

FREE RADICAL
POLYMERIZATION OF STYRENE
IN
CONTINUOUS AND BATCH REACTORS

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REACTORS

By

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SCOPE AND CONTENTS:

Polymerization of styrene was carried out in continuous and batch reactors using azobisisobutyronitrile as initiator and benzene as solvent. Monomer conversion, molecular weight distribution (MWD) and viscosity were measured.

Corrections to the conventional kinetic mechanism using results from the continuous reactor were determined. These corrections were applied to the batch reactor kinetic model and the conversion and MWD thus predicted were compared to experimental results. It was found that the corrections applied to the batch system were not adequate to give accurate predictions of conversion and MWD.

A short computer study of the effect of oscillating monomer flow and temperature, as opposed to steady flow, on a transient continuous reactor was also carried out. It was found from this study that at low conversions oscillations in monomer flow will not affect the time average conversion and molecular weight. Oscillations in temperature caused an

increase in time average conversion and a decrease in time average molecular weight as compared to results obtained when the reactor was operated at a steady temperature which was the average of the oscillating temperatures.

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ABSTRACT

Free radical polymerizations of styrene in benzene were carried out in continuous and batch reactor systems to determine the effect of viscosity on the conventional kinetic mechanisms. The correction correlations obtained from the continuous reactor conversions and MWD were applied to the batch reactor kinetic model and the results showed that further correction is required to predict accurate conversions and MWD's for the batch reactor.

The second part of the work was a computerized study of the effect of oscillating monomer flow and temperatures on the transient continuous reactor system. It was found that at low viscosities, oscillating monomer flow would not change the time average conversions and MWD from those obtained at the average monomer flow. The time average conversions and molecular weights obtained when temperature was oscillated differed from the results obtained at the average temperature. The molecular weights decreased and the conversions increased with oscillating temperature.

INTRODUCTION

The present work is a continuation of previous studies by Tebbens, Hui, and Duerksen of the kinetics of free-radical polymerization of styrene (1) (2) (3). A better understanding of the kinetics of free-radical polymerization at high conversions would lead to industrial application, since very little work has been done in the area of high conversions - the area with which this work is concerned.

At high conversions, styrene polymerization is greatly affected by viscosity. This fact was first reported by Tromsdorff (4) for the polymerization of methyl methacrylate. He discovered that the conversion and molecular weights were significantly increased over the values predicted by conventional kinetics. This phenomenon has been called the "gel" or "viscosity" effect.

Part I of this report is an experimental study of both an isothermal steady state continuous reaction system and an isothermal transient batch system. Polymerizations of styrene were carried out in benzene solution with azobisisobutyronitrile as initiator.

One objective of the experimental study was to investigate the high viscosity region (100 - 1000 cps.) in the continuous reactor system and to develop correlations for the effect of viscosity on rate constants and catalyst efficiency. In the batch system, the purpose was also to investigate the effect of viscosity on the rate constants and catalyst efficiency. The corrections to the kinetic rates (for viscosity effect) obtained from the CSTR experiments were applied to the BSTR model and the

predicted results were compared with the experimental data obtained using the batch system.

Part II of this report deals with a computer study of the effect of oscillating monomer flow and temperature on the conversion and molecular weight distribution (MWD) in a CSTR. This preliminary study was designed to investigate whether or not the operation of a polymerization reactor under non-steady state conditions would give higher conversion rates and a modified MWD, as compared to normal steady-state operation.

PART I
EXPERIMENTAL STUDIES
OF THE
EFFECT OF VISCOSITY
ON
STYRENE POLYMERIZATION KINETICS.

1. THEORY OF FREE RADICAL POLYMERIZATION KINETICS

1.1 Conventional Kinetics

The kinetic mechanism of free radical polymerization at low monomer conversions has been well established (5) (6). The reaction steps involved are: 1) initiation, 2) propagation, 3) chain transfer and 4) termination. These reaction steps may be described as follows:

	<u>Reaction Steps</u>	<u>Rate Constants</u>
<u>Initiation</u>		
(1)	Catalyst $\rightarrow 2R_C^\circ$	k_d
(2)	$R_C^\circ + M \rightarrow R_1^\circ$	
<u>Propagation</u>		
(3)	$R_1^\circ + M \rightarrow R_2^\circ$ \cdot \cdot \cdot	k_p
	$R_r^\circ + M \rightarrow R_{r+1}^\circ$	
<u>Chain Transfer</u>		
(4)	$R_r^\circ + M \rightarrow P_r + M^\circ$	k_{fm}
(5)	$R_r^\circ + S \rightarrow P_r + S^\circ$	k_{fs}
(6)	$R_r^\circ + C \rightarrow P_r + C^\circ$	k_{fc}
(7)	$R_r^\circ + P_q \rightarrow P_r + R_q^\circ$	k_{fp}
<u>Termination</u>		
(8)	$R_r^\circ + R_q^\circ \rightarrow P_{r+q}$	k_t
(9)	$R_r^\circ + R_q^\circ \rightarrow P_r + P_q$	k_{td}

The termination reactions do not affect the total number of radicals present in the system, but may affect the resulting activity of the radicals formed. For this reason, the new radicals may affect the propagation and termination reactions in a slightly different manner.

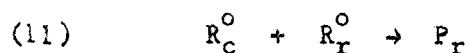
In styrene polymerization the termination of radicals is assumed to be by combination only, as represented by equation (8) and with negligible disproportionation.

1.2 Simplifying Assumptions

There are certain simplifying assumptions used when dealing with the polymerization of styrene. These are:

- 1) Reactivity of the radicals is independent of chain length.
- 2) Chain transfer to catalyst is negligible (6). This assumption eliminates equations (6) and (7).
- 3) The activity of radicals resulting from chain transfer is identical with all other free radicals.
- 4) The average chain length of radicals is large. This implies that consumption of monomer by initiation and chain transfer is very much smaller than by propagation.
- 5) The rate of change of concentration of free radicals is assumed much smaller than production or consumption rate of same. This is the stationary state hypothesis for free radicals.

Other steps which must be accounted for are recombination of primary radicals as follows:



The recombination in reaction (10) is accounted for by the use of an efficiency factor (f) related to the decomposition of catalyst in equation (1). The termination reaction (11) is usually ignored (6).

The validity of the above assumptions was shown experimentally by Tebbens (1). The use of the kinetic mechanism and assumptions above gave good agreement between experimental and theoretical conversions and MWD up to about a viscosity of about 10 centipoises.

It has been found (2) (7) (8) that these assumptions must be modified to predict polymerization in viscous media. There is also a solvent effect requiring modification of the assumption which identifies the transferred radicals with all other free radicals.

1.3 Corrections for Solvent Effect

The solvent effect gives reduced molecular weights as compared to those obtained in bulk polymerization. An extensive review of the solvent effect has been reported by Hui (2).

Corrections for the effect of solvent were applied to the kinetic equations outlined in Section 1.1 by Duerksen, Hamielec et al (9) (5). They applied the corrections reported by Henrici-Olivé and Olivé (10) (11).

Henrici-Olivé and Olivé postulated the formation of electron-donor-acceptor complexes between polymer radicals and solvent molecules. The competitive reactions between these complexes were believed to be the cause of the changes observed in k_t/k_p^2 . They proposed the following general equation correcting for the solvent effect:

$$(12) \quad \frac{(M)_{\text{bulk}}}{\phi_p(M)} = 1 + \frac{\tau_s(S)}{\tau_m(M)}$$

or

$$(13) \quad \frac{1}{\phi_p} = \frac{(M)}{(M)_{\text{bulk}}} + \frac{\bar{T}_s (S)}{\bar{T}_m (M)_{\text{bulk}}}$$

where

$$(14) \quad \phi_p = \frac{(k_t^{1/2}/k_p)_{\text{bulk}}}{(k_t^{1/2}/k_p)_{\text{solution}}}$$

\bar{T}_s/\bar{T}_m is a measure of the magnitude of the solvent effect. They proposed variation of k_p with concentration of solvent due to the electron complexes.

In the works of Duerksen, Hamielec et al, good agreement between experimental and theoretical results in CSTR and BSTR solution polymerizations were obtained by varying only k_t in the ratio $k_t^{1/2}/k_p$ rather than k_p as proposed by Henrici - Olivé and Olivé. An adjustment of k_p in this ratio gave identical results.

The adjustment of k_t for solvent concentration is used in all models employed in this investigation.

1.4 Corrections for Viscosity Effects

Polymerization of styrene in benzene solvent follows the conventional kinetic scheme as previously outlined up to about 10 centipoises viscosity. At higher conversions, the rate of polymerization rises more quickly. This phenomenon was first reported by Tromsdorff et al ⁽⁴⁾ in polymerization of methyl methacrylate initiated by benzoyl peroxide. It was observed that the rate of polymerization increased until it reached a maximum at about 70% conversion. This increase in polymerization rate was accompanied by a rise in molecular weight averages. These phenomena, often referred to as the "gel effect" may be explained in terms of relative rates of propagation and termination reactions. Either the termination

rate decreases or the propagation rate increases relative to the remainder of the reactions taking place.

Hui (2) has developed the background for the present interpretation of the gel effect. The works of Rabinowitch (12), Vaughan (13), Robertson (14), Benson and North (15) (16), and De Schrijver and Smets (17) were reviewed and the conclusions were drawn that the termination reaction becomes diffusion controlled at high viscosities, while the propagation rate remains virtually unchanged over a 1000 - fold change in viscosity. It was found by De Schrijver and Smets (17) in their studies of the decomposition of azobisisobutyronitrile in viscous media that there was an increase in the formation of waste product dimethyl-N-cyanoisopropylketenimine. They indicated an appreciable decrease in catalyst efficiency.

There is insufficient kinetic data available, however, to make direct application of these proposals to kinetic models.

1.5 Present Interpretation of Kinetics

Part I of this work is concerned with the prediction of conversions and MWD in both CSTR and BSTR systems using styrene in benzene, initiated by azobisisobutyronitrile (AZO).

The complete set of Arrhenius equations selected from the literature (9) for the particular rate constants is given below:

$$k_d = 1.58 \times 10^{15} \text{ EXP } (-15500/T)$$

$$k_p = 1.051 \times 10^7 \text{ EXP } (-3557/T)$$

$$k_{fm} = 2.31 \times 10^6 \text{ EXP } (-6377/T)$$

$$k_{fs} = 9.95 \times 10^{10} \text{ EXP } (-11000/T)$$

$$k_t = 1.255 \times 10^9 \text{ EXP } (-844/T)$$

$$k_{td} = 0.0$$

An initial catalyst efficiency of 0.6 has been assumed for all reaction conditions studied.

The derivation of the kinetic equations will not be included here, but may be found in the literature (1) (6) (2).

1.6 Equations Describing the CSTR System

The chemical reactions describing the mechanism of the polymerization reactions (equations 1-11, section 1.1) and the assumptions listed in Section 1.2 lead to the equations for the CSTR system.

In the CSTR the general mass balance holds for all components.

Accumulation = Flow in - Flow out - loss by reaction.

At steady state the accumulation is zero.

The steady state equations for the components in a monomer-solvent-catalyst polymerization are as follows:

Catalyst

$$(15) \quad (C) = (F_c / VQ W_c) / (1 + k_d V/VQ)$$

$$I = \text{initiation rate} = 2fk_d(C)$$

Total Radical

$$(16) \quad (R^{\circ}) = ((1 + 4Ik_t(V/VQ)^2)^{\frac{1}{2}} - 1) / (2k_t V/VQ)$$

$$(17) \quad (R^{\circ}) = \sum_{r=1}^n (R_r^{\circ})$$

Monomer

$$(18) \quad (M) = (F_m VQ / W_m - IV / VQ) / (1 + V/VQ(k_p + k_{fm})(R^{\circ}))$$

$$(19) \quad (PR) = \frac{(I + (S)k_{fs} + (M)k_{fm})(R^{\circ})}{(M)(k_p + k_{fm}) + k_{fs}(S) + k_f(R^{\circ}) + VQ/V}$$

$$(20) \quad (R_1^{\circ}) = \frac{I + (k_{fs}(S) + k_f(M))(R^{\circ})}{k_p(M) + k_{fs}(S) + k_f(M) + k_t(R^{\circ}) + VQ/V}$$

The probability of propagation is the term used to determine the probability whether a polymer free radical will propagate rather than disappear through transfer, termination or loss in the reactor effluent. The probability of propagation (Z) is given by the following:

$$(21) \quad Z = \frac{k_p(M)}{k_p(M) + k_{fs}(S) + k_f(M) + k_t(R^{\circ}) + VQ/V}$$

The concentration of polymer free radicals containing r monomer units is obtained from the recursion relationship:

$$(22) \quad (R_r^{\circ}) = Z^{r-1} (R_1^{\circ})$$

The mass balance equation for dead polymer containing r monomer units is:

$$(23) \quad (P_r) = (k_{fs}(S) + k_f(M))(R^{\circ}) V/VQ + 1/2k_t(V/VQ)(R_1^{\circ})^2 (r-1)Z^{r-2}$$

where $r \geq 2$

The differential MWD (weight fraction WF_r as a function of polymer chain length r) is given by:

$$(24) \quad WF_r = r(P_r) / ((M_0) - (M))$$

The number and weight average molecular weights, \overline{M}_n and \overline{M}_w , of the dead polymer are:

$$(25) \quad \overline{M}_n = \frac{\sum_{r=2}^{\infty} r P_r}{\sum_{r=2}^{\infty} P_r}$$

$$(26) \quad \overline{M}_w = \frac{\sum_{r=2}^{\infty} r^2 P_r}{\sum_{r=2}^{\infty} r P_r}$$

The monomer conversion is given by:

$$(27) \quad X_m = (M_0 - M) / M_0$$

1.7 Equations Describing the BSTR System

The same chemical equations and simplifying assumptions were used for the BSTR system as for the CSTR. The system differs, however, in the fact that the BSTR is in a transient condition.

The equations describing the BSTR are given below:

Initiation Rate

$$(28) \quad I = 2k_d f(C_o) \text{EXP}(-k_d t)$$

The stationary-state assumption for free radicals gives

$$(29) \quad (R^\circ) = (I/k_t)^{1/2}$$

Monomer Concentration

$$(30) \quad \frac{-dM}{dt} = k_p(M)(R^\circ)$$

Monomer Conversion

$$(31) \quad \frac{dx}{dt} = k_p(1-x)(2k_d f(C_o) \text{EXP}(-k_d t)/k_t)^{1/2}$$

Polymer of Chain Length r

$$(32) \quad \frac{dP_r}{dt} = (k_{fs}(S) + k_{fm}(M))(R_r^\circ) + k_{td}(R_r^\circ)(R^\circ) + 1/2k_t \sum_{n=1}^{r-1} (R_n^\circ) (R_{r-n}^\circ)$$

The probability of propagation factor for the BSTR system is given by the following equation:

$$(33) \quad Z' = \frac{k_p(M)}{k_p(M) + k_{fs}(S) + k_{fm}(M) + I^{1/2}(k_t)^{1/2}}$$

Using Z' , equation (32) becomes

$$(34) \quad \frac{dP_r}{dt} = (R^\circ)(1-Z')(Z')^{r-1} (k_{fs}(S) + k_{fm}(M_o)(1-x) + (R^\circ) \left(\frac{(r-1)k_t(k_{fs}(S) + k_{fm}(M_o)(1-x) + I^{1/2}(k_t)^{1/2})}{2k_p(M_o)(1-x)} + k_{td} \right))$$

The equations (28) and (34) describe the BSTR system. When viscosity corrections to k_t and f are made, as outlined in Section 1.4, the equations containing these factors cannot be integrated analytically. If these factors are assumed constant over a small time interval the following analytical solution is obtained for equation (31).

$$(35) \quad x_2 = 1 - \text{EXP}(\ln(1-x_1) + 2k_p \left(\frac{2f(C_0)}{k_d k_t} \right)^{\frac{1}{2}} (\text{EXP}(-k_d t_2/2) - \text{EXP}(-k_d t_1/2)))$$

2. EXPERIMENTAL

2.1 General Description

The polymerization of styrene in benzene initiated by azobisisobutyronitrile was studied experimentally. There were four experiments carried out in a CSTR system and four experiments in a BSTR system. All experiments were designed to yield information about polymerization rates and MWD at high viscosities. The conditions of the experiments are given in Table 1.

The conversion of monomer was determined gravimetrically. The weighed sample, diluted with dioxane if necessary, was poured slowly into a 10-20 - fold excess of methanol precipitating the polymer. The polymer was left covered for approximately 12 hours, then filtered and dried in a vacuum oven at approximately 40°C, for 12 hours. The dried polymer was weighed to determine conversion, and injected into the gel permeation chromatograph (GPC) to measure MWD. The Newtonian viscosity was measured on another portion of reaction sample with a Brookfield viscometer.

Azobisisobutyronitrile (Eastman Organic Chemicals) was recrystallized once from methanol. Benzene (Fisher Scientific certified grade) was used without further treatment. Uninhibited styrene was obtained from Polymer Corporation (Sarnia, Ontario) and was used without further purification. Samples of styrene were treated with an excess of methanol to determine whether polymer was present.

TABLE 1
REACTION CONDITIONS FOR EXPERIMENTS

CSTR	Monomer Conc. wt%	Solvent Conc. wt%	Catalyst Conc. wt%	Temp. °c	Residence Time (hr)
102 (a)	89.68	9.922	0.3986	85	3.318
(b)	89.68	9.922	0.3986	85	2.054
103 (a)	89.72	9.883	0.3963	85	2.50
(b)	89.72	9.883	0.3963	85	2.96
BSTR					
104	59.82	39.76	0.4074	75	
105	60.42	38.77	0.8021	75	
107	89.40	10.20	0.4064	85	
108	89.03	10.18	0.7867	75	
Temperature controlled to $\pm .2^{\circ}\text{c}$ Pressure = 1 atmosphere					

2.2 Apparatus and Procedures

CSTR

The CSTR reactor system is shown schematically in Fig. (1).

The reactor used is an enclosed stainless steel vessel, 3 inches in diameter and 4 inches in cylindrical height, with a hemispherical bottom. The reactor has four baffles placed at right angles. A turbine type impeller was located in the centre of the vessel approximately one-third from the bottom of the reactor. The feed and outlet pipes were located as shown in Fig. (1).

The vessel was kept under nitrogen pressure as shown. Temperature control of the reaction mixture was achieved between limits $\pm .2^{\circ}\text{c}$ by keeping the reactor in a constant temperature bath. The bath temperature was changed manually to control the temperature of the reaction mixture, which was indicated by a thermometer in the reactor.

The impeller speed in the reaction vessel was kept constant at 300 r.p.m. by a constant speed stirrer.

All piping joints were sealed by teflon gaskets.

The reaction mixture was prepared by weighing the correct amounts of monomer, solvent, and initiator into a feed mixing vessel, where they were thoroughly mixed while being kept under nitrogen pressure. The mixture was then forced into a refrigerated storage vessel by this nitrogen pressure. The storage vessel was kept at approximately 5°c throughout the period of a CSTR run. From the refrigerated feed storage tank, the feed mixture was pumped by a positive displacement metering pump into the reaction vessel. Samples were taken from the reactor effluent after

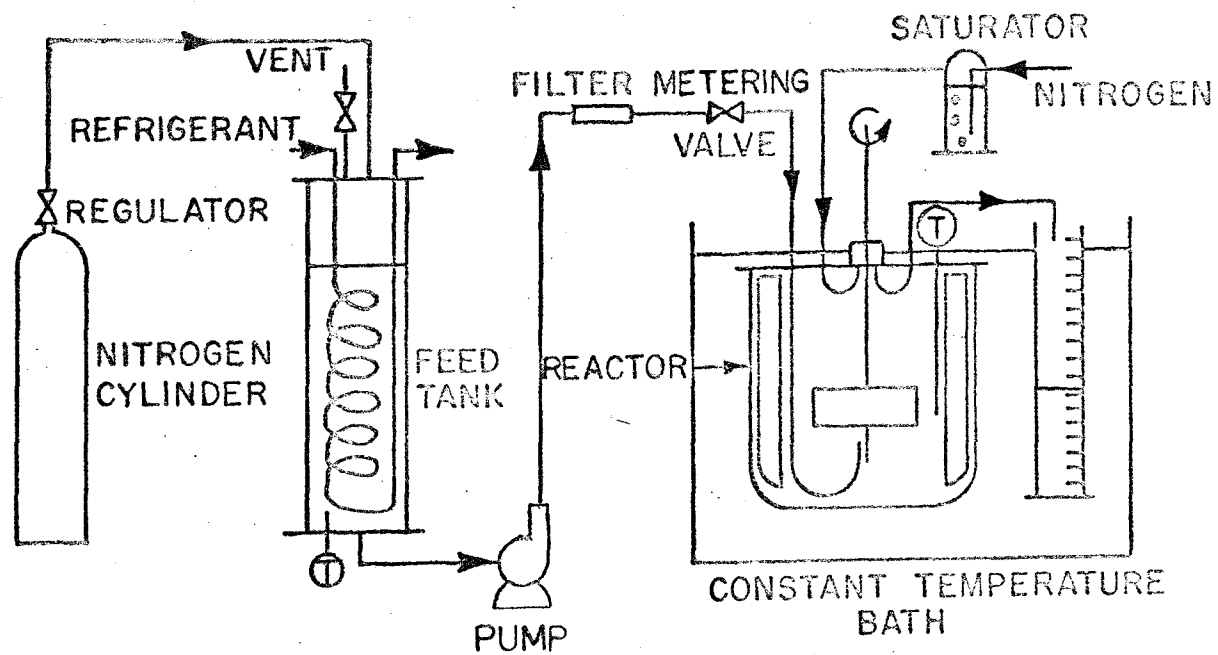


Figure 1. CSTR Reactor System

four reactor volumes had been displaced.

After one steady state had been reached, the flow rate to the reactor was changed and samples were taken periodically until the second steady state was reached. In this manner two steady state experiments were done using one feed mixture.

BSTR

The BSTR reactor system is shown schematically in Fig. (2).

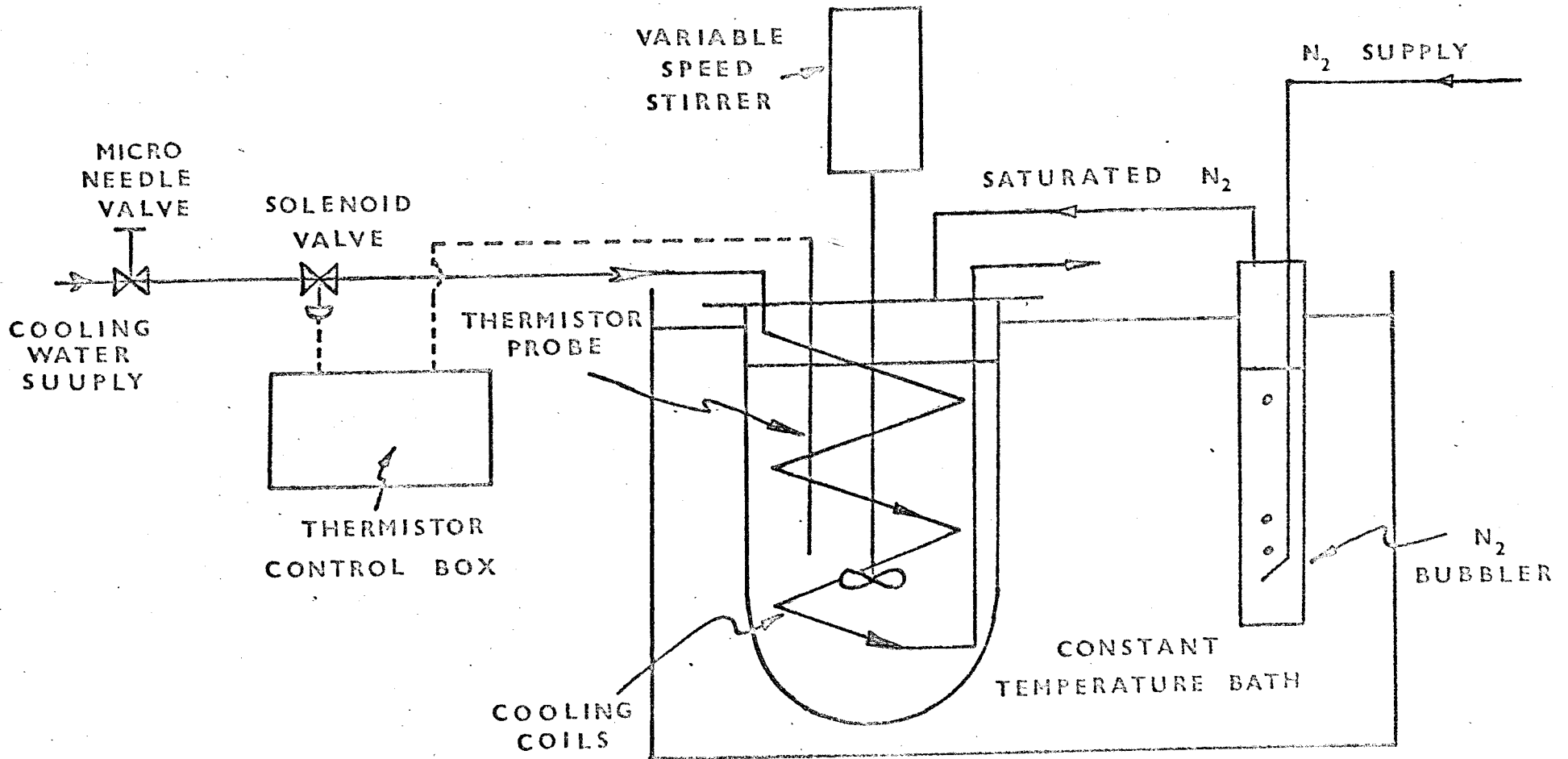
The BSTR reaction vessel was similar to that used in the CSTR system. Temperature control was achieved by the use of a thermocouple immersed in the reaction mixture, which allowed the use of a controller to control the flow of cooling water circulating in the coil inside the reactor. Control was on-off type to $\pm .2^{\circ}\text{C}$. The reaction mixture was kept stirred by a four bladed turbine-type impeller rotated at 300 r.p.m. by a constant speed stirrer. The reaction vessel was immersed in a constant temperature bath controlled at approximately 5°C higher than the reaction temperature. Nitrogen pressure was kept on the reaction vessel at all times.

The catalyst, solvent, and monomer were weighed separately to the reaction concentration. The solvent and catalyst were added to the reaction vessel, and brought to reaction temperature. The monomer was brought to reaction temperature in a separate vessel, and added to the reactor as soon as reaction temperature was reached.

Time zero was recorded when all the styrene had been transferred to the reactor.

Samples were taken periodically by forcing some of the reaction

Figure 2. BSTR Reactor System



mixture out of the reactor with nitrogen pressure.

2.3 The Gel Permeation Chromatograph

Several modifications to the instrument at McMaster University were recently carried out. A digital translator supplied by Waters Associates was installed, enabling the chromatogram heights and elution indicators to be punched onto paper tape. This taped information was then base-line corrected and processed with calibration curves determined by Duerksen to obtain frequency distributions (18). Corrections for imperfect resolution were made using the polynomial expansion method of Tung (19) (20). Resolution factors were obtained by the reverse-flow method.

The GPC conditions used were:

Solvent	Tetrahydrofuran
Flow Rate	2.0 ml/min
Temperature	22 - 24°c
Injection Time	30 sec. and 60 sec.
Sample Concentration	0.1 wt. %

3. RESULTS AND DISCUSSION

3.1 CSTR

The experimental results of CSTR Experiments 102 and 103 are shown in Figures (3) and (4). The transient results measured on the second steady state of each of the experiments show that steady state has been attained. The scatter in the data, especially in Experiment 103 is probably due to poor control of the liquid flow rate to the reactor at high viscosities. Some of the fluctuations in flow are probably due to imperfect mixing and segregated flow. Fluctuations in exit viscosity cause fluctuations in flow resistance and therefore flow rate.

As is indicated in Section 1.4 there is strong evidence that the termination rate constant and the catalyst efficiency are functions of viscosity. Duerksen has developed a method of searching for rate constants to give optimum agreement between experimental conversions and MWD with those predicted using conventional kinetic equations (see section 1.5)⁽³⁾.

The methods developed by Duerksen were applied in this work in the following manner: The experimental conversions were corrected for thermal polymerization and a computer program, based on the kinetic equations in Section 1.5, was used to calculate conversions as a function of the ratio $\frac{k_t f_i}{k_{ti} f}$. The value of $\frac{k_t f_i}{k_{ti} f}$ at which predicted and measured conversions agree was used in a Fibonacci search program to calculate the values of k_t and f which will give the minimum value of the function:

Figure 3. Conversion and Viscosity versus Time

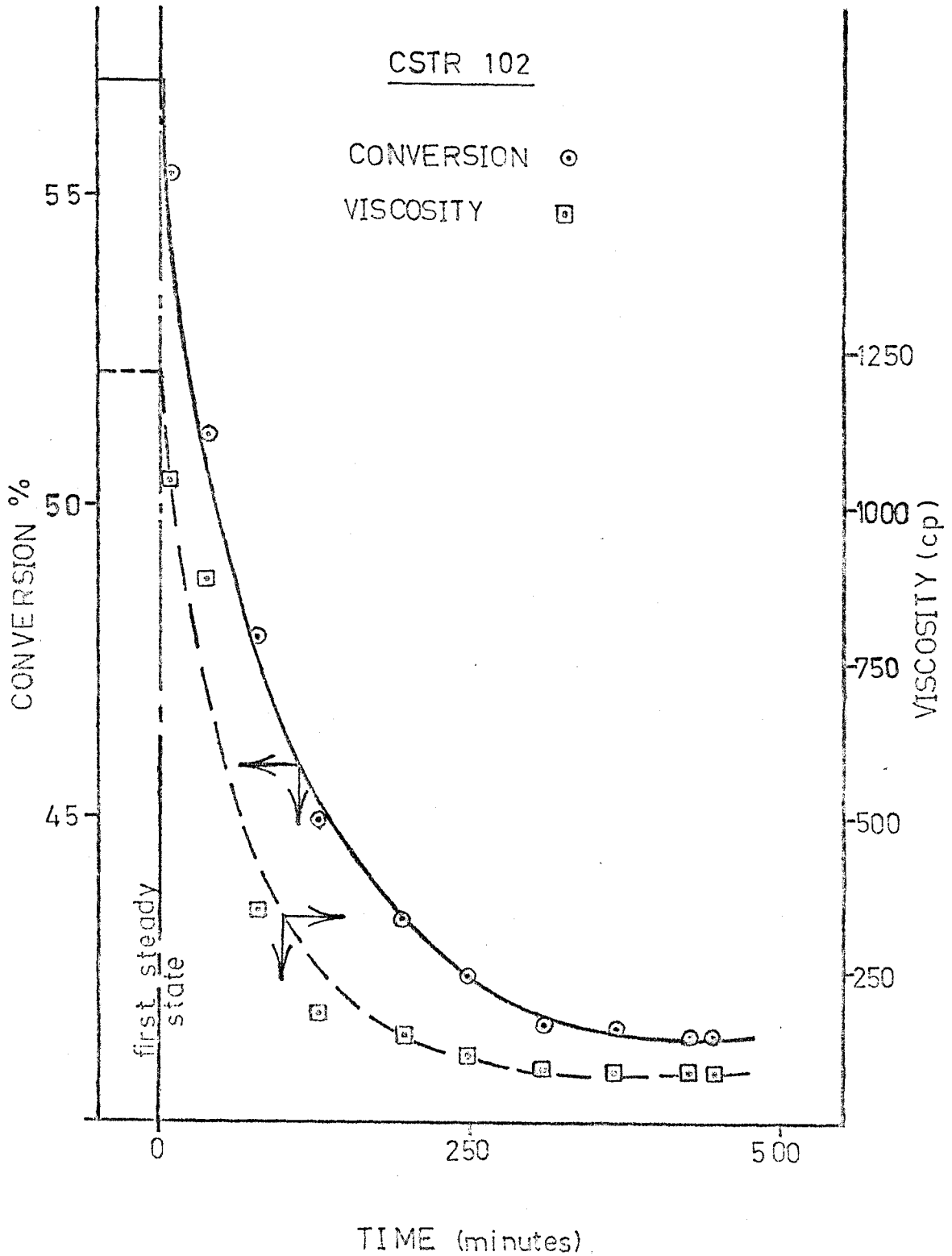
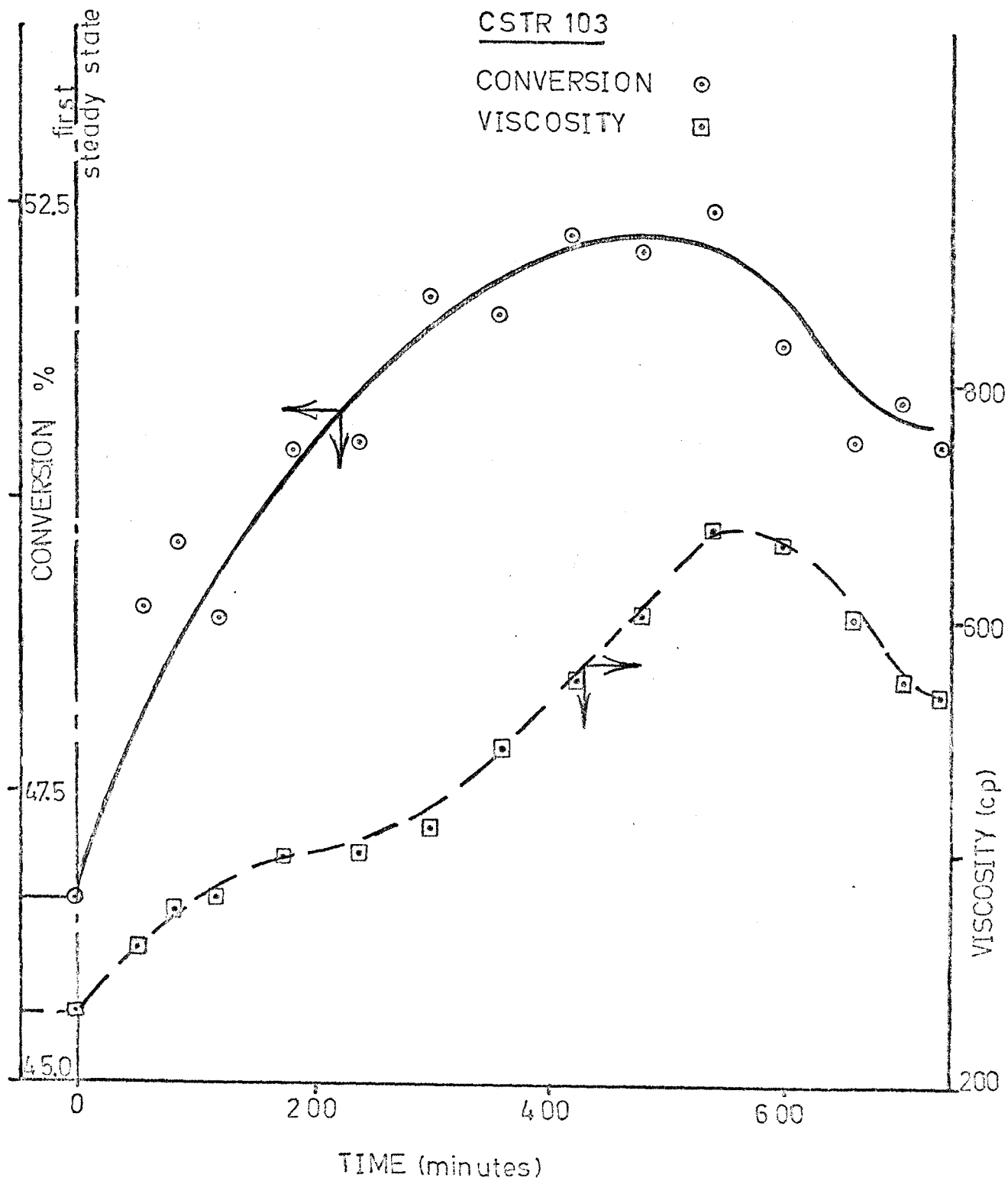


Figure 4. Conversion and Viscosity versus Time



$$(36) \quad F = \left((\overline{M}_n)_{\text{experimental}} - (\overline{M}_n)_{\text{theoretical}} \right)^2 + \left((\overline{M}_w)_{\text{experimental}} - (\overline{M}_w)_{\text{theoretical}} \right)^2$$

Using the above technique, the values of k_t and f listed in Table 2 were calculated. These results are also indicated in Figures (3) and (4) where they are shown as k_t/k_{t1} and f/f_1 plotted versus viscosity.

The data of Figures (5) and (6) were regressed, resulting in the following correlation equations.

$$(37) \quad \log k_t/k_{t1} = -0.0515 \log (1 + \text{vis}) - 0.0455 (\log (1 + \text{vis}))^2$$

$$(38) \quad \log f/f_1 = -0.0166 \log (1 + \text{vis})$$

These curves are shown in Fig. (10).

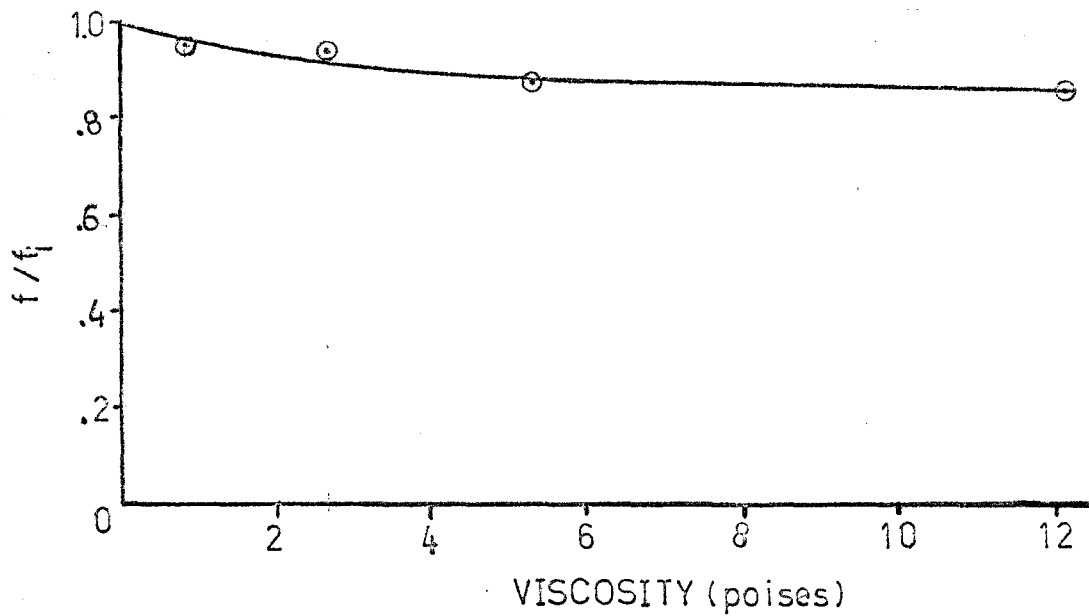
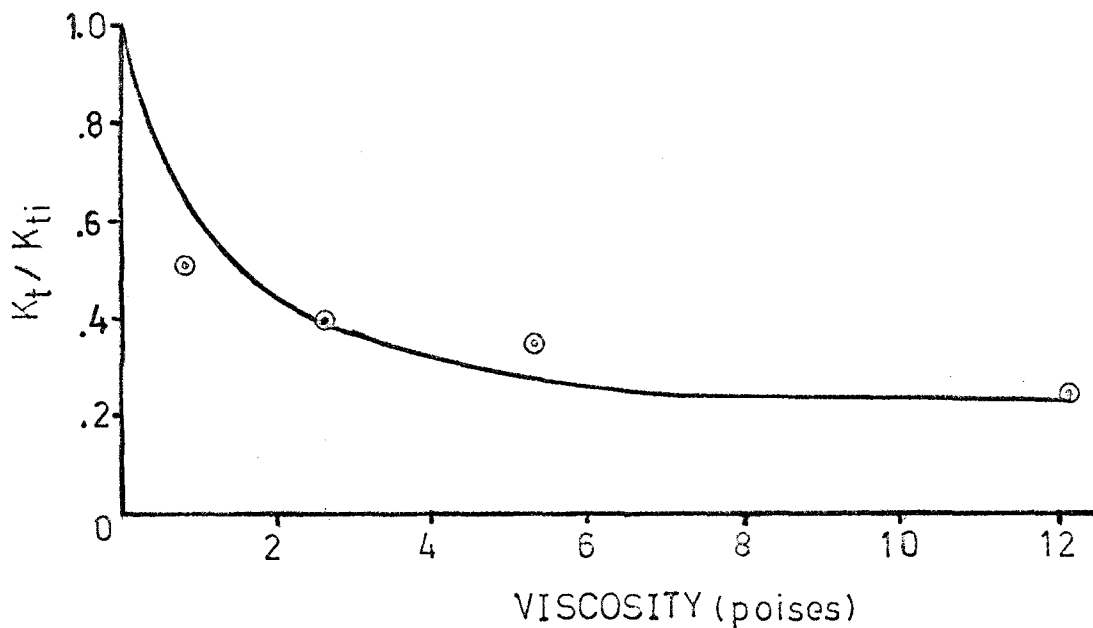
The experimental and theoretical MWD's are shown in Figures (7), (8) and (9). It may be seen that the theoretical MWD's have lower $\overline{M}_w/\overline{M}_n$ ratios than the experimental. This difference is seen to be increasing with viscosity. The poor agreement may be due to some dependence of k_t on chain length at high viscosity. This effect would probably be a result of orientation of the active end of the long polymer molecules. Also, there is possibly some discrepancy in the results due to the difficulty of controlling steady flow to the reactor. Another factor which may be of importance is mixing. Imperfect mixing and segregated flow may cause unusually high molecular weights to occur and thus increase \overline{M}_w and the $\overline{M}_w/\overline{M}_n$ ratio.

3.2 BSTR

The experimental results of conversion versus time and viscosity versus time for Experiments 104, 105, 107, and 108 are shown in

TABLE 2
CSTR RESULTS

CSTR Sample	102 - 3	102 - 13	103 - 3	103 - 12	
Conversion (thermal corrected)	.577	.406	.455	.493	
Viscosity (cp)	1214.	80.4	260.	537.	
k_{tf_i} / k_{ti_f} (calculated)	.291	.531	.474	.421	
$k_t \times 10^{-8}$ (calculated)	0.315	0.642	0.563	0.465	
f (calculated)	.512	.571	.567	.522	
$\overline{M}_n (x 10^{-4})$	EXP.	4.76	3.75	3.77	4.46
	THEOR.	5.12	3.89	4.10	4.63
$\overline{M}_w (x 10^{-4})$	EXP.	8.04	5.99	6.43	7.15
	THEOR.	7.77	5.89	6.21	7.03

Figure 5. f/f_i versus Viscosity (CSTR results)Figure 6. k_t/k_{ti} versus Viscosity (CSTR results)

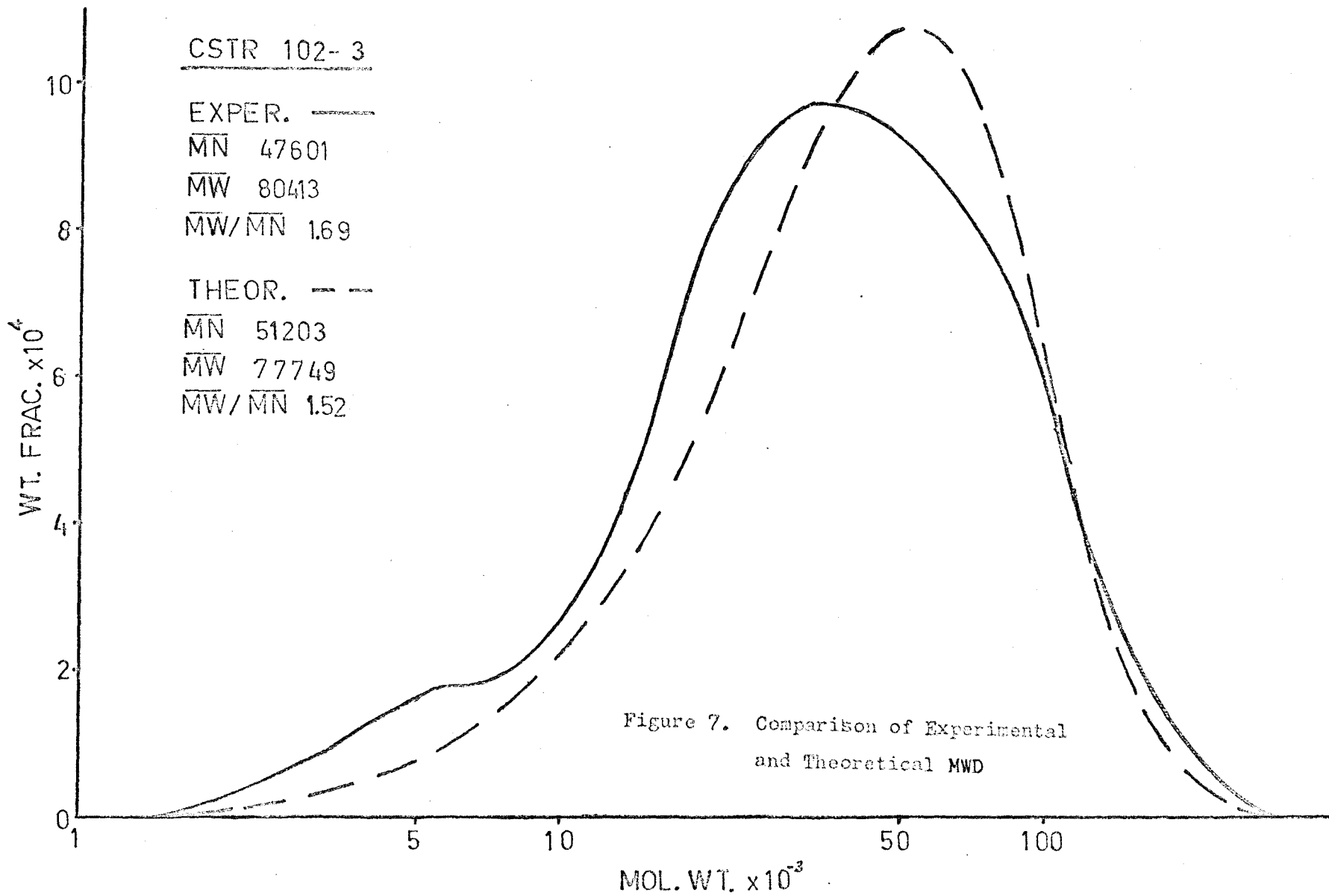


Figure 7. Comparison of Experimental and Theoretical MWD

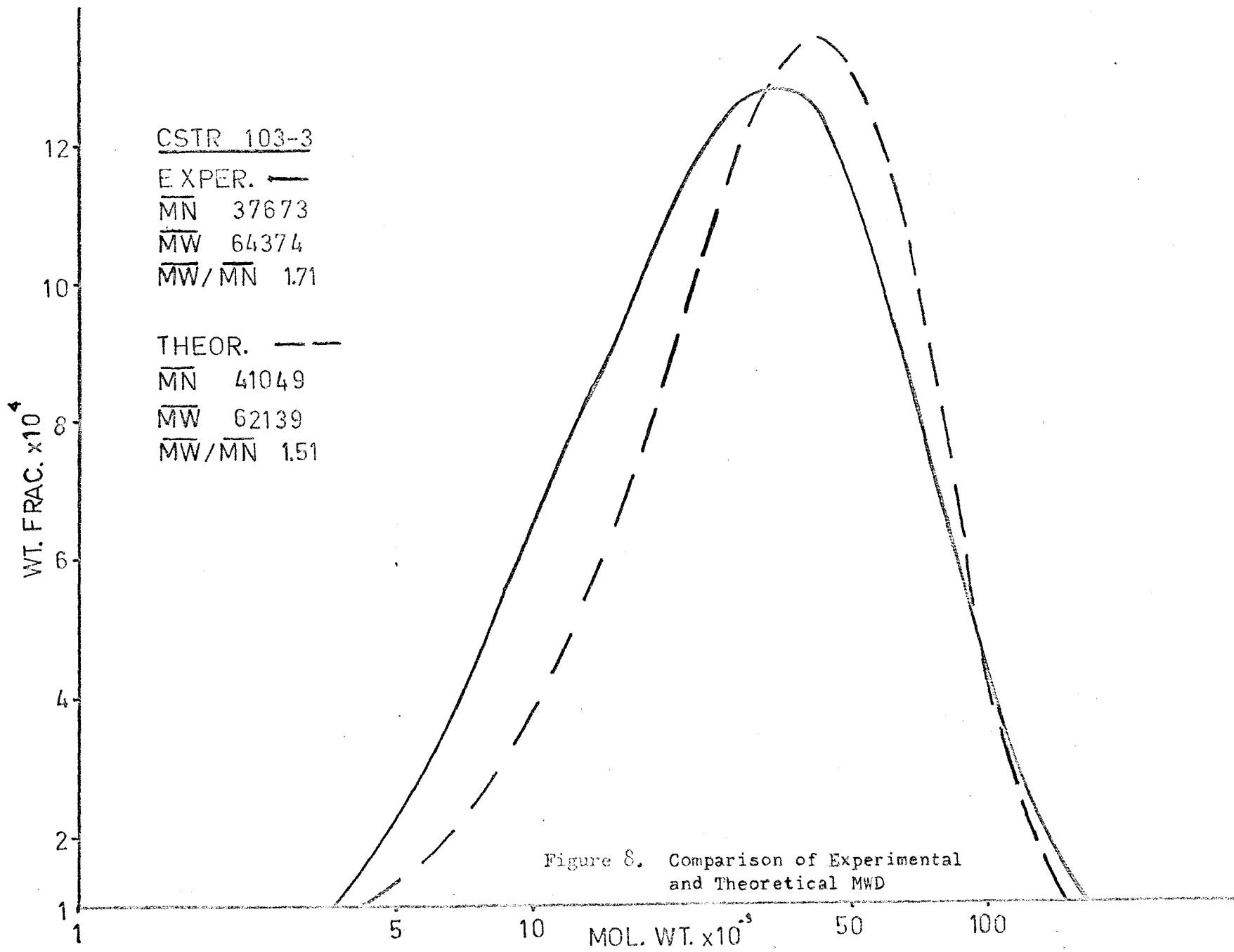


Figure 8. Comparison of Experimental and Theoretical MWD

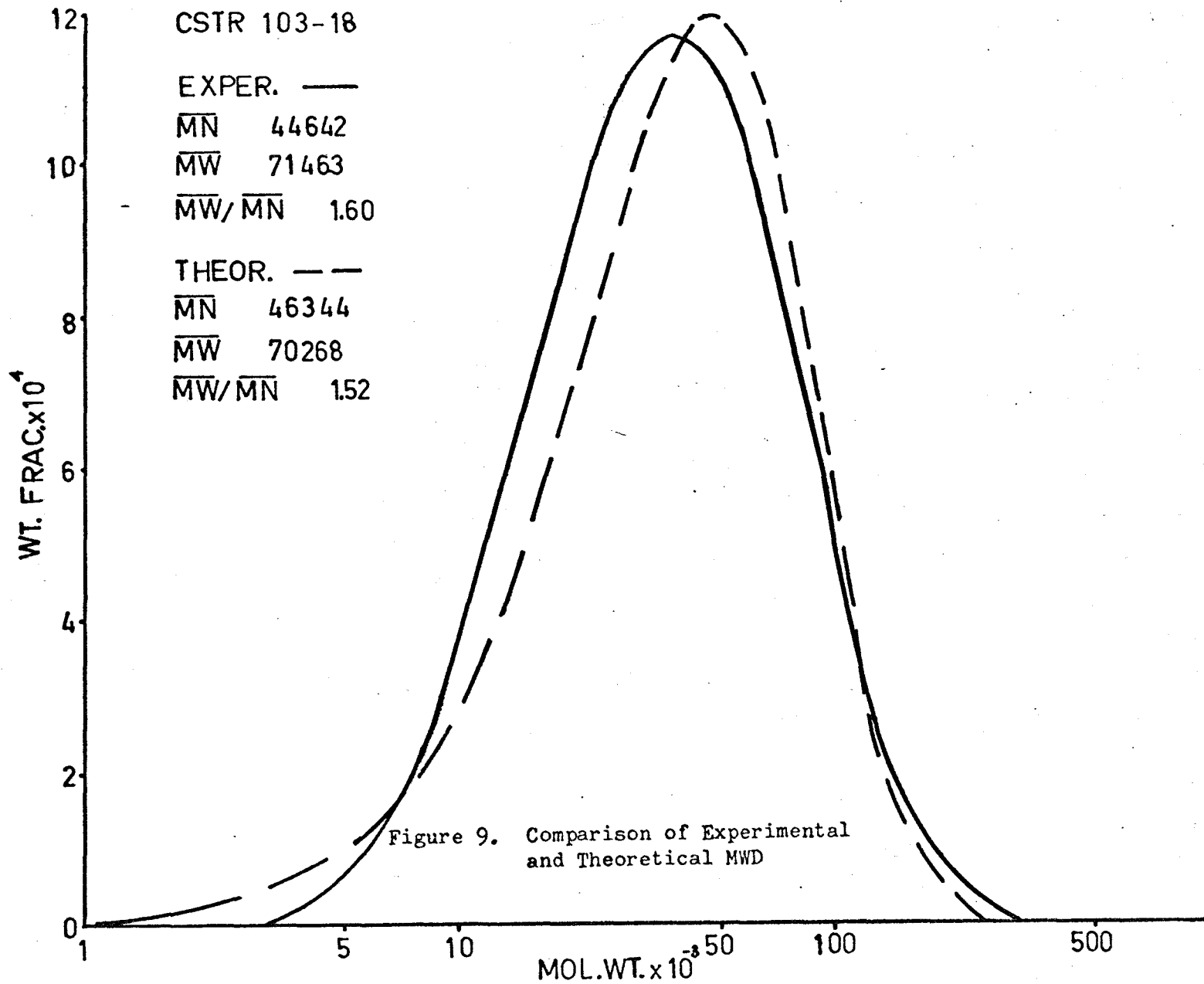
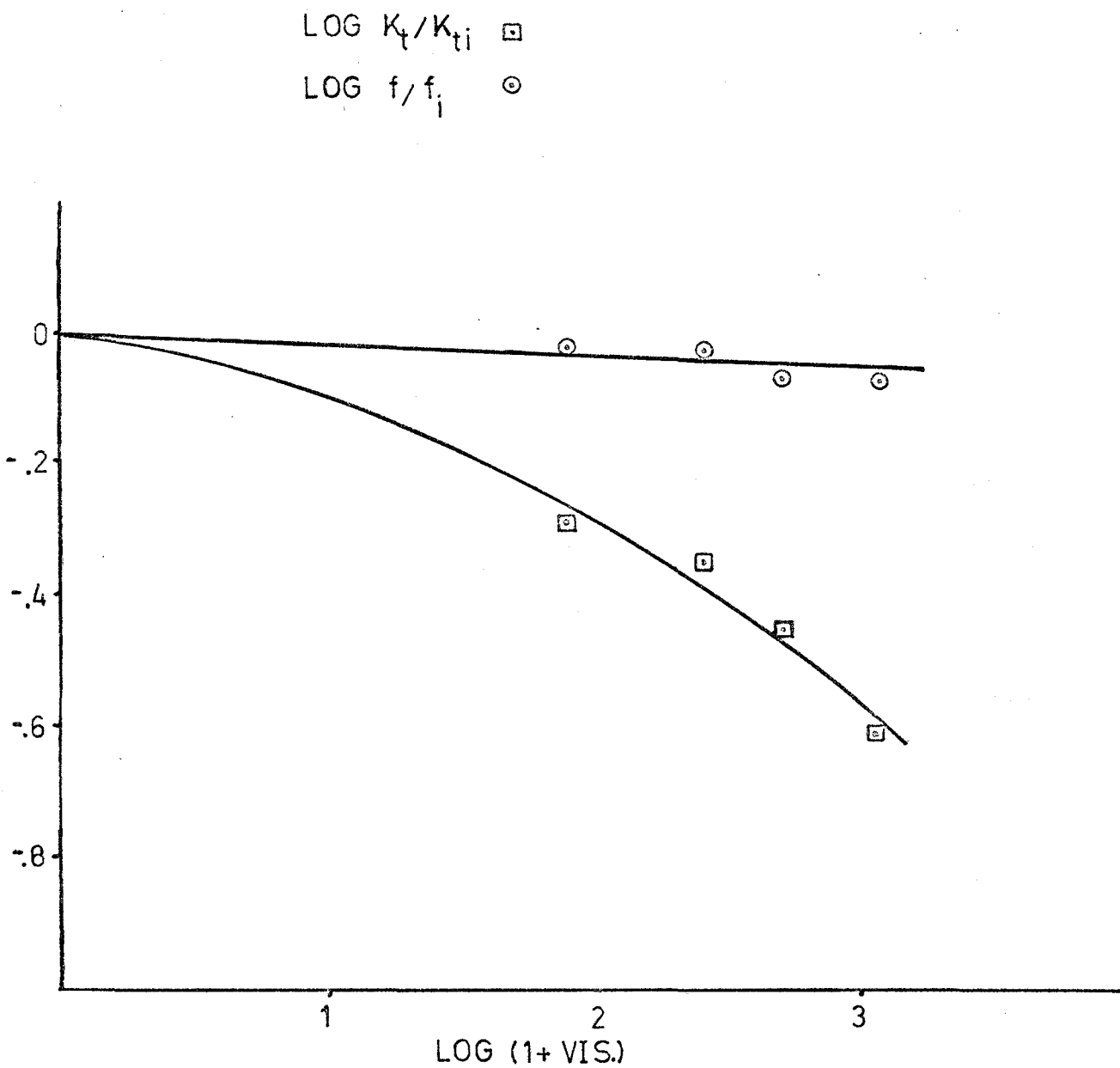


Figure 10
Regression Curves for $\log k_t/k_{ti}$ and $\log f/f_i$ versus Viscosity



Figures (11), (12), (13) and (14). In all these experiments it was noted that an increase in rate of conversion with time occurred simultaneously with a sharp increase in viscosity. This is evidence of the "gel" effect. The "gel" effect is not predicted by conventional kinetic equations as listed in Section 1.7 (eqns. 28-35). As previously stated, the effect may be explained by a decrease in the termination rate constant at high viscosity. A decrease in catalyst efficiency has also been proposed as a cause for the "gel" effect ⁽¹⁷⁾.

The conversion and MWD of each experiment, predicted by a computerized model based on the uncorrected kinetic relationships written by Tebbens ⁽¹⁾ and also by a model written by Hui ⁽²⁾ which corrects k_t and f as functions of viscosity, are shown in Figures (11), (12), (13) and (14). The experimental viscosities were used in the latter model.

The theoretical model with viscosity corrections, employing three different sets of correlation equations for $k_t f_i / k_{ti} f$ and f / f_i as functions of viscosity, were used, once for each of the three different viscosity correlation equations.

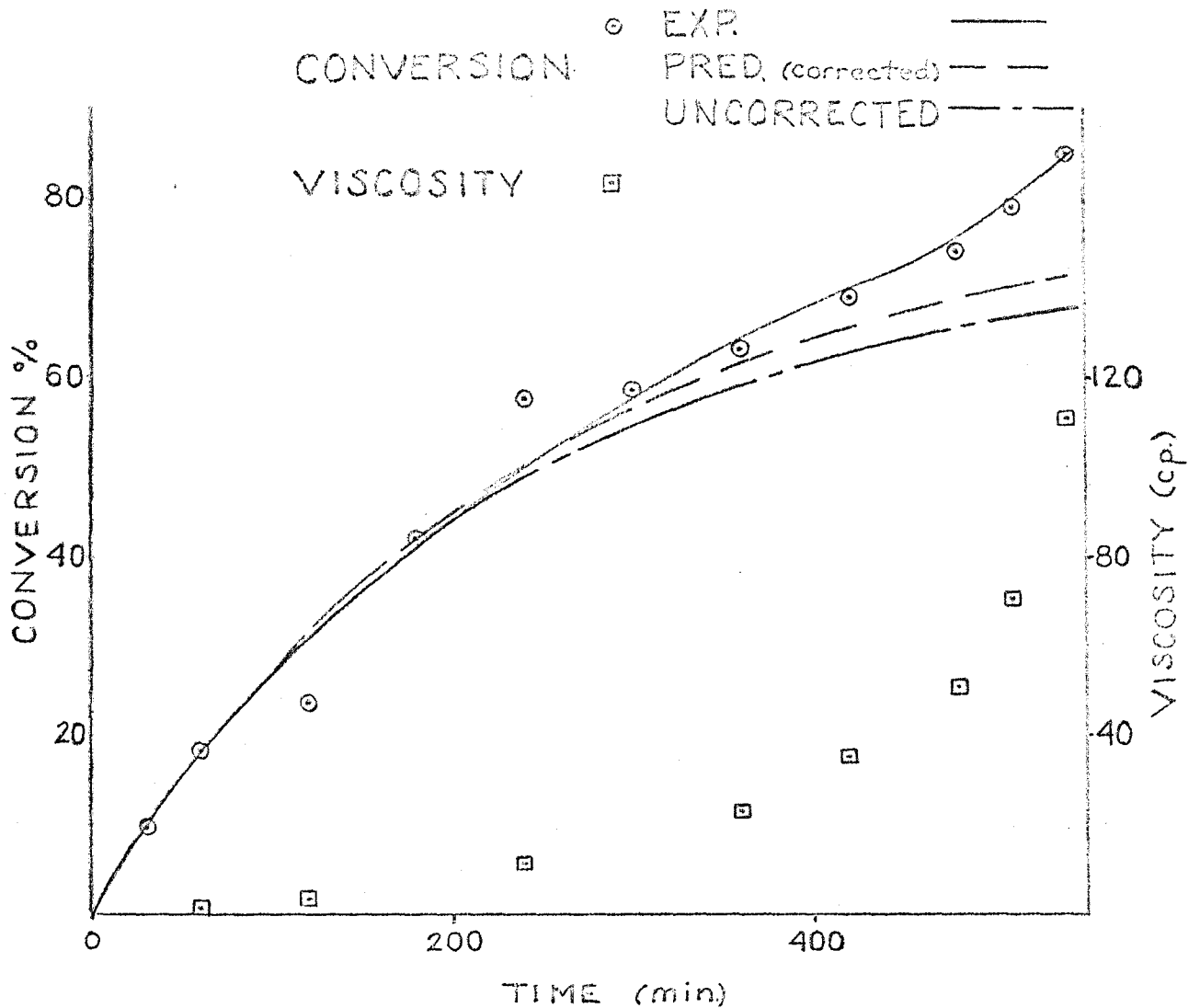
The results of these trials for Experiment 107 are shown, together with the experimental results and those calculated using no viscosity corrections, in Fig. (13). The correlation equation used for Case I was developed from CSTR experiments in this work; those for Case II were developed by Duerksen ⁽⁷⁾ for CSTR experiments using styrene and benzene and those for Case III were developed by Hui ⁽²⁾ for BSTR experiments using styrene and toluene.

The relationship between the reaction system and the viscosity

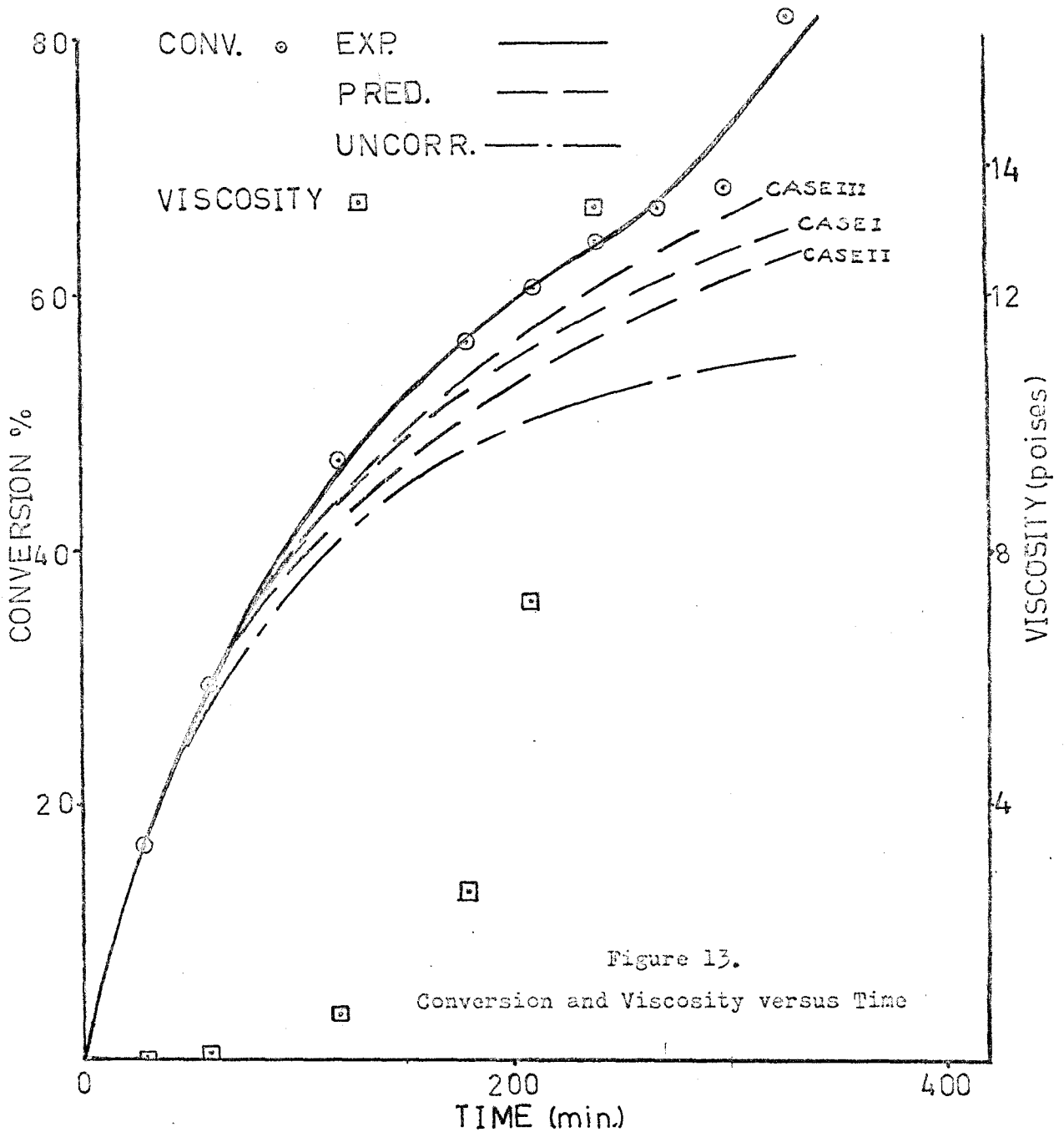
BSTR 105

Figure 12. Conversion and Viscosity versus Time

TIME	MOL. WTS. $\times 10^{-4}$					
	\overline{M}_N			\overline{M}_W		
	EXP	PRED	UC	EXP	PRED	UC
60	1.46	1.65	1.63	2.09	2.48	2.45
180	1.52	1.62	1.57	2.20	2.43	2.36
360	1.59	1.63	1.54	2.35	2.45	2.31
510	1.65	1.66	1.55	2.49	2.50	2.32



Time	$\overline{MN} \times 10^4$					$\overline{MW} \times 10^4$				
	EXP	CASE I	CASE II	CASE III	U.C.	EXP	CASE I	CASE II	CASE III	U.C.
60	2.29	2.74	2.79	3.32	2.72	3.38	4.13	4.19	5.07	4.09
120	2.69	3.17	3.09	3.95	2.81	4.34	4.93	4.77	6.55	4.28
180	2.98	3.45	3.40	4.47	3.02	4.76	5.65	5.67	8.32	4.71
240	2.84	3.69	3.66	4.74	3.14	5.57	6.56	6.89	9.54	5.07
300	3.38	3.85	3.79	4.82	3.23	6.56	7.37	7.63	9.89	5.43
360	3.68	3.89	3.80	4.82	3.27	7.33	7.65	7.72	9.92	5.60



effect on the kinetics is not very well understood. The mixing patterns in the two systems used here may have been of some importance, since the CSTR had baffles and the BSTR did not. The solvent used may also have had an effect since it is seen that the correlations used for the batch reactions in toluene do not predict results which agree with experiments done using benzene as solvent.

The difference in the results of Case I and Case II was expected, since the correlating equations differ quite markedly. The k_{tf_1}/k_{t_1f} ratios agree fairly closely, but there is a great difference in the f/f_1 ratios from Case I to Case II. It should be noted that for both Case I and Case II the values above viscosities of 1000 centipoises were not verified experimentally and the use of the correction equations above that value should not be considered reliable. Another factor which should be considered is that for Case II only one experiment was done for viscosities above 300 centipoises (7). Since the conditions used to determine the k_t and f variation with viscosity in Case I were obtained at viscosities in the range of 80-1000 centipoises, the data should apply in that range.

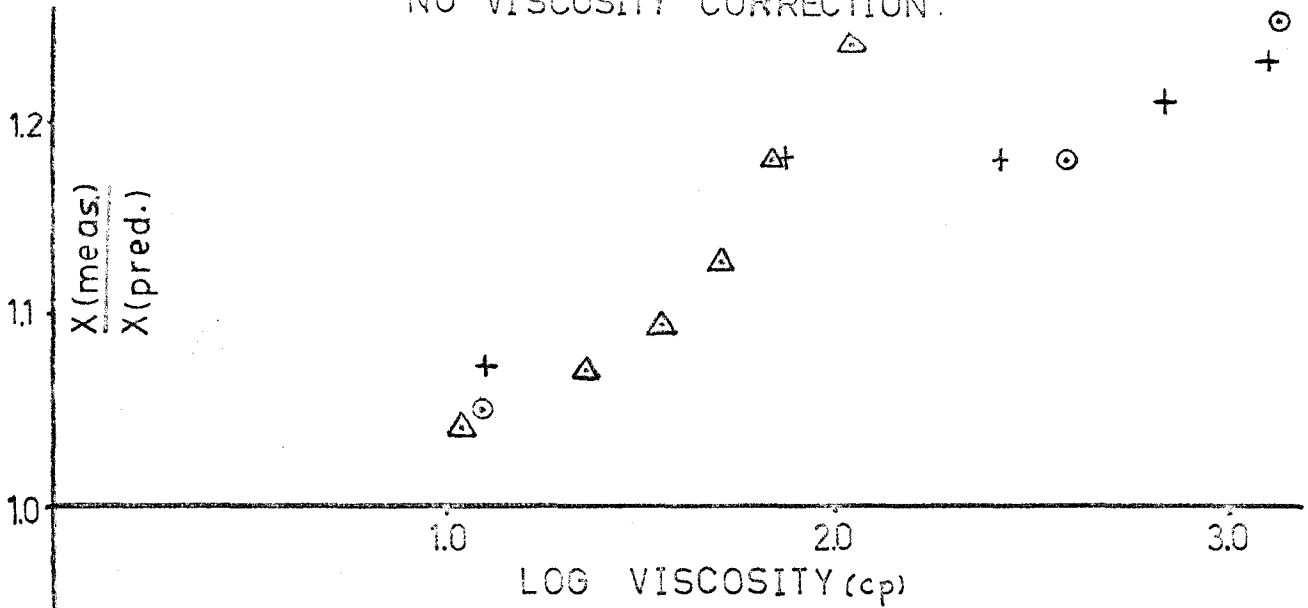
In Experiment 107, a viscosity of 1000 centipoises occurs at approximately 225 minutes. Conversion and molecular weight data up to that time show quite favorable agreement for both Case I and Case II, although Case I predictions are somewhat better for conversion. Up to the time of 225 minutes the conversions predicted by Case I agree to within 8% and the molecular weights to within 20%.

Figures (15) and (16) summarize the results of viscosity corrections to the BSTR data. The conversions have been predicted to within 20% of the measured values for all the experiments, and to within 10% of the experimental results for Experiments 107 and 108. The poor results for Experiments 104 and 105 occurred at the high range of conversion (see Figures (11) and (12)), and there appeared to be a stronger dependence of conversion on viscosity at that high region. It is possible that changes in rate constants other than those proposed here are affecting the results at this range of conversion.

One of the rate constants which could be changing is the propagation constant k_p . There is a strong possibility that rate of migration and proper orientation of the monomer molecules to reactive sites on the long polymer radicals is little affected at low viscosities, while it could be quite strongly affected at high viscosities. Since the correlating equations of k_t and f with viscosity are developed at high viscosity for Case I, they would include any effect of a decrease in k_p . When these correlations are applied to the low viscosity situation, where k_p should not be affected, they predict erroneous results since they are including a decrease in k_p .

The molecular weights are shown in Fig. (16) both before and after corrections for viscosity effects. It was found that the corrections used for k_t and f tended to over-correct the molecular weights, and in some cases the molecular weights calculated without viscosity correction were higher than those measured. This suggests that some degradation of polymer may have taken place - perhaps due to shearing of the molecules.

NO VISCOSITY CORRECTION.



- BSTR 104
- △ BSTR 105
- + BSTR 107
- ⊙ BSTR 108

Figure 15.
Comparison of Measured
and
Predicted Conversion

VISCOSITY CORRECTED
BASED ON CSTR RESULTS

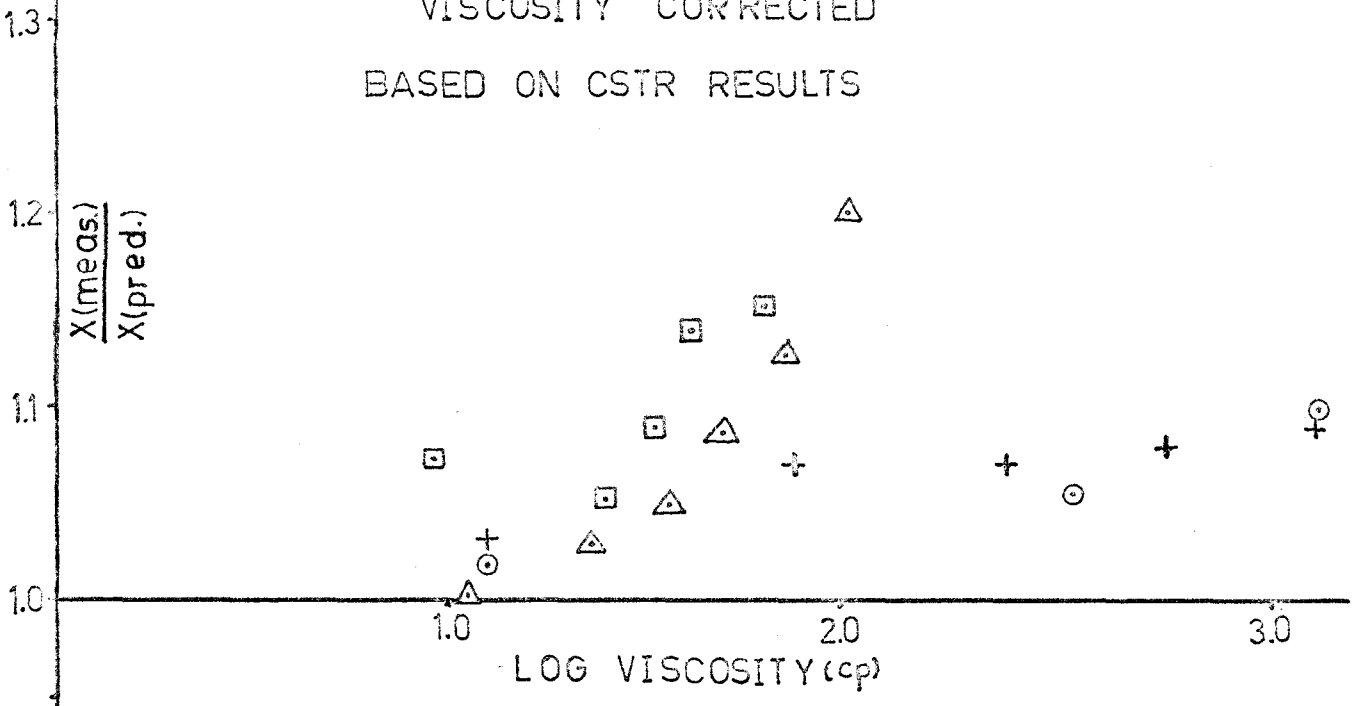
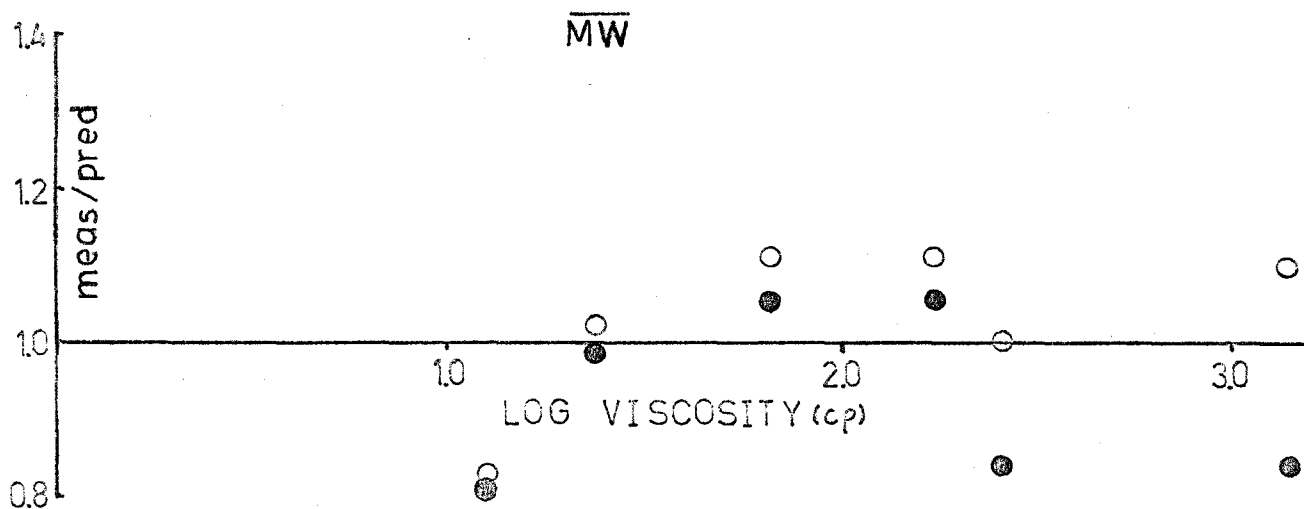
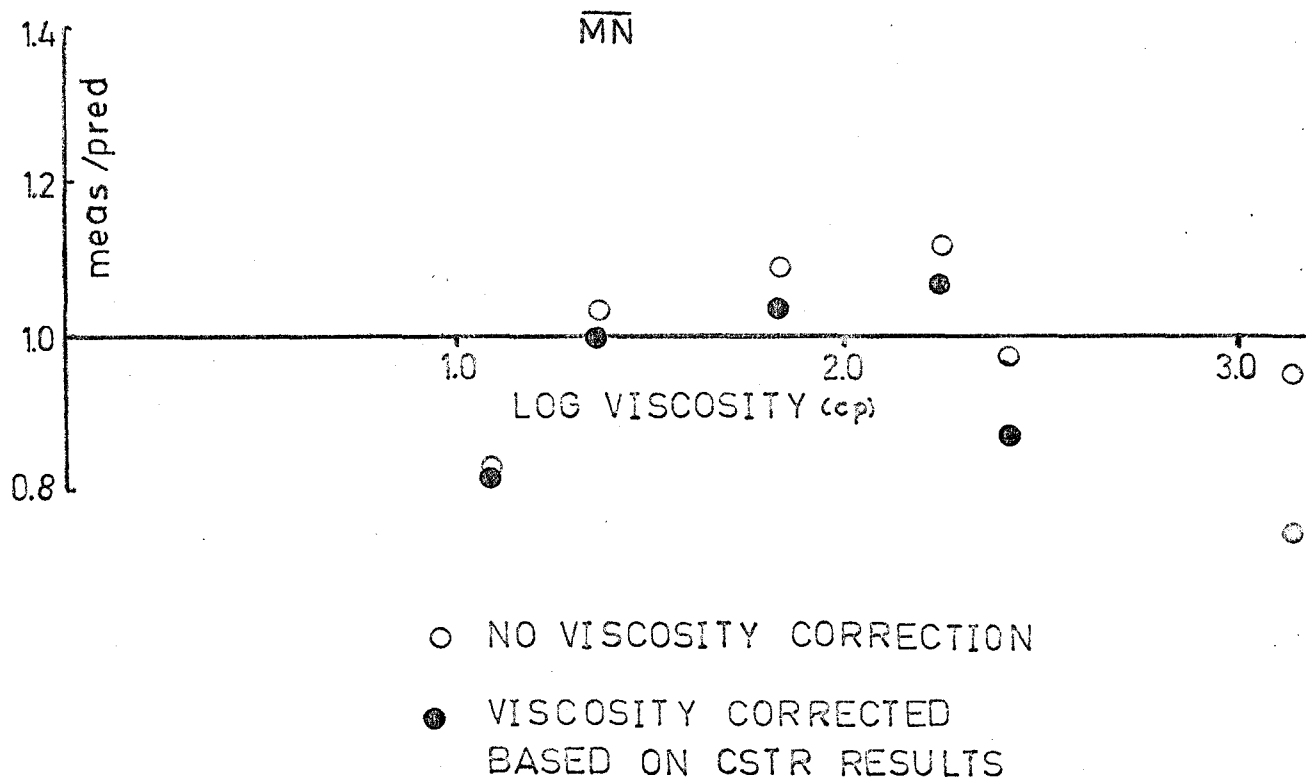


Figure 16.
Comparison of Measured and Predicted
Average Molecular Weights



There were sources of uncertainty in the results. The styrene used in these experiments had been stored for a number of months and may have had impurities dissolved in it during that time.

The means of measuring viscosities may also have been a source of errors, since the instrument used was not sufficiently reliable to determine accurate measurements at high viscosities (above 500 centipoises). There may have been non-uniform temperatures in the reactor causing deviations in both conversion and molecular weight.

There may have been errors in the predicted results due to the method of calculation. The values of k_t and f were assumed constant over a time increment during the calculation by the computerized model. Since the viscosity was found to increase very rapidly in all the experiments, the assumption of constant k_t and f over a small time interval may be valid only for very small intervals. The time interval used for most of the calculations was 300 seconds; this was decreased to 150 seconds for some trials and some improvement in the values of conversion were noted after the change.

4. RECOMMENDATIONS AND CONCLUSIONS

The results found in this work indicate that more work should be done at high viscosity under better controlled conditions and higher purity of feed components. Further work should be done to determine mixing effects and shear effects on the kinetic relationships. It is recommended that future high viscosity polymerization experiments be done in batch systems where the problems encountered with unsteady flow rates will not be present. Another improvement in the experimental technique would be to use a more accurate instrument for measuring viscosity. It is felt that the Brookfield viscometer used in this work is not sufficiently accurate at high viscosities.

The effect of the size of the time interval used in calculating the BSTR results should also be further investigated to determine whether the improvement in results when the step size is decreased is significant.

Further investigation of the correlations of k_t and f with viscosity should be carried out, and the kinetics should be more thoroughly studied for reactions over 70% conversions.

It should be noted that in this work there were no duplicate experiments or analyses done. There may be a large variance in the experimental results, particularly at high viscosity. There may also be errors due to impurities in the reacting components.

From the results obtained in this work it appears that there is an effect of viscosity on the termination rate constant and on the

the catalyst efficiency. It has been shown that correlations of k_c and f as functions of viscosity obtained from these experiments will improve the predictions of conventional kinetic equations to give better agreement between experimental and theoretical conversions and MWD's at high conversion and viscosity.

If the results are reproducible, this work would also indicate that corrections for k_c and f as functions of viscosity obtained from CSTR experiments will not predict accurate results for BSTR.

PART II
RESPONSE OF THE TRANSIENT CSTR
TO
SINUSOIDAL FLUCTUATIONS
IN
MONOMER FLOW AND TEMPERATURE

1. THEORY

The recent interest in studying the response of chemical reactors to non-steady state operation has prompted this computer study of the response of the continuous polymerization reactor (21) (22). The possibility that operating polymerization reactors at non-steady state conditions might yield higher conversions and molecular weights could promote many new approaches to design and optimization of such systems.

The computerized model consists of the set of equations describing the transient behaviour of a single CSTR developed by Hui and Hamielec (8), modified to allow oscillating flow and temperature.

The general mass balance for the transient analysis is similar to that for the steady state CSTR:

$$(1) \quad \text{Accumulation} = \text{Flow in} - \text{Flow out} - \text{Loss by reaction.}$$

In the case of the transient analysis the accumulation term does not equal zero as it does in the case of the steady state analysis.

The equations for the various components present in the CSTR system are as follows:

Catalyst

$$(2) \quad V \frac{d(C)}{dt} = F_c/W_c - VQ(C) - k_d(C)V$$

solving for (C):

$$(3) \quad (C) = \frac{F_c/V W_c}{k_d + VQ/V} - \left\{ \frac{F_c/V W_c}{k_d + VQ/V} - (C_0) \right\} \text{EXP} \left(-(k_d + VQ/V)t \right)$$

Initiation Rate

$$(4) \quad I = 2fk_d(C)$$

Total Free Radicals

$$(5) \quad V \frac{d(R^\circ)}{dt} = F_r/W_{Rr} - (R^\circ)VQ + (I - k_t(R^\circ)^2)V$$

Assuming stationary state for radicals present and assuming that there is no flow of radicals into the reactor, (R°) becomes:

$$(6) \quad (R^\circ) = \frac{-VQ/V + (VQ^2/V^2 + 4Ik_t)^{1/2}}{2k_t}$$

Monomer

$$(7) \quad V \frac{d(M)}{dt} = F_m/W_m - (M)VQ + (I - (k_p + k_{fm})(M)(R^\circ))V$$

Radical R_1°

$$(8) \quad V \frac{d(R_1^\circ)}{dt} = \text{Flow in} - (R_1^\circ)VQ + (I + (k_{fs}(S) + k_{fm}(M))(R^\circ) - (R_1^\circ)(k_p(M) + k_{fs}(S) + k_{fm}(M) + k_t(R^\circ)))V$$

$$(9) \quad (R_1^\circ) = \frac{I + (k_{fs}(S) + k_{fm}(M))(R^\circ)}{VQ/V + (k_p + k_{fm})(M) + k_{fs}(S) + k_t(R^\circ)}$$

Radical R_r°

$$(10) \quad V \frac{d(R_r^\circ)}{dt} = \text{Flow in} - (R_r^\circ)VQ + V[k_p(M)(R_{r-1}^\circ) - (R_r^\circ)(k_p(M) + k_{fs}(S) + k_{fm}(M) + k_t(R^\circ))]$$

Dead Polymer of Chain Length r

$$(11) \quad V \frac{dP_r}{dt} = \text{Flow in} - P_rVQ + V[R_r^\circ(k_{fs}(S) + k_{fm}(M)) + k_{td}(R_r^\circ)(R^\circ) + \frac{1}{2}k_t \sum_{n=1}^{r-1} (R_n^\circ)(R_{r-n}^\circ)]$$

Total Dead Polymer

$$(12) \quad V \frac{d(PR)}{dt} = \text{Flow in} - (PR)VQ + (I + (k_p + k_{fm})(M)(R^\circ))V W_m$$

The concentration of free radicals of chain length r may be

calculated from (R_1^0) through the use of the probability of propagation Z'' .

$$(13) \quad Z'' = \frac{k(M)}{VQ/V + (k_p + k_{fm})(M) + k_{fs}(S) + k_t(R^0)}$$

Solving for (R_r^0)

$$(14) \quad (R_r^0) = (R_1^0)(Z'')^{r-1}$$

The equations for monomer concentration (7) and total dead polymer (12) may be solved by numerical methods and the conversion calculated.

$$(15) \quad X = (PR)/((PR) + (M)W_m)$$

Using the above equations describing the transient behaviour of the CSTR, sinusoidal fluctuations to the monomer flow and the temperature were placed on the system. These fluctuations took the form:

$$(16) \quad F_m = F_{m0}(1 + a \sin wt)$$

$$(17) \quad T = T_0(1 + b \sin wt)$$

For polymerization to low conversions and to low viscosities, a reasonable assumption to make would be that the accumulation term in the mass balance equation (1) would be negligible (21). Using this assumption, a computer model was derived which was used to predict the time average conversion when the monomer flow rate was oscillating about the steady state flow rate in a sinusoidal manner.

The steady state equations (15) to (19) in Section 1.6 were used to predict the conversion for this model. The time average was found by integrating the conversions obtained at small time increments for the period of oscillation, then dividing the integrated value by the period.

$$(18) \quad X_{AV} = 1/T_p \int_0^{T_p} X dt$$

The integration was done by Simpson's Rule.

2. CASE STUDIES

Case studies were carried out to show the effect on conversion and MWD of oscillating monomer flow rate and temperature. The steady state conditions for both cases are given below:

Temperature	343° K
Monomer Flow	.04 gm/sec.
Catalyst Flow	.0002 gm/sec.
Solvent Flow	.02 gm/sec.

In the first study the monomer flow rate was varied according to the relationship:

$$F_m = .04 + .025 \sin \omega t$$

The frequency ω was 0.00087266 giving a period of 2 hours.

In the case with oscillating temperature, the following relationship was used:

$$T = 343 + 20 \sin \omega t$$

where again $\omega = 0.00087266$

The results of these two cases are shown in Figures (17) and (18).

The results shown in Fig. (17) indicated that oscillations in monomer flow, at least for low frequencies, would not affect the time average values of molecular weight and conversion. This would suggest that at low conversions the continuous polymerization reactor is linear with respect to monomer flow rate. At higher conversions, however, this may not be true since the viscosity of the reacting mixture would begin

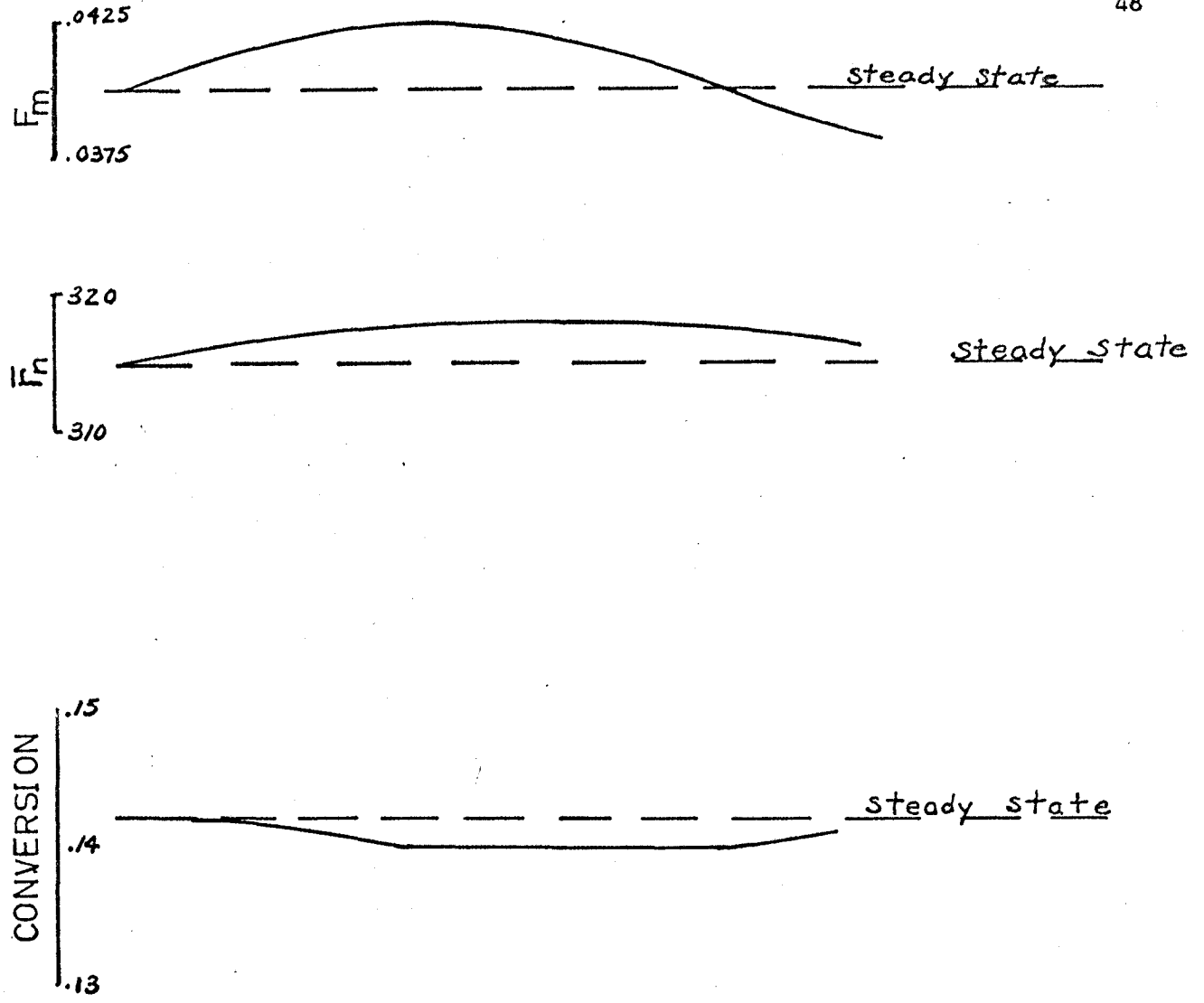
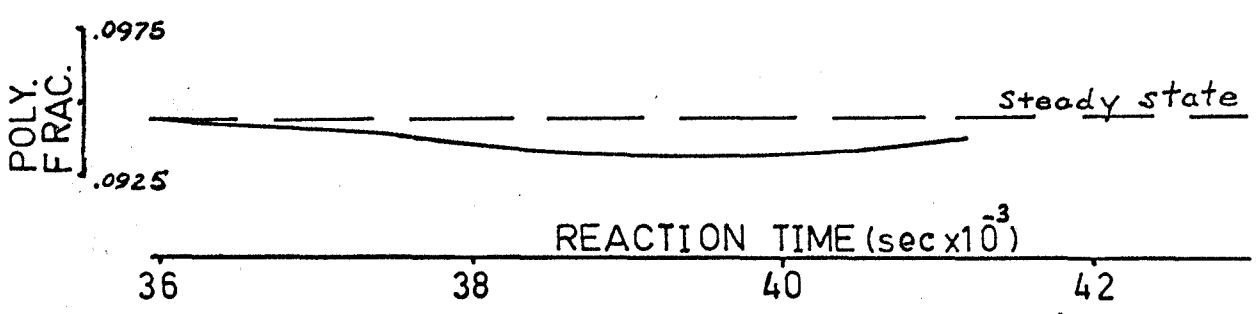


Figure 17. CSTR with Oscillating Flow



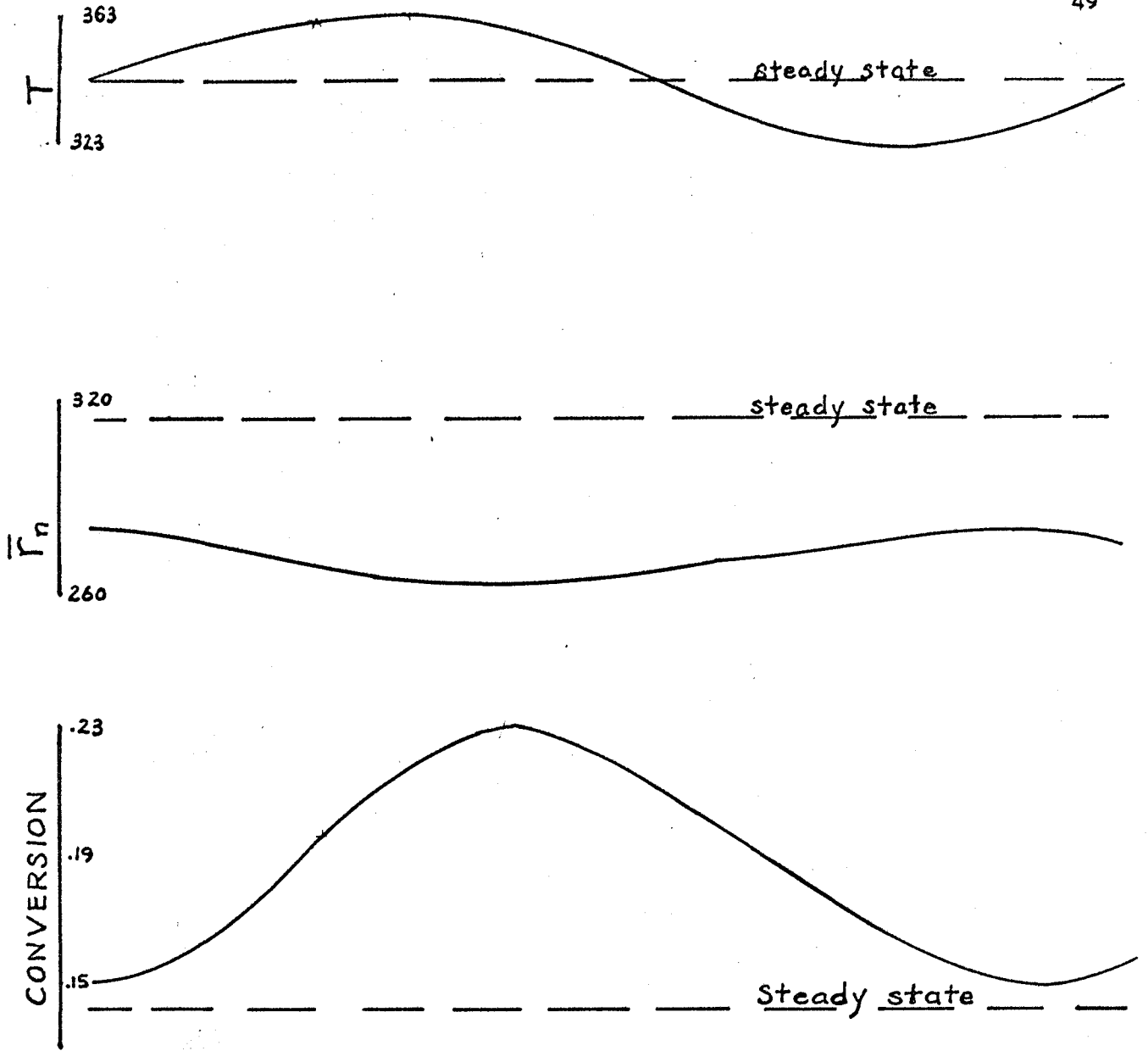
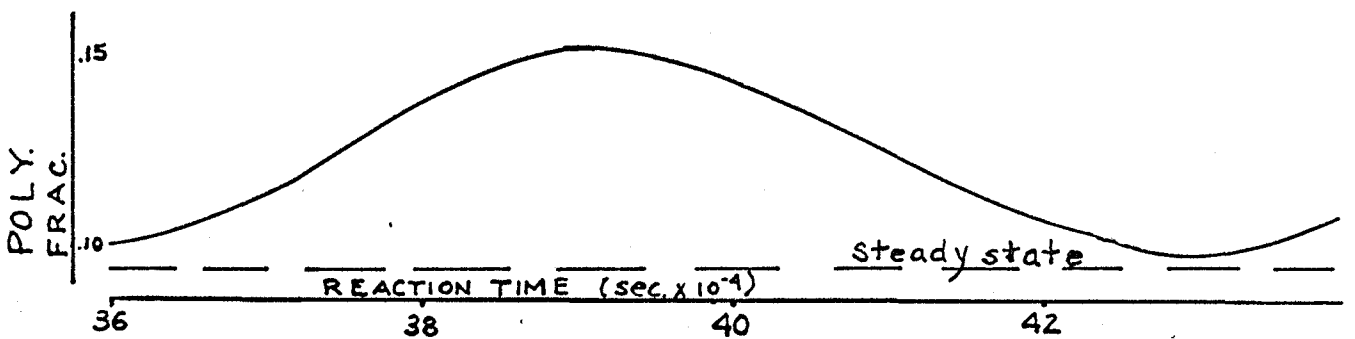


Figure 18. CSTR with Oscillating Temperature



to affect the conversion and molecular weight. The results of the CSTR experiments indicated that the viscosity of the system varies appreciably with the flow rate. The change in termination rate constant is a non-linear function of viscosity as indicated in Fig. (10), suggesting that if the viscosity were in the range of 100-300 centipoises, the time average conversion and molecular weight would vary from the steady state values.

Examination of Fig. (18) indicated that temperature fluctuations would cause the time average conversion and molecular weight to deviate from the steady state values. This is reasonable, since the rate constants are of the Arrhenius type and are of the form:

$$k = k_1 \text{ EXP}(-k_2/T)$$

In the range of temperatures 300-400°K these are very non-linear with respect to temperature and the time average values of the constants with varying temperature will be higher than the values at the average temperature. The increase in the rate constants will increase the average conversion and will decrease the average molecular weight.

The results of the model, assuming no accumulation were very similar to those obtained by the transient model, thus indicating that the assumption is valid for low frequencies.

3. RECOMMENDATIONS AND CONCLUSIONS

Further work should be done in the area of including viscosity corrections to the model. This refinement of the model would result in much better predictions of the actual reactor behaviour. An interesting study may also arise in the case where the reactor is operated part of the time as a batch reactor, and part of the time as a continuous reactor. If findings of these model studies showed favorable results, then laboratory experiments might be carried out to investigate the agreement of the model with the real system.

The results of this work would indicate that, in the region where viscosity has no effect, the continuous polymerization reactor would not be operated to any better advantage by fluctuating the monomer flow rate sinusoidally about an average value, than by keeping the monomer flow constant at the average value. Fluctuations in temperature will give higher conversion than if the temperature were kept at the average value, but the average molecular weight would decrease. However, the results obtained by oscillating the temperature may be due only to the non-linearity in the rate constant correlations, and not to the oscillating effect. This should be checked by comparing the steady-state conversion at each temperature with those obtained by the oscillating temperature.

NOMENCLATURE

a	-	a constant
b	-	a constant
BSTR	-	batch stirred-tank reactor
C	-	catalyst molecule or catalyst concentration in gm-mole/litre
CSTR	-	continuous stirred-tank reactor
EXP	-	exponential of
f	-	catalyst efficiency
F	-	flow rate in gm/sec
I	-	initiation rate for free radical
k	-	kinetic rate constant
ln	-	logarithm base e
log	-	logarithm base 10
M	-	monomer molecule or monomer concentration in gm-mole/litre
\overline{M}_n	-	number average molecular weight
\overline{M}_w	-	weight average molecular weight
MWD	-	molecular weight distribution
P_r	-	polymer molecule of chain length r or concentration of molecule in gm-mole/litre
PR	-	total concentration of all polymer species in gm-mole/litre
r	-	number of monomer units or chain length
R_r	-	radical of chain length r or radical concentration gm-mole/litre

- R° - total concentration of all free radical species
 gm-mole/litre
 S - solvent molecule or solvent concentration gm-mole/litre
 t - reaction time in seconds
 T_p - period of oscillation in seconds
 T - absolute temperature in degrees Kelvin
 V - reactor volume in litres
 VQ - volumetric flow rate in litre/second
 w - frequency of oscillation in sec^{-1}
 W - molecular weight
 WF - weight fraction
 Z, Z', Z'' - probability of propagation for CSTR, BSTR and transient
 CSTR respectively

Subscripts

- c - refers to catalyst
 i - initial values $k_{ti} f_i$
 m - refers to monomer
 o - initial value of concentration
 r - refers to chain length
 s - refers to solvent

Subscripts for rate constants

- d - refers to decomposition of catalyst
 fc - refers to transfer to catalyst
 fm - refers to transfer to monomer
 fp - refers to transfer to polymer

- p - refers to propagation
- t - refers to transfer by combination
- td - refers to transfer by disproportionation

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