-dM/dt) at 700 revolution/
minute . Therefore there is no mixing effect at τ =1 between
0 and 700 revolutions/minute agitator speeds for this case.
Thus, this confirms Hill and Felder's (3) and Chen and Hill's(1)
results, which state for an optical thickness (τ) equal to one,

Table I

Case I Results $\tau = 1$

Reaction Time (Hours)	Reaction Temperature (°C)	Catalyst % (g catalyst/ g monomer x 100) 0 RPM	700 RPM	Catalyst Injection cc/5 Min.	Product 0 RPM(NM) (grams)	700 RPM(PM) (grams)
1	83	2.00	1.99	= 1 all catalyst added at start of run	11.03	9.06
1	83	4.91	4.91		10.24	9.01
1	83	10.97	9.88	same	5.81	7.37
1	83	19.52	19.72	same	8.24	4.37
2	83	4.92	5.01	same	16.65	15.42

RPM = revolutions/minute agitator speed

Figure 4

Effect of Catalyst Level on Grams of Polymer Formed

⊙ =   0 Revolutions/Minute(NM)

⊛ = 700 Revolutions/Minute(PM)

1 Hour Reaction Time

$\tau = 1$

Figure 5

Case I: Grams Product Versus Reaction Time

⊗ =   0 Revolutions/Minute(NM)

⊙ = 700 Revolutions/Minute(PM)
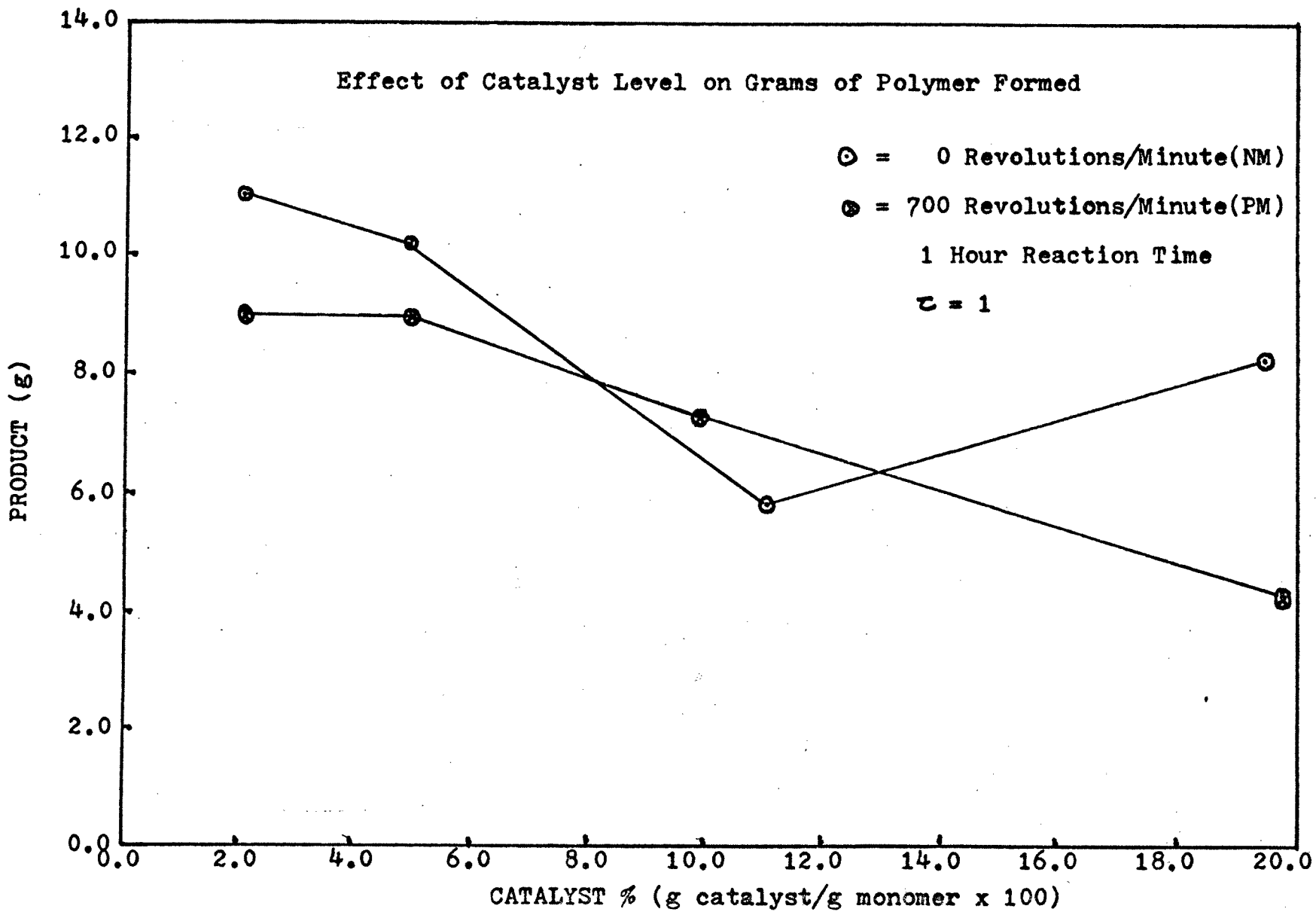
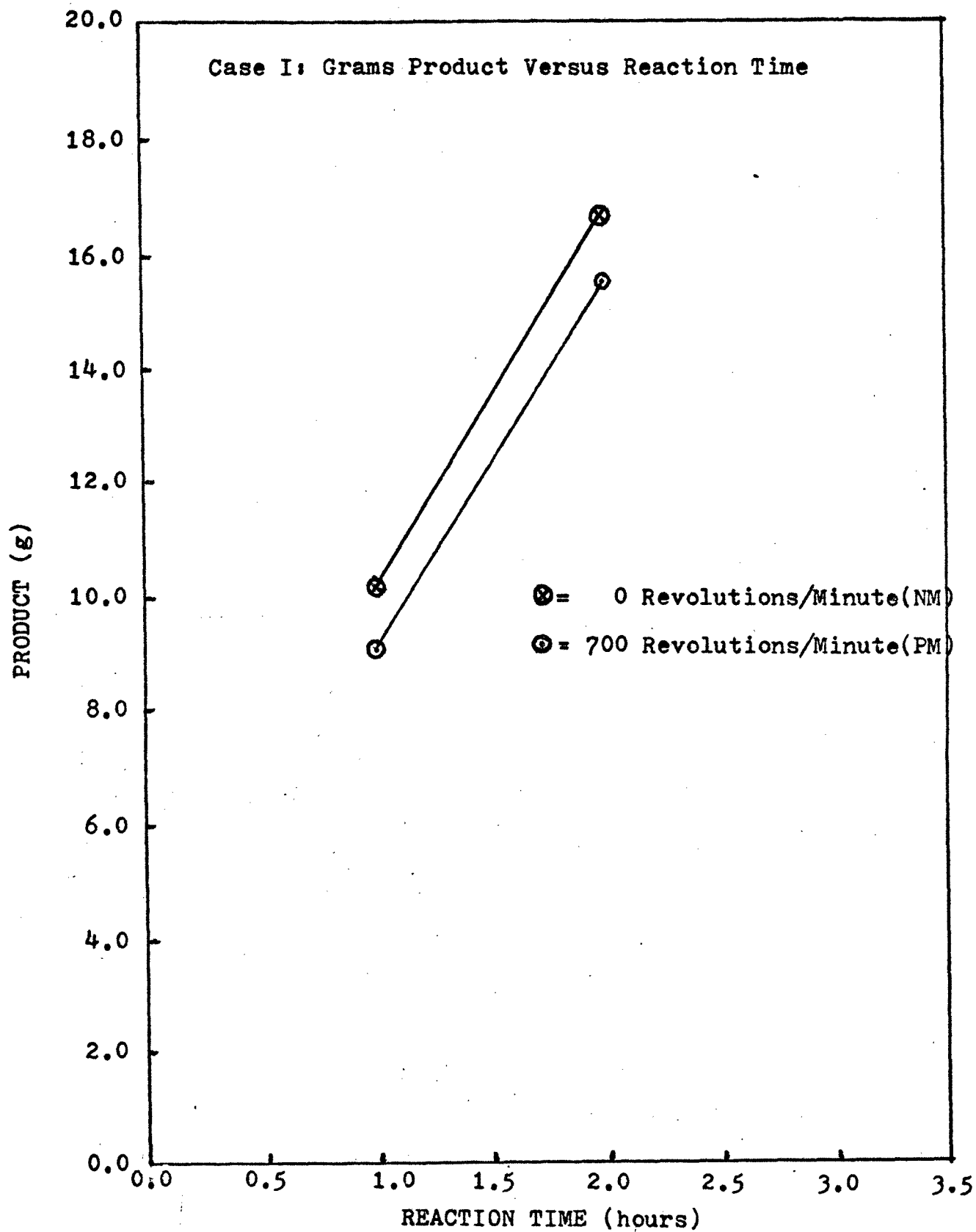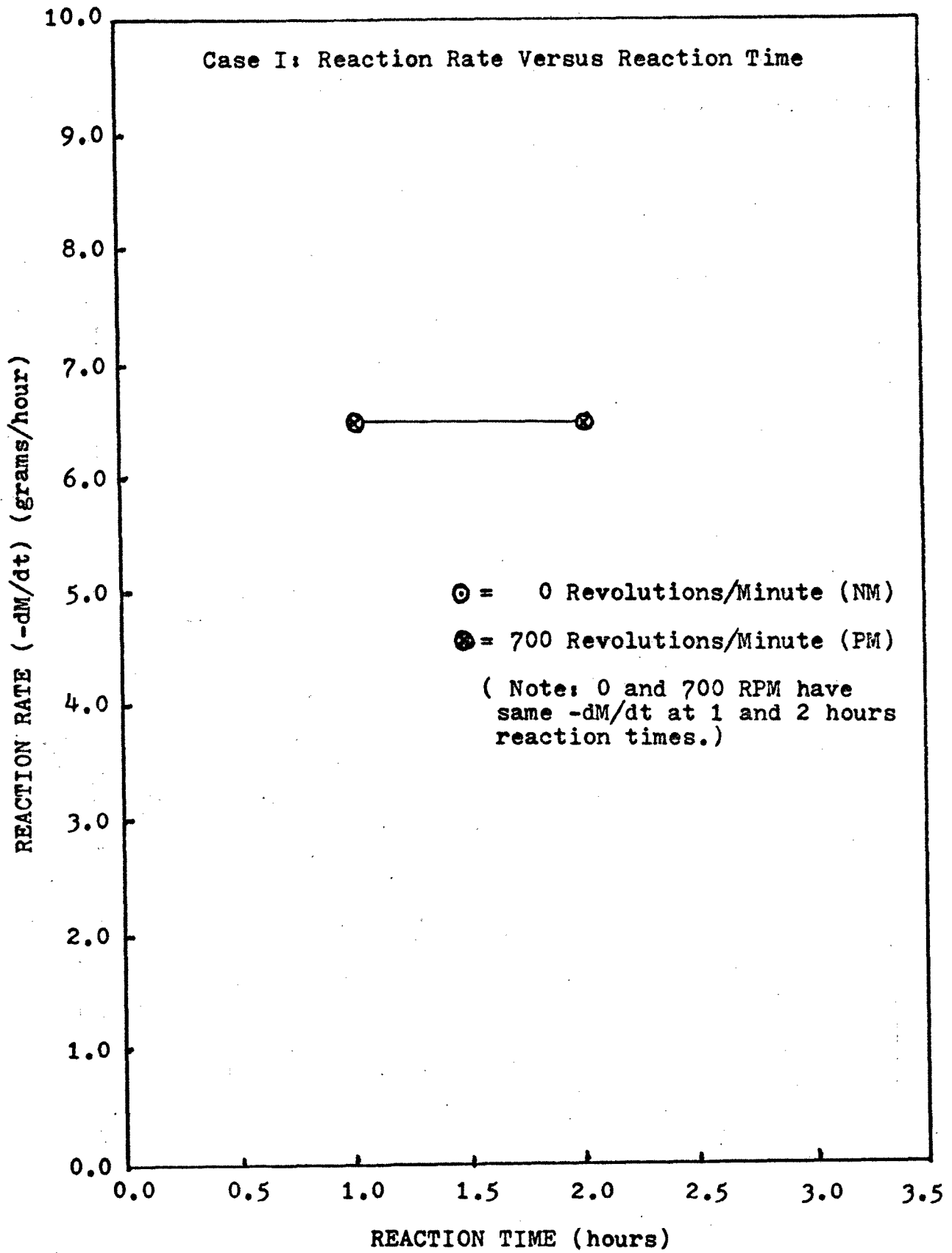Figure 6

there is little or no mixing effect or difference in product ratesbetween the PM and NM states at low conversion.

It should be noted that no mixing effects may be due to a reaction with a termination step of order equal to one. However, for this polymerization reaction, based on the reaction kinetics, the termination reactions are of an order equal to two. Thus, the presence or absence of mixing effects depends on the optical thickness or equivalent and agitator speed alone.

Case II. Having shown there is no mixing effect for $\tau = 1$ for 0 and 700 revolutions/minute agitator speeds, a series of runs were made with a $\tau = 35.7$. The runs were at a 5 percent catalyst level with reaction times from one half to three hours for both 0 and 700 revolutions/minute agitator speeds. The data, see Table II, was again treated as in case I. The product (grams) was plotted against reaction time (hours) for both the 0 and 700 revolutions/minute runs, see Figures 7 and 8. The slopes of both curves were taken at various reaction times to determine the product rates ($-dM/dt$) at these times. The product rates ($-dM/dt$) were then plotted against reaction times for both NM and PM cases. Both curves shown in Figure 8, were then extrapolated to zero time. At zero reaction time the PM (700 revolutions/minute) product rate was 20 percent greater than the NM (0 revolutions/minute) product rate. Again this coincides with Hill and Felder's (3) and Chen and Hill's (1) results, which state for a large

Figure 7
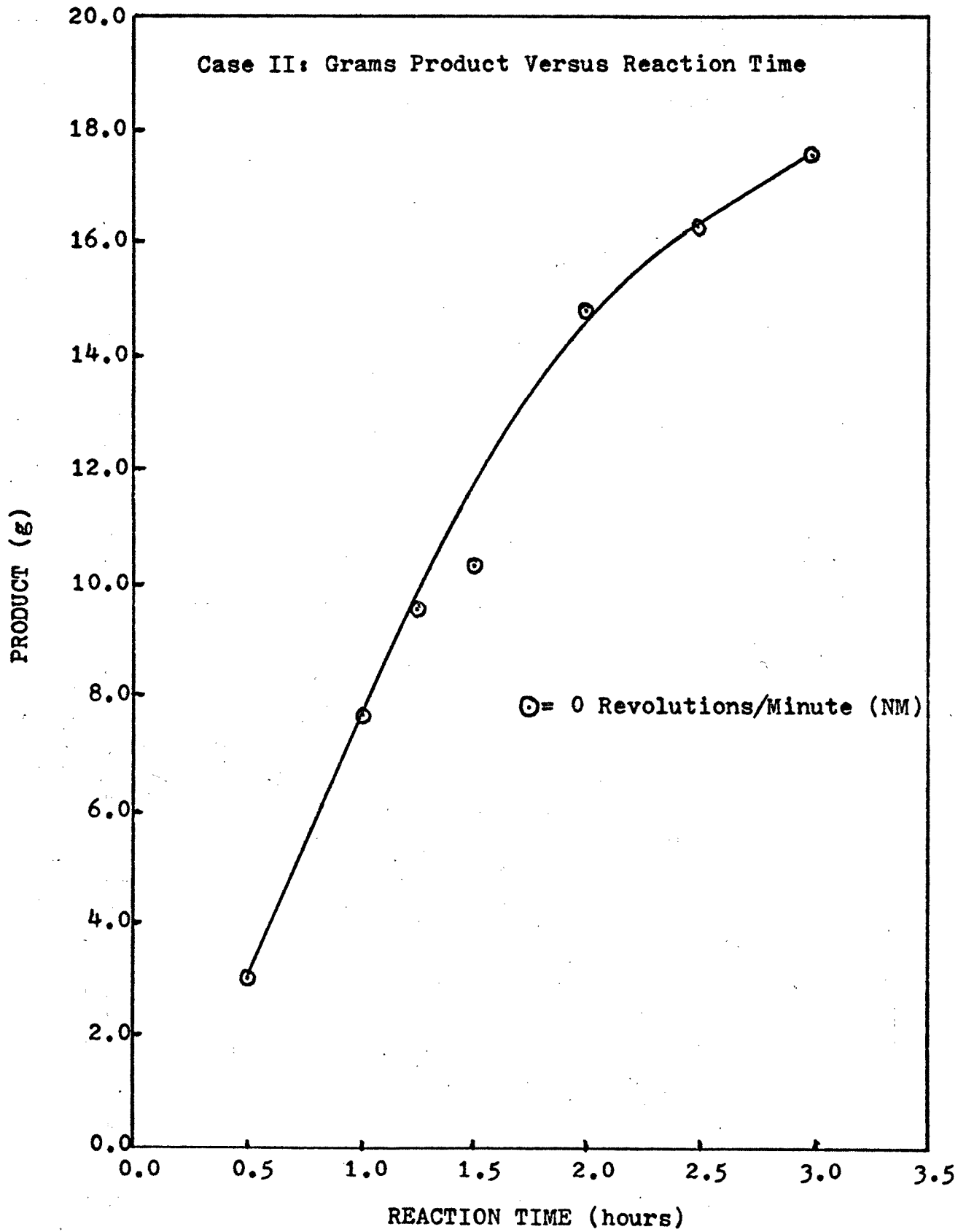
Table II

Case II Results $\tau = 35.7$

Reaction Time (Hours)	Temperature (°C) Reaction Mixture	Catalyst Solution	Catalyst % (g catalyst/ g monomer x 100) 0 RPM	700 RPM	Catalyst Injection cc/5 Min.	Product 0 RPM(NM) (grams)	700 RPM(PM) (grams)
0.5	83	83	5.05	5.06	5.0	3.06	1.83
1.0	83	83	4.94	4.95	2.5	7.73	7.36
1.25	83	83	4.97	4.96	2.0	9.57	9.10
1.5	83	83	5.08	4.99	1.67	10.33	10.91
2.0	83	83	4.90	4.97	1.25	14.83	14.87
2.5	83	83	4.94	4.97	1.0	16.34	16.35
3.0	83	83	4.99	4.98	0.83	17.60	17.55

RPM = revolutions/minute agitator speed

Figure 8

Case II: Grams Product Versus Reaction Time

= 700 Revolutions/Minute (PM)

Figure 9

τ, a large mixing effect will exist when comparing the product rates between the NM and PM states at low conversion.

Once the conversion reaches a certain level, the difference between the product rates for the NM and PM states becomes negligible, see Figure 9, over the two to three hour reaction time range. At this point, the conversion has reached a level where the assumptions used to develop the equations for the NM and PM states no longer hold .
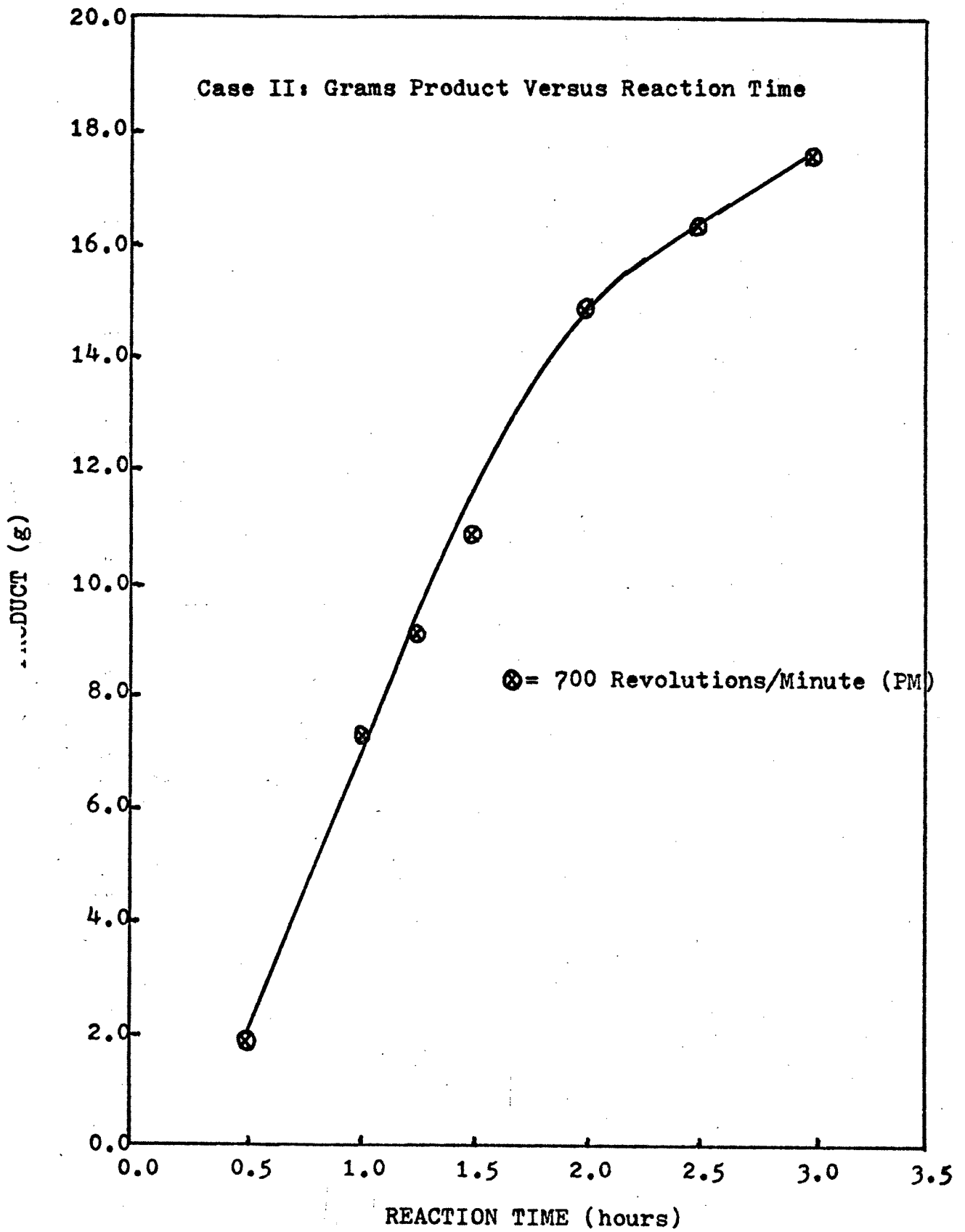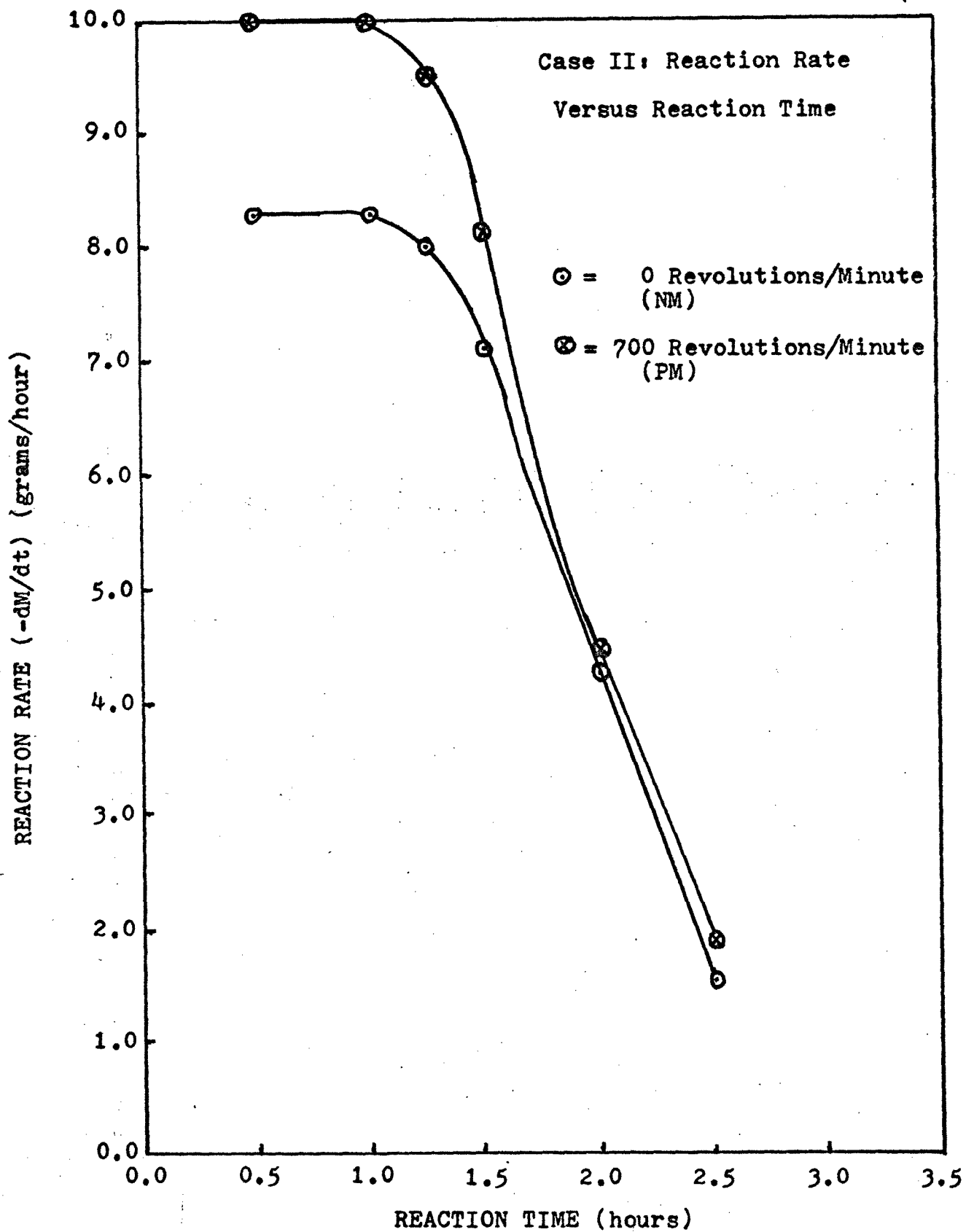
Summary

These experiments have studied the effect of agitation on the solution polymerization of styrene in a batch reactor, catalized with 2,2'azobisisobutyronitrile (Vazo-64) catalyst. The reaction temperature was maintained fairly constant and was considered isothermal. The reactor system was readily fitted to modified equations of Hill and Felder and Chen and Hill (3,1), per their papers' suggestion; where the radiation ititiation term $G_R I_o(\gamma)$ is replaced by $S_o(\gamma)$, a term expressing catalyst concentration, and the equation for optical thickness (τ) was modified to τ = total reactor volume/volume of catalyst solution, to express catalyst solution volume instead of irradiated reactor volume.

Two cases were studied, case I and case II. In case I the catalyst was uniformly distributed at the start of the run in the reaction mix, thus simulating a small optical thickness (τ), τ =1. A series of runs were then made in this

case for one hour reaction times and the percent catalyst was varied from 2 to 20 percent (grams catalyst/grams monomer x 100) at NM and PM states. Two runs were also made at a 5 percent catalyst level for two hour reaction times for both NM and PM states.

Case II involved a series of runs with reaction times from one half to three hours. Catalyst solution was injected at five minute intervals over the reaction time with a total of 5 percent catalyst injected at the end of the run or a total volume of 30 cubic centimeters of catalyst solution. Thus, a large optical thickness (τ), $\tau = 35.7$ was simulated for both the PM and NM states.

The experimental results from this study for cases I and II were then compared with the results from the theoretical reaction rate equations for the PM and NM states. The experimental results verify that $(-dM/dt)_{PM} \gtrless (-dM/dt)_{NM}$ for a large optical thickness, $\tau = 35.7$, and $(-dM/dt)_{PM} = (-dM/dt)_{NM}$ for $\tau = 1$, thus verifing previous theoretical work (1-3,4,6,7,12).

Thus Hill and Felder's (3) and Chen and Hill's (1) equations hold not only for photo or radiation initiated reactions but also for the nonuniformly initiated catalyst system studied for both NM and PM states. For this system however, their (1,3) equations become no longer valid once a conversion of 16.5 percent (grams polymer/grams monomer fed x 100) is reached. This is in agreement with both Hill and Felder (3) and Chen and Hill (1), per their theoretical development.

RECOMMENDATIONS

This thesis's experimental work dealt basically with the determination of the polymerization rate differences between perfect and no mixing states. Therefore, the apparatus used in these experiments was rather simple. Future work however, will require a more sophisticated apparatus and experimental technique. The equipment should comply with the following:

1. Agitator variability to cover a full range of speeds from 0 to over 1000 revolutions/minute, to ensure perfect mixing.

2. A method of continuous catalyst solution injection should be devised, with a highly variable rate of injection available.

3. An easier method to determine the polymerization rate should be devised (possibly a chromatographic technique), as well as a technique to determine the number and weight average molecular weights at any given time with a minimal sample size. This would enable many data points to be obtained from one run at various reaction times instead of just one point.

Once such an apparatus and techniques are developed, the following should be investigated:

1. Determine the effect of (τ) reactor volume/catalyst solution volume injected on reaction rate, number average molecular weight, and weight average molecular weight.

2. The effect of agitator speed in the range between perfect and no mixing states, on reaction rate and number and weight average molecular weights.

3. In addition , the effect of monomer concentration, solvent concentration, and temperature should be investigated.

NOTATION

G_R = radical yield, g.-mole/eV. absorbed

I_a = absorbed intensity, eV./(cc.)(second)

i,j = chain length, dimensionless

k_d = rate constant for reaction of catalyst radicals with momoner, cc./(g.-mole)(second)

k_i = rate constant for thermal decomposition of catalyst,1./(second)

k_p = propagation rate constant, cc./(g.-mole)(second)

k_t = k_{tc} + k_{td}, cc./(g.-mole)(second)

k_{tc} = rate constant for termination by coupling, cc./(g.-mole)(second)

k_{td} = rate constant for termination by disproportionation, cc./(g.-mole)(second)

m,M = monomer concentration, g.-mole/cc.

p_j = concentration of dead polymer of chain length, j monomer units, g.-mole/cc.

r_j = concentration of active polymer of chain length, j monomer units, g.-mole/cc.

s = concentration of catalyst, g.-mole/cc.

s_0 = initial concentration of catalyst, g.-mole/cc.

t = time, seconds

V = volume, cc.

V_c = reactor volume, cc.

$\underline{v}$ = position vector

X_n = number average chain length, dimensionless

X_W = weight average chain length, dimensionless

Ω = initiation rate as defined by Eq. (7) or (8) (Reactor Equations section), g.-mole/cc.-seconds

τ = optical thickness, reactor volume/catalyst solution volume, dimensionless

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APPENDIX

Calculations

The following development will generate equations for the perfect mix (PM) and no mix (NM) states , and prove the below equations to be true:

$$(-dM/dt)_{PM} \geq (-dM/dt)_{NM} \qquad (1)$$

$$X_n(t)_{PM} \geq X_n(t)_{NM} \qquad (2)$$

$$X_w(t)_{PM} \leq X_w(t)_{NM} \qquad (3)$$

Perfect Mix State. Based on the assumption that polymer chain lenght is great the following is a good approximation(3):

$$-dM/dt = k_p M \Sigma r_i(t) \qquad (4)$$

Now make a material balance for free radicals $r_i(t)$, i=1 to j

$$dr_1(t)/dt = \bar{\Lambda}(t) - k_p r_1(t)M - (k_{tc} + k_{td})r_1(t)\Sigma r_i(t) = 0 \qquad (5)$$

$$dr_2(t)/dt = k_p r_1(t)M - k_p r_2(t)M - (k_{tc} + k_{td})r_2(t)\Sigma r_i(t) = 0 \qquad (6)$$

$$dr_j(t)/dt = k_p r_{j-1}(t)M - k_p r_j(t)M - (k_{tc} + k_{td})r_j(t)\Sigma r_i(t) = 0 \qquad (7)$$

$$\text{where: } j = 2,3,\ldots..$$

Now add equations from i= 1 to .

$$d\Sigma r_i(t)/dt = \bar{\Lambda}(t) - (k_{tc} + k_{td})(\Sigma r_i(t))^2 = 0 \qquad (8)$$

Therefore , solving the rightside of equation (8) for $r_i(t)$:

$$\Sigma r_i(t) = (\bar{\Lambda}(t)/(k_{tc} + k_{td}))^{1/2} \qquad (9)$$

Substitute equation (9) into equation (4), then substitute $kt = k_{tc} + k_{td}$

$$-dM/dt = k_p M(\bar{\Lambda}(t)/(k_{tc} + k_{td}))^{1/2} = k_p M(\bar{\Lambda}(t)/k_t)^{1/2} \qquad (10)$$

Now make a material balance for the dead polymer $P_j(t)$, for $j = 1,2,3,\ldots..$.

$$-dP_j(t)/dt + k_{td}r_j(t)\Sigma r_i(t) + (1/2)k_{tc}\sum_{i=1}^{j-1} r_i(t)r_{j-i}(t) = 0 \qquad (11)$$

or

$$dP_j(t)/dt = k_{td}r_j(t)\Sigma r_i(t) + (1/2)k_{tc}\sum_{i=1}^{j-1} r_i(t)r_{j-i}(t) \quad (12)$$

Where $r_i(t)$ is the total polymer radical concentration at time t, and represents the effective initiation rate given by:

$$\bar{\Omega}(t) = 1/V_c \iiint_{V_c} \Omega(\underline{v},t)dV \quad (13)$$

where the vector $\underline{v}$, specifies position in the reactor and:

$$\Omega(\underline{v},t) = \Omega(\underline{v}) = G_R I_a(\underline{v}) \quad (14)$$

for radiation initiation.

For catalytic initiation:

$$\Omega(\underline{v},t) = k_i s(\underline{v},t) = k_i s_o(\underline{v})e^{-k_i t} \quad (15)$$

The number and weight average for the dead polymer size formed during the reaction are defined as follows:

$$X_n(t) = \Sigma i P_i(t)/\Sigma P_i(t) \quad (16)$$

$$X_w(t) = \Sigma i^2 P_i(t)/\Sigma i P_i(t) \quad (17)$$

where ΣP_i , $\Sigma i P_i$, and $\Sigma i^2 P_i$ are respectively the zeroth, first, and second moments of dead polymer size distribution.

Now looking at equation (12), with the aid of Euler's summation formula (1), the following is obtained:

$$dP_j(t)/dt = k_{td}r_j(t)\Sigma r_i(t) + (1/2)k_{tc}(\sum_{i=1}^{j-1} r_i(t)r_{j-i}(t)di + r_1 r_{j-1}) \quad (18)$$

Therefore based on the above, the zeroth moment is:

$$\Sigma P_i(t)/dt = (k_{tc} + (1/2)k_{tc})(\Sigma r_i(t))^2 \quad (19)$$

The first moment of the dead polymer size distribution is obtained by multipling j = 1 to i time equation (12) (material balance for dead polymer), then adding all the multilpied equations to obtain the following equation:

$$\Sigma iP_i(t)/dt = \Sigma ir_i(t)k_{td}\ r_i(t) + (1/2)\Sigma i\sum_{i=1}^{j-1}r_i(t)r_{j-i}(t) \qquad (20)$$

Now applying the below summation identity (1),

$$\sum_{j=1}^{\infty} j\sum_{i=1}^{j-1}r_i r_{j-i} = 2(\sum_{j=1}^{\infty}r_j)(\sum_{j=1}^{\infty}jr_j) \qquad (21)$$

The first momoment is as follows:

$$\Sigma i\ P_i(t)/dt = (k_{tc} + k_{td})\Sigma r_i(t)\Sigma ir_i(t) \qquad (22)$$

The above is repeated for the $\Sigma i^2 P_i(t)$ or second moment, except the terms are multiplied by i^2 or $1,4,9,\ldots i^2$, and the following equation is obtained:

$$\Sigma i^2P_i(t)/dt = \Sigma i^2r_i(t)k_{td}\Sigma r_i(t) + (1/2)k_{tc}\Sigma i^2\sum_{i=1}^{j-1}r_i(t)r_{j-i}(t) \qquad (23)$$

Applying the below summation identity ( ):

$$\sum_{j=1}^{\infty} j^2\sum_{i=1}^{j-1}r_i r_{j-i} = 2(\sum_{i=1}^{\infty}r_i)(\sum_{i=1}^{\infty}i^2r_i) + 2(\sum_{i=1}^{\infty}ir_i)^2 \qquad (24)$$

the below equation is obtained for the second moment:

$$\Sigma i^2P_i(t)/dt = (k_{tc} + k_{td})\Sigma r_i(t)\Sigma i^2r_i(t) + k_{tc}(\Sigma ir_i(t))^2 \qquad (25)$$

With expressions for the zeroth, first, and second moments for polymer size distribution, in terms of $\Sigma r_i(t)$, $\Sigma ir_i(t)$, and $\Sigma i^2r_i(t)$, these equations need now to be expressed in terms of $\bar{\Omega}(t)$ and M. Substituting $k_t = k_{tc} + k_{td}$ into equation (9), the following is obtained:

$$\Sigma r_i(t) = (\bar{\Omega}(t)/k_t)^{1/2} \qquad (26)$$

From the material balance for free radicals $r_i(t)$, $i = 1$ to j equations (5-7) are multiplied by $j = 1$ to i as before for the dead polymer moments, to obtain:

$$\bar{\Omega}(t) + k_pM(\Sigma jr_{j-1}(t)-\Sigma jr_j(t)) - (k_{tc} + k_{td})\Sigma ir_i(t)\Sigma r_i(t) = 0 \qquad (27)$$

It is easily shown that :

$$\Sigma jr_{j-1}(t) - \Sigma jr_j(t) = \Sigma r_j(t)$$

see below

	$\sum j r_{j-1}(t)$	$\sum j r_j(t)$
j = 1	0	$-r_1(t)$
j = 2	$2r_1(t)$	$-2r_2(t)$
j = 3	$3r_2(t)$	$-3r_3(t)$
	$\cdot$	$\cdot$
	$\cdot$	$\cdot$

Adding j=1 to i $r_1(t) + r_2(t) + \ldots r(t) = \sum r_i(t)$

Therefore; substituting $k_t = k_{tc} + k_{td}$

$$\sum i r_i(t) = (\bar{\Omega}(t) + k_p M \sum r_i(t))/k_t \sum r_i(t) \qquad (29)$$

A similar development for $\sum i^2 r_i(t)$ from the material balance for free radicals $r_i(t)$, i = 1 to i, from equations (5-7), except a multiplier of i^2 or $1,4,9,\ldots i^2$, is used to obtain the following equation:

$$\Omega(t) + k_p M(\sum i^2 r_{i-1}(t) - \sum i^2 r_i(t)) - (k_{tc} + k_{td})\sum i^2 r_i(t)\sum r_i(t) = 0 \qquad (30)$$

In a proof identical to equation (28) it is easily shown:

$$\sum i^2 r_{i-1} - \sum i^2 r_i = \sum r_i + 2\sum i r_i \qquad (31)$$

Thus the equation for $\sum i^2 r_i(t)$ is as follows:

$$\sum i^2 r_i(t) = \bar{\Omega}(t) + k_p M(\sum r_i(t) + 2\sum i r_i(t))/k_t \sum r_i(t) \qquad (32)$$

where $k_t = k_{tc} + k_{td}$ was substituted

Equations (29) and (32) must be simplified by applying the assumption that chain length is very long and therefore;

$$\bar{\Omega}(t) \ll k_p M \sum r_i(t) \qquad (33)$$

or in other terms applying equation (26)

$$\sum r_i(t) k_t \ll k_p M \qquad \text{or} \qquad \sum r_i(t) \ll k_p M/k_t \qquad (34A,B)$$

Now rearranging equation (29), and $\bar{\Omega}(t) = (\sum r_i(t))^2 k_t$ substituted, from equation (26), the following is obtained:

$$\sum i r_i(t) = \sum r_i(t) + k_p M/k_t \qquad (35)$$

Applying equation (34B):

$$\sum i r_i(t) = k_p M/k_t \qquad (36)$$

Rearranging equation (32), and substituting $\bar{\Omega}(t) = (\sum r_i(t))^2 k_t$:

$$\sum i^2 r_i(t) = k_p M/k_t ((k_t \sum r_i(t) + 2 k_p M)/k_t \sum r_i(t)) \qquad (37)$$

Applying equation (34A):

$$\sum i^2 r_i(t) = 2 k_p^2 M^2/k_t^2 \sum r_i(t) \qquad (38)$$

Substitute equations (26, 36, and 38), for $\sum r_i(t)$, $\sum i r_i(t)$, and $\sum i^2 r_i(t)$ respectively into equations (19, 22, and 25), for the zeroth, first, and second moments of polymer size distribution respectively, and simplify.

$$\sum P_i(t)/dt = ((k_{td} + (1/2)k_{tc})/k_t)\bar{\Omega}(t) \qquad (39)$$

$$\sum i P_i(t)/dt = (k_p M/k_t^{1/2})(\bar{\Omega}(t))^{1/2} \qquad (40)$$

$$\sum i^2 P_i(t)/dt = (k_p^2/k_t)(2 + k_{tc}/k_t)M^2 \qquad (41)$$

No Mix State. As in the perfect mix case, the polymer chain length is assumed great and as a good approximation ( ):

$$-dM/dt = k_p M \sum \overline{r_i(\underline{v},t)} \qquad (42)$$

and, the first three moments of the dead polymer size distribution are derived identically to equations (19, 22, and 25) except $\sum r_i(t)$, $\sum i r_i(t)$, $\sum i^2 r_i(t)$ are replaced by $\sum \overline{r_i(\underline{v},t)}$, $\sum \overline{i r_i(\underline{v},t)}$, and $\sum i^2 r_i(\underline{v},t)$ respectively.

$$\sum P_i(t)/dt = (k_{td} + (1/2)k_{tc})(\sum \overline{r_i(\underline{v},t)})^2 \qquad (43)$$

$$\sum iP_i(t)/dt = k_t \overline{\sum r_i(\underline{v},t)} \overline{\sum ir_i(\underline{v},t)} \qquad (44)$$

$$\sum i^2 P_i(t)/dt = k_t \overline{\sum r_i(\underline{v},t)} \overline{\sum i^2 r_i(\underline{v},t)} + k_{tc} \overline{(\sum ir_i(\underline{v},t))^2} \qquad (45)$$

Where an overlined quantity is the volume-averaged value of the quantity over the reactor volume.

Again, a material balance for the free radicals, r_i, are identical to equations (5-7) except $r_1(t)$, ... $r_i(t)$ are replaced by $r_1(\underline{v},t)$,..... $r_i(\underline{v},t)$ and the equations from 1 to i are then added and $k_t = k_{tc} + k_{td}$ substituted. Therefore:

$$d\sum r_i(\underline{v},t)/dt = \Omega(\underline{v},t) - k_t(\sum r_i(\underline{v},t))^2 = 0 \qquad (46)$$

thus,

$$\sum r_i(\underline{v},t) = (\Omega(\underline{v},t)/k_t)^{1/2} \qquad (47)$$

An identical development as was used to derive equations (29,32) to give the below equations:

$$\sum ir_i(\underline{v},t) = (\Omega(\underline{v},t) + k_p M \sum r_i(\underline{v},t))/k_t \sum r_i(\underline{v},t) \qquad (48)$$

$$\sum i^2 r_i(\underline{v},t) = (\Omega(\underline{v},t) + k_p M(\sum r_i(\underline{v},t) + 2\sum ir_i(\underline{v},t)))/k_t \sum r_i(\underline{v},t) \qquad (49)$$

Now simplifying these equations as per equations (36,38), the following equations are obtained:

$$\sum ir_i(\underline{v},t) = k_p M/k_t \qquad (50)$$

$$\sum i^2 r_i(\underline{v},t) = 2k_p^2 M^2/k_t^2 \sum r_i(\underline{v},t) \qquad (51)$$

Integrating equations (47,50,51) over the reactor volume the following overlined equations are obtained:

$$\overline{r_i(\underline{v},t)} = (1/V_c)\iiint_{V_c} \sum r_i(\underline{v},t)dV = (1/V_c k_t^{1/2})\iiint_{V_c} (\Omega(\underline{v},t))^{1/2}dV \qquad (52)$$

$$\overline{ir_i(\underline{v},t)} = (1/V_c)\iiint_{V_c} \sum ir_i(\underline{v},t)dV = k_p M/k_t \qquad (53)$$

$$\overline{i^2 r_i(\underline{v},t)} = (1/V_c)\iiint_{V_c} \sum i^2 r_i(\underline{v},t)dV = (2k_p^2 M^2/k_t^2 V_c)\iiint_{V_c} dV/\sum r_i(\underline{v},t) \qquad (54)$$

Substituting equations (52-54) into equations (42-45):

$$-dM/dt = (k_pM/k_t^{1/2}V_c)\iiint_{V_c}(\Omega(\underline{v},t))^{1/2}dV \quad (55)$$

$$P_i(t)/dt = ((k_{td} + (1/2)k_{tc})/k_tV_c)\iiint_{V_c}\Omega(\underline{v},t)dV \quad (56)$$

$$iP_i(t)/dt = (k_pM/k_t^{1/2}V_c)\iiint_{V_c}(\Omega(\underline{v},t))^{1/2}dV \quad (57)$$

$$i^2P_i(t)/dt = (k_p^2/k_t)(2 + k_{tc}/k_t)M^2 \quad (58)$$

Influence of Mixing. In summary, the following equations (10, 39-40)were developed for the perfect mix state and equations (55-58) for the no mix state, see below:

perfect mix

$$-dM/dt = k_pM(\bar{\Omega}(t)/k_t)^{1/2} \quad (59)$$

$$\Sigma P_i(t)/dt = ((k_{td} + (1/2)k_{tc})/k_t)\bar{\Omega}(t) \quad (60)$$

$$\Sigma iP_i(t)/dt = (k_pM/k_t^{1/2})(\bar{\Omega}(t))^{1/2} \quad (61)$$

$$\Sigma i^2P_i(t)/dt = (k_p^2/k_t)(2 + k_{tc}/k_t)M^2 \quad (62)$$

$$\text{where: } \bar{\Omega}(t) = (1/V_c)\iiint_{V_c}\Omega(\underline{v},t)dV \quad (63)$$

no mix

$$-dM/dt = (k_pM/k_t^{1/2}V_c)\iiint_{V_c}(\Omega(\underline{v},t))^{1/2}dV \quad (64)$$

$$\Sigma P_i(t)/dt = ((k_{td} + 1/2k_{tc})/k_tV_c)\iiint_{V_c}\Omega(\underline{v},t)dV \quad (65)$$

$$\Sigma iP_i(t)/dt = (k_pM/k_t^{1/2}V_c)\iiint_{V_c}(\Omega(\underline{v},t))^{1/2}dV \quad (66)$$

$$\Sigma i^2P_i(t)/dt = (k_p^2/k_t)(2 + k_{tc}/k_t)M^2 \quad (67)$$

Taking the integrals of equations (60-63, 65-67) over time, t:

perfect mix

$$\Sigma P_i(t) = ((k_{td} + 1/2k_{tc})/k_t)\int_0^t \bar{\Omega}(t)dt \quad (68)$$

$$\Sigma iP_i(t) = (k_pM/k_t^{1/2})\int_0^t (\bar{\Omega}(t))^{1/2}dt \quad (69)$$

$$\Sigma i^2P_i(t) = (k_p^2/k_t)(2 + k_{tc}/k_t)M^2\int_0^t dt \quad (70)$$

no mix

$$\Sigma P_i(t) = ((k_{td} + 1/2k_{tc})/k_t V_c)\int_0^t (\iiint_{V_c} \alpha(\underline{v},t)dV)dt \quad (71)$$

$$\Sigma i P_i(t) = (k_p M/k_t^{1/2} V_c)\int_0^t (\iiint_{V_c} (\alpha(\underline{v},t))^{1/2}dV)dt \quad (72)$$

$$\Sigma i^2 P_i(t) = (k_p^2/k_t)(2 + k_{tc}/k_t)M^2\int_0^t dt \quad (73)$$

Now compare perfect mix and no mix equations:

$$(-dM/dt)_{PM} = (k_p M/k_t^{1/2}(\bar{\alpha}(t))^{1/2} \quad ---- \quad (-dM/dt)_{NM} = (k_p M/k_t^{1/2}V_c)$$
(74) (75)
$$\iiint_{V_c}(\alpha(\underline{v},t))^{1/2}dV$$

Applying Schwartz's inequality (2,3)

$$(1/V_c)\iiint_{V_c}(\alpha(\underline{v},t))^{1/2}dV \leq (\tfrac{1}{V_c}\iiint_{V_c}\alpha(\underline{v},t)dV)^{1/2} = (\bar{\alpha}(t))^{1/2} \quad (76)$$

Thus,

$$(-dM/dt)_{PM} \geq (-dM/dt)_{NM} \quad (77)$$

An identical comparison of equations for the zeroth, first, and second moments for dead polymer size distribution in the perfect mix and no mix states results in the following:

$$(\Sigma P_i(t))_{PM} = (\Sigma P_i(t))_{NM} \quad (78)$$

$$(\Sigma i P_i(t))_{PM} \geq (\Sigma i P_i(t))_{NM} \quad \text{(fits Schwartz's} \quad (79)$$
$$\text{inequality (2,3))}$$

$$(\Sigma i^2 P_i(t))_{PM} = (\ i^2 P_i(t))_{NM} \quad (80)$$

Now comparing the number and weight average molecular weights for the perfect mix and no mix states, as defined in equations (16) and (17) respectively, it is easily seen:

$$(X_n(t))_{PM} = (\Sigma i P_i(t))_{PM}/(\Sigma P_i(t))_{PM} \quad (81)$$

$$(X_n(t))_{NM} = (\Sigma i P_i(t))_{NM}/(\Sigma P_i(t))_{NM} \quad (82)$$

Thus, using the relationships developed in equations (78) and (79) the following is obtained:

$$(X_n(t))_{PM} \geq (X_n(t))_{NM}$$

An identical comparison of $X_w(t)$ for perfect mix and no mix states gives the following:

$$(X_w(t))_{PM} \leq (X_w(t))_{NM}$$