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ON-LINE MEASUREMENTS AND CONTROL OF A BATCH POLYMERIZATION REACTOR

by

Saty R. Ponnuswamy

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

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To My Wife

Sakunthala

ABSTRACT

This thesis deals with the study of on-line measurement and control problems associated with the solution polymerization of methylmethacr[illegible] a batch reactor. An experimental reactor sys[illegible]ities for on-line measurements of polymer properties such as density, viscosity, torque on the stirrer and molecular weight distribution has been built as part of this work. A process control computer was used for on-line data acquisition and implementation of control policies on the reactor. An automatic sampling system that collects the samples of the reaction mixture periodically from the reactor and injects them into a size exclusion chromatograph (SEC) has also been developed. Computer programs were developed for automatic SEC data acquisition and data processing of this information to calculate number and weight average molecular weights. The analysis of the measurement data and demonstration of the correlation between density and conversion showed that the on-line densitometer can be used to give an indirect indication of conversion during the course of polymerization. The SEC was used as an on-line instrument to measure molecular weight averages.

A mathematical model of the reactor was developed and parameters of the model were estimated using the experimental data. Verification of the mathematical model was shown by the excellent agreement between model and experimental data. Open loop optimal control policies were

developed by the application of state-space theory to the model of the reactor. These policies were implemented on the reactor system. The results show that experimental and model conversion results were in good agreement whereas discrepancies of the order of 25-30 percent were observed for number and weight average molecular weight. Optimal feedback control policies were also derived and implemented on a simulated batch reactor. The feedback controller tracked the nominal conversion and molecular we[illegible]ofiles in the presence of disturbances in initiator concentration.

This study demonstrated that with the development of proper on-line instrumentation, advanced computer control of polymer properties such as conversion and molecular weight distribution is possible.

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I convey my special thanks to my wife who encouraged me to undertake this study for the doctoral degree.

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NOMENCLATURE

A_1 to A_6	Arrhenius factors for the terms k_1 to k_6
A_d, Ap, A_t	Arrhenius factors for dissociation, propagation and termination reaction, respectively.
A	3x3 state matrix in linear model,
b_1, b_2	constants in viscosity correlation.
B	3x1 control matrix in linear model.
C	$2f(1-k_{tc}/k_t)$
C_m	ratio of monomer transfer constant to propagation constant.
C_s	ratio of solvent transfer constant to propagation constant.
E_1 to E_6	activation energy for the terms k_1 to k_6, cal/mol.
E_d, Ep, E_t	activation energy for dissociation, propagation, and termination respectively, cal/mol.
e	error vector in parameter estimation.
f	initiator effiency.
F	3x3 state matrix in discrete model.
G	3x1 control matrix in discrete model.
H	Hamiltonian

H	3x1 disturbance matrix in discrete model.
I	initiator concentration, mol/L.
I_0	initial initiator concentration, mol/L.
I_s	nominal value of the initiator concentration, mol/L.
k_1	$kp\sqrt{2fk_d/k_t} = A_1\exp(-E_1/RT)$
k_2	$k_m\sqrt{2fk_d/k_t} = A_2\exp(-E_2/RT)$
k_3	$k_s\sqrt{2fk_d/k_t} = A_3\exp(-E_3/RT)$
k_4	$2kp^2k_s/\sqrt{2fk_d}k_t^{1.5} = A_4\exp(-E_4/RT)$
k_5	$2kp$[illegible]$k_s/\sqrt{2fk_d}k_t^{1.5} = A_5\exp(-E_5/RT)$
k_6	$(2+\nu)kp^2/k_t = A_6\exp(-E_6/RT)$
k_d	dissociation rate constant, 1/s.
k_i	initiation rate constant, 1/s.
k_m	transfer to monomer rate constant, L/mol-s.
kp	propagation rate constant, L/mol-s.
k_s	transfer to solvent rate constant, L/mol-s.
k_t	$k_{tc}+k_{td}$, L/mol-s.
k_{tc}	termination by combination rate constant, L/mol-s

k_{td}	termination by disproportionation rate constant L/mol-s.
M	monomer concentration, mol/L.
MW	molecular weight of the monomer.
M_n	number average molecular weight.
M_n^*	desired number average molecular weight.
M_t	true molecular weight of the polymer.
Mw	weight average molecular weight.
PD	polydispersity.
P_1, P_2, P_3	co-state variables.
P_x, P_y	concentration of dead polymer of chain length x and y respectively, mol/L.
Q	weighting matrix for states.
R	gas constant, cal/mol-°K.
R	weighting matrix for control.
S	solvent concentration, mol/L.
t	time, s.
tf	final time, s.
T	temperature, °K.
v	elution volume, mL.

V	volume of reaction mixture, mL.
$\mathbf{W}$	3x1 disturbance matrix in linear model.
w	3x3 weighting matrix in parameter estimation.
X	conversion
X^*	desired conversion.
u	control vector.
$\mathbf{Y}$	state vector
$\mathbf{Y}_m$	measured values of output vector.
$\mathbf{Y}p$	predicted values of output vector.
$\lambda_0, \lambda_1, \lambda_2$	zeroth, first and second moment of the live radical distribution respectively.
μ_0, μ_1, μ_2	zeroth, first and second moment of dead polymer distribution respectively.
ν	k_{tc}/k_t
η	viscosity of the polymer solution.
ρ_m, ρ_s, ρ_y	density of monomer, solvent and polymer respectively, g/mL.
Φ_s	volume fraction of solvent.

1. INTRODUCTION AND OBJECTIVES

Currently some 100 million metric tons per year of synthetic polymers are produced in the world in a wide variety of polymerization reactors. The total world sales of raw polymer is approaching $100 billion per year and sales of the final product after processing, molding and compounding is many times this figure. Hence the field of polymerization reaction engineering is of significant economic importance.

Until a decade or two ago, "polymers were mainly manufactured in batch reactors from faithfully prepared recipes scaled up from the chemist's beaker" (Ray(1983)). However with the growth of demand and increased price competition more efficient polymerization methods have been required. Manufacturers of high volume polymers are moving to fewer product lines, more uniform product and the use of continuous reactors. Similarly producers of low volume, high quality and high value polymers are realizing that their competitive edge comes from a deeper understanding of the relationship between polymerization conditions and the product quality.

Polymerization reaction engineers have been developing improved and efficient processes that can significantly reduce capital expenditure as well as operating costs. An example is the low pressure fluidized bed process of Union Carbide to produce low density linear polyethylene which can reduce the plant capital expenditure by 50% and energy consumption by 25% of the conventional high pressure polymerization process(Ray(1983)).

Significant economic advantages can also be obtained by operating the polymerization reactors in an optimal manner such that consistent product quality is maintained. Since any existing process can be operated in an efficient and optimal manner thereby reducing the operating costs, more attention has been paid to the optimum operation of the polymerization processes recently. As a result many operations in the polymer production have been automated and many of polymerization process variables such as temperature and pressure are being automatically controlled with the use of computers. The state of art of control of polymerization reactors has been reviewed by many authors (Amrehen(1977), Hoogendoorn and Shaw(1980), MacGregor et al.(1983)).

The benefits of automation and computer control of the polymerization reactors are many. Some of them are:

- Saving of manpower.
- Better control of quality of product.
- Shortening batch time in batch reactors.
- Minimum production of off-grade product in the product changeover in a continuous reactor.
- Optimum operation of plant through optimization programs.
- On-line measurement of process variables.
- Logging for process development and trouble shooting.
- Process alarms and automatic shutdown and hence better

safety.

Inspite of these benefits and much more, the progress in automatic control of the polymerization processes has been slow compared to other chemically simpler reaction systems such as ammonia synthesis, ethylene production, etc.

The slow progress in automatic control of polymerization processes has been attributed to the lack of development of on-line measuring devices. Hoogendoorn and Shaw(1980) pointed out the viscous nature of the polymerization mixture as the main contributing factor for the difficulty of on-line measurements. Polymer quality has been traditionally controlled by measuring the properties of the polymer product off-line and rejecting the off-grade product completely or blending it with good product such that the blended product has desirable properties.

In the past, on-line measurements of polymerization systems were mainly limited to temperature and pressure. With the advent of process control, especially due to digital computers, the impetus to determine product quality on-line has increased markedly. In response to this, there have been a number of attempts to develop new sensors to measure various polymerization process variables on-line and to modify the existing instruments so that they can be used for on-line measurements.

The availability of the process control computers and the recent development of on-line measurement techniques have considerably increased the scope of on-line control of product quality in polymerization reactors. Most of the earlier studies, particularly in academia, were limited to the theoretical prediction of batch reactor temperature policies, semi-batch initiator or monomer feed rate policies for the optimization of product quality in polymerization reactors. However, the success of these optimization efforts depends very much upon having valid dynamic models of the physical and chemical processes occurring in the complex polymerization systems. Hence considerable research has also been directed towards development of mathematical models to describe the polymerization processes under various conditions.

Optimization of product quality through feedback control can also be implemented on polymerization reactors. However the success of the optimal policies through feedback control are limited by the availability of on-line polymer characterization instruments. In recent years there has been considerable research in the area of on-line measurement and control of polymerization reactors. In fact the research is advancing so rapidly that it is anticipated that the 1980-s will see the implementation of higher level optimization and computer control schemes throughout the polymerization industry(MacGregor et al(1983)).

From the above it is clear that there is great incentive to study the problems associated with real time computer applications of optimal control policies to polymerization reactors. The present work was undertaken in response to these needs i.e. to develop techniques to measure, on-line, important process variables such as conversion and molecular weight distribution and to implement computer control on a polymerization reactor. Specifically the objectives of this study are summarized as follows:

1. Development of analytical techniques to measure on-line the density, viscosity, and molecular weight distribution of the polymer during the polymerization process.
2. Evalulation of these techniques with respect to their accuracy in estimating, on-line, important variables of the process such as conversion and molecular weight averages (number and weight average molecular weights).
3. Development of a reliable mathematical model of the process and estimation of the kinetic parameters of the model from the experimental data.
4. Application of optimal control theory to develop open loop and closed loop control policies to optimize the operation of the polymerization reactor.
5. Implementation of these optimal policies on a laboratory scale reactor using a real time process computer.

The above stated objectives were attempted on a free radical solution polymerization of methylmethacrylate in a batch reactor. However the on-line measurement and control techniques developed in this work can be easily extended to many other polymerization systems.

This thesis has been divided into eight chapters each of which closely follows the chronological development of the study. Chapter two contains a description of the experimental system which includes a five litre reactor, an automatic sampling system, a real-time process control computer and a number of measuring devices such as a densitometer, a viscometer and a size exclusion chromatograph.

In chapter three on-line and off-line measurement techniques used to monitor conversion and molecular weight distribution during the course of polymerization are described. A computer program developed for automatic data acquisition and on-line interpretation of size exclusion chromatograms (SEC) to determine molecular weight averages of the polymer is also described.

In chapter four, extensive experimental results obtained using the batch reactor system are presented. The effect of initiator, temperature and volume fraction of solvent on conversion and molecular weight is investigated.

A detailed mathematical model of a free radical solution polymerization of methylmethacrylate in a batch reactor is derived in chapter five. The model parameters are estimated from the experimental results obtained from the reactor system.

In chapter six open loop control policies are developed by applying optimal control theory to the mathematical model of the reactor derived in chapter five. These policies are then implemented on the laboratory scale reactor and the experimental results are compared with the theoretical predictions.

Chapter seven deals with the closed loop control of the polymerization reactor. The nonlinear model of the reactor is linearized and optimal feedback control policies are derived by working with a linearized model of the reactor. The closed loop policies are evaluated by simulation.

Finally in the eighth chapter the overall conclusions and the possible extensions of this work are presented.

This study is intended to provide the groundwork for a series of application studies on on-line measurements and real time computer control of polymerization reactors. It is hoped that the success of these studies and the knowledge gained during this research will have direct application to the control of industrial polymerization processes..

2. EXPERIMENTAL REACTOR SYSTEM

2.1 Introduction

As stated in chapter one, most studies on control of polymerization reactors have been limited to theoretical predictions of optimal policies required to produce a polymer product with desired properties in minimum time. It is true that very little work has been done on actual implementation of these control policies to a laboratory scale experimental reactor system. Chan and Huang (1981) first reported the implementation of optimal initiator policies on a 300 ml glass reactor for the case of solution polymerization of styrene. However their experimental system was a simple one and did not include facilities for on-line measurements and interfacing with a process computer. There is a great research incentive to study the problems associated with the real-time computer implementation of optimal control policies to a laboratory scale reactor system. Therefore a novel reactor was designed and built. This system consists of a five litre glass reactor, an automatic sampling system, a process control computer and a number of measuring devices such as a densitometer, a viscometer and a size exclusion chromatograph. In this chapter we describe in detail the experimental reactor system.

2.2 Reactor System

A schematic representation of the experimental set-up is shown in Figure 2.1. It is designed in such a way that different measurements from the system can be used for a variety of studies in polymerization reactions.

A detailed list of all the instruments and measurement devices used in the experimental system along with the technical specifications is given in Appendix A.

The reactor is a 5L jacketed cylindrical glass vessel of approximately 152 mm inside diameter and 280 mm height. It is calibrated and marked to show the volume of reaction mixture inside. The top of the reactor consists of a flared glass flange which is used to support the reactor by firmly gripping the glass flange by an outer stainless steel flange using a rubber gasket. The whole reactor assembly is supportd through the outer stainless steel flange to a framework consisting of four inclined steel legs and a circular plate at the top that is welded to the stainless steel flange. The legs are firmly bolted to the floor of the laboratory so that vibrations due to the stirrer motor are kept to the minimum.

A stirrer-motor assembly is mounted on the reactor to mix the reactants thoroughly. The stirrer has two turns of helical blades and is supported by a bearing at the centre of the lid. It is turned by a totally enclosed DC motor which is controlled by a controller that provides filtered DC power to the motor, changing the voltage as necessary to

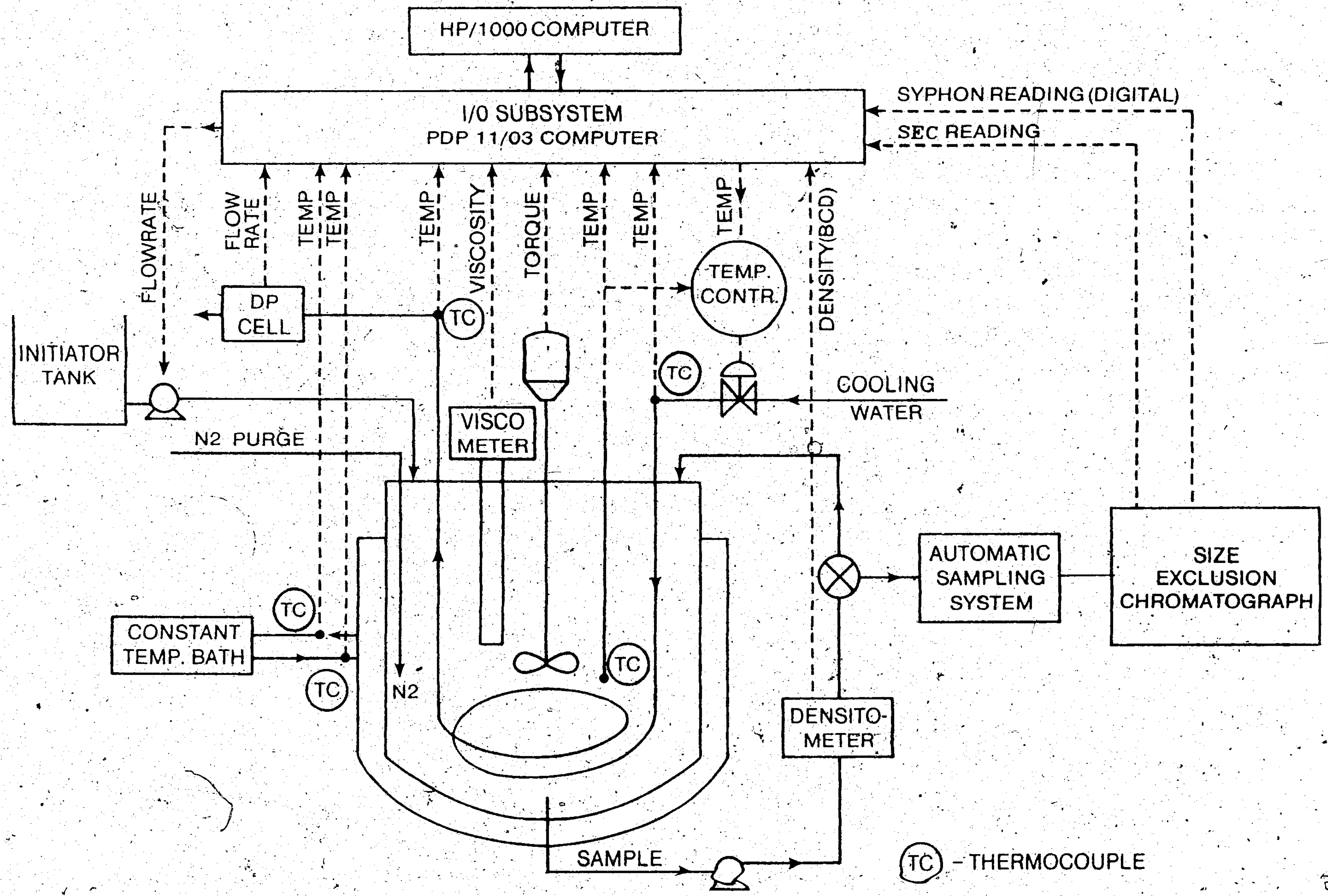

FIG. 2.1. SCHEMATIC DIAGRAM OF POLYMERIZATION REACTOR SYSTEM.

keep the speed constant. Because of the action of the controller the speed of the stirrer is maintained constant in spite of the increase in the load on the stirrer due to increasing viscosity of the reacting mixture during the course of polymerization. The torque on the stirrer is available for on-line data acquisition as a 0-10V output. It is found that the helical blades attached to the stirrer provided good mixing of the reaction mixture when operated at 750 RPM. Also the bearing and the motor support is good enough to provide stirring with minimum vibration.

The reaction mixture is continuously heated by circulating hot water through the jacket using a thermally protected centrifugal pump. The hot water flows through a rotameter and 1/2" diameter copper tubes. The constant temperature hot water tank has a capacity of 25 litres and is provided with agitators to keep the temperature uniform inside.

The cooling of the reaction mixture which is required during the exothermic reaction is achieved by the cold water flowing through 1/4" stainless steel cooling coils provided inside the reactor. The cooling water, whose flow rate is controlled by a Foxboro feed back controller, flows through a control valve and a Foxboro D/P cell that is used to measure the flowrate of the cooling water. The inlet and outlet temperatures of the cooling water are measured by thermocouples. Through the above mentioned facility of heating and cooling it is possible to maintain the desired temperature within the reactor within ±0.5°C.

A feedback controller is designed to control the temperature inside the reactor. For this purpose the temperature of the reaction mixture is measured by a copper-constantan thermocouple and the resulting millivolt signal is converted to a 10-50 ma signal through a Foxboro EMF converter. This 10-50 ma signal is fed to a PI Foxboro controller which produces the appropriate control signal (10-50 ma) to an electro-pneumatic converter. The output of the electro-pneumatic converter (3-15 psi) is fed to a diaphram control valve to regulate the flowrate of the cooling water. The Foxboro controller can accept remote setpoint, a facility that can be used for computer control of the reactor. The millivolt signal resulting from the thermocouple inside the reactor is also sent to the computer for on-line data acquisition of temperature.

A viscometer (Norcross Corporation Model M8B) is mounted on the lid of the reactor to measure viscosity during the course of polymerization. This viscometer operates on a falling piston principle. A piston is periodically raised by a lifting mechanism drawing a sample of the liquid to be measured down through the clearance between the piston and the cylinder into the space which is formed below the piston rod assembly. The piston is then allowed to fall by gravity, expelling the sample through the same path as it entered. The time required for the piston rod assembly to drop to the bottom of its travel is a measure of viscosity of the liquid and this measure is available as an electrical signal in the range of 1-5 volts for on-line data aquisition. The measuring element is rigidly mounted with the measuring tube in a vertical position as indicated by an air bubble level indicator mounted on the base of the measuring element. The calibration and measurement of viscosity will be dealt in detail in chapter three.

During polymerization the reaction mixture is continuously circulated through a densitometer by a reciprocating-revolving pump (Figure 2.2). This pump is valveless and can handle highly viscous fluids such as polymer solutions. According to manufacturer's specification it has an accuracy of one percent. In our experiments we experienced plugging of the pump at high viscosities. These problems were temporarily solved by removing the pump and cleaning the pump head with a solvent. The inlet of the pump was connected to the stopstock outlet at the bottom of the reactor through 1/8" flexible Teflon tubing. The Teflon tubing was found to perform well whereas Tygon tubing started to break at the higher temperature (about 75°C) of the reaction mixture. To ensure that density is measured at a constant temperature, the reaction mixture is first passed through stainless steel coils immersed in a thermostatic bath before entering the densitometer. The stainless steel coil is of sufficient length (50cm) so that the reaction mixture would reach the temperature of the thermostatic bath

(60°C), irrespective of the actual temperature of the reactor.

An on-line digital densitometer (Anton Parr, Austria Model DMA 450 marketed by Mettler Company, USA) is used to measure the density of the reaction mixture. This meter measures density by measuring the change in the natural frequency of a hollow oscillator when filled with different liquids or gases. It has a precision of 0.0001g/ml when the range of density is between 0.50 and 1.5 g/mL. Water is circulated around the density cell from a thermostatic bath so that density cell and its contents are kept at a constant desired temperature. The densitometer is provided with stainless steel adaptors so that continuous measurements can be made when reaction mixture flows through the density cell. The connections between the Teflon tubing and the adaptor are made by inserting the tube firmly into the sockets of the adaptors. In the event of the plugging of a valve or any part of the tube, the connections break open at the adaptors thereby avoiding pressure buildup and subsequent damage to the density cell. The measured density value is available as a BCD output for data acquisition by the computer. The measurement and calibration of the densitometer will be treated in detail in chapter three.

From the densitometer the reaction mixture flows through a three-way solenoid valve and back to the reactor. This valve is used to collect samples of reaction mixture automatically for the SEC sampling system. Initially used

Buna rubber and Viton valve seats plugged very often whereas the Teflon valve seats were found to perform well.

A size exclusion chromatograph (SEC Waters Associates Model 244) is employed to measure molecular weight distribution of the polymer in the reaction mixture. It separates the polymer molecules according to their size in solution by using microporous solids packed inside the columns of SEC. The concentrations of the separated polymers are detected using two detectors (UV absorption, or Refractive Index detector). Even though both of the detectors are available in the SEC employed in this work, it was found that only RI detector responds to the polymer polymethylmethacrylate. The RI detector has three possible outputs i.e. 10mV, 100mV, and 10mA one of which can be chosen by a selector switch. The RI responses are amplified filtered and transmitted to the computer for data acquisition. A computer program has been developed for automatic data acquisition and computation of molecular weight averages from the SEC measurements and will be discussed later in chapter three.

2.3 Automatic Sampling System

As mentioned earlier an automatic sampling system has been developed to collect samples at regular intervals from the reactor and prepare it for injection into the SEC. The schematic diagram of the system is shown in Figure 2.2. A 50 mL conical flask is used to collect the sample from the

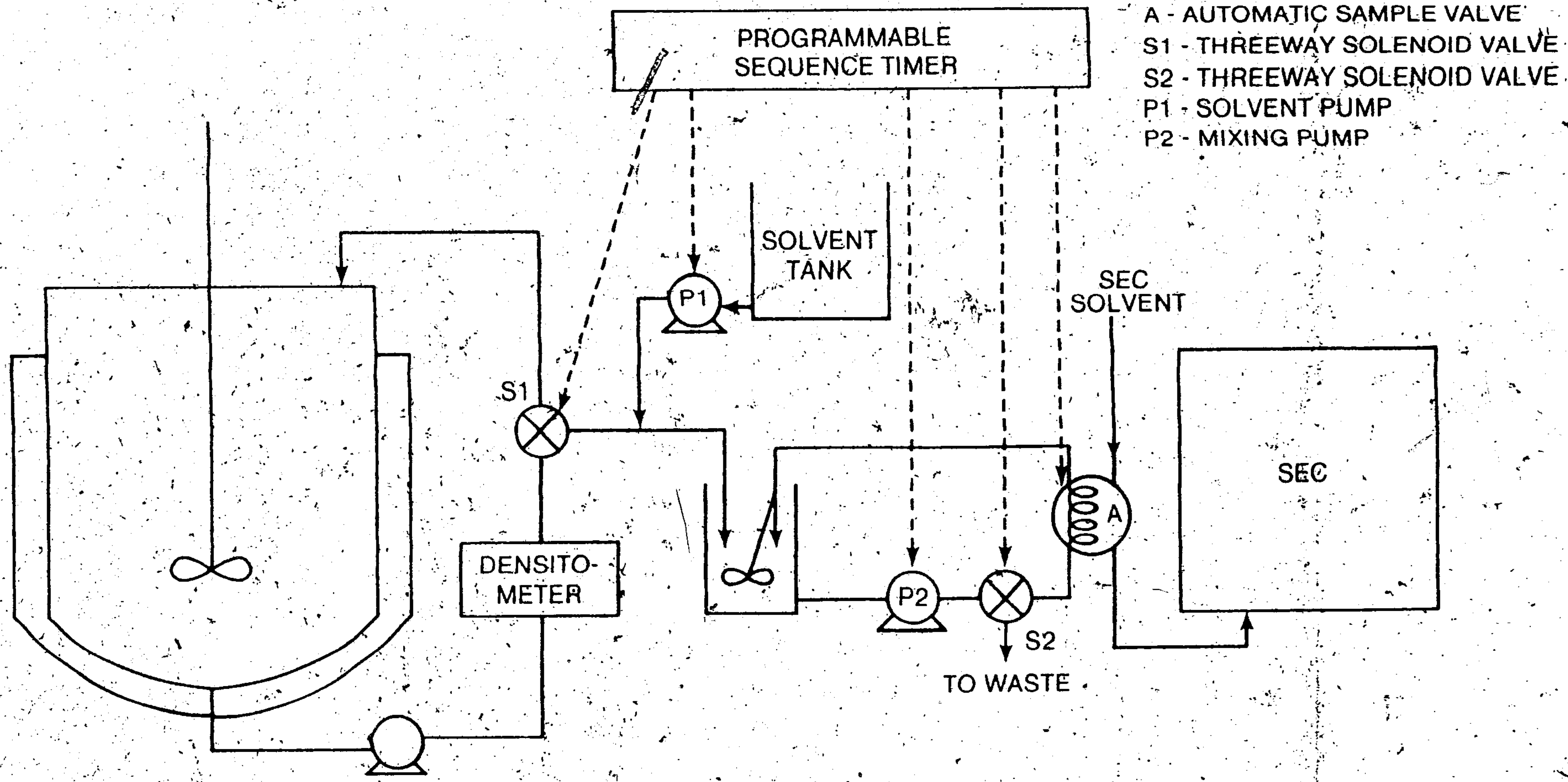

FIG. 2.2. AUTOMATIC SAMPLING SYSTEM FOR SEC.

Table 2.1 Sequence Timer Channel Allocation

Channel Number	Output Number	Channel Output
0-7	1	8
8-11	2	4
12-15	3	4
16	4	1
17	5	1
18	6	1
19	7	1
20	8	1
21	9	1
22	10	1
23	11	1
24	12	1
25	13	1
26	14	1
27	15	1
28	16	1

reactor. The sampling system also includes 1) two three-way solenoid valves 2) two metering pumps 3) a magnetic driven stirrer and 4) an automatic sample injection valve. A programmable microprocessor based sequence timer (Potter and Brumfield Company) that has twenty-nine channels and sixteen output relays is used for switching the pumps, solenoid valves and the magnetic stirrer on or off. The sample preparation is achieved by appropriate timing of the above devices. The essential steps of sampling system in the order of execution are:

- Step 1: collection of a certain quantity of polymer mixture in the sample vessel by switching on the threeway solenoid valve (S1) for a predetermined period of time.

- Step 2: dilution of polymer sample with a predetermined amount of solvent by operating the solvent pump (P1) over a period of time.
- Step 3: mixing of the sample with the solvent and circulation of the diluted polymer through the SEC sample loop by switching on the magnetic stirrer and pump(P2).
- Step 4: automatic injection of sample into SEC by switching on the automatic sample valve.
- Step 5: emptying contents of sample vessel to waste by switching on the solenoid valve (S2).
- Step 6: flushing sample vessel with more solvent by operating pumps P1 and P2.

The above mentioned procedure accomplishes automatic preparation and injection of the polymer sample into SEC.

Table 2.1 gives the assignment of channels to the output relays. Each channel can be programmed to switch on and off once during a cycle. Since eight channels(0-7) are assigned to the output relay number one, it can be switched on and off eight times in a cycle. Similarly from Table 2.1 it can be observed that output relays numbered two and three can be switched on and off four times in a single cycle whereas all other output relays can be switched on and off only once in a single cycle.

Even though there are 16 output relays available in the sequence timer, only six of them are needed for automatic

Table 2.2 Automatic Sampling System Program

Cycle Time = 15 min

Start Time min	Stop Time min	Total Time min	Output Number	Remarks
0.0	0.1	0.1	4	Polymer sample collected using solenoid valve(S1)
0.1	0.4	0.3	1	Dilution of polymer sample by pump(P2)
0.3	1.5	1.2	5	Mixing sample using magnetic stirrer.
0.3	1.5	1.2	3	Pumping sample through SEC loop and to waste(P2)
0.5	0.8	0.3	6	Sample injection by automatic sample valve
0.6	0.9	0.3	2	Discharging the polymer to waste(S2)
0.9	1.2	0.3	1	Pumping more solvent for cleaning(P1)
1.2	1.5	0.3	2	Discharging the solvent to waste(S2)

sampling. Table 2.2 gives the program used in this work with the start time and stop time of the various devices used in the automatic sampling system. Since it takes 10-12 minutes of time to analyze a polymer sample using SEC, a cycle time of 15 minutes is chosen for this program. Every fifteen minutes the program given in the Table 2.2 is executed by the sequence timer, starting a SEC analysis of the polymer sample.

2.4 Computer System

A Hewlet-Packard (HP/1000) minicomputer is used for data acquisition and control of the experimental reactor. This computer is maintained by Data Acquisition, Control, and Simulation Centre (DACS Centre) of the Department of Chemical Engineering.

The HP/1000 minicomputer employs a PDP 11/03 computer as an I/O subsystem to which various measurements from the reactor are interfaced. The PDP 11/03 computer performs the following functions; i) A/D conversion of analog signals and transmission of the digital signal to the main computer; ii) processing of thermocouple signals after providing cold junction compensation; iii) reading status of digital switches; and, iv) routing analog and digital outputs to appropriate devices. The system supports a plotter that can be used to plot data collected during an experiment. A hard copy terminal near the reactor site is used for entering commands as well as reporting experimental data. The data acquired by the computer is also stored in disc files for subsequent analysis.

The programs are written in Fortran IV, the language supported by the computer system. Real time data acquisition is done through CALL-s to standard ISA (Instrument Society of America) subroutines.

In addition another HP/1000 minicomputer which is dedicated to the task of gas chromatography has been used to do the GC analysis of the polymerization mixture. Details of the GC analysis will be given in chapter three.

2.5 Experimental Procedure

A free radical-initiated solution polymerization of methylmethacrylate in a batch reactor has been selected to study the problems associated with on-line implementation of optimal control policies. Toluene is chosen as a solvent because of its higher boiling-point (120°C) and its low rate constant for chain transfer reaction. Because the boiling-point is high, the toluene does not evaporate significantly at the temperature (60-80°C) of polymerization. The molecular weight distribution of the polymer formed during the course of polymerization is not affected by the presence of toluene due to the low value of its chain transfer rate constant(Brandrup and Immergut(1975)).

Commercial monomer methylmethacrylate (MMA) (supplied by Aldrich Chemical Company) contains 65 ppm hydroquinone monomethyl ether as inhibitor which is removed by vacuum distillation at 32-35°C. Both monomer and solvent are dried with anhydrous calcium chloride, since water also inhibits the reaction. Both monomer and solvent are purged with nitrogen to remove dissolved oxygen which inhibits polymerization. The initiator, benzoyl peroxide, supplied by Aldrich Chem. is dissolved in chloroform and recrystallized in methanol. The reactor is purged with nitrogen during polymerization to prevent oxygen from being dissolved into the reaction mixture.

Measured quantities of monomer and solvent are charged into the reactor and the reactor contents are heated to the required operating temperature, while the contents are mixed thoroughly by the stirrer. After the contents of the reactor have reached the reaction temperature, the initiator which has already been dissolved in toluene, is added to the reactor. Immediately afterwards the reactor is placed under computer monitoring for the purpose of on-line measurement of variables of the polymerization process. Off-line measurements are also carried out on the samples that are collected periodically from the reactor. These samples were also stored in a freezer so that they could be used for later off-line analysis if necessary.

A computer program has been developed for the purpose of on-line monitoring of various variables of the process. Every five seconds the program samples the following measurements during the course of polymerization:reactor temperature, inlet and outlet temperatures of hot water flowing through the jacket, inlet and outlet temperatures of the cold water flowing through the cooling coils, cold water flowrate, density and viscosity of the reaction mixture and finally the torque on the stirrer. The above measurements are corrupted by the noise of the measuring devices and also by the transmission noise and they should be filtered to smooth the data. A moving average filter that smoothes the current data by taking an average with certain number (typically 10) of past data is used in this program. The filtered data are reported at specified intervals of time (one or two minutes) at a hard copy terminal installed near the reactor. Also, these data are stored in disc files in the computer for later analysis.

In addition the program reads a digit switch every second to check whether a polymer sample has been injected into the SEC by the automatic sampling system. If a sample has been injected, as inferred from the ON status of the digit switch, the program automatically starts the SEC data collection and reports these data at specified time intervals on the hard copy terminal. After the polymer peak has eluted the SEC data collection is automatically terminated by the program. The details of the SEC program will be given later in chapter three.

2.6 Conclusions

The experimental facilities that are required for on-line measurement and computer control studies on a batch polymerization reactor have been described in this chapter. It can be appreciated that the experimental reactor system requires extensive instrumentation to measure on-line properties like density, viscosity, torque, temperature, molecular weight of the polymer etc. A process control computer was employed for on-line data acquisition and implementation of optimal control policies on the reactor system. A description of the software that was developed for data acquisition of all on-line measurements has also been given.

3. MEASUREMENT STUDIES

3.1 Introduction

As pointed out by Hoogendoorn et al. (1980) the measuring instruments are often the weakest link in polymerization reactor control circuits. Without some form of on-line polymer characterization, the monitoring and feedback control of polymer quality is not possible. Hence there is great incentive to develop on-line sensors to measure the polymerization process variables such as conversion and molecular weight distribution. There has been considerable advances in the development of on-line sensors recently(MacGregor et. at(1983)). In this chapter we describe some on-line techniques used in this work to measure density, viscosity, torque and molecular weight distribution in a solution polymerization process.

3.2 Previous Work

In the past, on-line measurements in a polymerization reactor were mainly restricted to temperature and pressure. Even temperature measurements can sometimes present problems in polymerization reactors due to fouling of the measuring elements(MacGregor et al.(1983)). Traditionally conversion has been measured by gravimetric methods which are time consuming and necessarily measured off-line. The molecular weight distribution of the polymer is usually measured off-line using a size exclusion chromatograph. There have been only a few attempts recently to develop on-line sensors to measure the above mentioned process variables.

Jo(1975) used an on-line refractometer supplied by Electron Machine Corporation (ECM) to monitor conversion in solution polymerization of vinylacetate. He modified the refractometer to increase turbulence and prevent polymer coating on the prism and reported trouble free operation of the instrument as well as accurate reproducible results for conversion. Schmidt and Ray(1981) have also used an on-line refractometer from ECM to monitor conversion in solution polymerization of methylmethacrylate and reported accurate results for conversion.

Abbey(1981) used an on-line densitometer (Anton Paar, Austria) for monitoring conversion in the cases of solution and emulsion polymerizations of methylmethacrylate and reported the following difficulties:

- pump failure from either monomer attack or polymer scale
- monomer phase separation in density cell
- lag time for rapid polymerization.

Schrock and Ray(1981) also used a DMA series densitometer in emulsion polymerization of methylmethacrylate and observed very good agreement between conversion from gravimetry and densimetry. They reported that at least a resolution of 0.5 per cent conversion is possible in the presence of sampling errors. Recently Pollock(1983) used the same type of densitometer to monitor conversion in emulsion polymerization of vinylacetate.

Though gas chromatograph is a sensitive and reliable instrument, it has not yet been extensively used in polymerization studies (Collins et al. (1973)). Guyot et al. (1981) used a gas chromatography with an automatic sampling system to monitor conversion in emulsion polymerization of vinylacetate. In some cases the gases contained in the head space of the reactor are analyzed and the composition and conversion of monomer in the reacting liquid are inferred through vapor-liquid equilibrium relationships. Recently Garcia-Rubio (1982) investigated the styrene acrylonitrile copolymerization kinetics using gas chromatography. Although some difficulties were experienced with the monomer extraction process at high conversion, in general very good descriptions of the copolymerization reaction were obtained in terms of the residual monomer composition.

Even though size exclusion chromatograph (SEC) is widely used to measure molecular weight distribution (MWD), only a few applications for on-line measurements are reported. Gregges et al. (1971) have modified a SEC for automatic sample injection and on-line data acquisition by a computer. Recently Meira et al. (1981) employed an SEC on-line for measuring MWD in the solution polymerization of methylmethacrylate and reported good reproducibility of SEC results. However they did not include an automatic sampling system which can collect samples from the reactor and inject into SEC after diluting with a carrier solvent. Roof et al. (1980) have field tested an on-line SEC in the case of a solution polymerization process over a period of three years and reported that their experience has proven that on-line polymer analysis by SEC is practical. They also developed an automatic sampling system to collect samples from the reactor and inject into the SEC.

Jo and Bankoff (1976) measured viscosity on-line in solution polymerization of vinylacetate and used the information to estimate the weight average molecular weight of the polymer product.

From the above it is clear that on-line sensors are still under development in polymerization processes. In the next section we will deal with on-line as well as off-line methods to measure conversion, molecular weight and viscosity in solution polymerization of methylmethacrylate.

3.3 Conversion Measurements

There are a number of methods available to measure the extent of conversion of monomer to high polymer during the course of polymerization. Probably the most direct method of determining conversion of monomer to polymer is to stop the polymerization, and isolate and weigh the resulting polymer. The chemical determination of the remaining functional groups at some stage of the polymerization is often practiced, particularly for step polymerization. This method not only leads to the extent of reaction but, through the use of Carothers equation relating extent of reaction and degree of polymerization, to the number average molecular weight in the case of linear polycondensation. Double bonds can also be determined chemically, so that this class of methods is applicable to chain polymerization as well. Examples of use of this method are reported in the literature (Patton(1962), Sorenson(1968), Kolthoff(1947), Lewis(1945)).

There is a linear relationship between the degree of conversion in a polymerization system and its volume, provided only that the monomer and polymer mix without change in volume. For following the volume change during polymerization, the reaction is carried out in a dilatometer, a vessel equipped with a capillary tube in which the liquid level can be measured precisely using a cathetometer. The decrease in volume on polymerization is large being 21% for methylmethacrylate and 27% for vinylacetate. In practice a few hundredths per cent polymerization can be detected (Billmeyer, Jr.(1971)). Example of the use of dilatometry to study the course of polymerization reaction has been reported by many authors (Paoletti(1964), Bell (1961), Niezette(1971)).

The determination of extent of reaction by means of refractive index is based upon the refractive index of the liquids, their chemical composition and their molecular structure. Since the structure of the polymer differs from the structure of monomer because of rearrangement of chemical bonds, the refractive index of the polymerization mixture is different from that of pure monomer. Since refractive index is also dependent on temperature, it is necessary to keep the temperature of the refractometer constant by precise temperature control. Generally, the dependence of refractive index on conversion is determined by calibration using polymerization mixtures whose conversions are known. Conversion can also be calculated by using the Lorentz-Lorentz equation (Collins et al. (1973)). Although the refractive index method requires removal of a single drop of sample of polymerization reaction mixture per determination, it is a simple and rapid means of following the polymerization. Naylor(1953) and Pulley(1968) used sealed cylindrical tubes as reaction vessels and measured refractive index *in situ* to follow the polymerization process.

On-line refractometers are available and their use to measure conversion in polymerization processes has been mentioned earlier in this chapter.

In addition to the above mentioned methods, the extent of reaction during polymerization can also be determined by densimetry, gas chromatography and infrared spectroscopy. Though the number of methods available to measure conversion in polymerization reactions are many, only a few of them can be used for on-line measurement. Three methods, namely gravimetry, gas chromatography and densimetry that have been used for on-line and off-line determination of conversion in solution polymerization of methylmethacrylate (studied in this work) are described in the following section.

3.3.1 Gravimetry

This is the most direct method of determining conversion of monomer to polymer. The sample of the polymerization mixture is withdrawn from the reactor in a vial and further polymerization of the collected sample is stopped rapidly by the addition of a fast-acting shortstop (in this case a few drops of solution of hydroquinone in distilled water). These vials are stored in a freezer so that gravimetric as well as gas chromatographic analysis can be done at any future time.

In this study the procedure reported by Jo(1975) has been used to isolate polymer from the sample. Samples of the reaction mixture are placed in preweighed aluminum dishes and weighed accurately using a Mettler electronic balance which has a resolution of 0.00001 g. The samples are then dried in a vaccum oven and finally heated to 60-80°C to remove the traces of monomer and solvent that could have been entrapped inside the polymer. The isolated polymer in the dish is cooled and weighed to a constant weight. Since the initiator added to the reactants in the beginning of the reaction remains with the polymer after vacuum drying, a correction is made in the conversion calculation to account for the weight of initiator in the isolated polymer. Because only a few drops of the solution of inhibitor are added to the sample, a correction for the weight of inhibitor is not done in our calculations.

This method of determining conversion is necessarily time-consuming, involving several hours of analysis, and moreover it becomes increasingly difficult to remove the traces of monomer and solvent from the polymer at high conversions where the viscosity of the sample mixture is also high. It was suggested to precipitate the polymer in the high conversion samples in methanol or heptane and then to isolate the precipitated polymer by vacuum-drying to avoid entrapped monomer or solvent in the polymer. However, it was found that both of the gravimetric procedures, namely direct vacuum drying and precipitation, gave almost similar results suggesting that conversion results obtained from gravimetry are prone to error especially at higher conversion levels. The residual monomer and solvent trapped inside the polymer sample can be removed by heating the vacuum oven to higher temperatures. However heating of the samples could also lead to further polymerization of the residual monomer to polymer and hence better results of conversion need not be obtained.

The presence of the residual monomer and solvent in the dried polymer has been confirmed by dissolving the dried polymer and injecting into an SEC. An SEC peak corresponding to the monomer and solvent elution volume has been observed thus confirming the presence of monomer and solvent .

3.3.2 Gas Chromatography

Though gas chromatography is perhaps better suited than any other method to follow the course of polymerization, it has not yet been extensively used. As a rule the presence of polymer in the reaction mixture does not hinder the use of GC. Since the methods for determining volatile components in polymer systems have been developed in great detail, GC methods can be used directly for determining the reaction kinetics from the changes in the concentration of the monomers consumed. Berezkin et al.(1977) compared the widely used dilatometry with GC methods to determine kinetic parameters in polymerization reactions and concluded that GC is the preferred method in most instances.

The following is a list of advantages of using GC method in the study of polymerization reactions (Berezkin et al.(1977)):

- The sample volume required for GC analysis is extremely small in the order of microlitres.
- Since GC analysis directly gives the mass fraction of the volatile components in the polymerization mixture, the results do not depend upon the temperature of the reaction. We need not worry about temperature effects as is the case with some other methods.
- By using an internal standard in the polymerization reaction mixture, one need not worry about the exact volume of the sample injected. Yet accurate results can be obtained about the compositions of the components in

the sample.

- GC analysis can also be extended to study any side reactions that may take place along with polymerization reaction.
- The sampling procedure can be automated so that GC methods can be used for on-line monitoring of polymerization reactions.
- GC methods can be easily extended to the study of copolymerization reactions with several monomers for which other methods may not be applicable or require extensive calibration.

The following are some of the problems that may be encountered when using GC methods in polymerization studies.

- The polymerization samples with higher viscosities corresponding to higher conversions can not be drawn into GC syringe easily for injection. However these samples could be diluted with a solvent which will facilitate easy injection into the GC.
- Since the polymer does not evaporate in the injection port, the polymer particles accumulate and block the injection port in course of time. The injection port can be removed and cleaned with a solvent.
- The injection port temperature should be such that there is no polymerization of monomer and also no depolymerization of polymer to monomer each of which can affect the results obtained from the GC.

In this work a HP gas chromatograph (Model 5710A) with a thermal conductivity detector is used. Argon is used as a carrier gas. The following operating conditions are employed to analyze the sample:

Column temperature : 102°C
Detector temperature : 150°C
Injection port temperature : 150 °C
Carrier gas flow rate : 15 mL/min
Sensitivity of the detector : 4
TC current : 150 ma
Carrier gas : Argon

For analyzing the samples of the reaction mixture, the hardware and software supplied by Hewlett-Packard Company have been used. The h[illegible] consists of a A/D converter and a HP/1000 minicomputer which is dedicated to the task of gas chromatography for a number of GC-s used in the Department of Chemical Engineering of University of Alberta. The software is a GC program that can automatically analyze the GC-readings, find the peaks and report compositions. The analysis is started by injecting the sample into the GC injection port and pressing a switch located on the A/D converter. The results are reported on a teletype terminal installed near the GC.

The solvent toluene does not take part in the reaction and so its weight fraction in the reaction mixture remains constant throughout the course of polymerization. Hence the solvent serves as an internal standard for the GC analysis of the monomer methylmethacrylate. During the course of polymerization the composition of monomer decreases with respect to the solvent and conversion of monomer to polymer can be easily calculated from the knowledge of initial compositions of monomer and solvent and the compositions obtained from the GC analysis. Since toluene serves as an internal standard, exact volume of injection of the GC sample need not be known.

For the purpose of comparison, the conversion results obtained from GC and gravimetry are presented in Figure 3.1. In Figure 3.1 T, Φ_s, and I_0 denote temperature, volume fraction of solvent and initial initiator concentration, respectively. It can be observed that conversion results from both of the methods agree very well (within 3%) upto 40 per cent conversion whereas after about 40 percent conversion the gravimetric results give higher values compared to the GC results. These higher conversion values from gravimetry especially at higher conversion range are attributed to two possible sources of error which have been already discussed in the section on gravimetry namely entrapped monomer and solvent in polymer and possible polymerization of monomer to polymer due to heating of samples. These errors are absent at lower conversion levels and hence better agreement of results are observed between the two methods.

In the GC method of analysis possible sources of errors are also due to polymerization of monomer to polymer inside

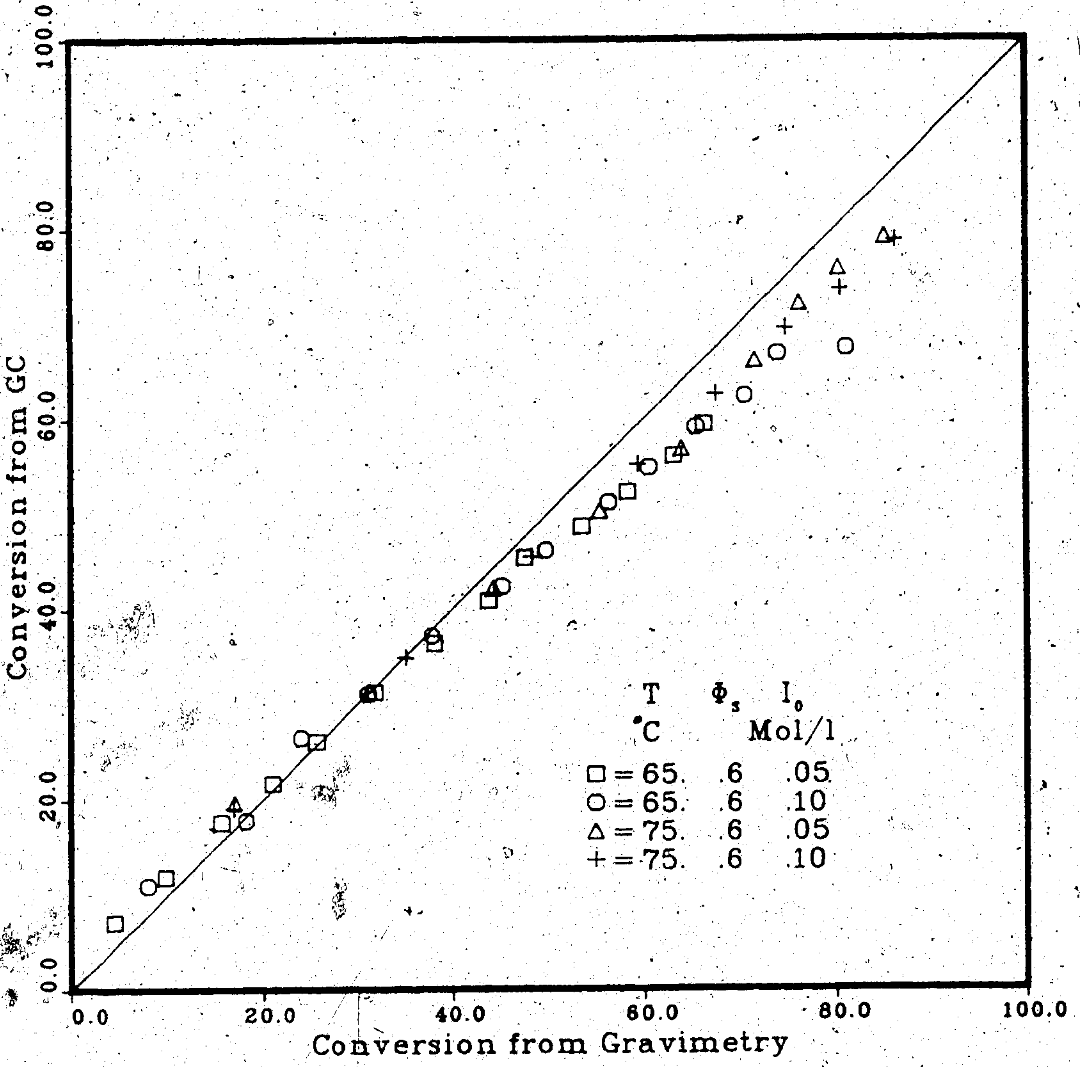

Fig 3.1 Comparison of Conversion Results fromGravimetry and GC

GC columns and the possible depolymerization of polymer to monomer in the injection port. The first source of error leads to conversion values from GC higher than true conversion. However, the vapor phase thermal polymerization of methylmethacrylate is negligible thus eliminating the error due to this source. The second source of error, i.e. depolymerization of polymer would lead to the GC conversion results lower than the actual conversions. But the actual injection port temperature of 150°C is much lower than the temperature at which depolymerization would occur. According to Odian(1981), depolymerization would become pronounced at temperatures higher than 200°C. It can be concluded from the above arguments that the GC method of analysis gives conversion results that are relatively accurate.

Even though, normally gravimetric methods are used to measure conversion in polymerization processes, one should be careful to avoid the sources of errors described here. In particular a quantitative check using size exclusion chromatography would be helpful to decide whether the amounts of monomer and solvent trapped inside the polymer are considerable. Only then would the validity of gravimetric results be established. For all subsequent conversion values needed for the study of polymerization reactions, the results obtained from the GC analysis have been used.

In retrospect, a better way of comparing conversion measurements from GC and gravimetric analysis would have been to prepare solutions of polymer, monomer and solvent by dissolving known weights of PMMA in a mixture of monomer and solvent and analysing the resulting mixture by the above methods. Since the weight fraction of the polymer in the mixture is known, we could have demonstrated the accuacy of one of the two or both methods.

3.3.3 Densimetry

Since the density of the polymer is higher than the density of the monomer, the density of the polymerization mixture increases during the course of the reaction, thus making density measurement an attractive method to follow the course of the polymerization reaction. Dilatometry which exploits this phenomenon of volume change (and hence density change) during the course of polymerization has been widely used earlier mainly to study kinetics of polymerization reactions. This section will deal with commercially available densitometers that can be used for continuous measurement of density and on-line control of conversion in polymerization reactions.

However, it should be mentioned that an on-line refractometer could also have been used to monitor conversion. In fact, we have recently purchased an on-line refractometer from the Electron Machine Corporation to evaluate its use in monitoring conversion.

Several companies supply densitometers which are suitable for automatic, continuous operation with sufficient precision for calculation of polymerization conversion. These break down into three classes based on the mode of operation:

- γ-ray absorption
- oscillatory frequency of a sample filled tube
- mass measurement at fixed volume.

Only one of these, an oscillator-based system distributed by Anton Paar has models with dead volume small enough for laboratory scale on-line determination of density.

The measuring principle of the instrument is based on the change of the natural frequency of a hollow oscillator when filled with different liquids or gases. The mass and thus the density of liquid or gas changes this natural frequency due to a gross mass change of the oscillator caused by introduction of liquids or gases. The oscillator consists of a hollow elastic glass tube which is electronically excited in an undamped harmonic fashion. With the simple relationship between the density of the sample and the natural frequency of the filled oscillator, it is possible to use the method for the determination of the density of the samples which are injected into or flowing through the oscillator.

For calculation of density we may consider an equivalent system represented by a hollow body of mass, M, which is suspended on a spring with an elasticity constant, C, its volume V filled with a sample of density ρ.

The natural frequency f of this system will be given by

$$f = \frac{1}{2\pi}\sqrt{\frac{C}{M+\rho V}} \qquad (3.1)$$

therefore, the period T is given as

$$T = 2\pi\sqrt{(M+\rho V)/C} \qquad (3.2)$$

Taking the square of this expression and introducing the constants

$$A=4\pi^2 V/C \qquad B=4\pi^2 M/C \qquad (3.3)$$

we obtain the equation for the density, ρ, of the sample from the period T as

$$\rho=(T^2 - B)/A \qquad (3.4)$$

Since the constants A and B contain the volume, spring constant and mass, they may be regarded as apparatus constants which may be determined from two calibration measurements of samples of known density such as air and water.

This suggested procedure by the supplier, Anton Parr, was used to calibrate the densitometer. The instrument is connected to an ultrathermostat and brought to the desired temperature by an adjustment on the thermostat temperature control. The display selector located at the top of the instrument is set to "T" to show the period of oscillation. Then approximately 0.7 ml of distilled water is injected through the lower opening of the oscillator cell using a plastic tipped hypodermic syringe. The sample must be homogeneous and free of even the smallest bubbles. The syringe is left in this position at the lower opening of the oscillator tube until the display shows a constant value indicating temperature equibrium.

Next the sample in the cell is withdrawn and the distilled water remaining inside the cell is evaporated by pumping air through the cell. After the cell has become dry, the air inside the cell is allowed to reach temperature equilibrium and the period of oscillation due to air is noted. From the values of periods of oscillations of distilled water and air, and from knowledge of densities of distilled water and air, the values of the constants A and B can be calculated using Equation (3.3). This procedure is repeated for the calibration at different temperatures.

Table 3.1 gives the results of the calibration for the DMA 450 series densitometer employed in this work. Once the instrument has been calibrated, normally it does not require recalibration until the density cell is replaced. This, in fact, has been confirmed by the author. When the instrument was recalibrated after several months of use, no significant changes in the calibration constants were observed.

Table 3.1 Calibration of Densitometer

Temp °C	Tw s	Ta s	ρ_w g/mL	ρ_a g/mL	A	B
30	5.5418	4.1759	.99568	.001046	13.3450	17.42418
40	5.5347	4.1735	.99225	.001013	13.33162	17.40459
50	5.5260	4.1710	.98807	.000981	13.31129	17.38418
60	5.5175	4.1688	.98324	.000952	13.29947	17.36623
65	5.5128	4.1678	.98059	.000938	13.29085	17.35809
70	5.5082	4.1669	.97781	.000924	13.28426	17.35078
75	5.5032	4.1661	.97489	.0009113	13.27400	17.34429
80	5.4959	4.1651	.97183	.000898	13.24177	17.33616

Tw: period of oscillation for distilled water

Ta: period of oscillation for air

ρ_w: density of distilled water

ρ_a: density of air

After calibration of the densitometer, density of the polymerization mixture can be measured easily. However, it is important that these density measurements should be converted to conversion measurements by developing appropriate correlations or equations. For this purpose two methods can be used.

The first one involves the development of an empirical correlation between density and conversion and use of this correlation to estimate conversion from density measurement. Figure 3.2 shows the variation of density with conversion for various polymerization conditions. For purpose of development of correlations, the density measurement is done off-line at a temperatute of 40°C which is significantly lower than the reaction temperature(60-80°C) in order to avoid further polymerization of the sample in the density cell. At 40°C polymerization of the mixture essentially stops and hence the calculated conversion values correspond to conversions at the times of collection of samples from the reactor. The conversion values used for this calibration are obtained from the GC measurements as the GC method is considered to be more accurate compared to gravimetry.

The density change with conversion during the polymerization process is shown in Figure 3.2 for various conditions. On closer examination it can be observed that two different straight lines can be fitted to the data: one for the initiator concentration 0.05 mol/l, the other for the concentration .10 mol/l. In fact the two solid lines

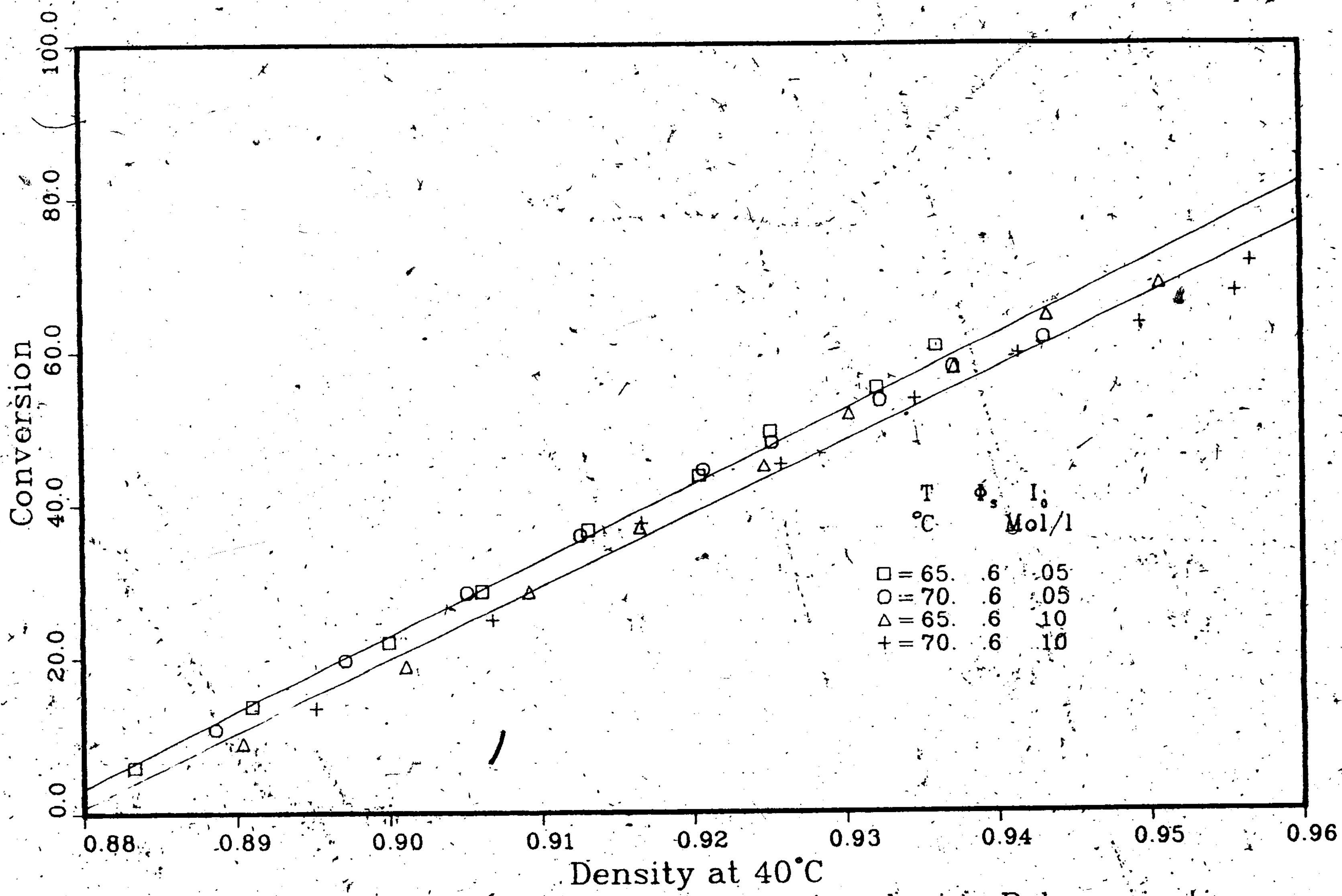

Fig. 3.2 Variation of Density with Conversion during Polymerization

shown in the Figure 3.2 are the least square fit of the data for the two initiator levels. However, it is noted that if the volume fraction of the solvent is changed, a different straight line has to be fitted for the experimental points. It is obvious that this procedure of fitting a straight line for each experimental condition is not convenient. Hence a second method of relating density and conversion has been developed as described below.

Abbey (1981) assumed ideal mixing of polymer, monomer and solvent or water phase and developed mathematical equations relating the density of the polymerization mixture and conversion in the cases of solution and also emulsion polymerization of methylmethacrylate. Schmidt and Ray (1981) also used a mathematical relationship to get conversion in the case of emulsion polymerization of methylmethacrylate. A mathematical equation relating the density to the conversion will be developed assuming ideal mixing of polymer, monomer, solvent and also the initiator. Since the initiator also affects the density of the polymerization mixture, as shown in Figure 3.2, the effect of initiator on the density must be taken into account.

Let W be the total weight of the initial polymerization mixture. The total weight is given by the Equation (3.5).

$$W=W_m+W_s+W_i \qquad (3.5)$$

where W_m, W_s and W_i are the initial weights of monomer, solvent and initiator, respectively. The total weight of the polymerization as well as the weights of solvent and initiator remain constant throughout the course of polymerization. Since monomer is converted to polymer, the weight of the monomer decreases while the weight of the polymer increases by an equal amount. The density of the polymerization mixture increases due to higher density of the polymer compared to the monomer. Let X be the weight fraction of the initial monomer converted to polymer. At a conversion X, the following mass balances will hold good.

the weight of polymer = $W_m X$.
the weight of monomer = $W_m (1-X)$
volume of polymer = $W_m x/\rho_y$
volume of monomer = $W_m (1-X)/\rho_m$
volume of solvent = W_s/ρ_s
volume of initiator = W_i/ρ_i

The total volume V of the polymerization mixture can be obtained by adding the volumes of monomer, polymer, solvent and initiator assuming ideal mixing of the above components. Total volume V is given by:

$$V = \frac{W_m X}{\rho_y} + \frac{W_m (1-X)}{\rho_m} + \frac{W_s}{\rho_s} + \frac{W_i}{\rho_i} , \qquad (3.6)$$

where ρ_y, ρ_m, ρ_s and ρ_i are the densities of polymer, monomer, solvent and initiator respectively. The density of the mixture will be given by

$$\rho_{mix} = W/V \tag{3.7}$$

Substituting for W and V from Equations(3.5) and (3.6) respectively in Equation(3.7), an expression for monomer conversion X is obtained as:

$$X = \frac{W_m(1-1/\rho_m)+W_s(1-1/\rho_s)+W_i(1-1/\rho_i)}{(\rho_{mix}W_m/\rho_y - W_m/\rho_m)} \tag{3.8}$$

In the RHS of Equation(3.8) all the quantities except density of the mixture are known at the beginning of the reaction. Thus by measuring density, conversion X can be calculated. However it should be noted that density also changes with temperature. To eliminate the effect of temperature, the density of the polymerization mixture is measured at a constant temperature.

Equation (3.8) has been used to calculate conversion from the measured values of density at a temperature of 40°C for various conditions of polymerization. These results are compared to the conversion results obtained from GC measurements in Figure 3.3. It can be easily observed that the conversion results from both of these methods agree very well, confirming our earlier deduction that the gravimetric results are prone to error at higher conversion level. This equation can also be used in situations where the density measurements are available under changing temperatures of the reaction mixture if the densities of monomer and solvent are known as functions of temperature. Hence its use should

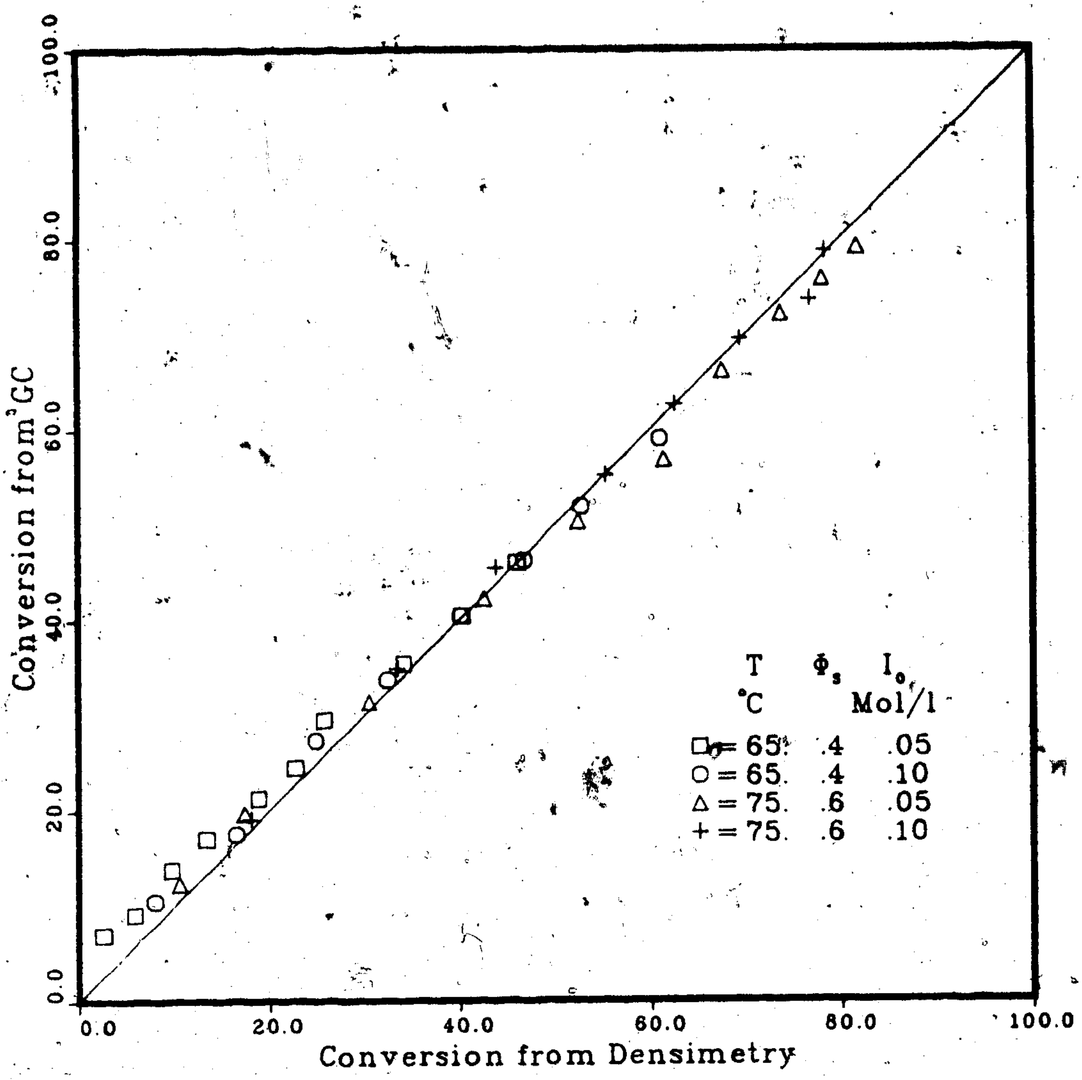

Fig. 3.3 Comparison of Conversion Results from Densimetry and GC

be superior to that of the empirical relationship shown in Figure 3.2.

The densitometer is capable of measuring density to a resolution of 0.0001 g/mL. The resolution with respect to conversion in the case of solution polymerization of methylmethacrylate can be calculated by knowing the initial density and the final density at 100 per cent conversion. In the case of bulk polymerization of methylmethacrylate a resolution of 0.04 per cent conversion can be expected whereas in the case of solution polymerization with 60 per cent solvent (toluene) a resolution of 0.20 per cent conversion can only be expected. Schrock and Ray (1981) have reported that in the presence of measurement errors, they could get a conversion resolution of 0.5 per cent in emulsion polymerization of methylmethacrylate.

The above discussion indicates that the densitometer has sufficient resolution to measure conversion in polymerization reactions and can also be used for on-line monitoring of conversion.

3.4 Size Exclusion Chromatography(SEC)

SEC has become one of the most important instruments in polymer engineering because of its ability to measure molecular weight distribution (MWD). SEC separates polymer molecules with molecular weights from 1000 to as high as 10 million according to their size in solution. The separation is accomplished by passing a solution of molecular mixture of interest through a column containing particles of a microporous solid which has solvent in [illegible] interstices and in its pores. Since any pore acces[illegible] to larger molecule is also accessible to a smaller molecule, larger molecules are excluded from more pores than are the smaller ones and come out of the column first. This separation is illustrated schematically in Figure 3.4.

Moore (1964) of Dow Chemical Company first disclosed the use of cross-linked polystyrene gels for separating synthetic polymers soluble in organic solvents and with that event conventional size exclusion chromatography (SEC) was born and came rapidly into extensive use to get MWD information for synthetic polymers. Modern high-performance SEC has resulted from the development of small, more rigid porous particles which can withstand relatively high pressures (2000-3000 psi) and provide high performance in terms of resolving polymer species. A number of very good references are available that deal with SEC separation techniques in polymerization studies (Yau et al.(1979), Boni(1976), Hamielec (1976)).

A large number of equipment manufacturers market systems and components for performing SEC separation. The information concerning the vendors and the equipment that can be used for high-performance liquid chromatography are listed by McNair and Chandler(1976) and Snyder and Kirkland(1979).

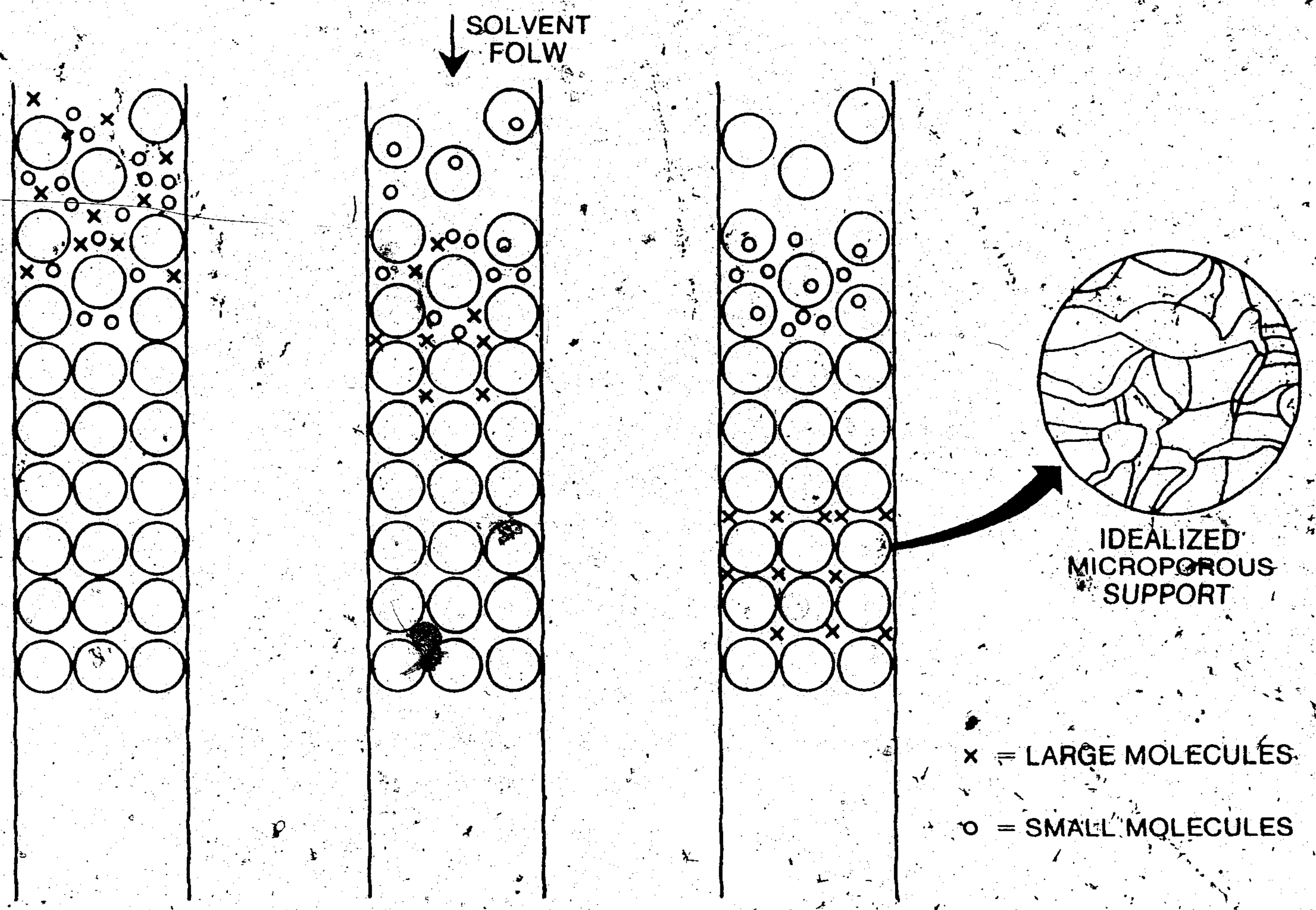

FIG. 3.4. SCHEMATIC OF THE SEPARATION PROCESS IN SEC.

An SEC supplied by Waters Associates (Model 244) was used in this work to measure the molecular weight distribution of the polymer polymethylmethacrylate. The Waters Associates model consists of the following components:

- a high pressure solvent delivery pump
- a UV absorbance detector
- a refractive index (RI) detector
- a sample injection system
- μ-Styragel columns
- a syphon at the outlet of the columns.

Tetrahydrofuran is used as the carrier solvent and also as the solvent to dissolve the polymer. This SEC has been modified by replacing the sample injection system with an automatic sample valve and by incorporating an automatic sampling system which collects the samples of the reaction mixture from the reactor and injects into the SEC after diluting with the carrier solvent. The automatic sampling system which facilates the on-line measurement of MWD has already been described in detail in chapter two.

Even though the SEC is provided with a UV as well as a RI detector, only the RI detector was used in this work because of its response (being a universal detector) to the polymer methylmethacrylate. The RI detectors are universal in the sense that they respond to a wide variety of chemicals. The UV detector does not respond to the polymer PMMA. The RI detector responses (0-10mv) are amplified, filtered and sent to the HP/1000 computer for on-line data acquisition.

3.4.1 SEC Program

A computer program has been developed in order to collect the SEC data automatically and process them to calculate the number average and weight average molecular weights. The SEC program accomplishes the following functions:

1. Initiation of SEC data acquisition
2. Identification of start of SEC peak
3. Identification of end of SEC peak
4. Termination of SEC data collection
5. Processing of SEC data for molecular weight averages.

Initiation of SEC data acquisition is accomplished by reading a digit switch associated with the switching of the automatic sample valve. This digit switch which is located in the programmable sequence timer turns on at the instant of injection of polymer sample into the SEC. The program reads the on-status of the switch and starts the process of SEC data acquisition. Since the actual SEC peak which contains the essential data elutes a few minutes after the injection, a dead time can be specified in the program during which SEC data will not be collected. However time count is started from the moment of injection. Few minutes after the injection the digital switch is turned off so that at the time of next injection, it can again be turned on starting another SEC analysis.

Logic to Identify the Start of the Peak

The SEC data that are necessary for the calculations of molecular weight averages lie between the start point and the end point of the SEC peak. Hence it is important to devise proper logic to correctly identify the start point of the SEC peak. For this purpose initially 20 SEC readings are collected at the appropriate sample interval which in this case is three seconds. These readings are stored in an array and starting from the first reading, each reading in the array is analysed to check five consesecutive readings showing an increasing trend. The first reading which satisfies the above criterion is considered to be the start point of the SEC chromatogram. This criterion works well upon proper differentiation between baseline drift and SEC peak. For this purpose each successive SEC reading after the start point is required to be higher than the previous value by a certain value (10mV), which is usually higher than the baseline drift value(≤5mV). If all the points fail to satisfy the criterion for the start point of the SEC peak, it implies that the SEC peak has not yet started eluting. Since the SEC data outside SEC peak are not needed, the program rejects the initial five data and proceeds to collect five more data points so that there are again twenty points to repeat the same logic to find the start point of the peak. After the start point of [illegible] peak has been identified a logical variable LSTAT which is initialized to .FALSE. is set to .TRUE. and this variable helps the program to recognize the occurrence of the peak and the future readings are not analyzed for the start point of the peak.

Logic to Identify the End Of The Peak.

After the start point has been identified, the next important point is the end point of the chromatogram. For this purpose, the program first identifies the peak point corresponding to the maximum value of the chromatogram readings. For identifying the peak point of the chromatogram, the SEC data are arranged in an array and since the peak point can occur only after the start point, each reading in the array after the start point is analyzed to check whether it satisfies the criterion for the peak point. A peak is considered to have been identified if five consecutive readings show a decreasing trend. The first reading after the start point which satisfies the above criterion is the peak point of the chromatogram. If a peak point is not found, the program stores a point from where the search for the peak point should start next time and proceeds to collect five more SEC data. The same criterion for the peak point is repeated but this time starting with the stored value of the search point, thus reducing the computer search time. After a peak point has been identified a logical variable LPEAK which is initialized to .FALSE. [illegible] set to .TRUE. and the program proceeds to identify the e point of SEC chromatogram:

To identify the end point of the SEC chromatogram the SEC data are placed in an array and each reading after the peak point is analyzed to check whether it satisfies the logic for the end point. A point is considered to have satisfied the criterion for end point if five consecutive readings have SEC readings that lie within a bound. The first reading after the peak point that satisfies the above criterion is considered to be the end point of the chromatogram. If all the readings fail to satisfy the criterion, a search point is stored and the program collects five more SEC data to repeat the criterion. After the end point has been identified a logical variable LSTOP which is initialized to .FALSE. is set to .TRUE. and the program stops data collection. It is possible that sometimes a solvent peak or initiator or monomer peak may start eluting before the end of polymer peak settles to a constant value in which case the SEC chromatogram ends in a valley. The identification of end point of SEC chromatogram corresponding to an end in a valley is also handled by the program. However by selecting SEC columns which can achieve good resolution of polymer peak, an end in valley can be easily avoided.

After identification of the end point of the SEC peak, the program stops the data collection and reinitializes the above mentioned logical variables to .FALSE. so that another search for the start, peak and end points can be made in the next polymer sample injection. Then the program proceeds to calculate the molecular weight averages.

The SEC data that had been collected can also be plotted using an HP plotter. Figure 3.5 gives a typical chromatogram obtained in one of the SEC analyses.

3.4.2 Molecular Weight Calculations

The SEC data are processed to calculate number average and weight average molecular weights taking into account the following:

- Base line drift
- Dispersion
- Variation in solvent flowrate

Base Line Drift

It is noted that the number average molecular weight is affected considerably if the base line drift is not accounted for in the molecular weight calculations. Base line drift is corrected by noting the initial base line value and the final base line value corresponding to the end of the SEC peak and assuming a linear drift from the initial to the final base line value.

Normalization

Since the chromatogram above the base line is only needed in the calculation of molecular weight averages, the

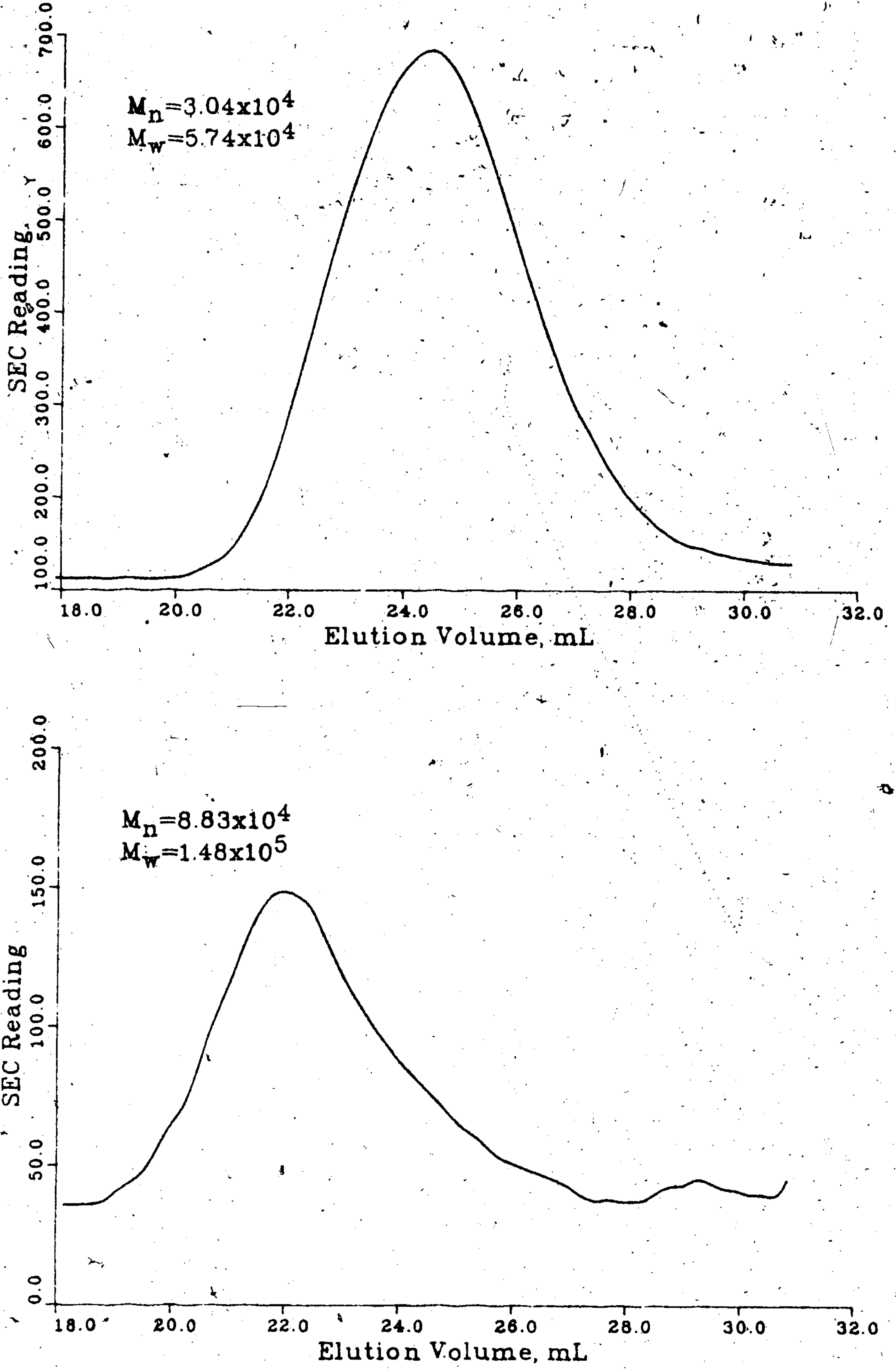

Fig. 3.5 Typical SEC Chromatograms

base line values are subtracted from the corresponding SEC readings. The area of the resulting chromatogram is calculated and a normalized chromatogram is obtained by dividing each reading by this area. The normalized chromatogram has the area of unity and simplifies further calculations to get molecular weight averages. In the normalization procedure it is assumed that the detector response factor is independent of molecular weight.

Dispersion Correction

Axial dispersion of solute molecules of a single species results in the elution of a single species occurring over a range of elution times, giving a distribution of elution times for each species of the solute. The chromatogram of the sample as measured by the detector is the superposition of these distributions. Interpretation of a chromatogram must therefore account for this superposition.

If there were no column dispersion, i.e. at infinite resolution, the weight concentration and the molecular weight at any SEC elution volume, y, are $W(y)$ and $M_t(y)$ respectively, where $M_t(y)$ is the true calibration relationship. If we let a Gaussian function $G(v-y)$ describe the fraction of species at y which gets spread over to v, we can consider the molecular weight mixture at any elution volume v to be made up by species coming from all different y elution volumes. The molecular weight of these species are

M_i and their weight concentrations detected at v are W(y)G(v-y). The total detector response observed at elution volume, v, is given by

$$F(v) = \int_{-\infty}^{\infty} W(y)G(v-y)dy \qquad (3.9)$$

The above is the well known Tung's equation for axial dispersion and has the form of the convolution integral as shown by Hamielec and Ray(1969). The solution or deconvolution of the above equation is needed to correct for the effect of dispersion. A number of methods have been proposed (Balke et al.(1969), Provder and Rosen(1971), Yau et al.(1977)) to correct for the dispersion effect in SEC and a method proposed by Yau et al.(1978) is used in this study. The details of the mathematical derivation of this method is presented in Appendix B.

Narrow PMMA molecular weight standards were used to obtain σ^2 values of SEC chromatograms. However, it should be noted that the observed variances of SEC chromatograms are not only due to the column dispersion but also due to the polydispersities of the narrow standards. The PMMA standards obtained from the manufacturer were characterized only for the peak molecular weights, whereas they were not accurately characterized for their polydispersity values. Hence, it was not possible to accurately take account of the variance contribution of the polydispersities of the narrow standards in calculating number and weight average molecular weights.

In this work, dispersion correction was done based on the observed variances of SEC chromatograms of the narrow standards only. If the variance contribution of the known polydispersity values were taken into account, it should change the results of number average and weight average molecular weights slightly. A computer simulation experiment was done using a raw SEC chromatogram to study the effect of variance values on number and weight average molecular weights. For a variance value of 0.40, the number and weight average molecular weights, and polydispersity values obtained were 8.23×10^4, 1.35×10^5 and 1.65, respectively. When the variance value was changed from 0.4 to 0.0, the M_n, Mw and polydispersity values obtained were 7.83×10^4, 1.40×10^5 and 1.75, respectively. Thus the changes in M_n, Mw and polydispersity values were 4.8, 3.7 and 11 percent, respectively. We observe that the variance affects the polydispersity values considerably. However, in our calculation of number and weight average molecular weights, the errors due to not taking account of the polydispersity of the narrow samples will be less than the error values just reported, because the σ^2 values due to column dispersion will be only smaller than the σ^2 values of SEC chromatograms of the narrow standards, but will be never zero.

Correction for Solvent Flowrate Variations

Since the molecular weight calculations are sensitive to the variations in the flowrate of the carrier solvent, the average flowrate for each run is measured and used in the calculations. A syphon that would discharge its contents when it is full, is fitted at the outlet of the SEC columns. At the time of discharge of the SEC solvent from the syphon a digit switch is closed. The average flowrate is easily calculated from the volume of the syphon and the readings of the computer times at which the syphon discharged the solvent.

3.4.3 Molecuar Weight Calibration

The traditional technique for relating elution volume to molecular weight has been to determine the elution volumes of sample with relatively narrow MWD that have been characterized as to molecular weight by independent means. The most commonly used standards are anionically polymerized polystyrenes, prepared by Pressure Chemicals Inc.(Pittsburgh, Pa.). Since the relation between the size and molecular weight strongly depends on the polymer structure and it is the size that determines elution volume, a calibration curve obtained with a particular polymer will not be accurate for a polymer with a different structure. Since narrow MWD sample are only available for a limited number of polymer types, means for generating a universal calibration curve that would be applicable to others, independent of their structure, has been the subject of considerable study (Boni(1976)). Hamielec(1976) and Yau et al.(1979) discussed in detail the methods that can be used to calibrate the SEC.

Since narrow MWD standards are available (Polymer Laboratories Inc., Stow, Ohio), the molecular weight calibration curve is established directly by injecting different standards into the SEC and finding peak elution volumes for a particular set of operating conditions. In this work the SEC is operated under the following conditions:

Columns : μ-Styragel Columns 10^3, 10^4, 10^5 °A
Solvent : Tetrahydrofuran(THF)
Flowrate : 3.0 ml/min
RI detector: 8x

Six narrow MWD standards (molecular weights ranging from 45,000 to 680,000) were used in this study to obtain the molecular weight calibration curve for the SEC. In Table 3.2 peak elution volumes (along with duplicate values) and the variance of the SEC peaks of the narrow standards are reported. A semilog plot of molecular weights and elution volumes shown in Figure 3.6 suggests that a semi-logarithmic relationship of form given in Equation (3.10) can be fitted to the data,

$$\ln(M_t) = a_0 + a_1 v \qquad (3.10)$$

where a_0 and a_1 are constants and v is the elution volume. In fact the solid line shown in the Figure 3.5 is the least squares fit of all the data.

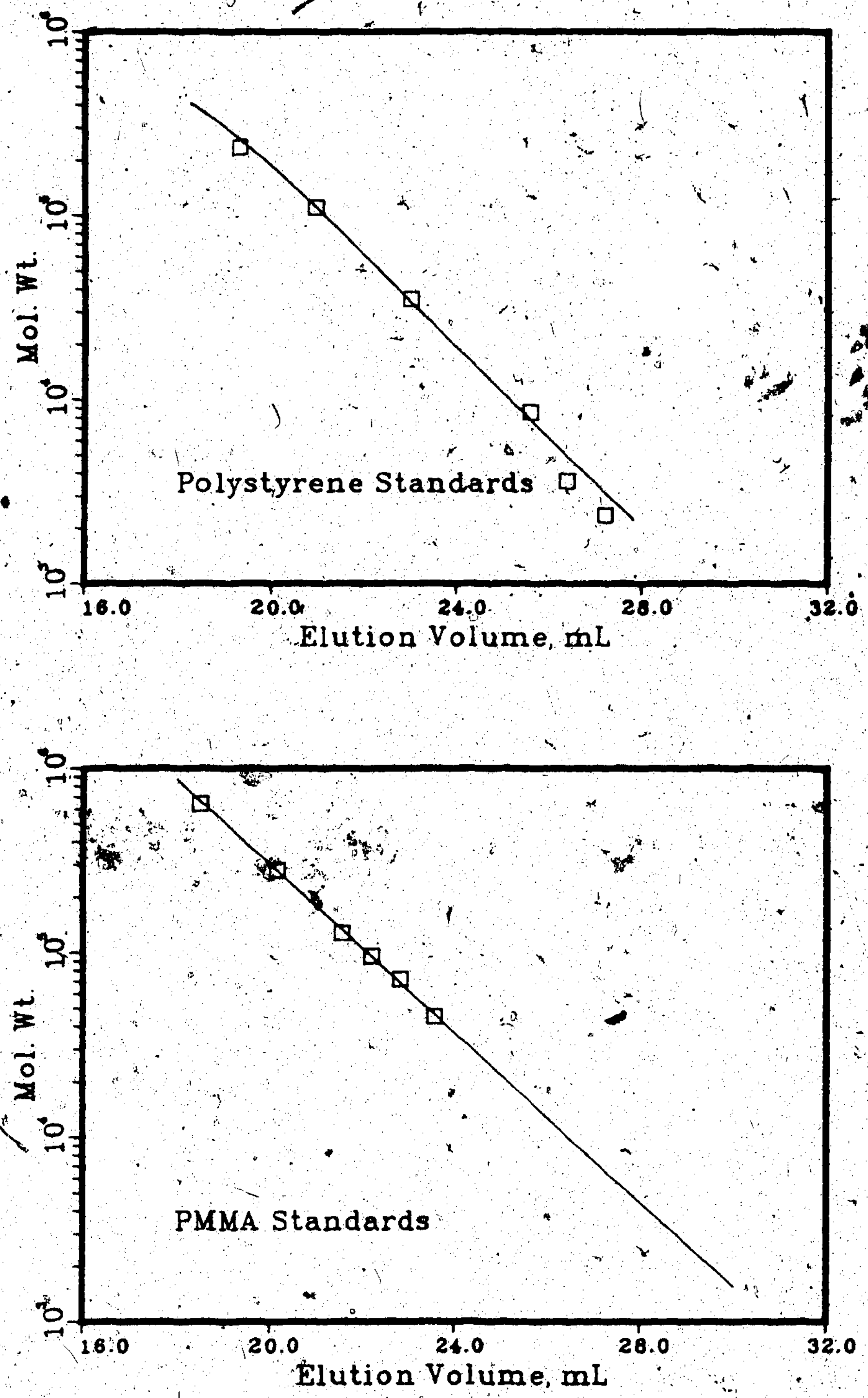

Fig. 3.6 SEC Calibration

Table 3.2 Molecular Weight Calibration

Molecular Weight	Retention Volume (ml)	Variance σ^2
45200	23.56 23.53	0.3316 0.4084
72000	22.82 22.80	0.3390 0.3753
96000	22.20 22.17	0.4247 0.3987
128000	21.56 21.57	0.3527 0.3663
280000	20.16 20.18	0.3485 0.3738
640000	18.52 18.61	0.3782 0.3898

It should be mentioned here that PMMA molecular weight standards are available in the range 45,000 to 680,000. Hence it is important to establish whether the set of SEC columns could be used for molecular weights below 45000 and whether the semi-logarithmic relationship could be extrapolated for molecular weights less than 45000. For this purpose, we injected polystyrene molecular weight standards ranging in molecular weights from 2000 to 200,000. The molecular weight-elution volume relationship for the polystyrene standards are shown in Figure 3.6. From this relationship, it can be concluded that the SEC columns were able to resolve molecular weights as low as 2000. According to the manufacturer's (Waters Associates) specification, the set of columns (10^3, 10^4 and 10^5 °A) could be used for the molecular weights from 500 to 8,000,000.

From the elution volume and molecular weight plot shown in Figure 3.6 for polystyrene standard, we can fit a straight line for the molecular weights ranging from 2000 to 200,000. Even though we do not have narrow PMMA standards for molecular weights lower than 45000, we can reasonably assume the semilogarithmic relationship for molecular weights up to 2000 by analogy with polystyrene standards. Of course, we can expect that this assumption can lead to some error in the calculation of number average and weight average molecular weights particularly at molecular weights less than 45000.

Two typical SEC chromatograms, one corresponding to a high molecular weight sample (M_n=8.83x10^4, Mw=1.48x10^5) and the other corresponding to a low molecular weight sample, (M_n=3.04x10^4, Mw=5.74x10^4) are shown in Figure 3.5. We can observe that for the low molecular weight sample, the elution volumes range from 20 mL to 29 mL. Since the elution volume for the 45000 molecular weight sample of PMMA is only 23.6 mL, we note that extrapolation of the molecular weight-elution volume relationship is necessary for elution volumes greater than 23.5 mL. We could have used a universal calibration curve based on polystyrene standards to avoid extrapolation.

Usually the molecular weight-elution volume relationship is expressed in the form:

$$M_t = D_1 \exp(-D_2 v) \qquad (3.11)$$

From Equations (3.10) and (3.11) the constants D_1 and D_2 are obtained as,

$$D_1 = \exp(a_0), \qquad D_2 = -a_2 \qquad (3.12)$$

The D_1 and and D_2 values obtained from Equation(3.12) along with the reported value of average variance in Table 3.2 are used to calculate the number and weight average molecular weights as shown in Appendix B.

It should be pointed out that the SEC calibration should be repeated often to compensate for column deterioration. While small fluctuations in temperature or flowrate may not upset the calibration, changing columns, solvent, or the nature of the polymer samples will require recalibration of the SEC experiment. After several months of use, we observed only a slight change in the calibration curve of the SEC used in our study.

3.5 SEC Error Analysis

A number of experiments have been conducted to check the reproducibility of SEC results. A sample of the polymerization reaction mixture diluted with the solvent THF was injected seven times into the SEC and the number and weight average molecular weights obtained are reported in Table 3.3.

From Table 3.3 it can be observed that the averages of the number and weight average molecular weights are 42000. and 76400., respectively. The percent relative standard deviation for the number and weight average molecular weights are calculated as 5.3 and 4.1, respectively. These results are comparable to the reproducibility studies reported by Balke(1973).

The accuracy of molecular weight average determined from a SEC experiment is dependent [illegible] factors which are discussed by Yau et al.(1979). [illegible] important that the samples are diluted [illegible] to prevent the overloading of the columns and significant band broadening due to viscous streaming. A rough guide for sample dilution is that an injected sample should have a viscosity no greater than twice the viscosity of the mobile phase. For high molecular weight polymers concentrations less than 0.10 weight percent are often required to eliminate undesirable effects.

3.6 Viscosity Measurement

Even though number average and weight average molecular weights can be measured using the SEC, there is a delay of 10-15 minutes before these measurements become available to take any control action during the course of polymerization. Hence, it is desired to have more rapid on-line measurements of the molecular weight averages. In this context the viscosity of the polymerization mixture has been measured to get an estimate of the molecular weight average of the

Table 3.3 Reproducibility Results of SEC

Injection Number	Number Average Mol. Weight	Weight Average Mol. Weight
1	3.95E4	7.50E4
2	3.97E4	7.31E4
3	4.33E4	7.70E4
4	4.45E4	8.04E4
5	4.13E4	8.15E4
6	4.01E4	7.48E4
7	4.54E4	7.31E4
Average	4.20E4	7.64E4
Std. deviation	2.23E3	3.13E3

polymer.

It is known that the viscosity of linear polymer solutions are related to the molecular weight of the polymer (Flory(1953)). Since PMMA is a linear polyme[illegible]n expression relating the molecular weight and the viscosity of the polymerization mixture could be developed. In addition to molecular weight, the viscosity of the polymerization mixture is also affected by monomer conversion, temperature of the reaction and concentration of the solvent. Influence of all of the above variables on the viscosity of the reaction mixture should be taken into account when developing mathematical models to estimate the molecular weight average from measurement of viscosity.

Jo(1975) measured the viscosity on-line for the case of solution polymerization of vinylacetate in a CSTR and estimated the weight average molecular weight from the following correlation:

$$\ln(\eta) = b_1 + b_2 X Mw^n \tag{3.13}$$

In the above equation η, X, Mw are the viscosity, monomer conversion and weight average molecular weight respectively. The constants b_1 and b_2 and n had been determined from his experimental data.

Alhough a number of on-line viscometers are available in the market (Huskins(1982)), only a few of them can be considered suitable for use in the laboratory-sized reactor. Most of them required large sized process streams or large sized reactors, the emphasis of application being on industrial-scale processes. Finally, an industrial-type viscometer supplied by Norcross Corporation which could also be used for laboratory application was chosen for this study.

This viscometer operates on a falling piston principle which is better explained by referring to Figure 3.7. The measuring element consists of a cylindrical tube which is mounted vertically on the reactor lid. The lower part is immersed in the reaction mixture and a piston-rod assembly is located inside the measuring tube. During the filling phase the piston-rod assembly is lifted by an air-actuated mechanism drawing a sample of the polymer mixture down through the clearance between the measuring tube and the piston. During the measuring phase, the piston rod assembly is allowed to fall under gravity, expelling the same sample

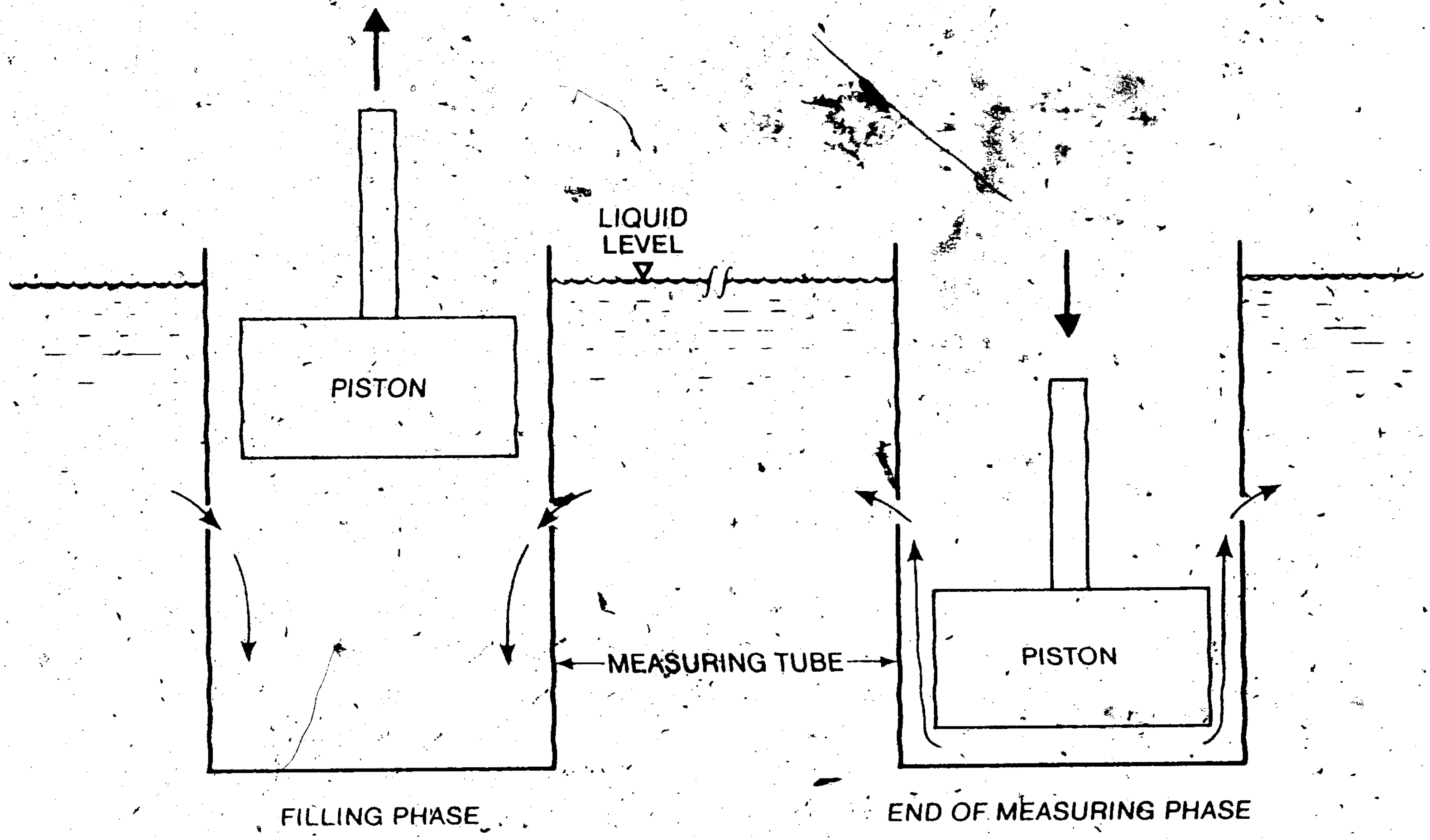

FIG. 3.7. SCHEMATIC OF THE FALLING PISTON VISCOMETER.

through the holes in the measuring tube. The time required for the piston-rod assembly to drop to the bottom of the tube is a measure of viscosity and this measure is available in the range of 1-5V for on-line data acqusition. The element is continuously self-cleaning owing to the reverse flushing that takes place during the normal up-and-down motion of the piston. In this instrument viscosity measurement is taken every minute which is considerably faster than the 10-15 minutes analysis time for SEC measurement.

The viscosity range that can be measured using a single piston is limited to a single decade (i.e. 1cp-10cp, 10cp-100cp etc.). Since during the course of polymerization the viscosity can increase from 1cp to as high as 100cp, it is necessary to change the piston when the viscosity values exceed the maximum range. However the piston can be changed easily in two to three minutes time which is negligible compared to the total reaction time of 1-5 hours.

The viscometer is calibrated for each piston separately using viscosity standards available in the market(Can-Am Instruments Ltd, Mississauga, Canada). The calibration curve obtained for two pistons are shown in Figure 3.8. The computer readings are converted to viscosity values using this calibration curve. In the next chapter the viscosity measurements along with the analysis to estimate the molecular weight of the polymer will be presented.

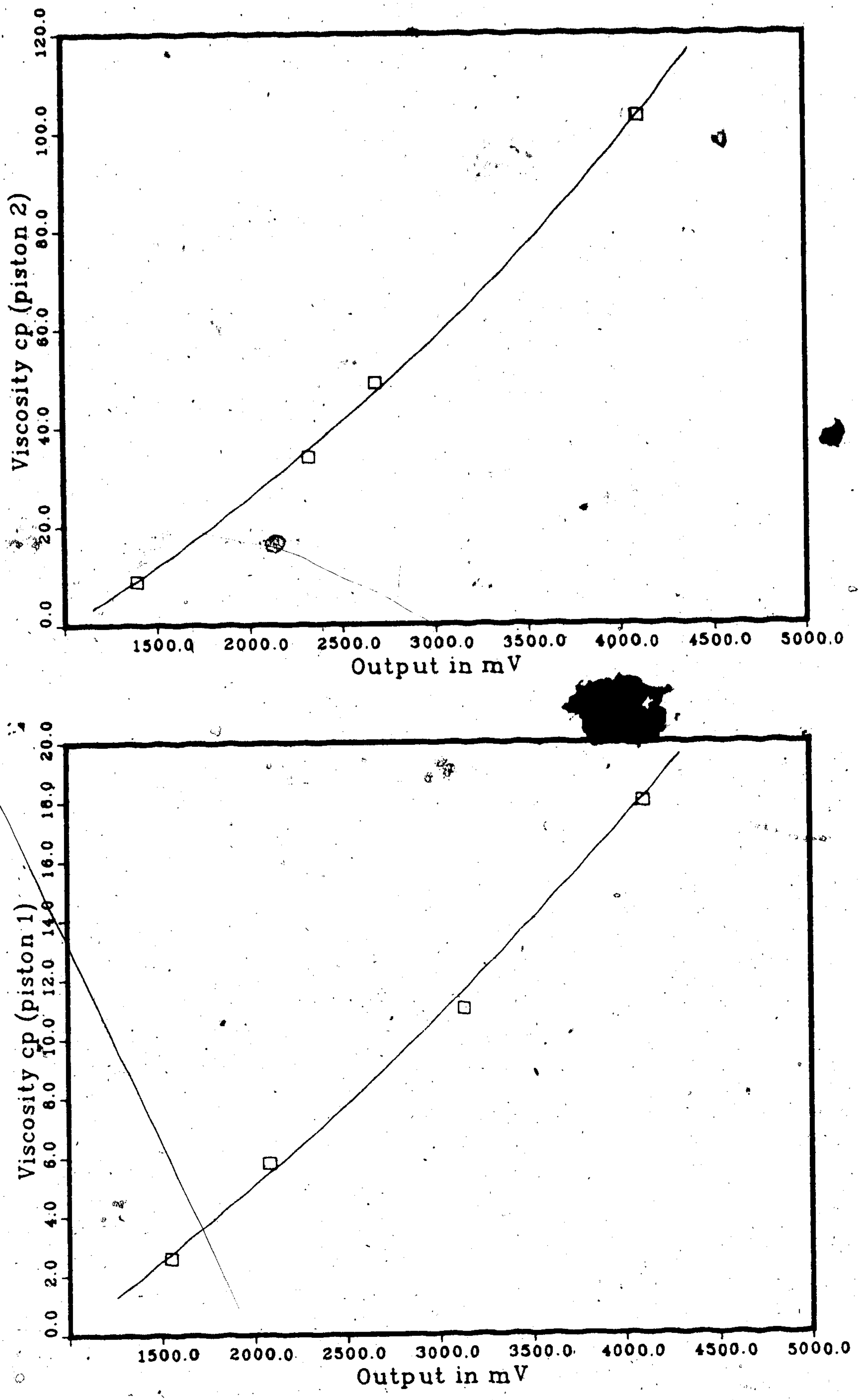

Fig. 3.8 Viscometer Calibration

3.7 Torque Measurement

Since the viscosity of the polymerization mixture increases during the course of polymerization, the torque exerted on the constant RPM stirrer by the reaction mixture also increases. By measuring the torque exerted on the stirrer, it is possible to estimate the molecular weight average of the polymer produced during the course of polymerization. In fact, Jo(1975) monitored on-line the torque on the stirrer in order to measure the viscosity of the reaction in a solution polymerization process. In turn the viscosity measurement was used to estimate the weight average molecular weight of the polymer as described in the previous section.

The stirrer-motor assembly used in this experimental study has been already described in chapter two. The torque exerted on the stirrer is available in the range of 0.10V output for on-line data acquisition. Since torque measurement is continuous, molecular weight averages could be estimated instantaneously if a reliable correlation relating torque and molecular weight of the polymer is developed.

Though the torque measurement could have served as an additional measurement for estimation of the molecular weight of the polymer produced during the reaction, in this study the torque measurement could not serve that purpose. The torque measurements were found to be noisy due to unpredictable friction at the bearing site of the stirrer.

Since it was not possible to predict the torque exerted on the stirrer only due to the polymerization mixture, these measurements were not analysed to develop correlations.

3.8 Conclusions

Various on-line as well as off-line technique[illegible] measure monomer conversion, molecular weight averages, viscosity and torque on the stirrer for a free radical solution polymerization process have been described in this chapter. Comparison of conversion measurements from gravimetry, gas chromatography and densimetry confirms that gas chromatography and densimetry results are more accurate than gravimetric results. Further it has been concluded that gravimetric conversion results are prone to error especially at higher levels of conversion and hence these results should be accepted only after careful consideration.

A description of computer software that was developed for on-line acquisition of the SEC data and analysis to calculate the number and weight average molecular weights of the polymer is also given. This software along with the automatic sampling system form an important contribution to the automatic analysis of polymerization reaction mixtures.

4. EXPERIMENTAL RESULTS

4.1 Introduction

In chapters two and three the experimental reactor system and the techniques of measuring various process variables in the solution polymerization of MMA in a batch reactor were described in detail. It is important to generate experimental data on the polymerization processes for the following purposes. Various on-line measurements such as density, viscosity and SEC can be analyzed to develop correlations to estimate important process variables such as conversion, number and weight average molecular weights. These experimental results can also be used to check the validity of the mathematical model of the reactor as will be shown in chapter five. Also by designing appropriate experiments we can understand the effect of various inputs such as temperature and initiator concentration on the polymerization process.

A total of 15 experiments were conducted with different combinations of initiator concentrations and temperatures. The experimental procedures described in section 2.5 were followed to measure process variables such as temperature, density, viscosity, torque, number average and weight average molecular weights. All of these variables were recorded on the HP/1000 computer through an on-line data acquisition program. The experimental data obtained are summarized and reported in Appendix G. For experiments (1-7) the number and weight average molecular weights are not reported because of the experimental difficulties with the SEC in getting reliable values. Some of the SEC columns plugged and had to be replaced with new columns. Later it was found that some of the earlier measurements done using the old columns could not be reproduced well and hence they were discarded. Although torque measurements were recorded, they were not reported because of the unreliability of these data, as discussed earlier in section 3.7. In the following sections the analysis of the experimental results will be presented.

4.2 Reproducibility of the Experimental Data

The results from a polymerization experiment are dependent on many different factors: purity of monomer and solvent, the condition of the initiator, the presence of any inhibitor in the reaction mixture, the purity of the nitrogen blanket, the actual temperature of the reaction mixture, etc. A good reproducibility of the experimental results gives confidence in the accuracy of the results in spite of the difficulties in maintaining identical experimental conditions. Hence it is important to repeat some of the experiments keeping identical conditions to check if the results are reproduced at all. This lends credibility to the experimental set-up as well as the measurement techniques and the instruments.

Figure 4.1 shows the reproducibility results for conversion, viscosity, number average and weight average molecular weights for a case where the temperature, solvent ratio and initial initiator concentration were 70°C, 0.6 and 0.05 mol/L respectively. From this figure it can be observed that we are able to duplicate conversion results very well, the maximum difference being only 5 per cent. There are differences to the order of 10-15 per cent in the reproducibility of number average and weight average molecular weights and even larger differences of the order of 20-25 per cent can be observed in the reproducibility of viscosity values. The same trends are observed in Figure 4.2 in which reproducibility results are presented for the following experimental conditions: temperature=75°C, solvent ratio=0.6 and initial initiator concentration=0.10 mol/L.

From the above results it can be concluded that conversion, number average and weight average molecular weights can be duplicated within reasonable accuracy when identical experimental conditions are maintained. However, viscosity results could not be reproduced well enough and the reason for this can be explained as follows. The viscosity of the polymerization mixture depends on monomer conversion, molecular weight of the polymer and also the temperature of the polymerization mixture. Since the errors in any of the variables affect the viscosity, the poor reproducibility is most probably due to the cumulative effect of small errors in all of these variables.

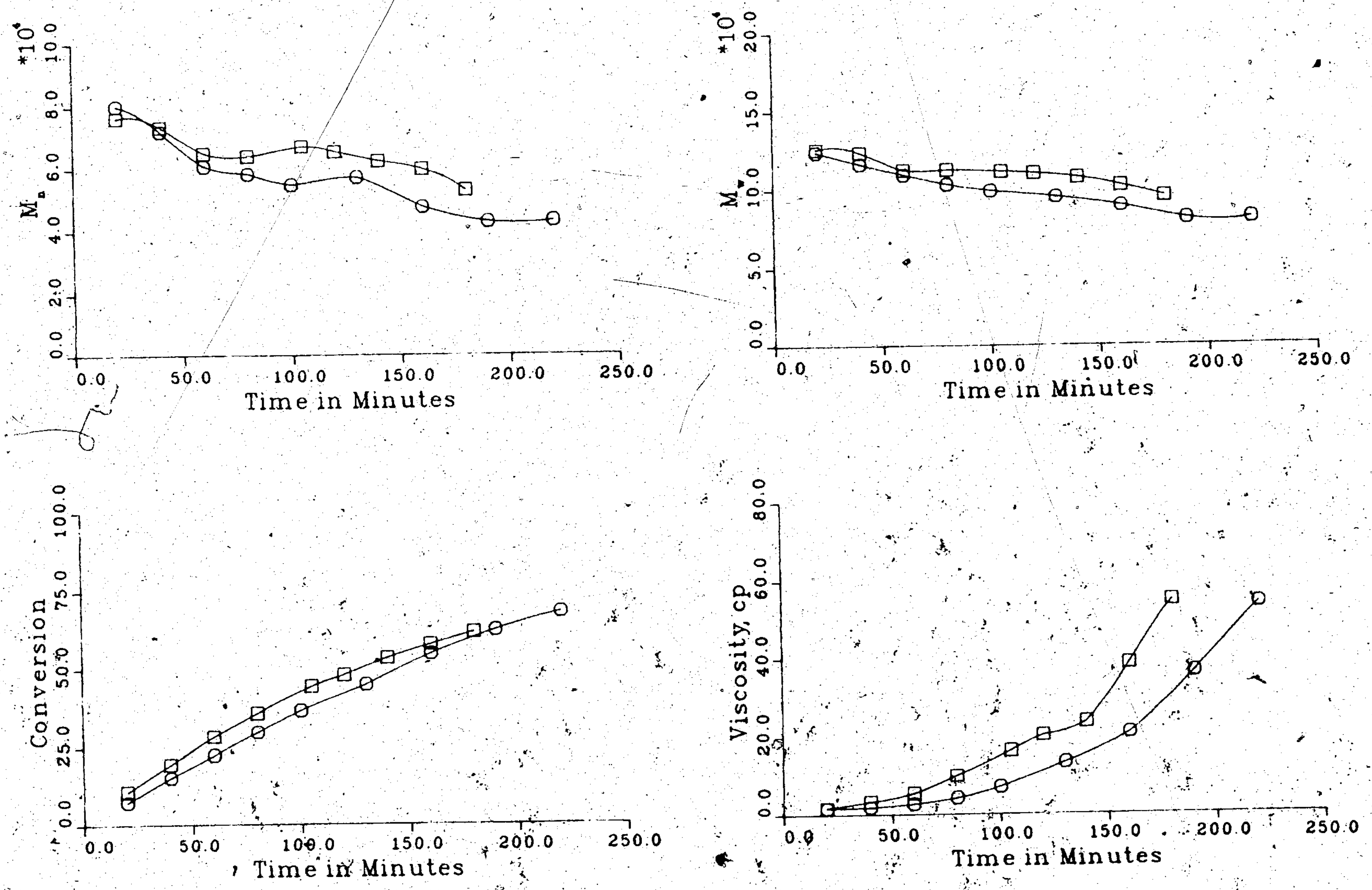

Fig. 4.1 Reproducibility Results of Polymerization Experiments-I
$T = 70^\circ C$ $\Phi_s = 0.6$ $I_0 = 0.05$ mol/l

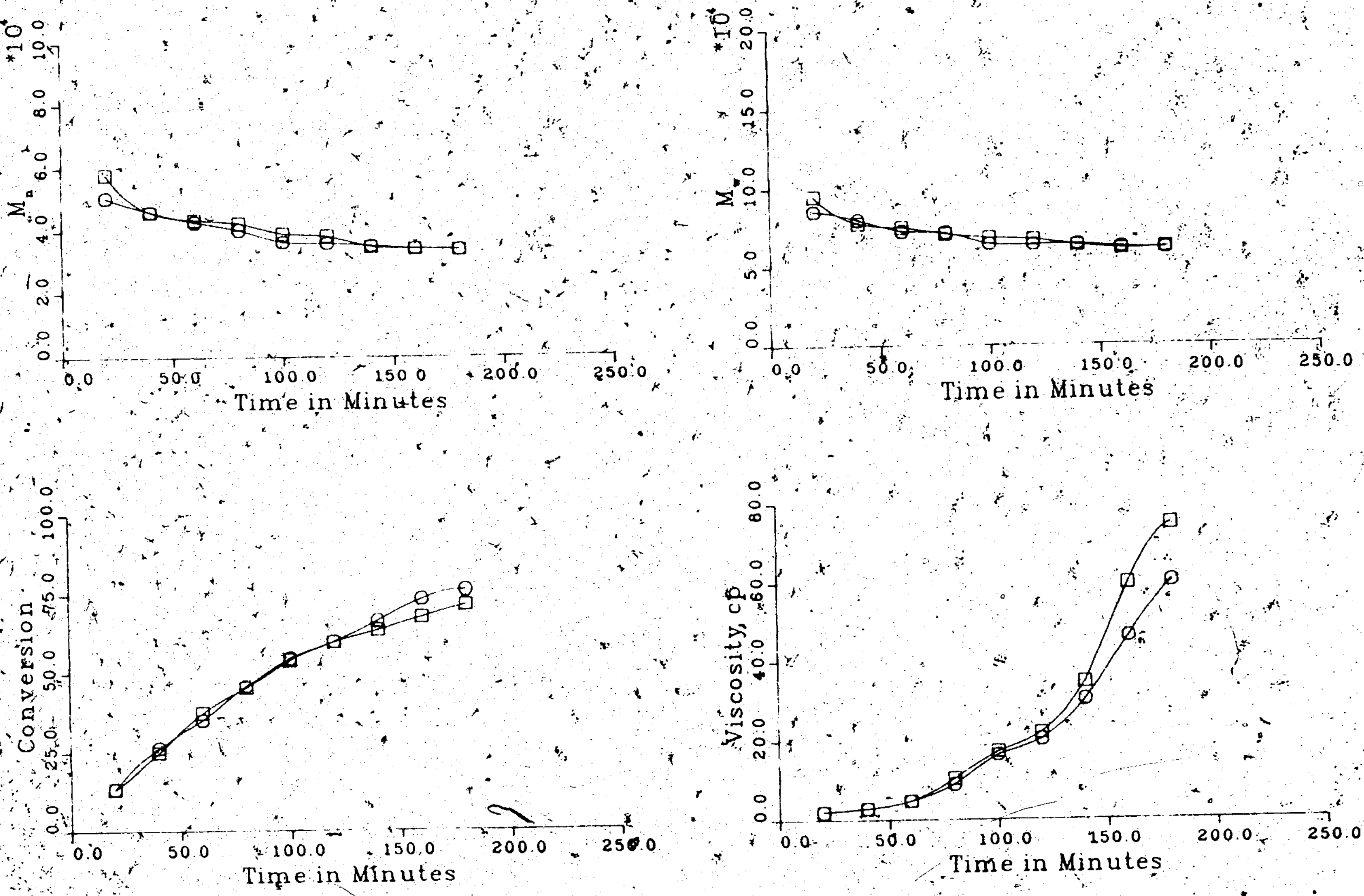

Fig. 4.2 Reproducibility Results of Polymerization Experiments-II
T=70°C Φ_s=0.6 I_0=0.10 mol/l

4.3 Effect of Solvent Concentration

A number of experiments were conducted to study the effect of solvent concentration on the rate of polymerization in the batch reactor system. These experiments are helpful to decide whether the gel effect, in which the rate of polymerization increases with increasing conversion is significant, and thus whether it should be taken into account in developing the mathematical model of the reactor. In Figure 4.3, the conversion-time histories obtained for solvent volume fractions of 0.4, 0.5 and 0.6 (temperature=75°C I_0=0.05 mol/L) are presented. No marked differences can be observed in the conversion-time histories for different solvent fractions. The same result was also observed for experiments conducted at 65°C for different solvent fractions. The shape of the conversion-time histories in Figure 4.3 shows a decreasing slope of the curves throughout the course of polymerization which means the rate of polymerization decreases during course of the reaction. If a pronounced gel effect were present, the rate of polymerization would increase with increase in conversion. From these experimental results, we can neglect the gel effect phenomenon in the modeling of the polymerization reactor. The gel effect can be neglected in this work because of high solvent fractions (0.6) employed and also because of the limited extent of conversion at which the viscosity of the polymerization mixture is not very high. On the other hand it is known that in bulk

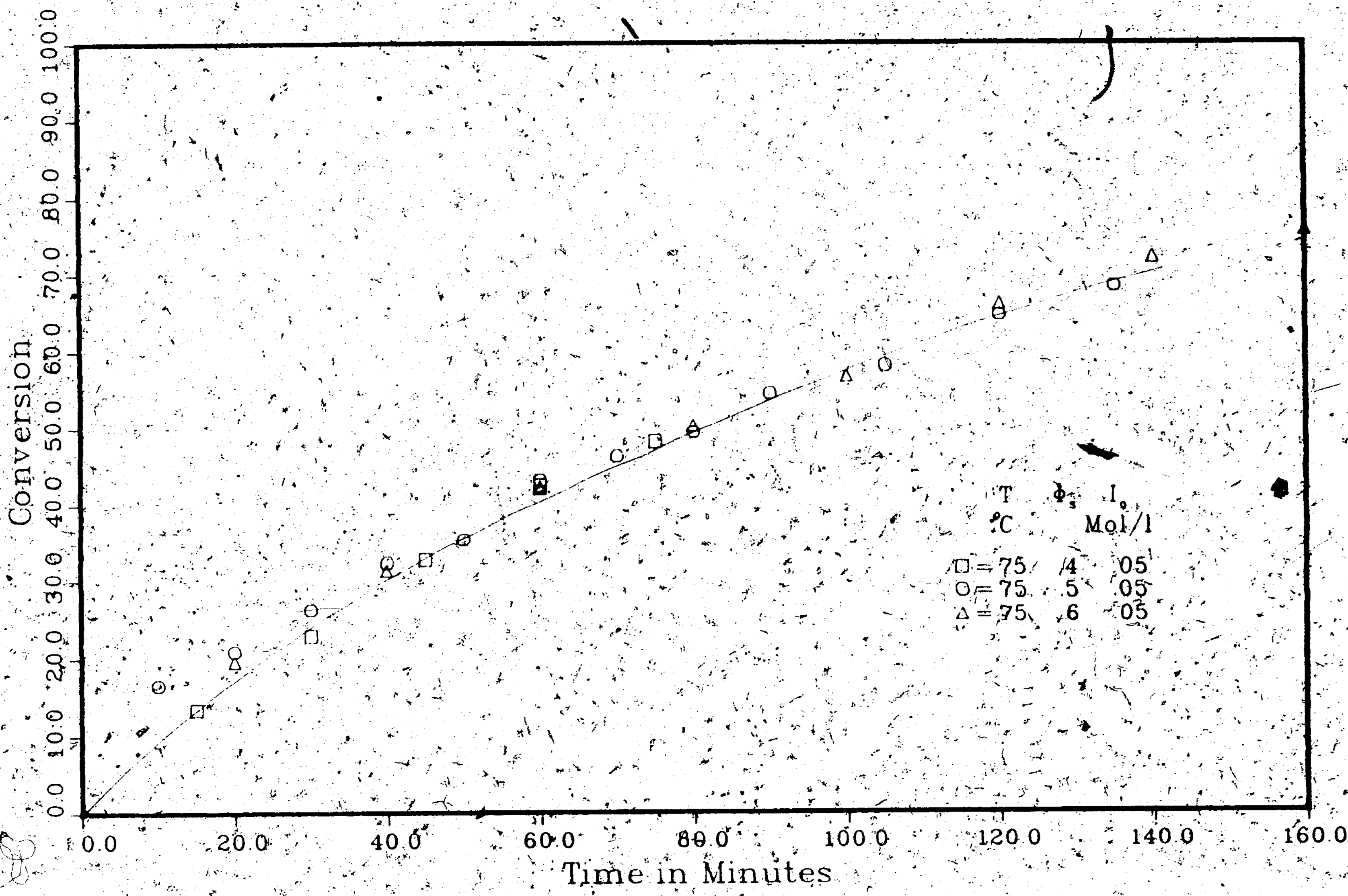

Fig. 4.3 Effect of Solvent Ratio on Rate of Polymerization

polymerization of MMA, the polymerization reaction shows gel effect at conversion as low as 10 per cent (Odian(1981)). The presence of solvent in the polymerization mixture reduces the viscosity of the [illegible] and postpones the occurrence of gel effect to hi[illegible] values.

4.4 Effect of Initiator Concentration

A series of experiments were conducted to study the effect of initial initiator concentration on the course of polymerization. Two levels of initial initiator concentration (0.05 and 0.10 mol/L) and three levels of temperatures (65°C, 70°C and 75°C) were employed to generate the necessary experimental data. Figures 4.4 to 4.6 show the effect of increasing the initial initiator concentration on the conversion-time histories. It has been established that the polymerization rate is directly proportional to the square root of initiator concentration (Odian(1981)). Hence increasing initiator concentration should increase the rate of polymerization. This can be clearly observed in Figures 4.4-4.6.

Also Figures 4.4 to 4.6 show the effect of initiator concentration on the development of number average and weight average molecular weights, respectively. Sacks et al.(1973) proved that in conventional free radical polymerizations taking place at constant temperature, the instantaneous value of number average molecular weight of the polymer produced would decrease during the course of

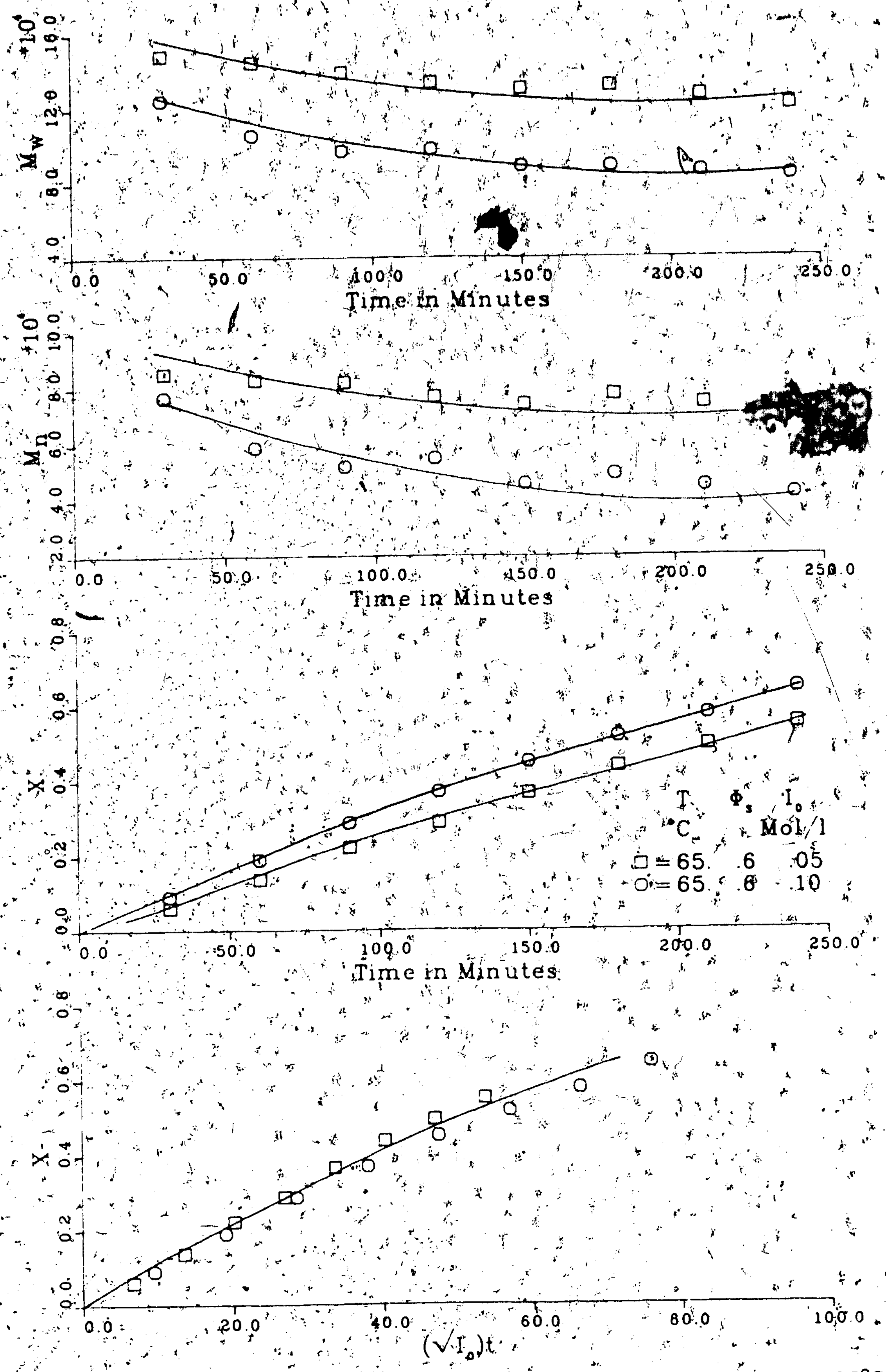

Fig. 4.4 Effect of Initiator Concentration on Polymerization at 65°C

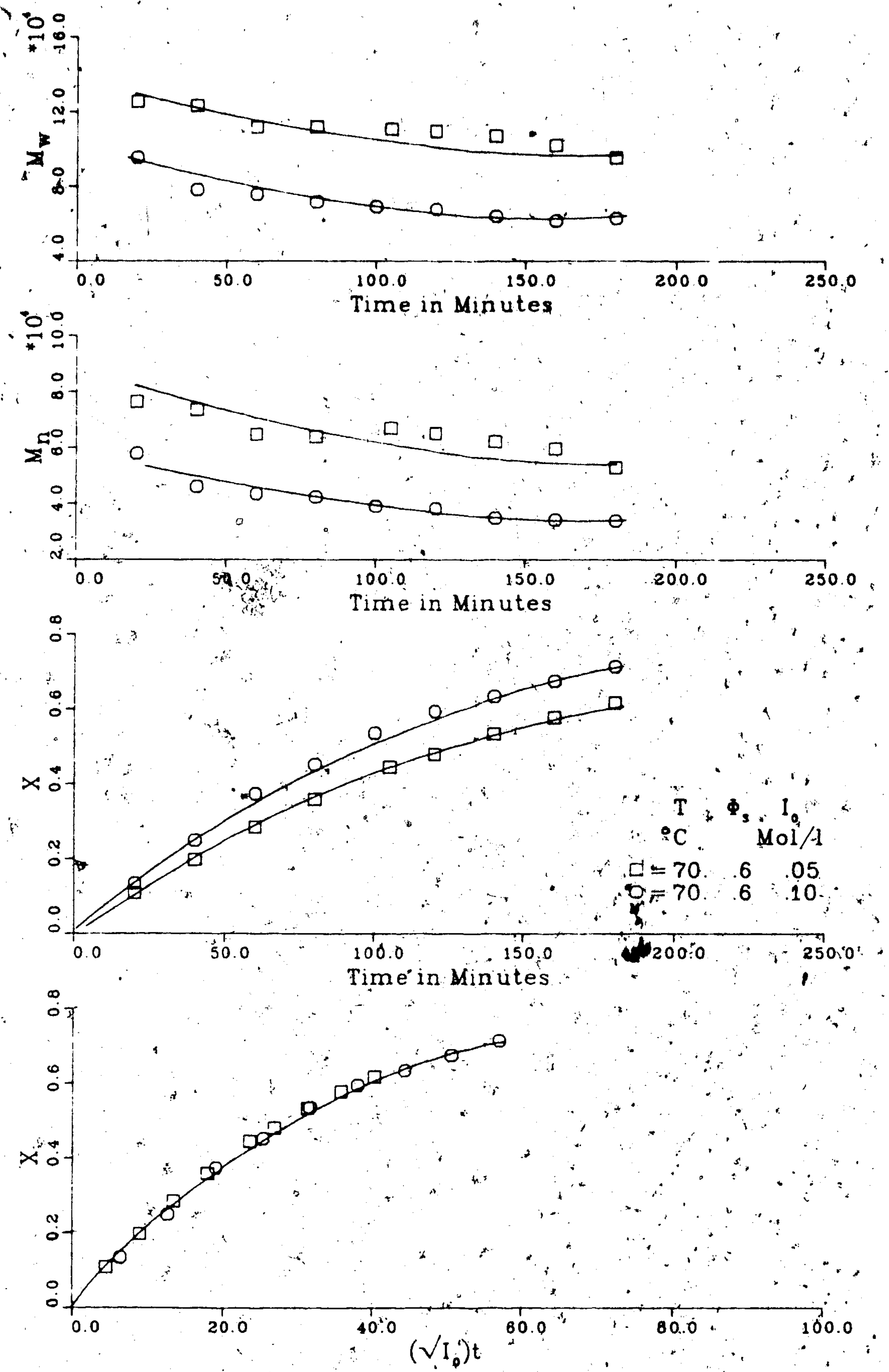

Fig. 4.5 Effect of Initiator Concentration on Polymerization at 70°C

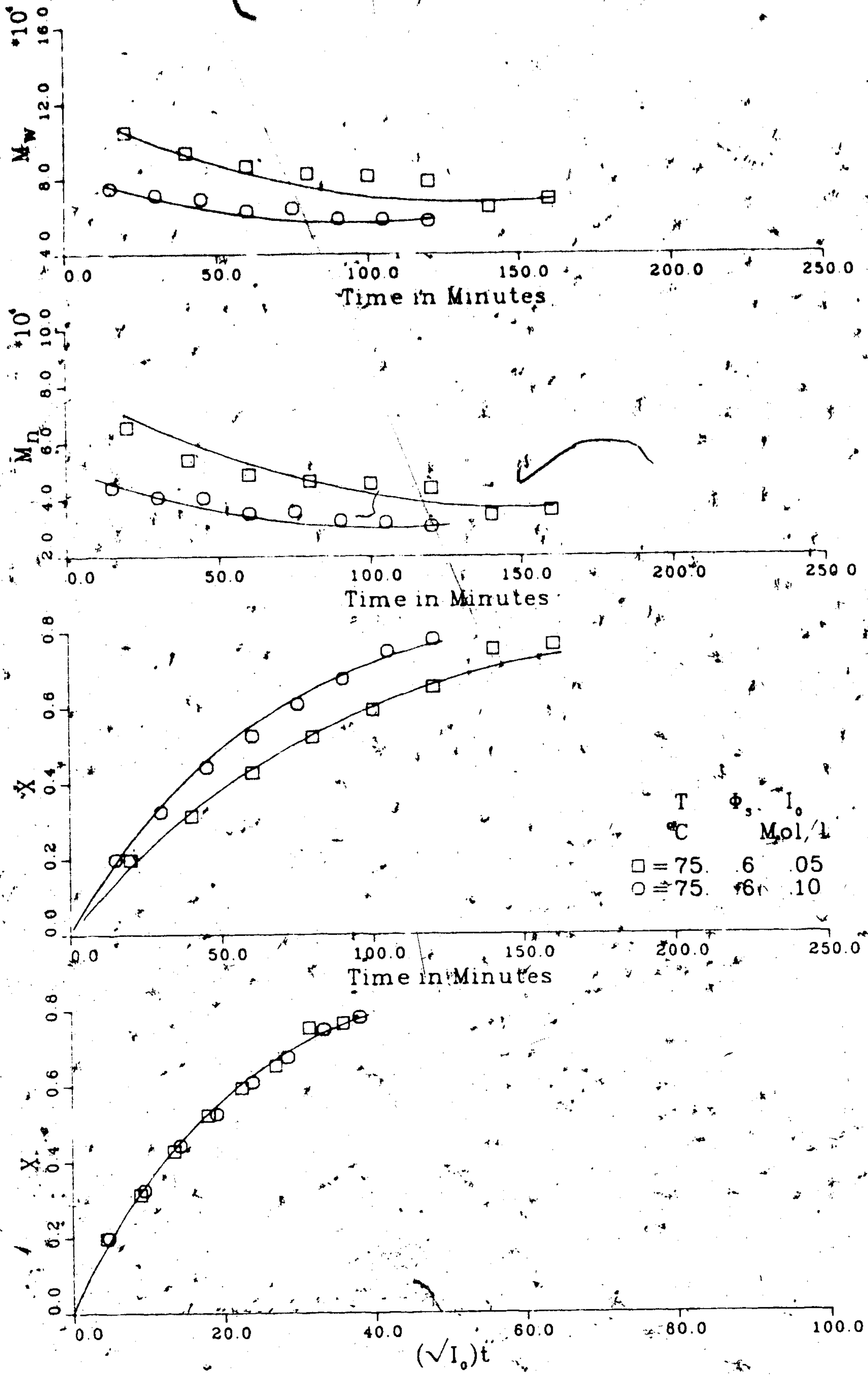

Fig. 4.6 Effect of Initiator Concentration on Polymerization at 75°C

polymerization, when transfer to monomer and solvent do not control molecular weight. The same trend would be observed by the weight average molecular weight. Also, the kinetic chain length, and hence degree of polymerization, is shown to be inversely proportional to the initiator concentration (Odian(1981)). Hence with increase in initiator concentration, the number average as well as weight average molecular weights should decrease. We observe in Figures 4.4 to 4.6 that with increase in initiator concentration, the number and weight average molecular weights decrease. Similar experimental results for number and weight average molecular weights have been reported by Chen and Huang(1981) for the solution polymerization of styrene in a batch reactor.

A master plot is drawn by plotting conversion versus $(\sqrt{I_0})t$ for different temperatures as shown in Figures 4.4 to 4.6. Since the data points for different initiator concentrations coincide, we can infer that the rate polymerization is proportional to the square root of the initiator concentration.

4.5 Effect of Temperature

A number of experiments have been conducted in order to study the effect of temperature on different variables of the polymerization process. The effect of temperature on the rate of polymerization is shown in Figures 4.7 and 4.8. It can be observed from these figures that the rate of

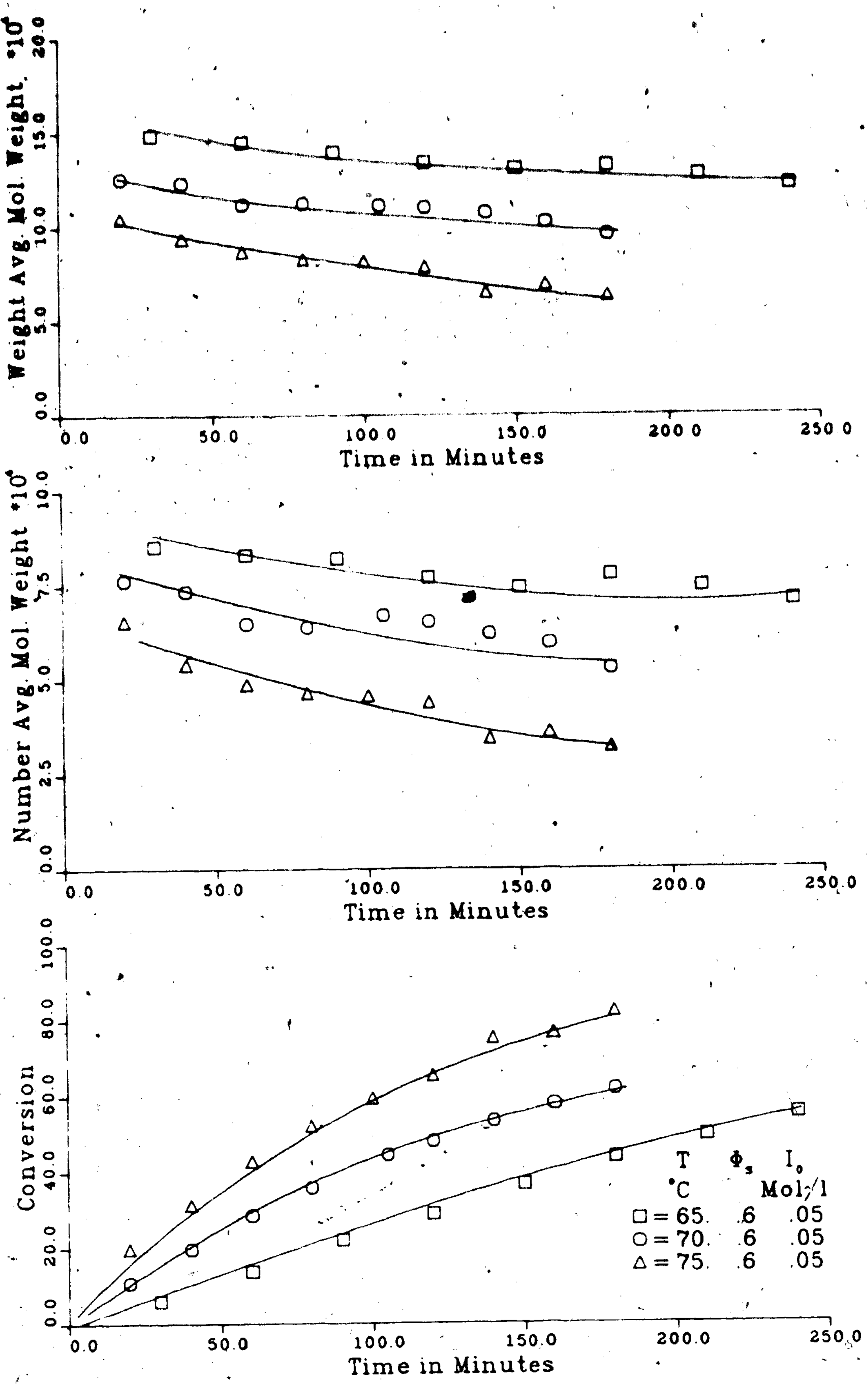

Fig. 4.7 Effect of Temperature on Polymerization-I

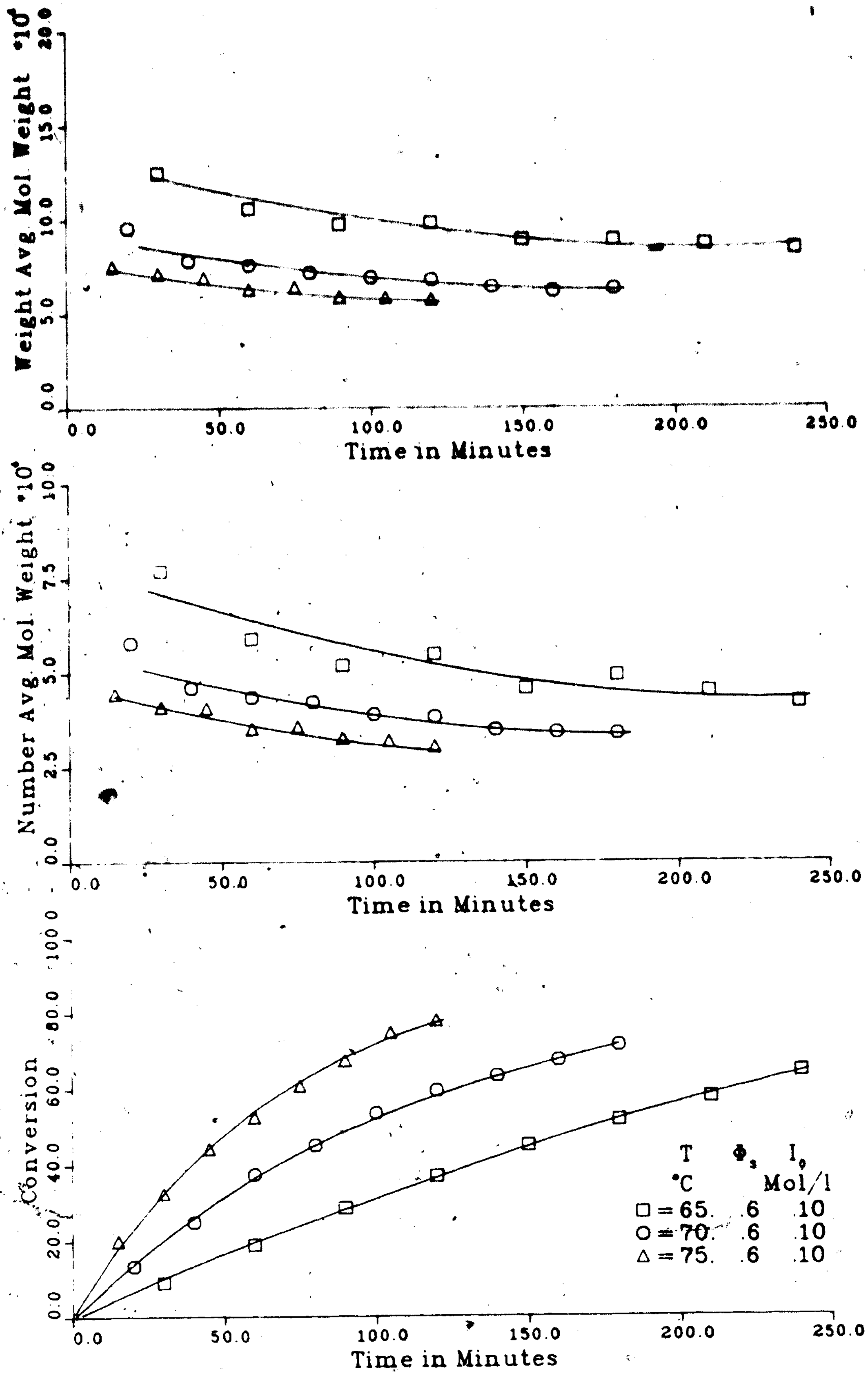

Fig. 4.8 Effect of Temperature on Polymerization_II

polymerization increases with increase in temperature.

The effect of temperature on the rate of polymerization is determined by the value of activation energy for the rate of polymerization. The activation energy for the rate of polymerization can be derived as $(E_p+E_d/2-E_t/2)$ where E_p, E_d, and E_t are activation energies for propagation, dissociation and termination reactions, respectively. The E_p, E_d and E_t values for MMA polymerization are 9600, 33700, 1000 cal/mol, respectively. From these values, the activation energy for rate of polymerization is calculated as 25,500 cal/mol. Hence, it is clear that the rate of polymerization will increase with temperature. This can be observed in Figures 4.7 and 4.8.

The effect of temperature on number average and weight average molecular weights is also shown in Figures 4.7 and 4.8. Odian(1981) has shown that except for photochemical polymerizations where the degree of polymerization increases with temperature, in all other cases the degree of polymerization and hence the molecular weight averages should decrease with increase in temperature. This decrease in number and weight average molecular weight can be clearly observed in Figures 4.7 and 4.8.

These experimental results establish that initiator concentration and temperature significantly affect the rate of polymerization, number and weight average molecular weights. These two variables can be employed to control conversion and molecular weight averages. Open loop control policies using initiator concentration and temperature as control variables are developed in chapter six.

4.6 Analysis of Viscosity Data:

In chapter three the method of measuring viscosity on-line using an industrial viscometer was described. Viscosity values were measured at various temperatures and initiator concentrations during the course of polymerization. Figures 4.9 to 4.11 present the experimental values of the viscosity of the polymerization reaction mixture. From these figures it can be clearly observed that at the same conversion and temperature, the viscosity values are less for the experiments which employed higher initiator concentration. It has been explained (see section 4.4) that at higher initiator concentrations, lower molecular weight polymers are produced. Hence the effect of molecular weight on the viscosity is clearly indicated in these figures.

Viscosity is a function of many variables. Though mathematical equations have been developed relating molecular weight for dilute solutions of the polymer, for concentrated solutions such relations are lacking (Rodriguez(1982)).

Jo(1975) developed a semiempirical model to estimate the weight average molecular weight of the polymer from the measurement of viscosity during the course of polymerization. Since all the experiments were conducted at a constant temperature, they did not take into account the

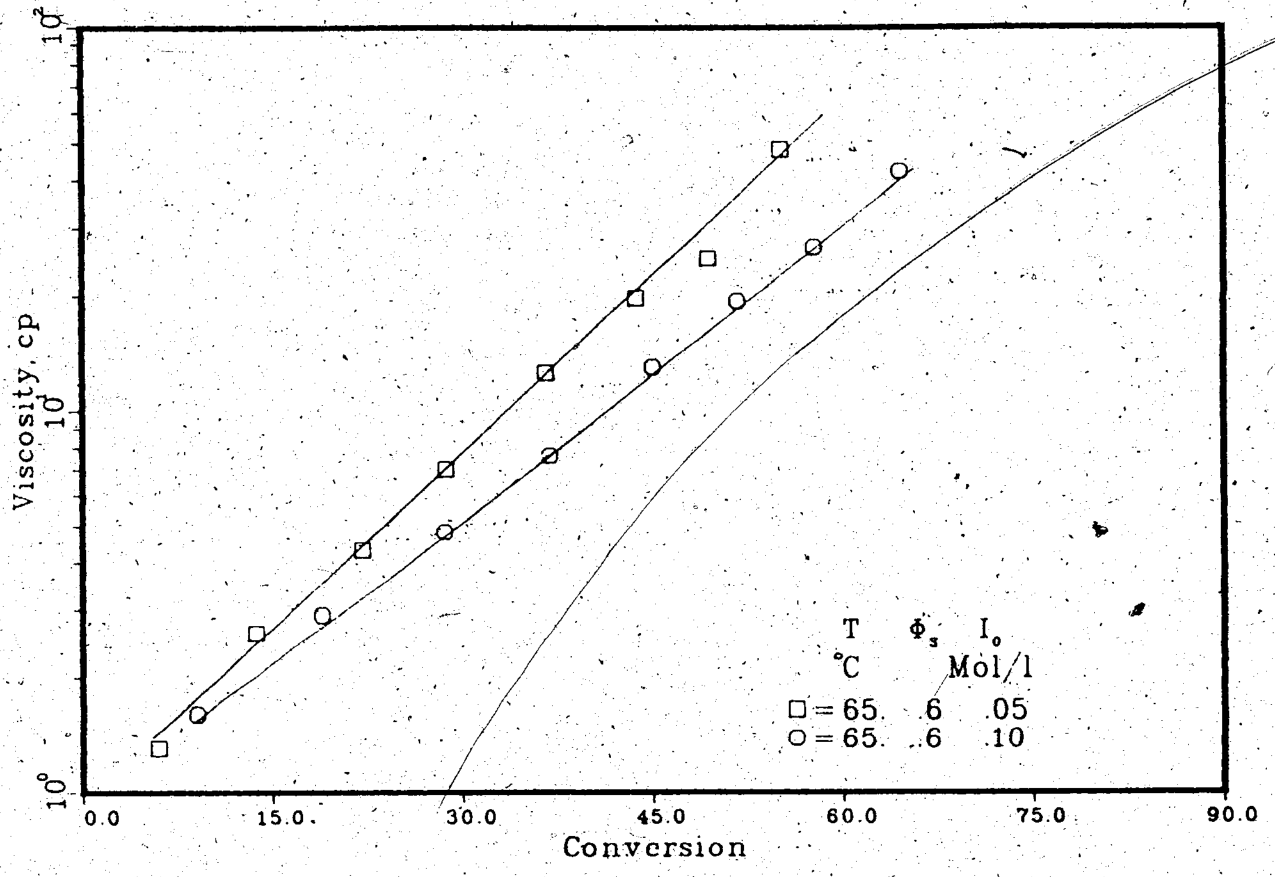

Fig. 4.9 Variation of Viscosity with Conversion at 65°C

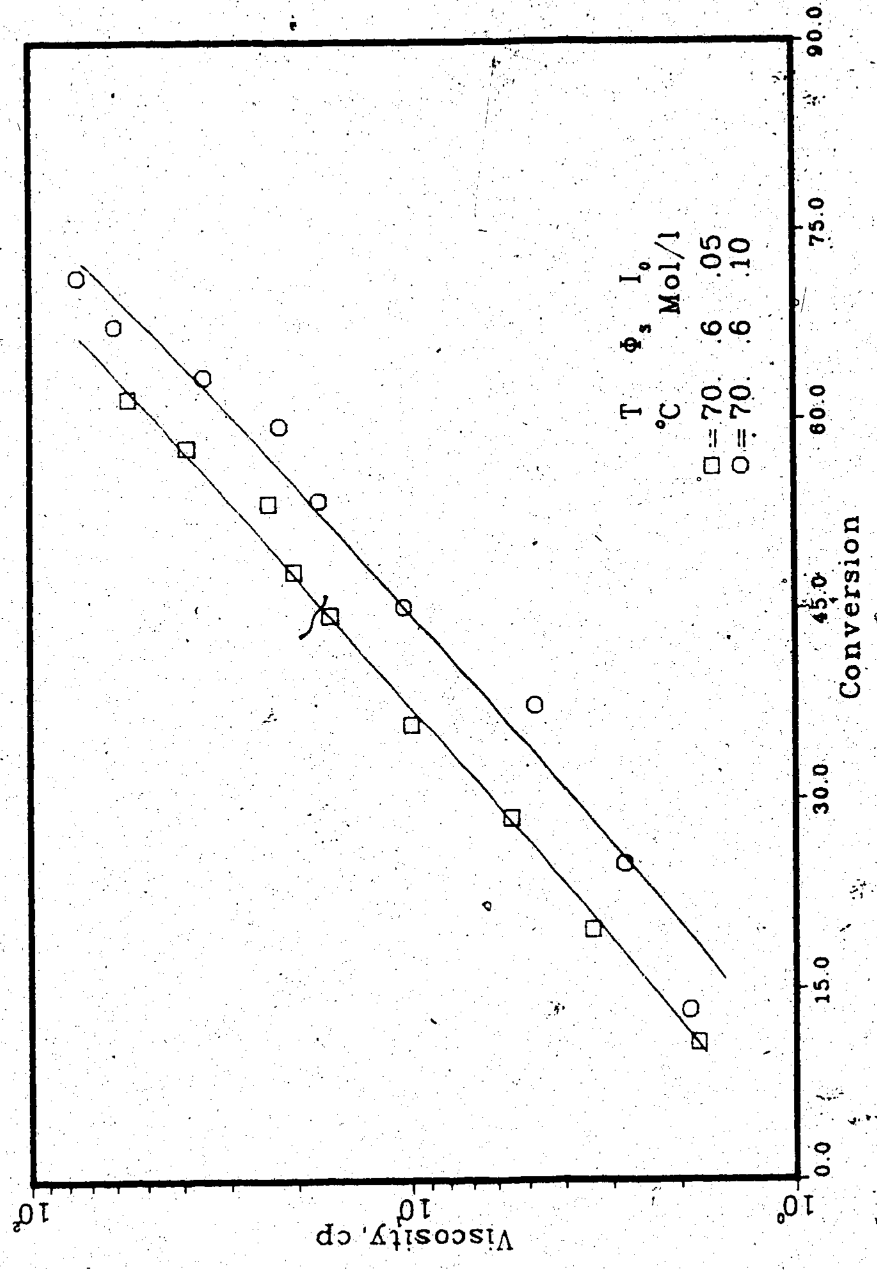

Fig. 4.10 Variation of Viscosity with Conversion at 70°C

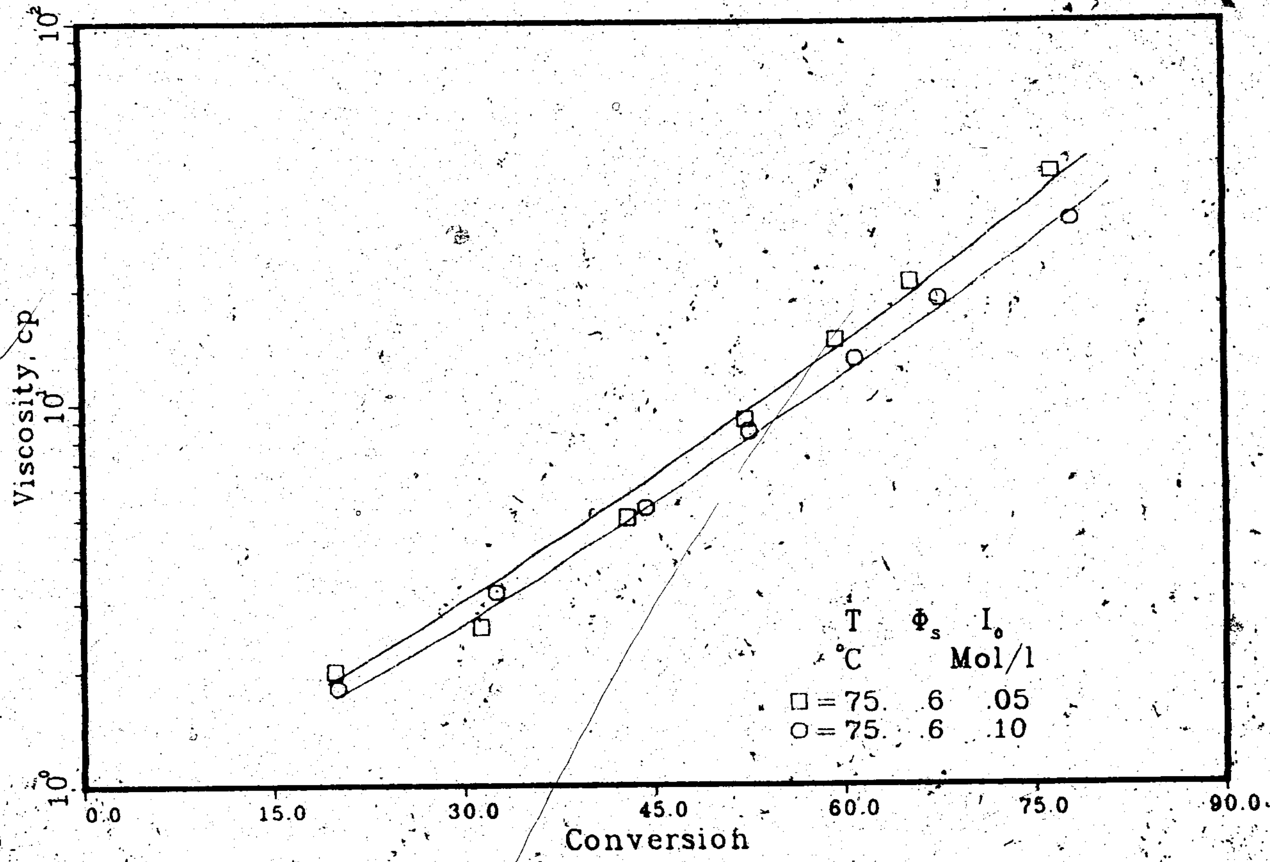

Fig. 4.11 Variation of Viscosity with Conversion at 75°C

variation of viscosity with temperature in their model.

Recently Hamer(1983) developed two types of correlations to estimate viscosity of the polymerization mixture in solution polymerization of vinylacetate.

The first and the simpler version was based on the correlation suggested by Spencer and Williams(1947).

$$\eta = A\,\exp[\,F(X_y;E)\,(\frac{B}{RT} + C\sqrt{(.001Mw + D)}\,] \qquad (4.1)$$

where

$$F(X_y;E) = RX_y - E, \qquad X_y \geq 4E^2$$
$$= X_y/4E, \qquad X_y \leq 4E^2$$

where X_y is the weight fraction of polymer in solution. A, B, C, D and E are constants. Equations of this form, although difficult to support theoretically were found to be useful for fitting early experimental results with concentrated polymer solutions. (Flory(1940), Ferry et al.(1951)).

The second viscosity correlation was based on the free volume concepts and chain entanglement theories discussed in detail by Berry and Box(1968), Graessly(1974) and Ferry(1980). We will not deal with the details of the mathematical derivation here as our aim in this study is to develop empirical relationships that can be used to obtain molecular weight values from measurements of viscosity.

Since in this study the objective is to estimate the molecular weight from the measurement of viscosity, the empirical correlation(Equation 3.13) used by Jo(1975) was modified to take account of the variation of viscosity with temperature. The following correlation was used.

$$\ln(\eta) = (a_1 + \frac{a_2}{T}) + (a_3 + \frac{a_4}{T})X/M_n \qquad (4.2)$$

where η, T, X and M_n are viscosity, temperature, conversion and number average molecular weight respectively. The parameters a_1, a_2, a_3, and a_4, must be estimated from the experimental data.

Viscosity values obtained from six experiments were used to estimate the four parameters appearing in the empirical equation.

Figure 4.12 shows the comparison between the experimentally measured viscosity and the viscosity values estimated from the Equation 4.2. From these results it can be observed that the model predicts the viscosity reasonably well. The correlation is reasonably good at least in the low viscosity region. Equation (4.2) can be rearranged to get M_n from the measurement of viscosity as:

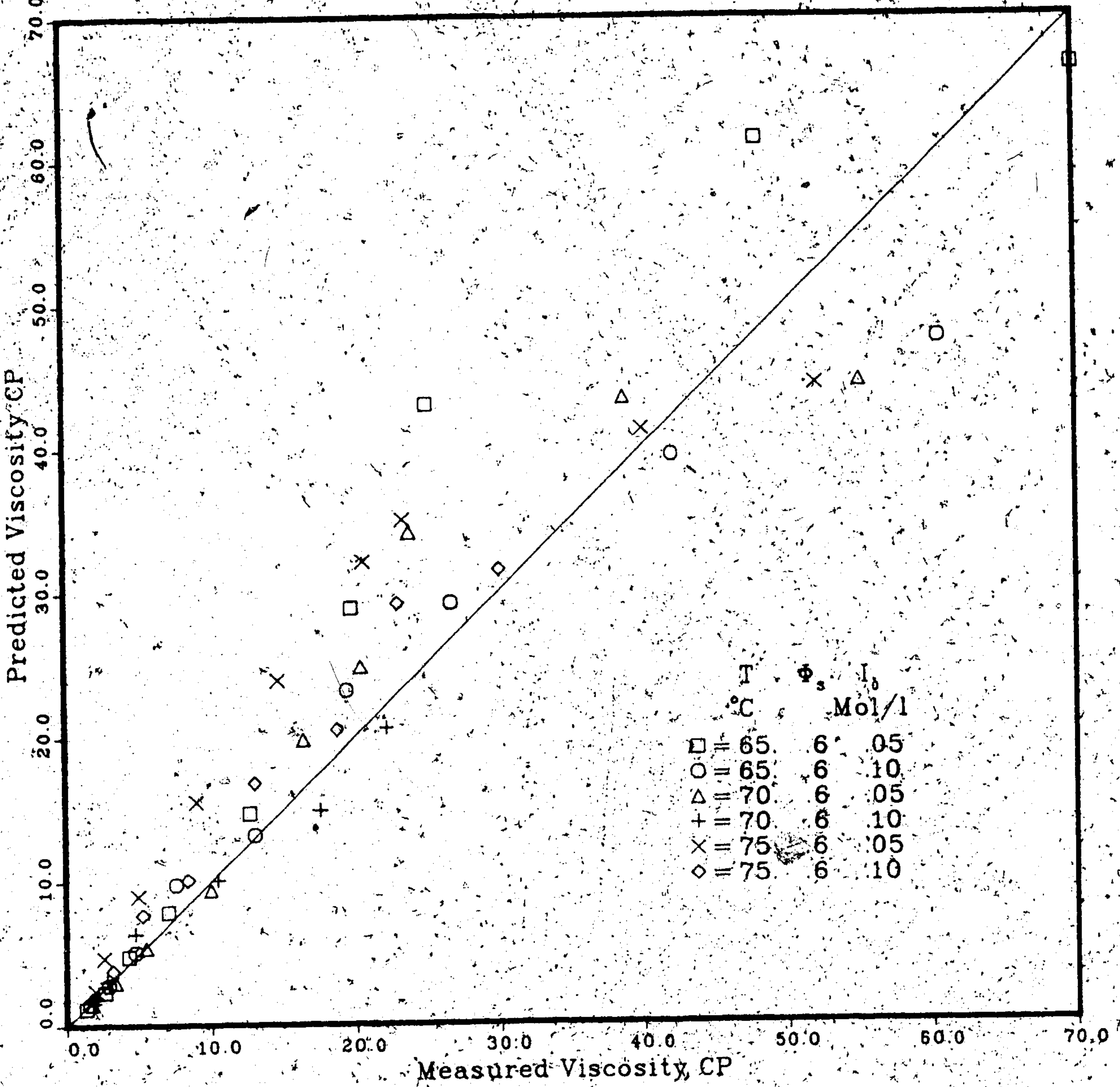

Fig. 4.12 Comparison of Measured and Predicted values of Viscosity

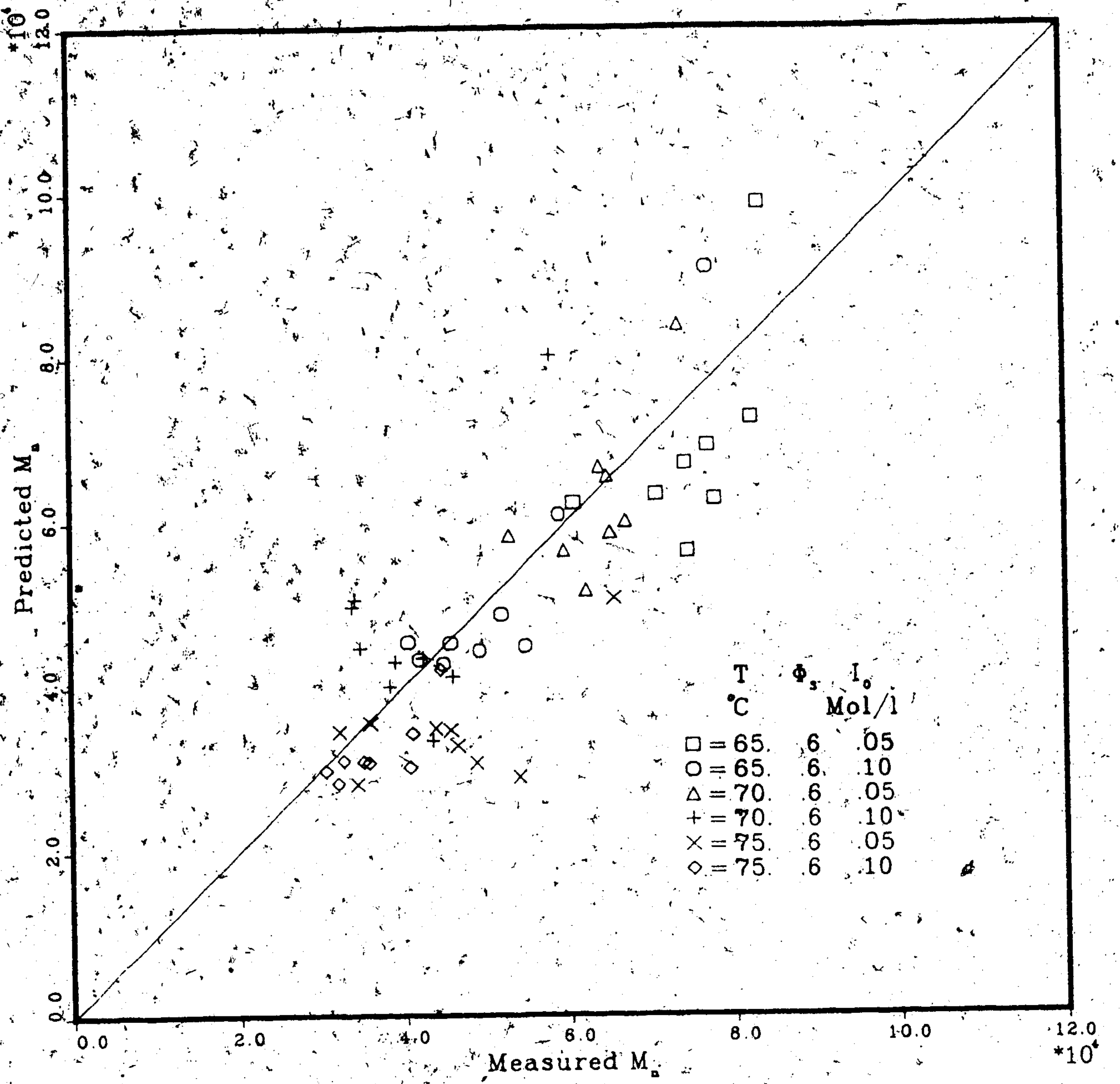

Fig. 4.13 Comparison of Measured and Predicted M_n Values

$$M_n = \left\{ \frac{\ln(\eta) - a_1 - a_2/T)}{((a_3 + a_4/T)X)} \right\}^2 \qquad (4.3)$$

The experimental M_n values and the M_n values predicted from Equation (4.3) are plotted in Figure 4.13. From this figure it can be observed that M_n is predicted well at high viscosity solutions, whereas considerable discrepancy exists at molecular weights predicted for low viscosity solutions.

From these results it can be deduced that molecular weight of the polymer can be determined on-line from measurement of viscosity, conversion and temperature. We have observed that the M_n is estimated with better accuracy at higher viscosity values whereas in dilute solutions having lower viscosity the estimation of M_n is poor and unreliable.

Our analysis of viscosity data is not exhaustive and complete by any means. We tried various forms of semi-empirical functions to estimate number average molecular weight from viscosity measurement. However, none of them could estimate the number average molecular weight with better accuracy over the whole viscosity range. Perhaps, application of free volume theory to the viscosity data could have provided better estimates of molecular weight.

It should be pointed out here that the control action is not completely dependent on the molecular weight estimated from the viscosity measurement. These estimates could be updated when the molecular weight averages become available from SEC measurement. This combined viscosity and SEC measurements of molecular weight averages could provide better control of the polymerization reactor. As an alternative recently introduced, Bondagel columns by Water Associates are able to perform SEC analysis of polymer in about 5 minutes. With these columns, on-line molecular weight determination using SEC has become possible in very short analysis time.

4.7 Torque Measurements

Figure 4.14 shows the torque measurement obtained using the experimental reactor system. The torque exerted on the stirrer by the polymerization mixture increases during the course of polymerization. The torque measurements were done with an intention that they would provide additional measurements to estimate viscosity and therefore indirectly the average molecular weights. However these measurements turned out to be unreliable because of the friction at the bearing site of the stirrer. Hence these measurements were not analyzed to estimate the molecular weights.

4.8 Conclusions

In this chapter extensive experimental data obtained using the reactor have been presented. The analysis of the data revealed that initiator concentration and temperature

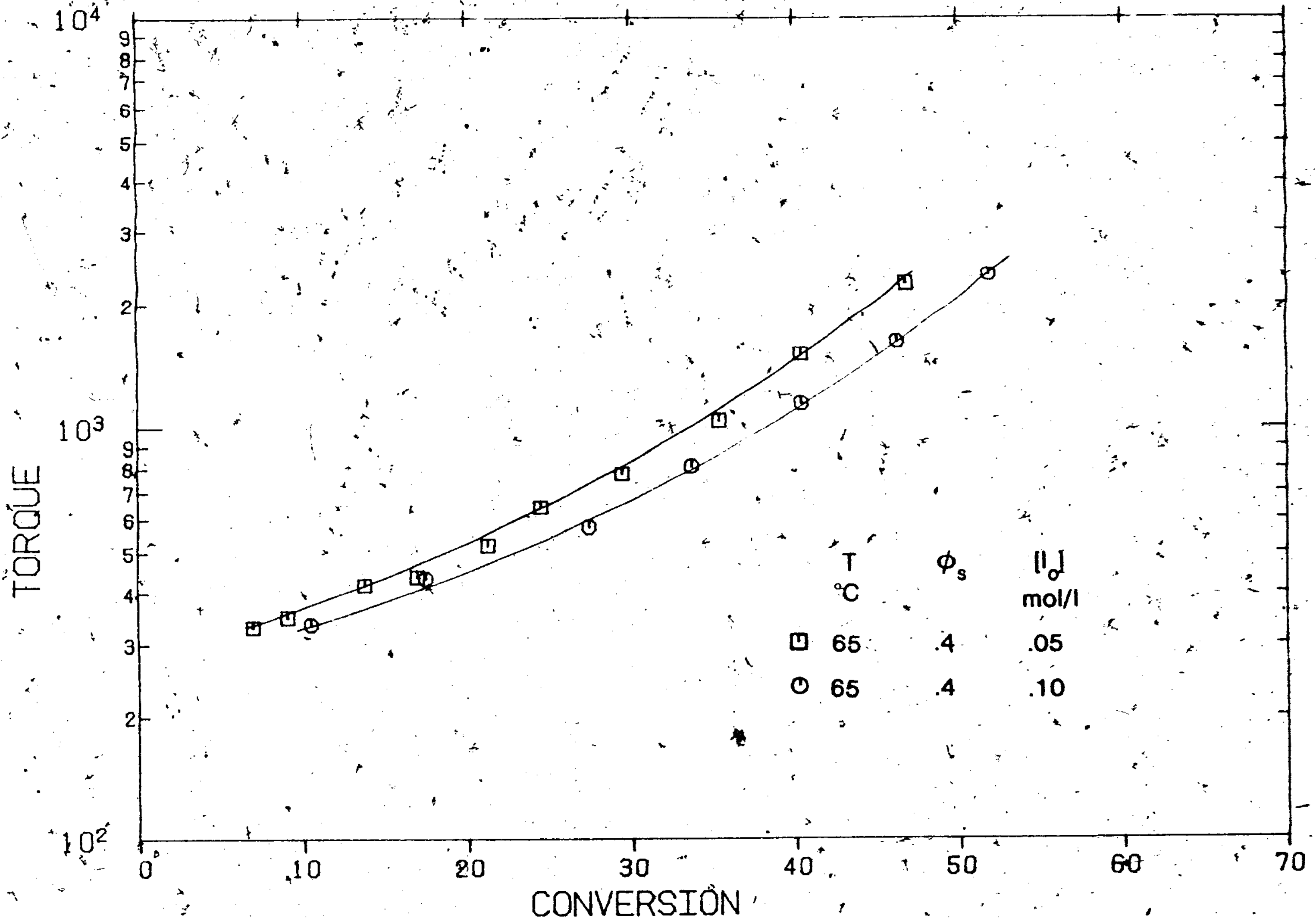

Fig. 4.14 Variation of Torque with Conversion

of the reaction considerably affect the rate of polymerization and the number average and weight average molecular weights of the polymer formed during polymerization. Hence these two variables, temperature and initiator concentration, can be employed as manipulated variables to control monomer conversion and molecular weight averages in the polymerization reaction. The analysis of viscosity data showed that at a higher viscosity of the polymerization mixture, the M_n values are predicted well whereas considerable discrepancy exist in M_n values predicted in dilute solutions of the polymer, where viscosity is also low. The experiments on reproducibility of the results showed that conversion and molecular weight averages are reproduced well when identical experimental conditions are maintained. This lends credibility to the instruments and measurement techniques used in this study.

5. MODELING AND PARAMETER ESTIMATION

5.1 Introduction

A reliable mathematical model of the polymerization process is required in order to calculate the optimal control policies that will improve the performance of the batch reactor. Free radical polymerization of vinyl monomers is a well studied process and a description of the elementary chemical reactions occurring in the process is readily available in most standard texts on polymer chemistry (Odian(1981)). The more fundamental properties, often of importance to the chemical engineer, such as conversion and molecular weight distribution are the result of elementary reactions occurring in the polymerization process and their relative rates. By developing a mathematical model of the process from these elementary reactions, it is possible to find the effect of control variables such as temperature and initiator concentration on monomer conversion and molecular weight distribution(MWD) during the course of polymerization.

In the past, a number of investigators have reported a variety of models to describe the free radical polymerization of methylmethacrylate(MMA) in a batch reactor. Matheson et al.(1949) measured the average life time of PMMA radicals as a function of temperature in photosensitized polymerization of liquid monomer. By combining their experimental results with those of Schulz and Blaschke(1942), and Schulz and Harborth(1947), they obtained the rate constants for propagation, termination and transfer to monomer for conversions up to 10 percent. They attributed the accelerated polymerization rate occurring in the latter stages of the reaction to a decrease in the termination rate constant.

Nandi(1957), Ferington and Tobolsky(1957) have reported experimental results that were obtained with a wide variety of initiators under different isothermal conditions for bulk polymerization of MMA. Using their experimental results they calculated the rate constant for chain transfer to monomer and the ratio $kp/\sqrt{k_t}$ where kp and k_t are the rate constants for propagation and termination reactions, respectively. Their results were in good agreement with the results of Matheson et al.(1949).

Hayden and Melville(1960) measured the increase in temperature in an adiabatic polymerization reactor as a function of time and reported that after about 10 percent conversion the polymerization rate and the life time of the polymer radical chains increased. This increase was attributed to the increasing viscosity of the reaction mixture resulting in a decrease of the collision rate of the growing radicals. They found that beyond 40 percent conversion, the activation energy for the propagation reaction also increased while the corresponding velocity coefficient decreased due to the monomer addition step becoming diffusion controlled. Paul et al.(1973) also observed a similar decrease in the propagation rate constant.

Balke(1972) investigated the bulk free radical polymerization of MMA to high conversions. Using size exclusion chromatography (SEC) and gravimetric analysis he followed changes in the MWD and conversion during polymerization and developed a mathematical model for this process.

Mahabadi and Meyerhoff(1979) proposed a new model to estimate the rate constant for primary radical termination using the radical life time, the rate of polymerization and the rate of initiation. By applying this model to high conversion polymerization experimental data, they showed the dependence of conversion on termination and initiation rate constants.

Schmidt and Ray(1981) developed a mathematical model to describe the free radical solution polymerization of methylmethacrylate in a CSTR. They also developed expressions to account for the gel effect based on the free volume correlation of Ross and Laurence(1976).

A mathematical model to describe the free radical solution polymerization of MMA in a batch reactor is developed in the following sections.

5.2 Description of the Reaction Mechanism

A general description of the chemical reactions taking place during the free radical solution polymerization of MMA initiated by benzoylperoxide is as follows:

Initiator Decomposition:

$$I \xrightarrow{k_d} 2fR_0$$

Initiation:

$$R_0 + M \xrightarrow{k_i} R_1$$

Propagation:

$$R_x + M \xrightarrow{kp} R_{x+1}$$

Transfer to Monomer:

$$R_x + M \xrightarrow{k_m} P_x + R_1$$

Transfer to Solvent:

$$R_x + S \xrightarrow{k_s} P_x + R_1$$

Termination by Disproportionation:

$$R_x + R_y \xrightarrow{k_{td}} P_x + P_y$$

Termination by Combination:

$$R_x + R_y \xrightarrow{k_{tc}} P_{x+y}$$

where I denotes the initiator molecules, R_0 the initiator radicals, R_x and R_y denote the live radicals of chain lengths x and y respectively. M is the monomer, and P_x and P_y represent the dead polymer of chain length x and y respectively. k_d, k_i, kp, k_m, k_s, k_{td}, and k_{tc} are the rate constants for initiator dissociation, initiation, propagation, transfer to monomer, transfer to solvent, termination by disproportionation and termination by combination respectively.

Using the above kinetic scheme, general population balance equations that describe the time variation of the concentration of different species in the batch reactor can be written. To simplify the mathematical formulation of the problem the following assumptions are made.

1. All the reactions are irreversible and elementary.
2. Reaction rate constants are independent of chain length.
3. Reactor contents are perfectly mixed and there are no temperature gradients in the reactor.

These assumptions are common and are well documented in the literature on the modeling of free radical polymerization reactions. Although chain transfer to monomer and solvent are usually neglected in most other modeling studies reported in the literature, they are included in this model development.

The volume of the reaction mixture decreases during the course of polymerization due to the increase in the density of the reaction mixture as the result of monomer conversion to polymer. This volume change is accounted for in the modeling of the batch reactor. By assuming that the reaction volume varies linearly with the monomer conversion, the volume of the reaction mixture, V, at a conversion, X, can be expressed as:

$$V = V_0 \ (1+\epsilon X) \tag{5.1}$$

where V_0 is the volume of the reaction mixture at conversion $X=0$ and ϵ is the fractional volume change at $X=100\%$. The monomer conversion X is defined as:

$$X=(M_0V_0 - MV)/ M_0V_0 \tag{5.2}$$

From Equations (5.1) and (5.2) it can be easily shown that the change in the reaction volume is related to the monomer conversion by

$$\frac{1}{V}\frac{dV}{dt} = \frac{\epsilon}{\epsilon X+1}\frac{dX}{dt} = \frac{-\epsilon}{M_0 + \epsilon M}\frac{dM}{dt} \tag{5.3}$$

The general equation for the species, i, in the batch reactor can be written as:

$$R_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{1}{V}\frac{d(C_iV)}{dt} = \frac{dC_i}{dt} + \frac{C_i}{V}\frac{dV}{dt} \tag{5.4}$$

Combining Equations (5.3) and (5.4) we obtain:

$$\frac{dC_i}{dt} = R_i - \frac{C_i}{V}\frac{dV}{dt} \tag{5.5}$$

where N_i represents the number of moles of the species, i, in the reactor; C_i the concentration, and R_i denotes the rate of appearance (disappearance) of species, i. In the following section, the mass balance equations for the different species in the reactor are derived directly from Equation (5.5).

5.3 Derivation of the Model Equations

According to the above kinetic scheme, the mass balance equations, for initiator, monomer, live macroradicals and dead polymer chains are expressed as:

$$\partial I/\partial t = -k_d I - (I/V)(dV/dt) \tag{5.6}$$

$$\partial M/\partial t = -k_i M R_0 - (kp+k_m) M \sum_{x=1}^{\infty} R_x - (M/V)(dV/dt) \tag{5.7}$$

$$\partial R_1/\partial t = k_i M R_0 - kpMR_1 - k_t R_1 \sum_{x=1}^{\infty} R_x + (k_s S + k_m M) \sum_{x=1}^{\infty} R_x - (R_1/V)(dV/dt) \tag{5.8}$$

$$\partial R_x/\partial t = -kpMR_x + kpMR_{x-1} - (k_m M + k_s S) R_x - k_t R_x \sum_{y=1}^{\infty} R_y - (R_x/V)(dV/dt) \tag{5.9}$$

$$\partial P_x/\partial t = (k_s S + k_m M) R_x + k_{td} R_x \sum_{y=1}^{\infty} R_y + (k_{tc}/2) \sum_{y=1}^{x-1} R_y R_{x-y} - (P_x/V)(dV/dt) \tag{5.10}$$

In the above equations k_t is the sum of k_{td} and k_{tc}. The last two equations represent an infinite number of differential equations since x can vary mathematically from 2 to ∞. Therefore the above description of the process results in a model with an infinite number of differential equations. To reduce the order of the mathematical model we introduce the moments of the live and dead polymer distributions.

It should be pointed out here that the concept of instantaneous molecular weight (Hamielec(1976)) could also be used to develop the mathematical model of the reactor. This method gives the molecular weight distribution in addition to the number and weight average molecular weights of the dead polymer.

Define the k-th moment of the live radicals as:

$$\lambda_k = \sum_{x=1}^{\infty} x^k R_x \tag{5.11}$$

and the k-th moment of the dead polymer species as

$$\mu_k = \sum_{x=2}^{\infty} x^k P_x \tag{5.12}$$

From Equations (5.6)-(5.10) we can easily obtain equations for the leading moments of the live and dead polymer distributions.

$$d\lambda_0/dt = 2fk_dI - k_t\lambda_0{}^2 - (\lambda_0/V)(dV/dt) \qquad (5.13)$$

$$d\lambda_1/dt = 2fk_dI+kpM\lambda_0+(k_sS+k_mM)(\lambda_0-\lambda_1) - k_t\lambda_0\lambda_2$$
$$-(\lambda_1/V)(dV/dt) \qquad (5.14)$$

$$d\lambda_2/dt = 2fk_dI + 2kpM\lambda_1 + (kpM+k_mM+k_sS)\lambda_0$$
$$-(k_mM+k_sS)\lambda_2 - k_t\lambda_0\lambda_2 - (\lambda_2/V)(dV/dt) \qquad (5.15)$$

$$d\mu_0/dt = (k_sS + k_mM)\lambda_0 + k_{td}\lambda_0{}^2 + k_{tc}\lambda_0{}^2/2$$
$$-(\mu_0/V)(dV/dt) \qquad (5.16)$$

$$d\mu_1/dt = (k_sS+k_mM)\lambda_1 + k_t\lambda_0\lambda_1$$
$$-(\mu_1/V)(dV/dt) \qquad (5.17)$$

$$d\mu_2/dt = (k_sS+k_mM)\lambda_2 + k_t\lambda_0\lambda_2 + k_{tc}\lambda_1{}^2$$
$$-(\mu_2/V)(dV/dt) \qquad (5.18)$$

The leading moments μ_0 and μ_1 denote respectively the concentration of the terminated polymer and the total amount of monomer associated with the terminated polymer. The moments λ_0 and λ_1 have a similar meaning for the growing radical distribution.

From Equations (5.3), (5.7) and (5.11) we obtain the rate of monomer consumption as:

$$dM/dt = -kpM\lambda_0(M_0 + M\epsilon)/M_0 \qquad (5.19)$$

In Equation (5.19) it is assumed that the monomer consumption and monomer production due to initiation and chain transfer to monomer and solvent are negligible. Thus the rate equation for the change of volume can be obtained from Equations (5.3) and (5.7) as:

$$(1/V)(dV/dt) = kp\lambda_0\epsilon M \,/\, M_0 \tag{5.20}$$

In order to simplify the kinetic equations a quasi steady state approximation (QSSA) for live radicals is usually made. According to this approximation the net rate of production of radicals is assumed to be zero. This implies that the number of radicals produced by the initiation process must be approximately equal to the number of radicals consumed through the termination reactions. In practice it is found that QSSA is usually valid for all but the first few seconds of the free radical polymerization reactions.

Using the QSSA assumption the LHS terms in Equations (5.13)-(5.15) can be set to zero. Further neglecting any volume change, the resulting algebraic equations are solved to obtain the moments of the live polymer distribution.

$$\lambda_0 = \sqrt{2fk_dI \,/\, k_t} \tag{5.21}$$

$$\lambda_1 = [2fk_dI + (kpM+k_mM+k_sS)\lambda_0] \,/\, (k_sS+k_mM+k_t\lambda_0) \tag{5.22}$$

$$\lambda_2 = \lambda_1 + (2kpM\lambda_1)/(k_sS+k_mM+k_t\lambda_0) \tag{5.23}$$

Substituting Equations(5.21)-(5.23) into Equations (5.16)-(5.18) we finally obtain:

$$d\mu_0/dt = (k_s S + k_m M)\lambda_0 + (k_{td} + k_{tc}/2)\lambda_0^2 \quad (5.24)$$

$$d\mu_1/dt = (k_s S + k_m M)\lambda_1 + k_t \lambda_0 \lambda_1 \quad (5.25)$$

$$d\mu_2/dt = (k_s S + k_m M)\lambda_2 + k_t \lambda_0 \lambda_2 + k_{tc} \lambda_1^2 \quad (5.26)$$

The total monomer consumption will be equal to the sum of the first moments of the dead and live polymer distributions.

$$M_0 - M = \mu_1 + \lambda_1 \quad (5.27)$$

Differentiating Equation(5.27) with respect to time and neglecting the contributions of the term λ_1 compared to μ_1, we obtain:

$$d\mu_1/dt = M_0 (dX/dt) \quad (5.28)$$

From Equations(5.28) and (5.19) monomer conversion rate can be expressed as:

$$\frac{dX}{dt} = \sqrt{2fk_d I}\,\frac{kp(1-X)}{\sqrt{k_t}} \quad (5.29)$$

The physical and mechanical properties of the polymer are related to the number average(M_n) and weight average(Mw) molecular weights and these averages are related to the moments of the dead polymer distributions as:

$$M_n = MW\,(\mu_1 + \lambda_1)\,/\,(\mu_0 + \lambda_0) \qquad (5.30)$$

$$Mw = MW\,(\mu_2 + \lambda_2)\,/\,(\mu_1 + \lambda_1) \qquad (5.31)$$

where MW is the molecular weight of the monomer. Since λ_k is negligible compared to μ_k, Equations(5.30) and (5.31) can be simplified to the following equations:

$$M_n = MW\,\mu_1/\mu_0 = MW(XM_0)/\mu_0 \qquad (5.32)$$

$$Mw = MW\,\mu_2/\mu_1 = MW\,\mu_2/(XM_0) \qquad (5.33)$$

From Equations(5.6), (5.24), (5.26)and (5.29) one can determine the time variation of I, X, μ_0 and μ_2 which are initiator concentration, monomer conversion, zeroth and second moment of dead polymer respectively.

It can be appreciated that the original Equations(5.13)-(5.18) have been considerably simplified by the introduction of the moments and the quasi-steady state approximations. These four nonlinear differential equations now can describe the solution polymerization of MMA in a batch reactor.

In the development of the above mathematical model it has been assumed that the reaction rate constants do not vary during the course of isothermal polymerization. However experimental results reported on free radical polymerization of MMA show the presence of an autoacceleration (gel effect) in the polymerization rate as the reaction proceeds(Odian(1981)). This dramatic increase of the polymerization rate is due to the increase in viscosity of the reaction mixture which reduces the mobility of the live macroradicals and therefore the rate of termination reaction. It should be noted that at very high conversions (above 60%) the propagation reactions may also become diffusion-controlled, reducing the rate of polymerization.

It is important to include the decrease of the termination reaction due to the gel effect in the mathematical model of the polymerization reactor. Many mathematical expressions have been developed for the gel effect based on empirical and free volume approaches (Friis and Hamielec(1976), O'Driscoll et al.(1979), Ross and Laurence(1976), Marten and Hamielec(1979)).

Recently Schmidt and Ray(1981) extendended the free volume correlation of Ross and Laurence(1976) to the solution polymerization of MMA to predict the gel effect as a function of monomer conversion, temperature and solvent concentration. The gel effect is calculated by assuming that glass transition occurs at a free volume of 0.025 (Beuche(1962)).

In this study the gel effect was initially taken into consideration after the free volume correlation developed by Schmidt and Ray(1981). However the experimental results presented in Figure 4.3 show that there is no significant gel effect present at the conditions of polymerization. High solvent/monomer ratios and lower conversions used in this study assure negligible gel effect during the course of polymerization.

5.4 Parameter Estimation

A nonlinear state space model for the solution polymerization of MMA in a batch reactor was developed in section 5.3. These differential equations can be solved to obtain the time variation of I, M, μ_0, and μ_2 during the course of polymerization by specifying the numerical values of the kinetic parameters of the model. Using the reported values of the kinetic parameters by Schmidt and Ray(1981)for solution polymerization of MMA, significant discrepancy between the experimental and model predicted results was observed. Since there was considerable scatter of the values of the kinetic parameters reported in the literature, it was decided to reestimate the parameters of the model using our own experimental data.

The parameters that appear in the set of four nonlinear differential equations that represent the reactor model are k_d, kp, k_{td}, k_{tc}, k_s, k_m and f. In the following we will discuss how the numerical values of various parameters of the model were obtained.

In MMA polymerization it is generally assumed that termination reaction occurs predominantly by disproportionation mechanism. However polydispersity values($M_w/M_n \simeq 1.7-2.0$) obtained in this work suggest that both modes of termination reactions should be taken into account. Odian(1981) reported that at 60°C, termination by combination account for about 40 percent of the total termination reactions in MMA polymerization.

When k_{tc} was set equal to k_{td}, the theoretical polydispersity values varied from 1.88 upwards, matching the experimental polydispersity values better. If the termination by combination mechanism was neglected the theoretical polydispersity values would vary from 2.0 upwards. However, it should be noted that the contribution of the disproportionation mechanism to the total termination mechanism increases with increase in temperature in MMA polymerization (Odian (1981)). This effect of temperature on the modes of termination reactions was not taken into account in our parameter estimation studies.

It is known that not all the initiator radicals produced in the dissociation reaction are able to initiate a polymer chain because of many side reactions. The initiator efficiency f is defined as the fraction of radicals formed in the primary step of initiator dissociation which are successful in initiating a polymer chain. The values of f for most initiators lie in the range of 0.3-0.8 (Hamielec(1976)). In this work a value of 0.5 was chosen which is also the value used by other workers (Schmidt and Ray(1981)).

It is noted that the rate constants for chain transfer reactions to monomer and solvent are very low compared to propagation rate constant. The numerical values of the chain constants were taken from Brandrup and Immergut(1975) and are reported in Table 5.1. The kinetic parameters which were estimated in this work using the experimental data are k_d, kp and k_t.

But the kinetic terms kp and k_t appear in the model equations in such a way that their values can not be found individually, but only the ratio kp^2/k_t can be estimated from the experimental data. Since the individual kinetic constants are reported in the literature, we re-adjusted all the parameters simultaneously so that the experimental and model results match. Also we checked that the values of the estimated parameters are well within the range of values reported in the literature.

Each kinetic constant consists of two parameters through the Arrhenius relationship:

$$k_j = A_j \exp(-E_j/RT) \qquad (5.34)$$

where

k_j = kinetic constants k_d, kp, or k_t

A_j = Arrhenius factor A_d , Ap , or A_t

E_j = Activation energy E_d , Ep , or E_t

According to Equation (5.34) a total of six parameters consisting of three Arrhenius factors and three activation energies have to estimated. The above problem reduces to a standard problem of estimating numerical values of parameters in a system of differential equations. Numerical procedures for solving this problem have been reported in

Table 5.1 Numerical Values of k_m and k_s Parameters
(Brandrup and Immergut(1975))

Temp °C	$C_s \times 10^4$ $C_s = k_s/kp$	$C_m \times 10^4$ $C_m = k_m/kp$
60	.190	.00515
70	.567	-
80	.910	.0240

the literature and are given below.

Rosenbrock(1966) dealt with the problem of estimating parameters in differential equations by minimizing the sum of squares of errors between the measured values and computed values of the states. He also gave an analytical procedure to calculate the confidence intervals for the parameters by linearizing the model equations.

Donnelly and Quon(1970) used a quasilinearization method to identify parameters in systems of ordinary differential equations derived for chemical engineering problems. Hosten(1979) carried out a comparative study of short cut procedures for parameter estimation for an experimental catalytic reaction system. He reported that Maximum Likelihood treatment is a laborious task requiring up to 100 times the computer time required by short cut methods. However since short cut estimates do not possess desirable statistical properties, it is important to follow up any such procedure with rigorous treatment such as Maximum Likelihood. Recently Wantenbe and Himmelblau(1983) examined a number of aspects of estimating coeffecients in kinetic models. They reported about a class of methods in which the derivatives in the differential equations are approximated by a proper difference relation to yield a set of algebraic equations that can be solved to obtain values for the coefficients.

In this work a finite difference Levenberg-Marquardt method (Becks and Arnold(1977), Bard(1974)) available in the IMSL Library (ZXSSQ) has been used in combination with a routine (DGEAR, IMSL Library, Gear(1971)) to integrate the system of ordinary differential equations for estimating the parameters.

The idea behind the Levenberg-Marquardt (L-M) method which combines the Gauss method with the steepest descent method is the following. The steepest descent method often works well in the initial iterations, but the approach to the minimum becomes progressively slower. On the other hand, the Gauss method works well and converges fast in the neighbourhood of the minimum but gives troubles or even diverges when the initial guesses are away from the minimum. This L-M method starts as the steepest descent method and progressively switches to the Gauss method when the minimum of the objective function is reached, thus ensuring convergence as well as fastness of the algorithm.

For the parameter estimation of the reactor model, the differential equations representing the batch reactor are numerically integrated assuming an initial set of parameters. At times t_i at which measured data are available, the computed values of the outputs Yp_i are compared with the measured values of the outputs Y_{mi}. An error vector, $e(_i)$ at the time t_i is formed as follows:

$$e_i = (Y_{mi} - Yp_i) \tag{5.35}$$

If a is the vector of the six parameters consisting of the Arrhenius factors and activation energies, then a scalar function J(a) can be formed by summing the weighted squares of the errors as:

$$J(a) = \sum_{i=1}^{n} e_i{}' w e_i \tag{5.36}$$

where w is a 3x3 weighting matrix and n is th[illegible]otal number of times measurements are made. Note that at each time t_i three measurements namely conversion, number and weight average molecular weight are made. This is a case of a multiresponse problem in contrast to single response problem in which only a single measurement is made at each time. The function J(a) is minimized by a proper choice of the vector a of parameter using the L-M method.

One of the main difficulties involved in the least squares estimation procedure is how to carry out successfully the optimization of J(a) for a highly nonlinear model. Because of the complex nature of the model solutions, local optima can be expected to be encountered, hence the choice of the initial guesses for the parameters is important. Since the numerical values of states in the model are of different magnitude, a Gear routine (DGEAR in IMSL library) which can handle stiff differential equations with the provision for automatic step size and error control was used.

The kinetic parameters reported by Schmidt and Ray(1981) were used as the initial values, since it is known that kinetic parameters that would be estimated would not differ significantly from these values. The data obtained from six different experiments were used for the purpose of parameter estimation. Table 5.2 gives the details of the experimental conditions and the number of data points used from each experiment to estimate the parameters. A total of 159 data points were used.

Since the initial guess of the parameters was good, the program converged fairly quickly in five iterations. These parameter estimates along with the values of the kinetic constants are listed in Table 5.3.

Figures 5.1 and 5.2 show the "goodness" of fit of the parameters in predicting the conversion-time histories for various experimental conditions. The experimental points along with the model predictions (solid lines) clearly show the agreement between predicted values and the experimental values are quite good in all the six experiments.

Figures 5.3 and 5.4 compare the experimental and predicted values of number average molecular weight. It can

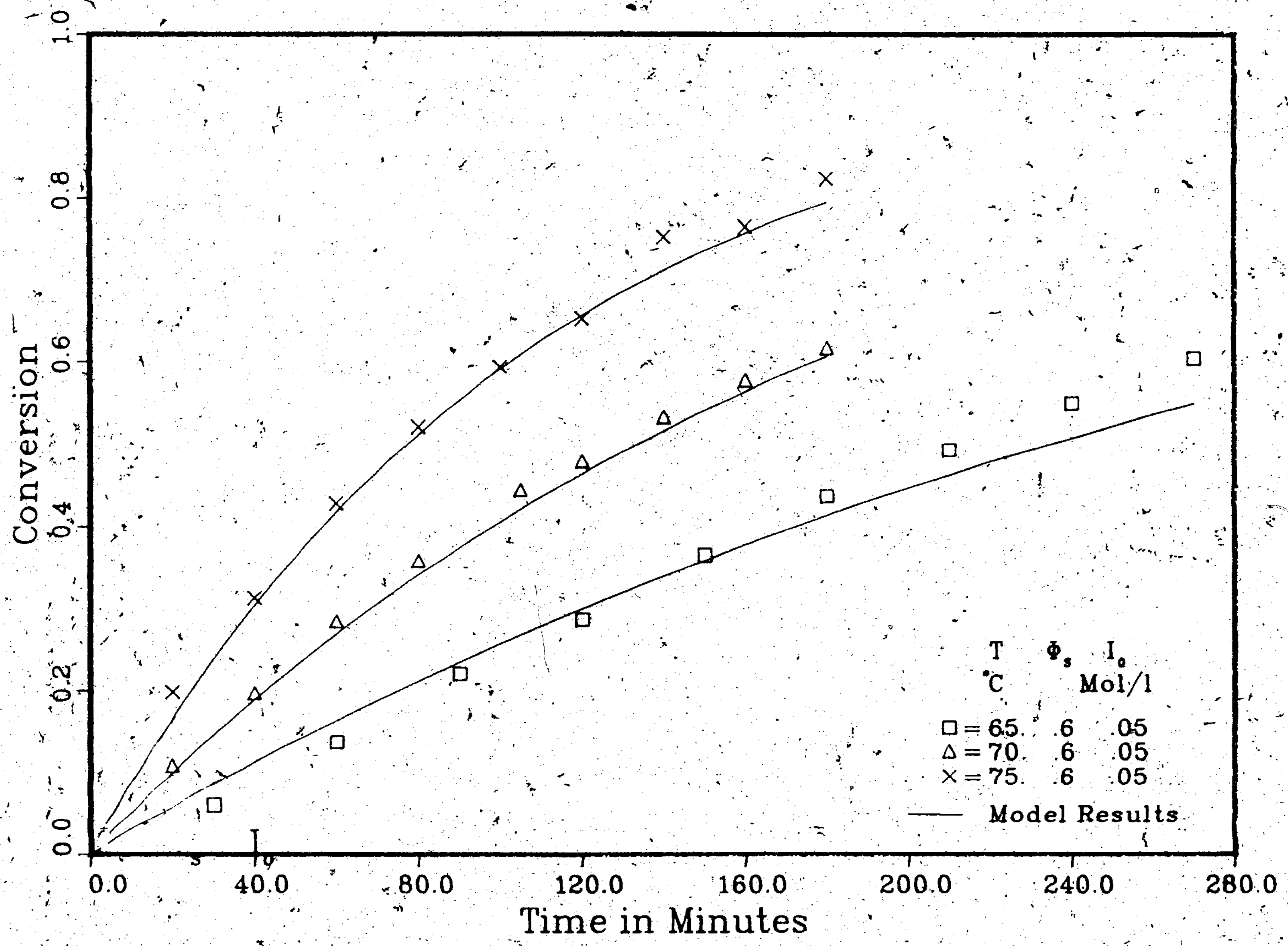

Fig. 5.1 Comparison of Experimental and Model Results for Conversion-I

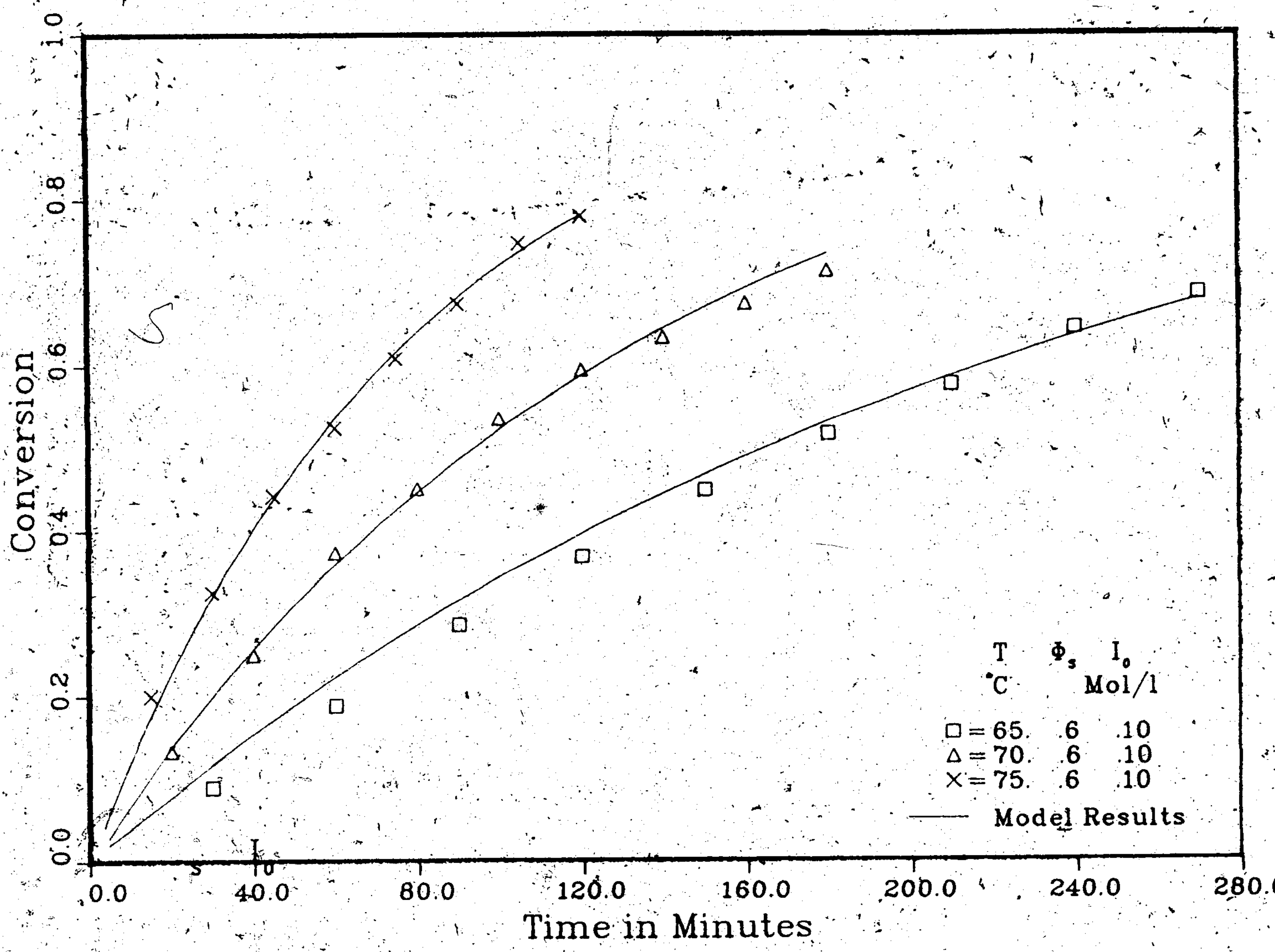

Fig. 5.2 Comparison of Experimental and Model Results for Conversion-II

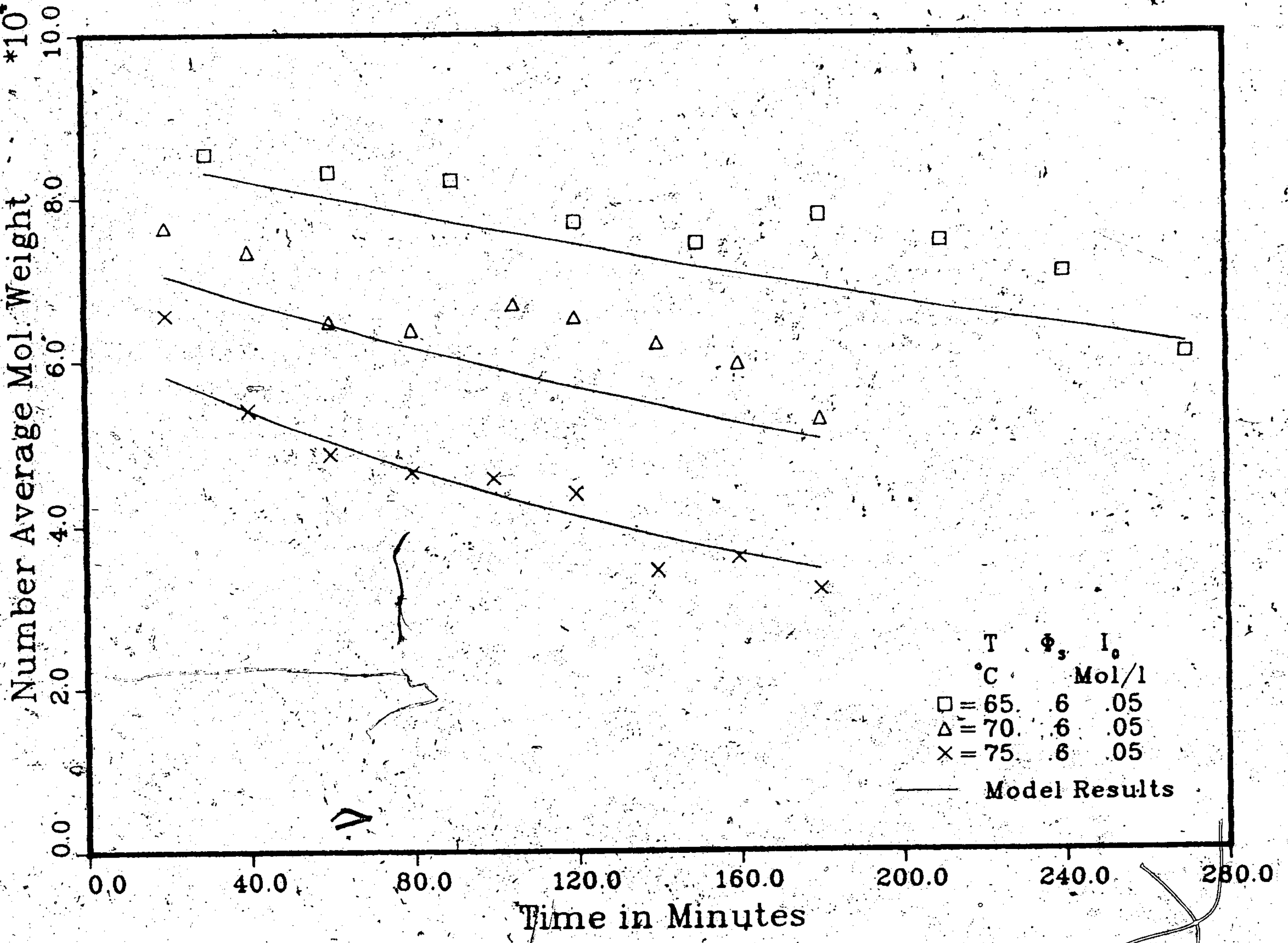

Fig. 5.3 Comparison of Experimental and Model Number Average Molecular Weight-I

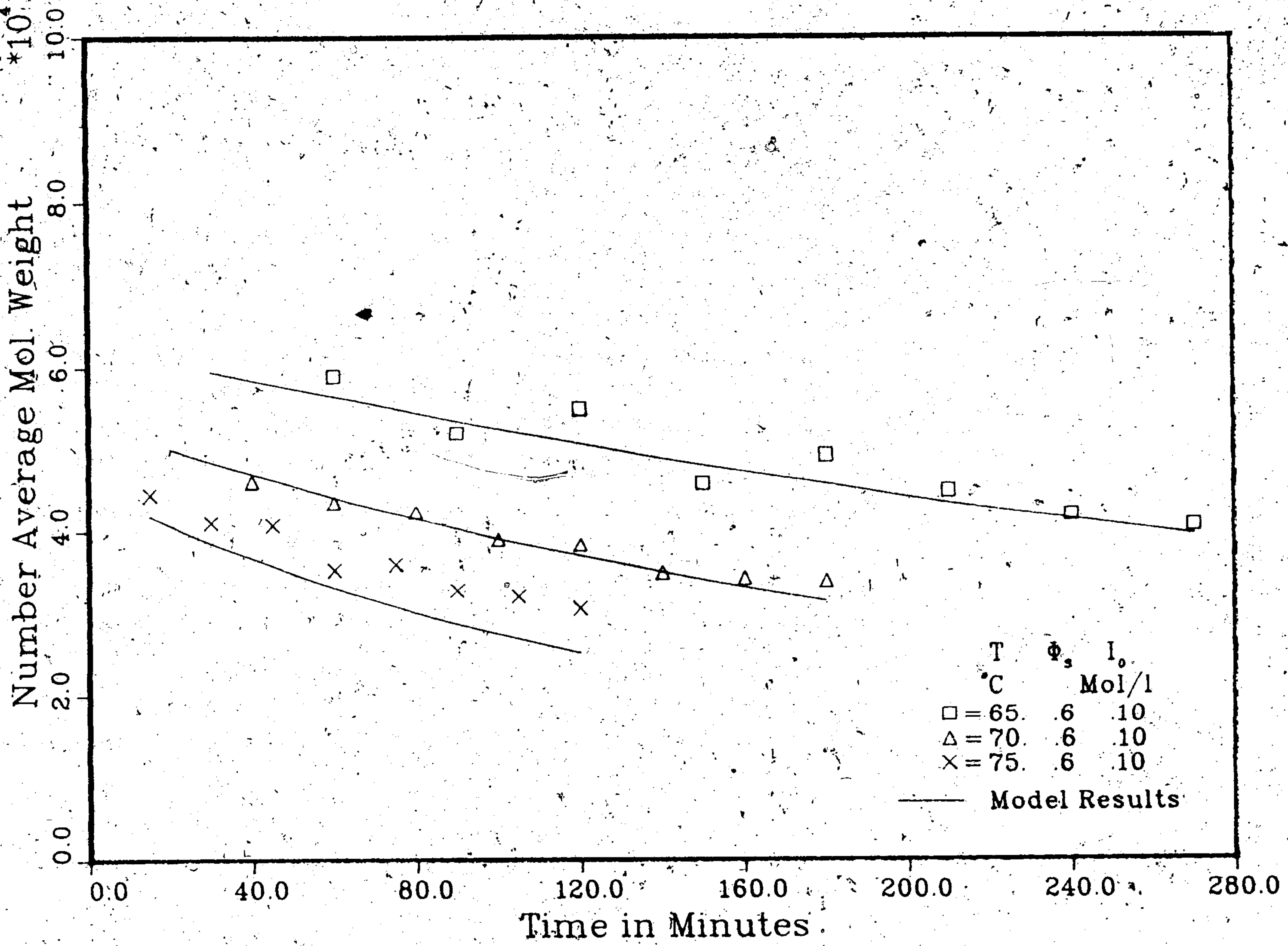

Fig. 5.4 Comparison of Experimental and Model Number Average Molecular Weight-II

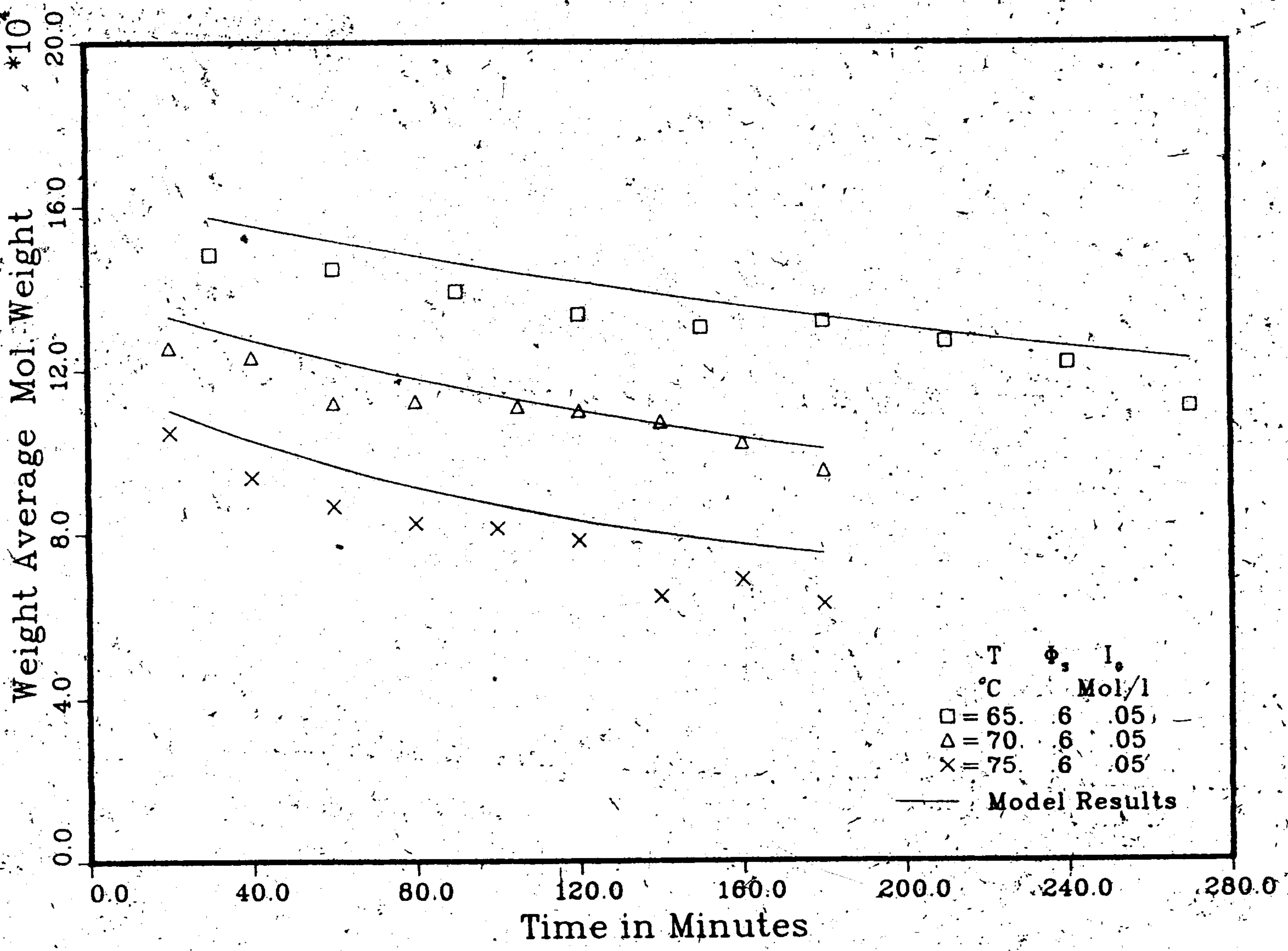

Fig. 5.5 Comparison of Experimental and Model Weight Average Molecular Weight-I

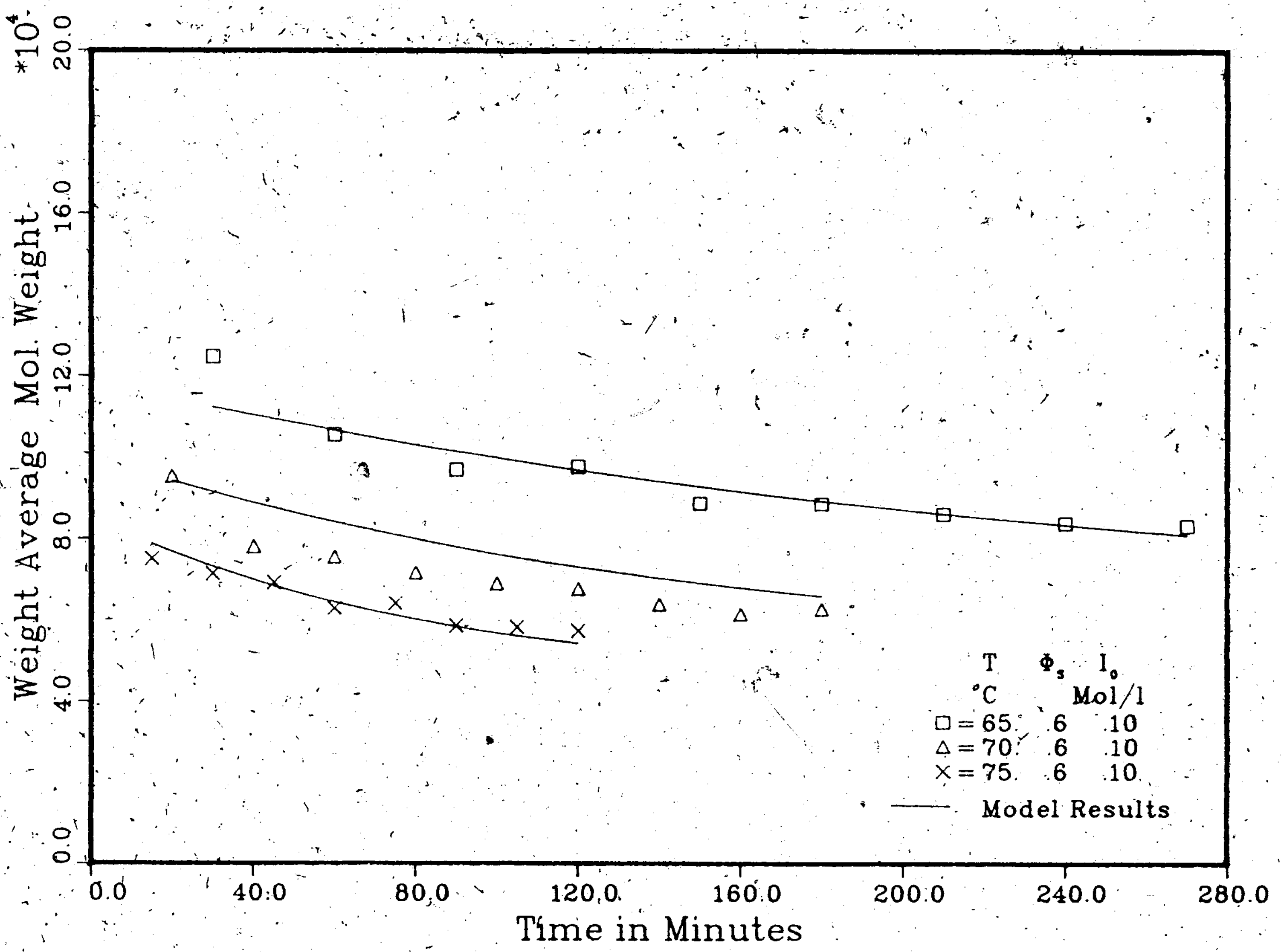

Fig. 5.6 Comparison of Experimental and Model Weight Average Molecular Weight-II

Table 5.2 **Experimental Data used for Parameter Estimation**

Exp no	T °C	solvent Ratio	I_0 mol/L	X	M_n	Mw	Total Data
1	65	.6	.05	9	9	9	27
2	65	.6	.10	9	9	9	27
3	70	.6	.05	9	9	9	27
4	70	.6	.10	9	9	9	27
5	75	.6	.05	9	9	9	27
6	75	.6	.10	8	8	8	24

Total number of data points = 159

$$W = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/50000 & 0 \\ 0 & 0 & 1/80000 \end{bmatrix}$$

Table 5.3 Estimated Values of the Kinetic Parameters

$A_d = 3.751 \times 10^{16}$ $E_d = 33740$
$Ap = 1.201 \times 10^{9}$ $Ep = 9630$
$A_t = 2.113 \times 10^{8}$ $E_t = 1014.$

Typical values of k_d, kp and k_t at different Temperatures

T °C	$k_d \times 10^4$ 1/s	kp L/mol-s	$k_t \times 10^{-8}$ L/mol-s
65	.0490	681.7	4.648
70	.1022	840.6	4.751
75	.2085	1030.0	4.854

be observed that though the model predicts the number average molecular weight well, some of the experimental points do differ from the model results. The accuracy of number average molecular weight measurements from size exclusion chromatography has been discussed earlier in Section 3.4. A measurement error in the range of 10 percent can be expected.

Figures 5.5 and 5.6 show the comparison of experimental and predicted weight average molecular weights for various experimental conditions. A similar argument that has been advanced with respect to number average molecular weight holds good since weight average molecular weight has also been measured using SEC.

It should be mentioned here that the model prediction of conversion, number average and weight average molecular weights considerably improved after the parameter estimation. The values of kinetic constants taken from literature did not predict the experimental values well. Therefore the newly estimated parameter values are used in the derivation of optimal control policies in chapter six.

5.5 Conclusions

In this chapter a mathematical model has been derived for the free radical solution polymerization of MMA in a batch reactor. By using the moments of the polymer chains and the quasi steady state approximation (QSSA), the order of the model was reduced significantly.

The model parameters were estimated from our experimental data by using a nonlinear parameter estimation routine (ZSSQ IMSL Library) due to Marquardt(1963). It is found that when the estimated parameters are used, the model predicts experimental values of conversion, number and weight average molecular weights reasonably well.

6. OPEN LOOP CONTROL STUDIES

6.1 Introduction

In the polymerization industry there is considerable economic incentive to develop real time computer control policies that will increase production and produce a polymer with desired final physical and mechanical properties. As discussed in chapter five a homopolymer is mainly characterized by the molecular weight distribution and its mean values e.g. number average (M_n) and weight average (M_w) molecular weights. These two variables greatly affect the final chemical, physical and mechanical properties of a polymer product. Therefore if we want to produce a polymer with specified final properties, we must be able to exercise control of these variables (M_n and M_w) during the course of polymerization. In the past most of the studies on the optimal control of polymerization reactors have been limited to theoretical predictions of the optimal control policies such as optimal temperature and optimal initiator addition policies to produce a polymer with desired final conversion and desired molecular weight averages. Few if any studies have reported actual implementation of such optimal policies to laboratory scale polymerization reactors. Hence there is an obvious need to demonstrate and evaluate computer implementation of these optimal control policies to a laboratory scale reactor.

In this chapter we develop optimal control policies by applying state-space based control methods to the model of the batch polymerization reactor derived in chapter five. These policies are implemented on the experimental batch reactor system and the results compared with the theoretical predictions. However in open loop control of the reactor no feedback corrective action is taken should there be any process upsets or disturbances entering the system.

6.2 Control of Polymerization Reactors

Compared to the successful application of optimal control theory to other chemical processes (distillation, evaporator etc.) there have been only a few successful attempts at the optimal control of polymerization reactors (Kiparissides (1978)). Several valid reasons exist for this lack of progress of application of the optimal control theory to polymerization reactor systems:

1. Polymerization reactions are highly complex and at least until relatively recently it was difficult to describe such systems by low order models.
2. The formulation of a mathematical objective function to optimize the performance of the polymerization reactors is not easy.
3. On-line measurements of important polymerization process variables such as conversion and molecular weight distribution until fairly recently has not been available.

6.2.1 Previous Work

In the past several investigators have applied optimal control theory to polymerization reactors to determine the temperature and initiator addition policies that minimize the reaction time and produce a polymer with desired final molecular weight distribution. Hoffman et al. (1964) developed policies for monomer or initiator addition to a batch polymerization reactor to produce a polymer product with desired final conversion and number average molecular weight and at the same time having minimum polydispersity. They concluded that in polymerization reactor systems in which gel effect is absent, the narrowest molecular weight distribution of the polymer is obtained when the instantaneous degree of polymerization is maintained constant throughout the course of polymerization. Beste and Hall(1966) extended this study of molecular weight distribution control to the batch polymerization reactors and determined addition policies of initiator and monomer.

In one of the earliest applications of optimal control theory to polymerization reactors Shatkan(1965) determined the temperature histories to obtain a polymer with desired final conversion in minimum time for the case of an ideal batch polymerization reactor. According to this policy, the temperature must be raised at a predetermined rate until it reaches an upper limit and maintained at this level until the desired target set is reached.

Ray(1967) calculated the optimal temperature and initiator concentration policies for a series of polymerization reactors by minimizing a performance index which is a function of deviations of conversion, number average degree of polymerization and polydispersity from their desired values. He applied a peak-seeking method to compute the best temperature and initiator concentration in each tank. Hicks et al.(1969) formulated a similar objective function and applied Pontryagin's Maximum Principle to optimize the performance of a free radical polymerization reactor: (i) by controlling the polymerization temperature while keeping a constant initiator concentration, and (ii) by using both temperature and initiator concentration as control variables. The latter attempt proved unsuccessful due to computational difficulties.

Yoshimoto et al.(1968) applied the Maximum Principle to a free redical solution polymerization reactor to obtain the desired average degree of polymerization and conversion in minimum time. Their results are similar to those of Shatkan(1965). In a later study Yoshimoto et al.(1971) determined optimal temperature policies to obtain specified conversion and average molecular weight in minimum time for the case of a thermally initiated polymerization reactor. They demonstrated that there exists a unique initial temperature and thermal history that permits to reach the selected final conversion and average molecular weight in minimum time. However their model did not take account of the gel effect caused by the diffusion controlled termination reactions.

Nishimura et al.(1968) also applied the Maximum Principle to an ideal radical polymerization reactor to obtain the optimal temperature and initiator concentration policies. They implemented these policies to a solution polymerization of styrene in a batch reactor and found good agreement between the experimental results and theoretical predictions.

Osakada and Fan(1970) calculated sub-optimal temperature and initiator feed rate policies in an attempt to obtain a desired molecular weight distribution. The near optimal policies were represented by two polynomial functions of time the coefficients of which were found by a simplex pattern search technique (Nelder and Mead(1969)).

Sacks et al.(1972) applied the Maximum Principle to determine temperature and initiator policies that minimize the time to obtain a final desired conversion and number average molecular weight. They showed that the optimal initiator policy is one of maintaining constant initiator concentration throughout the course of polymerization. The same authors (Sacks et al.(1973)) studied the effect of temperature variations on the molecular weight distribution of the polymer. By using the Maximum Principle they found that the temperature policy which minimizes the breadth of the molecular weight distribution should produce a polymer with constant instantaneous number average molecular weight throughout the course of polymerization. The temperature policy which maximizes the breadth of the molecular weight distribution is one of requiring step changes in temperature between prespecified maximum and minimum values.

Chen et al.(1978,1980,1981) conducted a series of studies on optimal control problems related to free radical polymerization of styrene in a batch reactor by considering the polymerization temperature and the initiator concentration as two control variables. They derived optimal temperature and initiator policies that are required to obtain a polymer with desired final conversion and number average molecular weight in minimum time. Experimental verification of their policies for the case of solution polymerization of styrene in a batch reactor revealed that there was good agreement between experimental and calculated conversion values throughout the course of the polymerization reaction. However appreciable deviations existed between experimental and calculated number average and weight average chain lengths.

Masterson(1977) and Clough et al.(1978) applied the Maximum Principle to solve the minimum time problem for batch polymerization of styrene. They obtained a product with desired conversion, desired number average and weight average molecular weight by controlling temperature and initiator feedrate. The numerical solution of the above problem has proven challenging. They used a target set concept in the sense that they searched for final values of conversion, number and weight average molecular weights in the "target set" which satisfied the initial conditions of the state variables.

Wu et al.(1980) presented a graphical solution to the minimum time problem of styrene polymerization. Their performance index depended only on conversion and number average molecular weight at the end of reaction. Applying the Maximum Principle, they were able to obtain the the optimal variation of temperature with time. Their theoretical predictions were in agreement with experimental measurements of conversion and number and weight average molecular weights.

Farber(1983) applied optimal control theory to bulk polymerization of styrene in a batch reactor to obtain a polymer with desired conversion and molecular weight averages in minimum time using temperature as the control variable. Recently Thomas(1981) and Thomas and Kiparissides(1984) applied the optimal control theory to a batch polymerization reactor for MMA to calculate the near-optimal temperature and initiator policies that are required to produce a polymer with a desired final conversion and desired number average and weight average molecular weights. They numerically solved the resulting two-point boundary problem to obtain the optimal control policies by introducing a "target set concept" which significantly simplified the numerical solution.

6.3 Statement of the Control Problem

From the previous review of literature on the optimal control of batch polymerization reactors it becomes evident that most of the studies were directed to the derivation of theoretical optimal control policies using the model of the reactor, and only very few implemented these policies to an actual reactor in an effort to verify experimentally the theoretical results. Such a verification is not only important but also necessary to successfully close the wide gap existing between the theory and practice in chemical process control (Foss and Denn(1976), Athans(1976)).

In the following sections optimal control policies for the solution polymerization of MMA in a batch reactor will be developed using the mathematical model of the reactor derived in chapter five.

A variety of optimization problems can be formulated for the batch solution polymerization reactor depending upon the objective function that has to be minimized and the selection of control variables. The reaction temperature and the initiator concentration are usually selected as the control variables. These two variables affect the rate of polymerization and the molecular weight distribution of polymer as seen in chapter four.

The following problems have been formulated and solved for the free radical solution polymerization of MMA in a batch reactor.

Problem 1: Find the optimal isothermal temperature and the optimal initial initiator concentration to produce a polymer with desired conversion and desired number average molecular weight in minimum time.

Problem 2: Find the time optimal initiator addition policy for a given polymerization temperature to produce a polymer with desired conversion and desired number average molecular weight in minimum time.

Problem 3: Find the optimal temperature policy for a given initial initiator concentration to produce a polymer product with desired final conversion and desired number average molecular weight in minimum time.

Problem 4: Find the optimal temperature policy for a given initial initiator concentration to produce a polymer product with desired final conversion and number average molecular weight and with minimum polydispersity.

The first problem reduces to a static optimization problem. Problems two and three require a minimum time formulation based on the Pontryagin's Maximum Principle. The fourth, minimum polydispersity problem, turns out to be a free terminal time problem.

6.4 Optimal Isothermal Temperature and Optimal Initial Initiator Concentration Policy (Problem 1)

The objective of this static optimization problem is to find the optimal isothermal temperature and the optimal initial initiator concentration to produce a polymer with desired final conversion and desired number average molecular weight in minimum time. A solution to this problem is obtained by using the Lagrange multiplier technique.

The mathematical model of the free radical solution polymerization of MMA in a batch reactor has been derived in chapter five. The model equations were further simplified as shown in Appendix C.

The model equations are

$$dI/dt = -k_d I \tag{6.1}$$

$$dM/dt = -k_1 M\sqrt{I} \tag{6.2}$$

$$d\mu_0/dt = Ck_d I + k_2 M\sqrt{I} + k_3 S\sqrt{I} \tag{6.3}$$

$$d\mu_2/dt = (k_s S + k_m M)\lambda_2 + k_t \lambda_0 \lambda_2 + k_{tc} \lambda_1^2 \tag{6.4}$$

where

$$\lambda_0 = \sqrt{2fk_d I/k_t} \tag{6.5}$$

$$\lambda_1 = \frac{2fk_d I + (kpM + k_m M + k_s S)\lambda_0}{(k_m M + k_s S + k_t \lambda_0)} \tag{6.6}$$

$$\lambda_2 = \lambda_1 + 2kpM\lambda_1 / (k_m M + k_s S + k_t \lambda_0) \tag{6.7}$$

$$k_1 = kp\sqrt{2fk_d/k_t} = A_1\exp(-E_1/RT) \quad (6.8)$$

$$k_2 = k_m\sqrt{2fk_d/k_t} = A_2\exp(-E_2/RT) \quad (6.9)$$

$$k_3 = k_s\sqrt{2fk_d/k_t} = A_3\exp(-E_3/RT) \quad (6.10)$$

$$C = 2f(1 - k_{tc}/\ 2k_t) \quad (6.11)$$

Equations(6.1) through (6.11) completely describe the solution polymerization of MMA in a batch reactor. For a constant temperature Equation(6.1) can be analytically solved to give

$$I = I_0\ \exp(-k_d t) \quad (6.12)$$

where I_0 is the initiator concentration.Substituting Equation(6.12) into Equation(6.2) and integrating the resulting equation we get

$$M = M_0\ \exp[\ \sqrt{I_0}\ 2\frac{k_1}{k_d}\{\ \exp(-\ \frac{k_d t}{2})\ - 1\}] \quad (6,13)$$

where M_0 is the initial monomer concentration. Equation(6.3) can be integrated as:

$$\mu_0 = \int_0^t Ck_d I\ dt + \int_0^t k_2 M\sqrt{I}\ dt + \int_0^t k_3 S\sqrt{I}\ dt \quad (6.14)$$

From Equation(6.12) and (6.13), the integrals in the Equation(6.14) are evaluated as:

$$\mu_0 = CI_0[1-\exp(-k_d t)] + 2\frac{k_3}{k_d}S\sqrt{I_0}[1-\exp(-k_d t/2)]$$

$$+ \frac{k_2}{k_1}M_0\{1-\exp\{2\frac{k_1}{k_d}\sqrt{I_0}\,[\exp(-k_d t/2)-1]\}\} \qquad (6.15)$$

The desired conversion X^* and desired number average molecular weight M_n^* can be expressed in terms of desired monomer concentration (M^*) and desired zeroth moment of the polymer(μ_0^*) as:

$$M^* = M_0(1-X^*) \qquad (6.16)$$

$$\mu_0^* = M_0 X^* MW/M_n^* \qquad (6.17)$$

where MW is the molecular weight of the monomer. Equation(6.13) can be solved for the final time as

$$tf = -\frac{2}{k_d}\ln\{1 + \frac{k_d \ln(a)}{2k_1\sqrt{I_0}}\} \qquad (6.18)$$

where

$$a = M^* / M_0 \qquad (6.19)$$

Substituting Equation(6.18) into Equation(6.15) and rearranging we get

$$\mu_0^* - CI_0 \left[1-\left\{1+\frac{k_d \ln(a)}{2k_1\sqrt{I_0}}\right\}^2\right] + \frac{k_3}{k_1} S\ln(a)$$

$$-\frac{k_2}{k_1} M_0(1-a)=0 \qquad (6.20)$$

Now the optimization problem can be formulated as follows:

$$J= \min_{I_0,\,T} \; tf \quad \text{subjected to Equation(6.20)} \qquad (6.21)$$

An objective function $J(I_0,T)$ can be formed incorporating the constraint Equation(6.20) using a Lagrange multiplier.

$$J(I_0,T)= -\frac{2}{k_d} \ln(1+ \frac{k_d \ln(a)}{2k_1 I_0}$$

$$+\gamma\{\mu_0^* -CI_0[1-\left(1+\frac{k_d \ln(a)}{2k_1\sqrt{I_0}}\right)^2] - \frac{k_2}{k_1}M_0(1-a)+\frac{k_3}{k_1}S\ln(a)\} \qquad (6.22)$$

where γ is the Lagrange multiplier. From Equation(6.22) the optimal conditions are

$$\partial J/\partial I_0 = 0 \qquad (6.23)$$

$$\partial J/\partial T = 0 \qquad (6.24)$$

From Equations(6.23) and (6.24), Equation(6.25) can be derived after considerable algebraic manipulation.

$$-2k_1 I_0 E_d - Ck_2 S \ln(a)(E_1-E_2) + Ck_3 M_0 (1-a)(E_1-E_3) + k_d\sqrt{I_0}\ln a(E_1-E_d)$$

$$-k_d(E_1-E_d)\sqrt{I_0}\ln(a)\,\frac{2k_1 I_0 + k_d\sqrt{I_0}\ln(a)}{2k_1 I_0}$$

$$-\{E_d k_d\sqrt{I_0}\ln(a)\}\ln\{\frac{2k_1 I_0 + k_d\sqrt{I_0}\ln(a)}{2k_1\sqrt{I_0}}\} = 0 \qquad (6.25)$$

The optimal values of initial initiator concentration I_0 and isothermal temperature T were obtained by simultaneous solution of Equations (6.25) and (6.20) for which the Newton-Raphson method was used.

Table 6.1 gives the optimal values of I_0 and T that must be used to obtain a polymer product with the desired conversion and number average molecular weight in minimum time.

From the results in Table 6.1 it can be observed that the combined policy leads to almost total depletion of initiator, the initiator conversion being 99 percent in all the cases. This situation in which the initiator is fully consumed before all of monomer is converted to polymer is called dead-end polymerization. Chen and Cheng(1978) also obtained similar results in batch bulk polymerization of styrene. The isothermal temperature obtained are high in the range of 103-123°C whereas the initial initiator concentration are very low in the range of 0.006-0.004 mol/l. It can also be observed that when desired number average molecular weight is increased keeping desired final

Table 6.1 Simulation Results of Optimal Isothermal and Initial Initiator Concentration Policy

X^*	M_n^*	I_o mol/l	T °C	tf min	Initiator Conversion
.70	50000	.0066	123	9.5	.99
.70	70000	.0047	117	19.7	.99
.70	90000	.0036	112	34.0	.99
.80	50000	.0075	114	25.0	.99
.80	70000	.0054	108	52.0	.99
.80	90000	.0041	103	90.0	.99

conversion constant, the isothermal temperature as well as the initial initiator concentration decreases. However total time to produce higher molecular weight polymer increases as expected.

These optimal temperature and initial initiator concentration policies reported in Table 6.1 were not implemented on the experimental reactor system because of difficulties of maintaining high temperatures inside the reactor.

These results should be interpreted with caution. Probably the model itself is not valid at these high temperatures and hence one may question the accuracy of the quantitative results. However the qualitative predictions obtained from the model should be valid. Since the rate of reaction is high at high temperatures, considerable amount of heat will be released by the exothermic MMA polymerization. The reactor should have enough cooling capacity to carry out the reaction at high temperatures.

6.5 Time Optimal Initiator Concentration Policy (Problem 2)

The objective in this problem [illegible] find an optimal initiator concentration policy for a given temperature of the reaction to produce a polymer with desired final conversion and final number average molecular weight in minimum time. This problem reduces to the standard minimum time problem in optimal control theory for which standard procedures of solution are available.

It should be pointed out here that only desired conversion and desired number average molecular weight are specified whereas the weight average molecular weight is allowed to be free from any constraint. In polymerization systems in which the gel effect is absent, as is the case here, the polydispersity values do not change very much suggesting that the weight average molecular weight is an almost constant multiple of M_n. Hence the number average and weight average molecular weights can not be changed independently when the gel effect is absent.

Now let us apply optimal control theory to the model of the reactor given by Equations (6.1)-(6.11).

For the isothermal process the objective is

$$\min(t\ ) = \int_{0}^{tf} dt \tag{6.26}$$

The Hamiltonian for the above problem is given as:

$$H = -1 - P_1 k_1 M\sqrt{I} + P_2\{Ck_d I + k_2 M\sqrt{I} + k_3 S\sqrt{I}\} \tag{6.27}$$

P_1 and P_2 are co-state variables which must satisfy the following canonical equations.

$$dP_1/dt = -\partial H/\partial M \tag{6.28}$$

$$dP_2/dt = -\partial H/\partial \mu_o = 0 \tag{6.29}$$

From the Equation(6.29) it is clear that P_2 is a constant. If the control variable is unconstrained the conditions for optimality are given by:

$$\partial H/\partial I = 0 \tag{6.30}$$

$$H = 0 \tag{6.31}$$

From Equations(6.30) and (6.31) I can be obtained as

$$I = -1/(Ck_dP_2) = \text{constant} \tag{6.32}$$

Here I is constant because P_2 is constant and k_d is constant for a given temperature.

Integrating Equation(6.3) after substituting for dt from Equation(6.2) we get

$$\mu_o = \frac{k_3}{k_1} S\ln(\frac{M_0}{M}) + \frac{k_2}{k_1}(M_0-M) + CIk_dt \tag{6.33}$$

From Equation(6.2)

$$\ln(M/M_0) = \ln(1-X) = -k_1\sqrt{I}t \tag{6.34}$$

From Equation(6.34) I is obtained as

$$I = \frac{\{\ln(1-X)\}^2}{(k_1 t)^2} \tag{6.35}$$

From Equations(6.35), (6.17) and (6.30) tf can be obtained as

$$tf = \frac{(1-\nu)k_t\{\ln(1-X^*)\}}{kp^2[\ M_0X^*MW/M_n{}^* + C_sS\ln(1-X^*) - C_mM_0X^*} \tag{6.36}$$

where

$$C_m = k_m/kp \qquad C_s = k_s/kp \qquad \nu = k_{tc}/k_t \tag{6.37}$$

Substituting Equation(6.36) in Equation(6.35) I can be obtained as

$$I = \frac{kp^2\{M_0X^*MW/M_n{}^* + C_sS\ln(1-X^*) - C_mM_0X^*\}^2}{(1-\nu)^2\ 2fk_dk_t\{\ln(1-X^*)\}^2} \tag{6.38}$$

Given X^* and $M_n{}^*$ the optimal initiator concentration which is constant for a given isothermal temperature can be calculated from Equation (6.38). The minimum time required is obtained from Equation(6.36). Since the initiator dissociates during the course of polymerization, fresh initiator has to be continuously added to maintain I at constant level. Deriving a simple mass balance for the initiator, the initiator feedrate F is obtained as

$$F = I k_d = -1/CP_2 = \text{constant} \qquad (6.39)$$

The above equation indicates that the optimal initiator feedrate is also constant.

However in conventional polymerization reactions, the initiator decomposition rate is so slow that the initiator concentration remains constant throughout the duration of polymerization. Therefore the initiator policy turns out to be single charge of initiator at the beginning of the reaction. But in dead end polymerization reactions where the initiator dissociates at an appreciable rate, fresh initiator has to be added during the course of polymerization to keep the initiator concentration constant. It has already been mentioned that dead end polymerizations occur in systems that employ high temperatures and low initiator concentrations.

Table 6.2 gives the optimal initiator concentration values that were obtained to produce a polymer with desired X^* and $M_n{}^*$ in minimum time for the given isothermal temperature.

The results in Table 6.2 shows that at constant X^* and $M_n{}^*$, when the temperature is increased, the optimal initiator concentration as well as the total time of the reaction decreases. This suggests that to have appreciable time savings the isothermal temperature should be chosen as the maximum allowed temperature of the reactor and the optimal initiator concentration shoud be employed to get polymer with desired X^* and $M_n{}^*$.

Since the optimal initiator concentrations are almost constant for the temperatures employed in our reactor system, separate experiments were not carried out to verify the results shown in Table 6.2. However some of the isothermal experimental results reported in chapter four correspond to the conditions shown in Table 6.2. Table 6.3 compares the experimental results with the results shown in Table 6.2. The above results clearly show that there is very good agreement between the experimental results and the theoretical predictions.

6.6 Minimum Time Temperature Policy (Problem 3)

In this problem the objective is to find the optimal temperature policy at a given initial initiator concentration to produce a polymer with desired conversion and number average molecular weight in minimum time. Sacks et al.(1973) solved the above problem for the bulk free radical polymerization systems and deduced that the optimal temperature policy should keep the rate of production of primary radicals constant. Since the concentration of the initiator decreases with time, the temperature should be increased to keep the initiator dissociation rate constant. However in conventional polymerizations in which the rate of dissociation of the initiator does not decrease significantly, the optimal temperature policy turns out to be one of constant temperature throughout the polymerization process.

Table 6.2 Optimal Initiator Concentration Policy

Temp °C	X^*	M_n^*	I mol/L	tf min
65	.50	50000	.1040	161
70	.50	50000	.0735	109
75	.50	50000	.0520	74

Table 6.3 Comparison of Experimental and Optimization Results:
Optimal Initiator Concentration Policies.

Time min	T °C	I mol/L	X^*	X	M_n^*	M_n
161	65	.10	.50	.46	5.0E4	4.8E4
74	75	.05	.50	.49	5.0E4	4.8E4

The mathematical derivation and numerical techniques necessary to calculate the optimal temperature profile for the given problem are discussed in detail in Appendices C and D.

In Appendix C, the Pontryagin's Maximum Principle is applied to the mathematical model of the batch reactor in order to minimize an objective function representing final time and weighted sums of squares of deviations of M and μ_0 from their desired values at the final time. The objective function is given as:

$$\min J = tf + w_1\{M(tf) - M^*\}^2 + w_2\{\mu_0(tf) - \mu_0^*\}^2 \qquad (6.40)$$

In the above equation w_1 and w_2 are weights. A two point boundary value (TPBV) problem involving the state and co-state variables is obtained as a result of application of optimal control theory.

There are a number of numerical methods available (Kirk(1970)) to solve this difficult TPBV problem. A gradient method (Thomas(1981)) is used to obtain numerically the optimal temperature profile. The minimum time problem is solved as a series of fixed terminal time problems. For this purpose a fixed time and an initial temperature profile is assumed at first. The temperature profile is updated by solving the TPBV problem using the gradient technique. The minimum time is found by solving the TPBV problem for different final times and selecting the smallest one for which convergence is possible.

This method to find the optimal temperature profile has many disadvantages. The initial guess to the optimal temperature profile has to be a good one, otherwise serious convergence problems could occur. The step changes that are made in the steepest descent direction has to be properly controlled. Small steps in the steepest descent direction result in too much computer time before the solution is reached whereas large steps could lead to oscillations and divergence from the solution.

In Appendix D the optimal temperature profile for the given problem is developed by using a simplified model of the batch reactor, in which transfer reactions to monomer and solvent are neglected. However it should be pointed out that the transfer reactions are neglected only to derive the optimal control policy; they are included in the state equations for model description during the simulation runs. From earlier simulation studies it has been established that neglecting transfer reactions does not affect conversion results whereas molecular weight results do show changes of approximately 10 percent.

As shown in Appendix D the simplified model facilitates the direct solution of the minimum time problem of the batch reactor. Solution of the optimal control problem is obtained by iterating upon the initial value of one co-state variable , P_2. The TPBV problem is thus avoided.

Computer programs have been developed for both of the methods to find the optimal temperature policies. Since both methods gave almost similar temperature profiles, the method obtained from the simplified model was used for all the problems because of its computational efficiency.

In Figure 6.1 the optimal temperature profile obtained is plotted for different desired number average molecular weights. It can be observed that the temperature profiles are almost isothermal which is an expected result for conventional polymerization systems. It has been explained that the optimal temperature policy should be an increasing

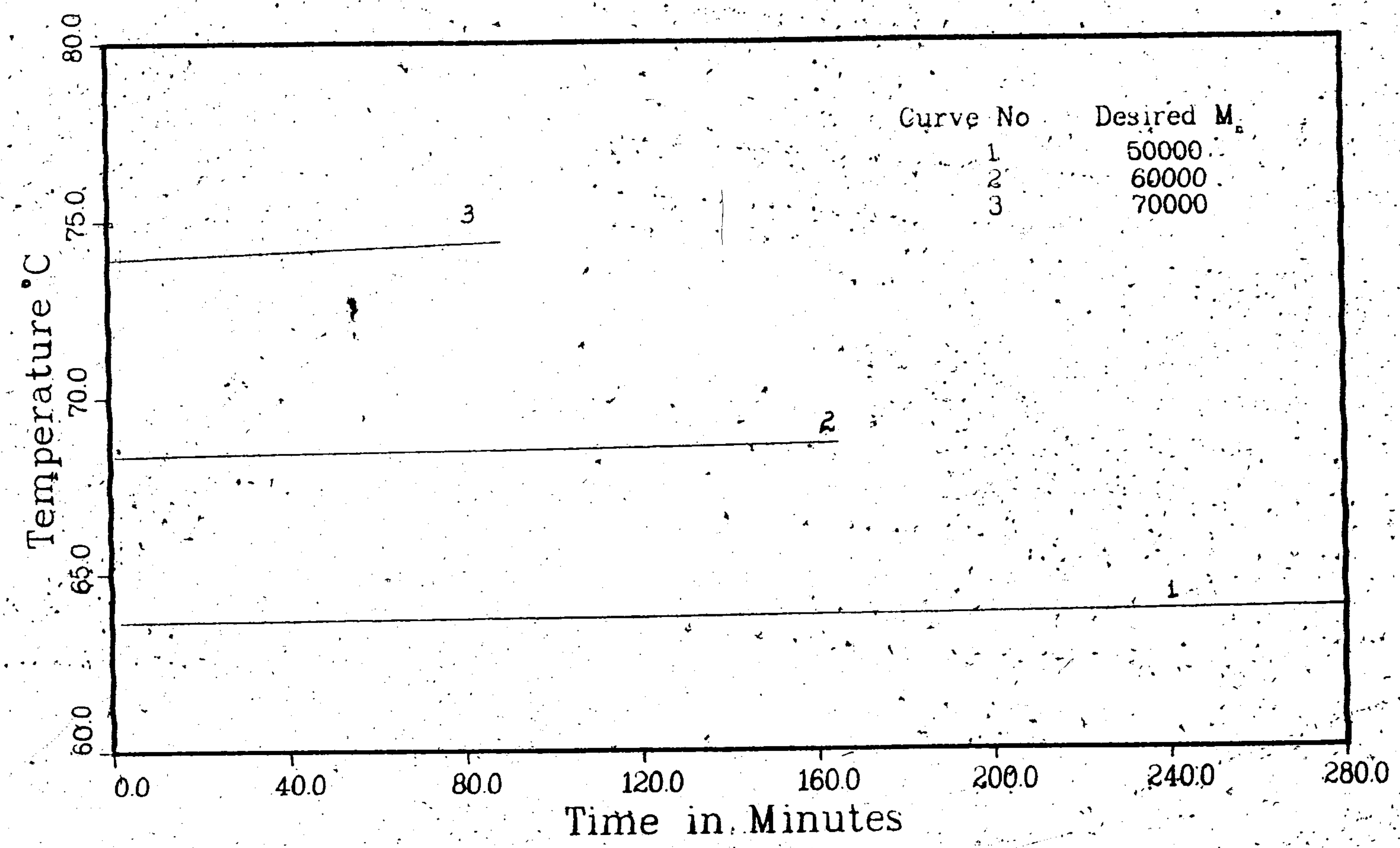

Fig. 6.1 Temperature Profile for Minimum Time Policy

Desired $x=0.5$ $\Phi_s=0.6$ $I_0=0.050$ Mol/l

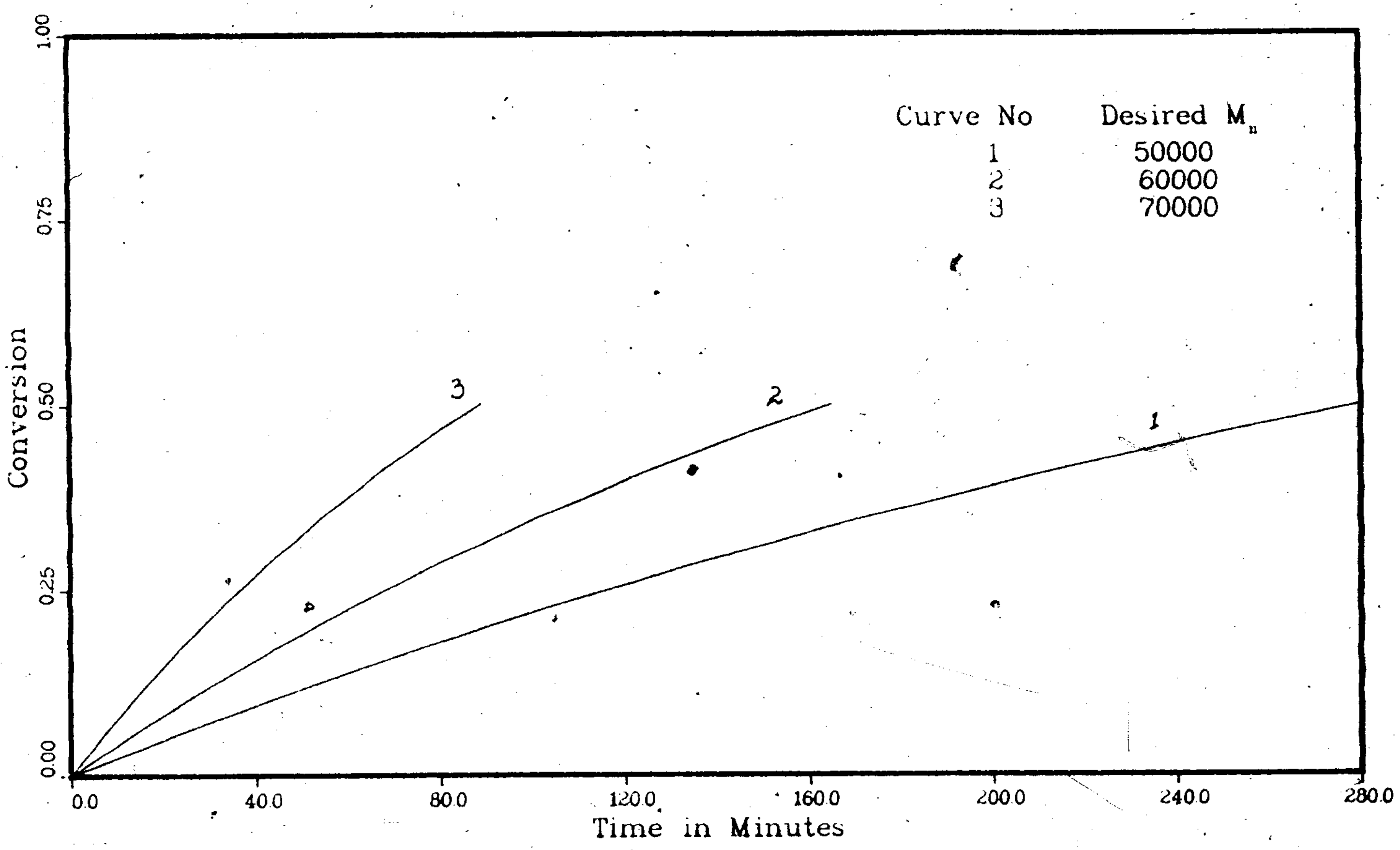

Fig. 6.2 Conversion Profile for Minimum Time Temperature Policy

Desired $x=0.5$ $\Phi_s=0.6$ $I_0=0.050$ Mol/l

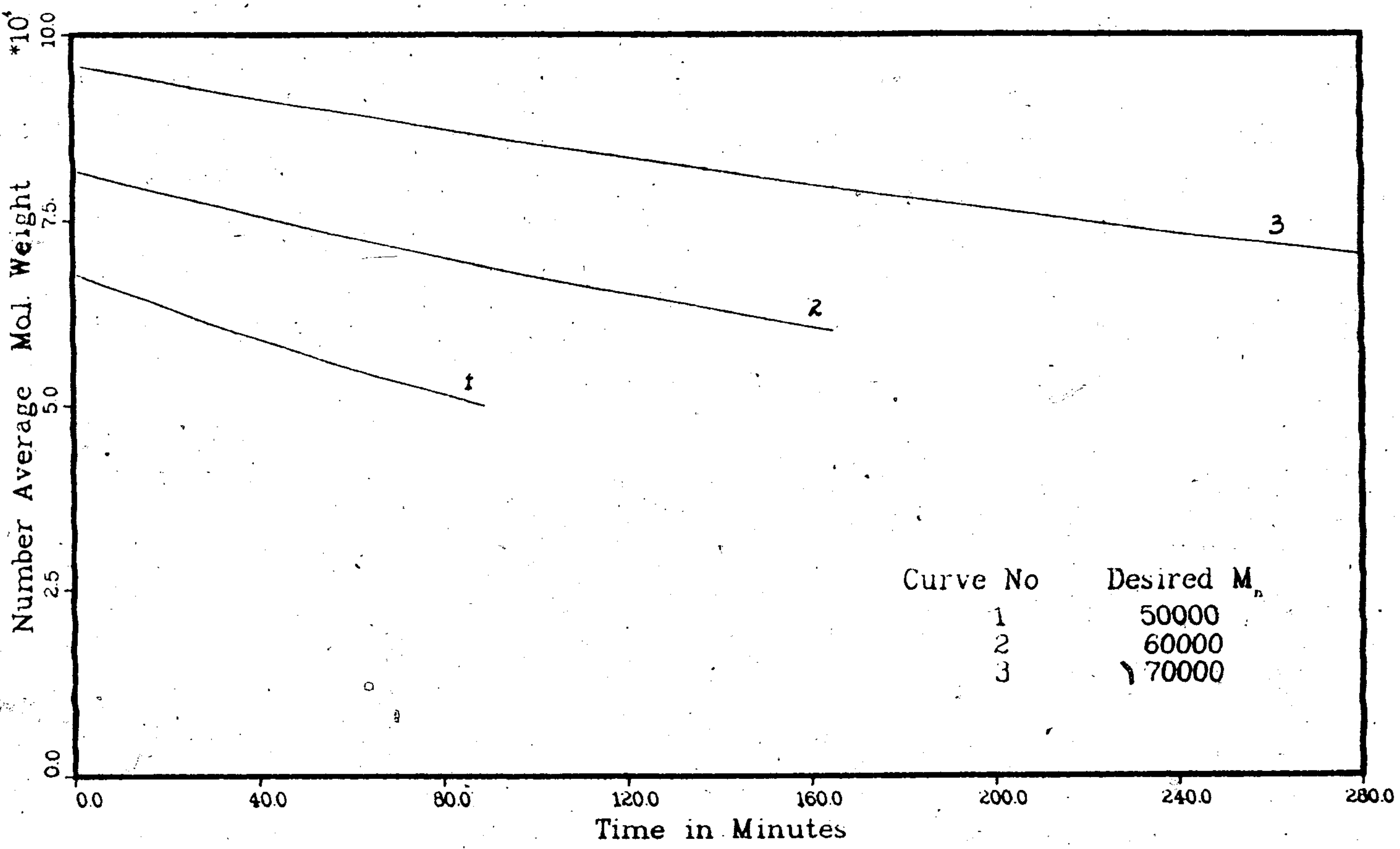

Fig. 6.3 Number Average Molecular Weight for Minimum Time Temperature Policy

Desired $x=0.5$ $\Phi_s=0.6$ $I_0=0.050$ Mol/l

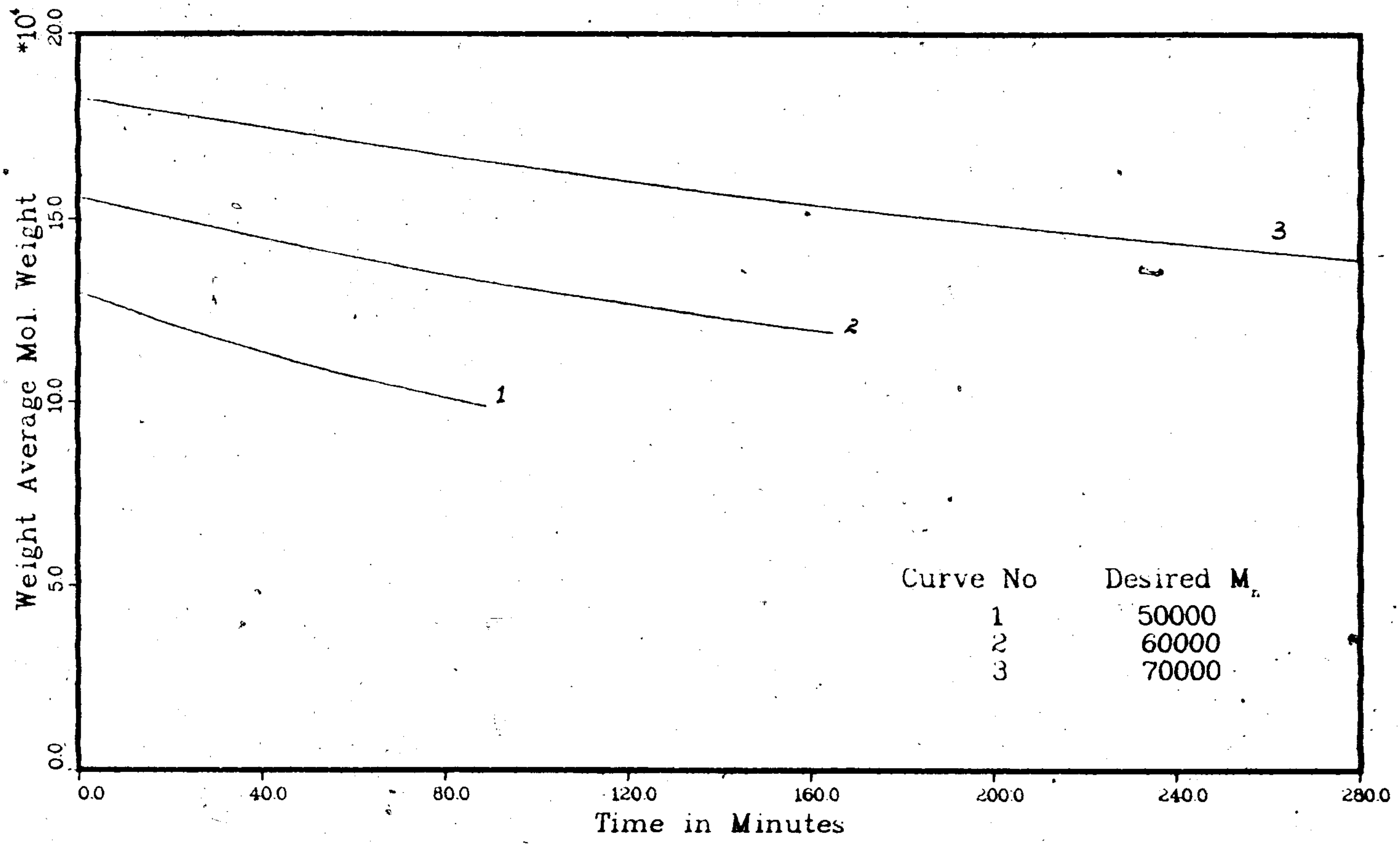

Fig. 6.4 Weight Average Molecular Weight for Minimum Time Temperature Policy

Desired $x=0.5$ $\Phi_s=0.6$ $I_0=0.050$ Mol/l

policy in order to keep the rate of dissociation of initiator constant during the course of polymerization. The increasing trend of the temperature policy can be clearly observed in curve no.3. From Figure 6.1 it can also be observed that when the desired M_n is decreased, the temperature of polymerization increases whereas the total time of the reaction decreases. However as pointed out by Chen and Cheng(1978) these optimal temperature policies do not achieve considerable time saving compared to isothermal policies. Figure 6.2 shows the conversion profiles that are obtained when optimal policies are used.

Figures 6.3 and 6.4 show the number average and weight average molecular weights development, respectively, in the polymerization process when the optimal temperature profiles are used. It can be observed that for this policy, high molecular weight polymers are produced at the beginning and progressively lower molecular weight polymers are produced such that at the end of reaction, the desired M_n value polymer is obtained. Obviously this leads to broadening of the molecular weight distribution.

Two of the temperature policies shown in Figure 6.1, corresponding to desired M_n values of 50000 and 60000, have been implemented on the experimental reactor system. The experimental results are documented in section 6.8.

6.7 Minimum Polydispersity Policy (Problem 4)

The aim in this problem is to develop the optimal temperature policy for a given initial initiator concentration to produce a polymer product with minimum polydispersity and with desired final conversion and number average molecular weight.

Hoffman et al.(1964) derived initiator and monomer addition policies to produce a polymer product with minimum breadth of molecular weight distribution. He reasoned that to have the minimum polydispersity, the instantaneous number average molecular weight of the polymer produced should be constant throughout the course of polymerization. Sacks et al.(1973) later proved mathematically Hoffman's (1964) reasoning. They also showed that in conventional polymerization the optimal temperature policy is one of decreasing temperature during the course of polymerization. It can be readily observed (Figure 6.3) that at a constant temperature, the number average molecular weight produced in the polymerization process decreases with time. In order to keep the instantaneous number average molecular weight constant, the temperature of the reaction must be decreased during the couse of polymerization.

Optimal control theory has been applied to the simplified model of the batch reactor in which transfer reactions have been neglected. The detailed mathematical development along with the numerical procedure is given in Appendix E. As mentioned in Section 6.6, through the use of the simplified model, the computational procedure to obtain the optimal temperature policy is considerably simplified by avoiding the TPBV problem.

In Figure 6.5 the optimal temperature policies to obtain desired final conversion ($X^*=0.5$) and desired number average molecular weight are shown. The optimal temperature decreases with time during the course of polymerization, a result that is expected from the earlier discussion in this section. When higher molecular weight polymer is desired, the temperature decreases and the total reaction time to obtain the desired conversion is considerably increased. Figure 6.6 shows the conversion profiles for the optimal temperatures used in the reaction.

In Figures 6.7 and 6.8 the development of number average and weight average molecular weights during the polymerization process are shown. It can be observed that for the minimum polydispersity temperature policy, constant instantaneous number average and weight average molecular weights are produced throughout the course of polymerization. Figure 6.9 shows polydispersity values that are constant throughout the polymerization. It should be noted that polydispersity will increases in the case of isothermal polymerization.

Two of the policies were selected and implemented on the reactor system in order to compare the experimental results with theoretical prediction. These results are discussed in the next section.

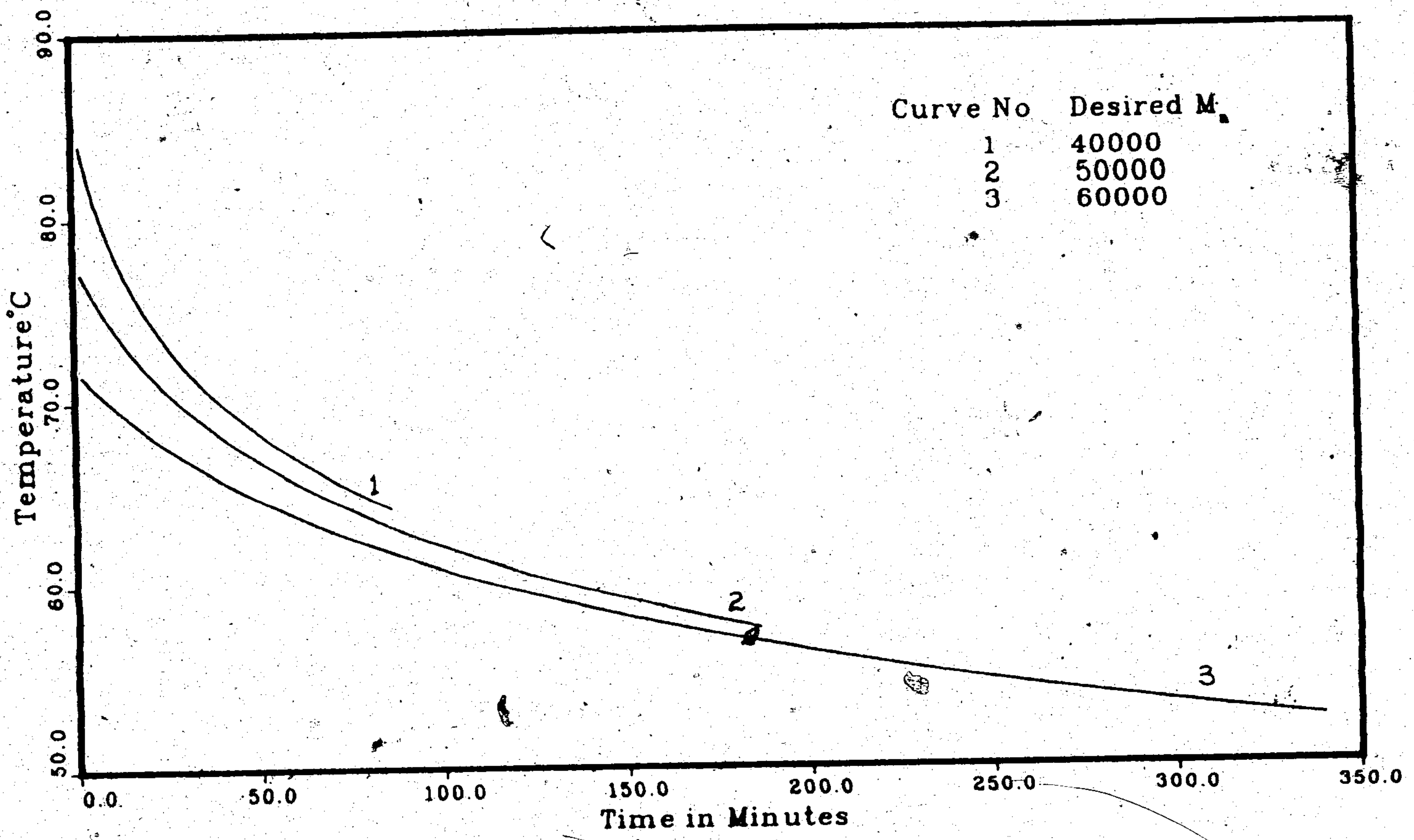

Fig. 6.5 Temperature Profile for Minimum Polydispersity Policy

Desired x=0.5 Φ_s=0.6 I_0=0.075 Mol/l

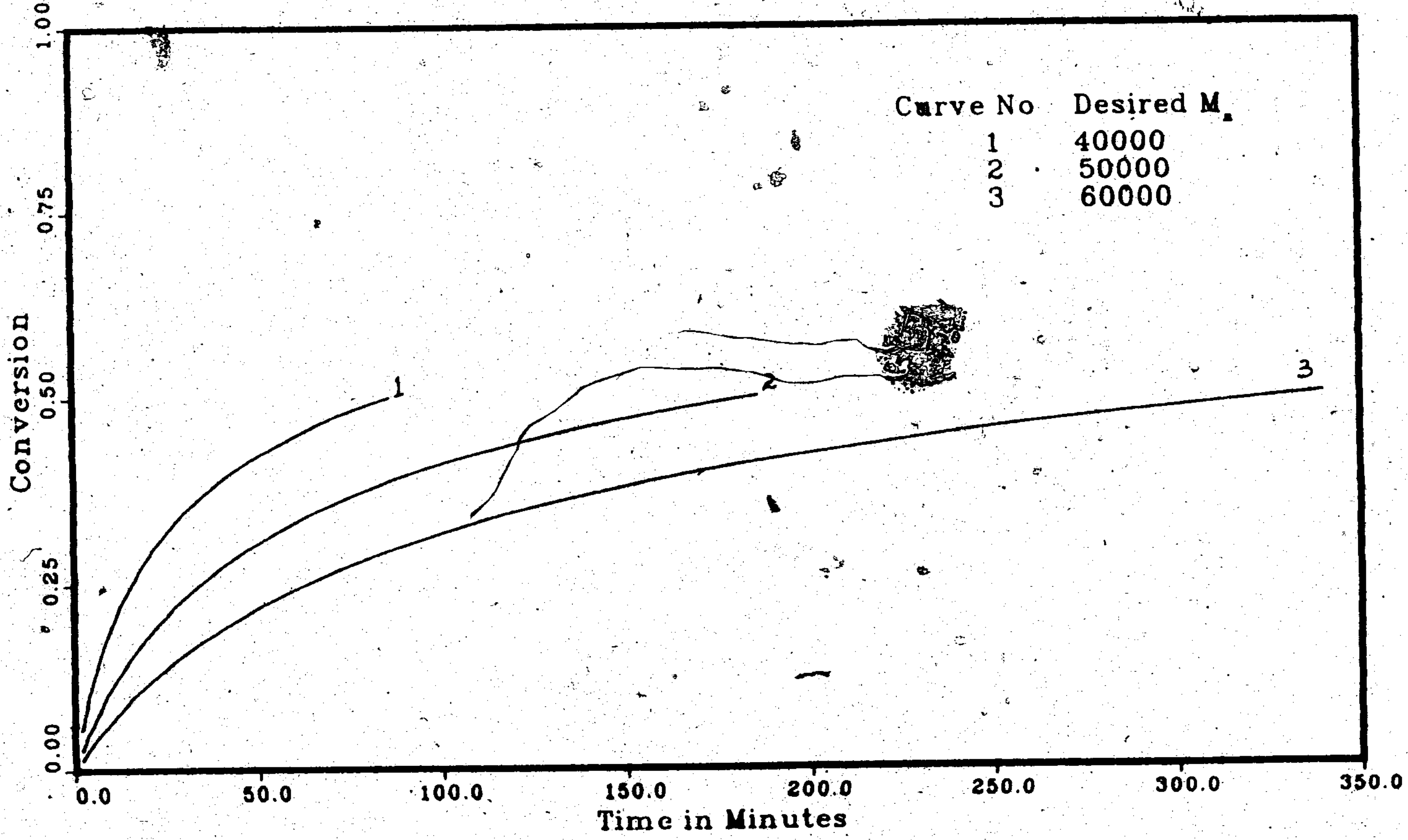

Fig. 6.6 Conversion History for Minimum Polydispersity Policy

Desired x=0.5 Φ_s=0.6 I_0=0.075 Mol/l

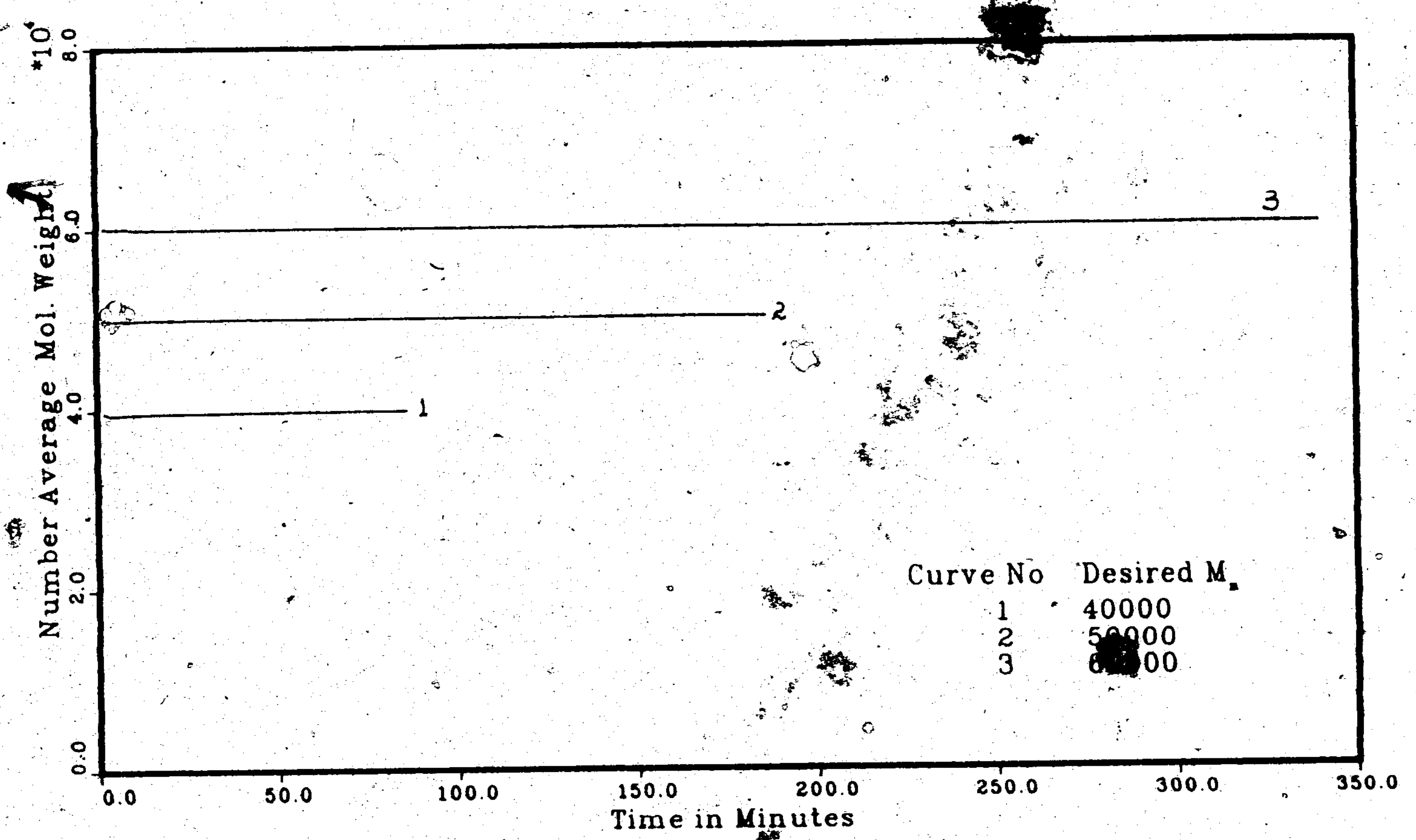

Fig. 6.7 Number Average Molecular Weight for minimum Polydispersity Policy

Desired x=0.5 Φ_s=0.6 I_0=0.075 Mol/l

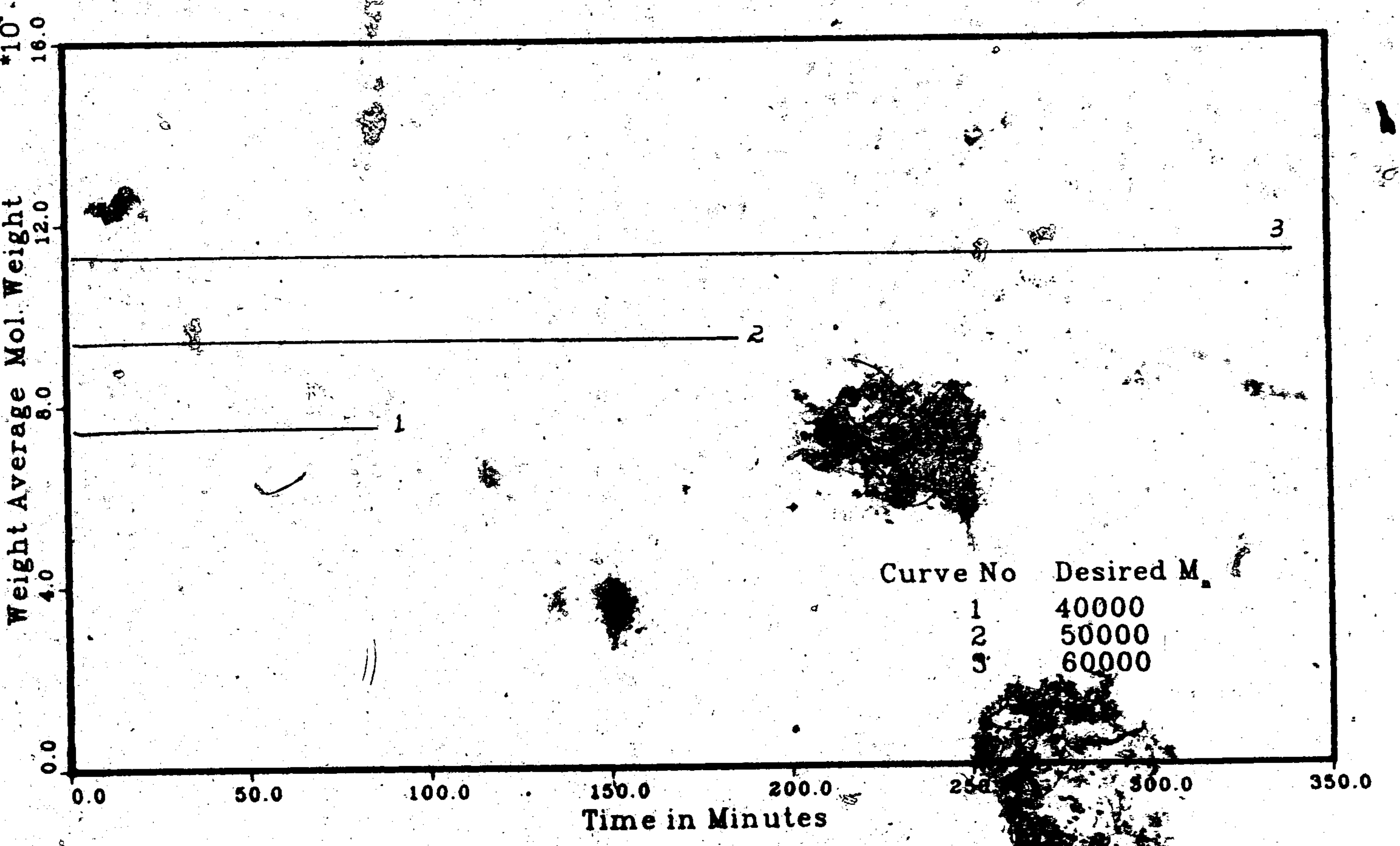

Fig. 6.8 Weight Average Molecular Weight for minimum Polydispersity Policy

Desired x=0.5 Φ_s=0.6 I_o=0.075 Mol/l

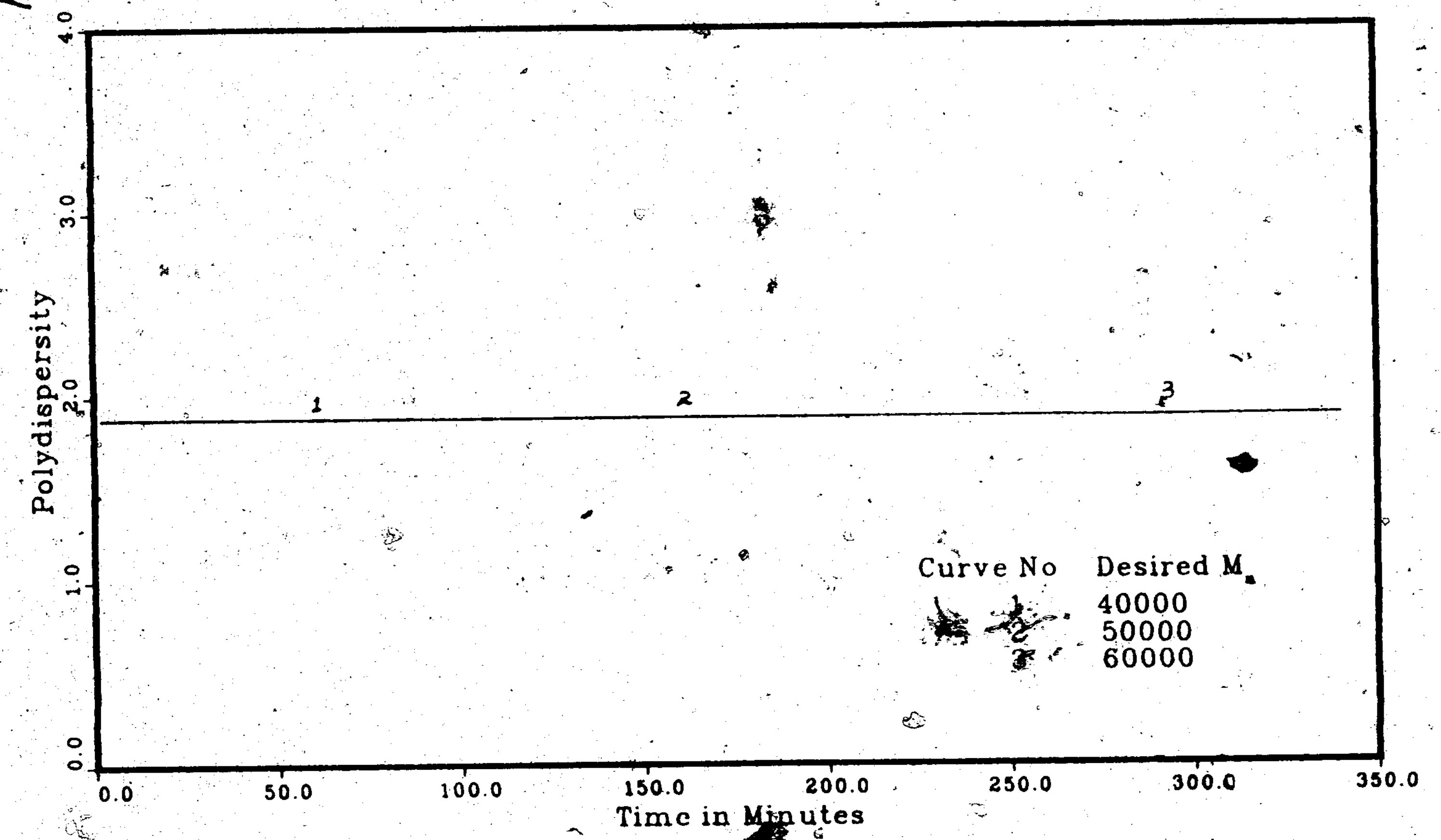

Fig. 6.9 Polydispersity Values for Minimum Polydispersity Policy

Desired x=0.5 Φ_s=0.6 I_0=0.075 Mol/l

6.8 Experimental Verification of Optimal Control policies

In the previous sections, theoretical optimal control policies were obtained for a variety of problems in the batch polymerization reactor using the mathematical model. However it is important to verify experimentally these policies to demonstrate and evalulate on-line experimental open loop control of the polymerization reactor.

For this purpose the open loop temperature policies, which are stored in a disc file, are read by the computer at the time of implementation and sent as remote set point values through a current output station to the local Foxboro temperature controller. The controller mainpulates the cooling water flowrate through the coils inside the reactor and brings the reactor temperature to the desired set point value.

The experimental procedure described in section 2.5 has been followed. Conversion was measured using gas chromatography. Number average and weight average molecular weights were measured using the SEC.

In total four policies were implemented, two from minimum time temperature policies and the other two from the minimum polydispersity temperature policies. The experimental results along with the theoretical results are presented in Figure 6.10 through 6.13. It can be observed that in all the cases the local temperature of the reactor closely followed the set point temperature provided by the computer.

The experimental conversion results agree closely with the model conversions in three of the four experiments in which a maximum difference of only three percent is observed. However in Figure 6.13 it can be observed that the experimental and model conversions agree well in the first one-hour of the reaction and afterwards the experimental conversion values are less than model values, the difference being about 10 percent at the end of the reaction. This discrepancy observed for conversion results in the Figure 6.13 can be explained as follows. The parameters used in the model have been estimated based on the experiments conducted in the temperature range 65-75°C whereas in this particular experiment the temperature is varied from 63°C to 52°C. Since the parameter values are extrapolated, an error in the values of model parameters and consequently the model prediction of conversion values are expected. It should be noted that in the same experiment, in the initial period when the temperature was around 63-60°C, the experimental and model conversions agreed very well. For the other three experiments, the temperatures employed are within the range 65-75°C used to estimate the parameters and hence very good agreement between model and experimental conversions are observed.

In all the four cases, the experimental number average and weight average molecular weights are lower than the theoretically predicted values from the model. The experimental number average molecular weight values are less

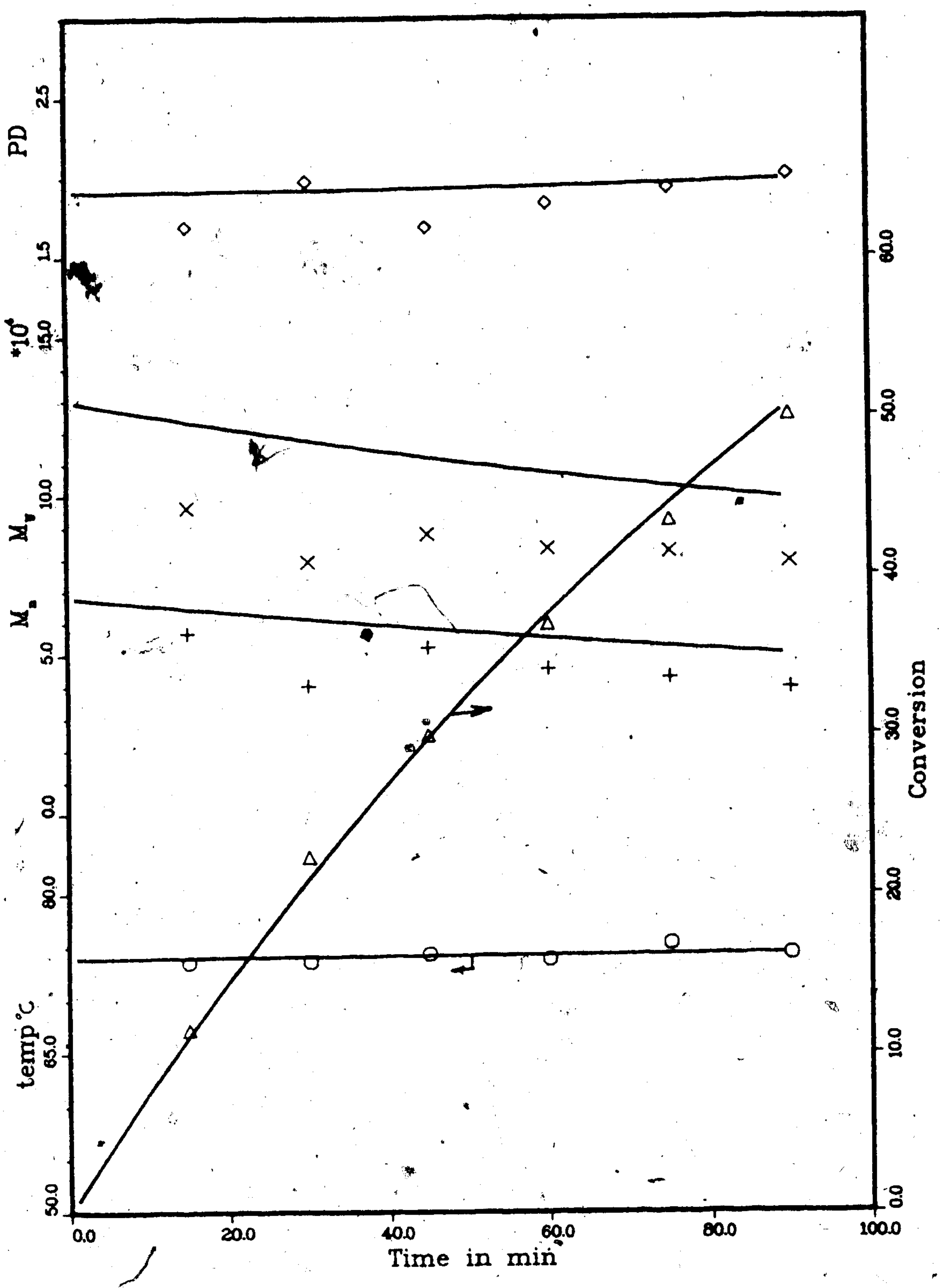

Fig. 6.10 Experimental Results of Minimum Time Policy - I

Desired $x=0.5$ Desired $M_n=50000$ $\Phi_s=0.6$ $I_0=0.050$ mol/l

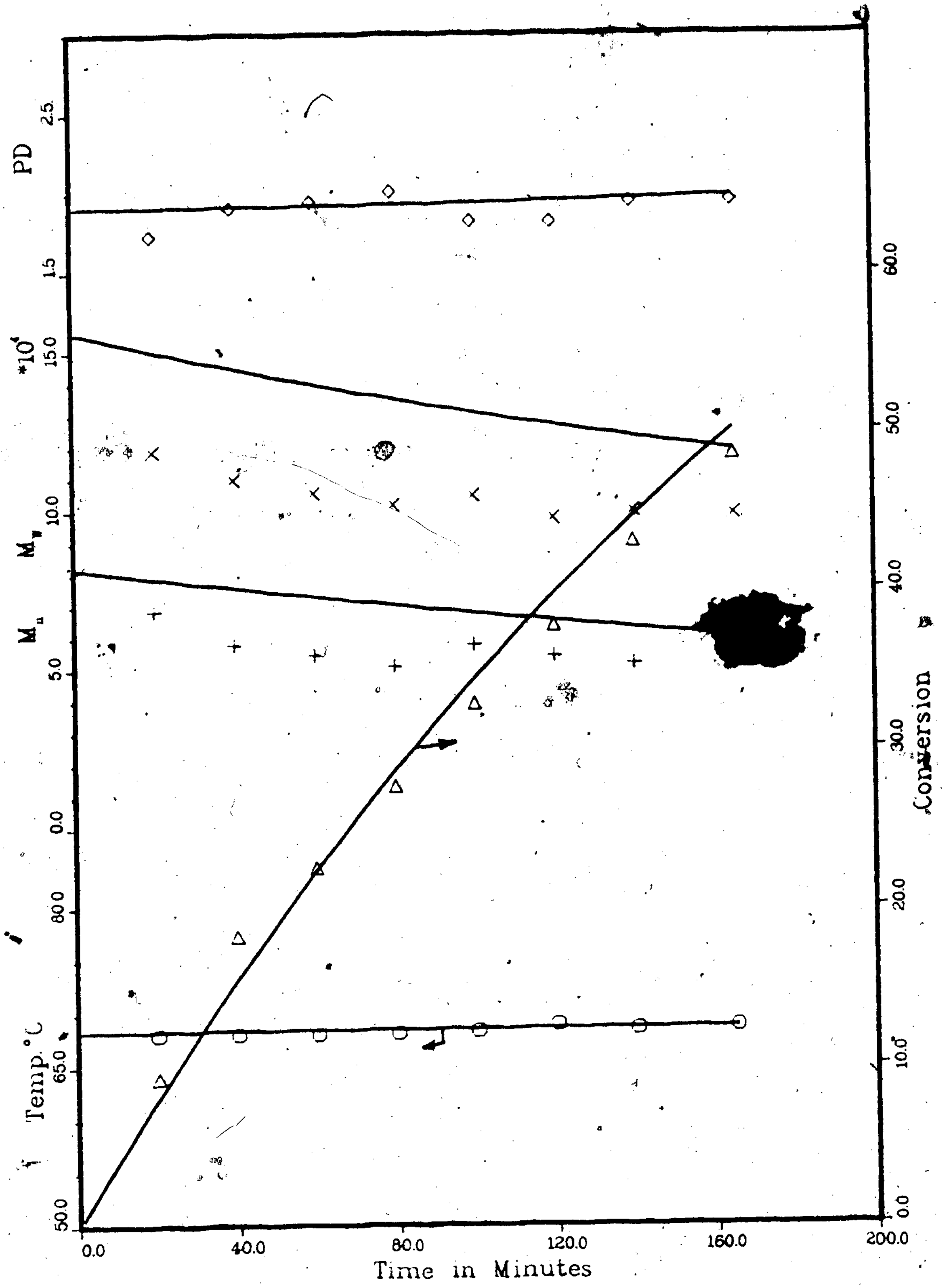

Fig. 6.11 Experimental Results of Minimum Time Policy-*II*

Desired $x=0.5$ Desired $M_n=60000$ $\Phi_s=0.6$ $I_0=0.050$ mol/l

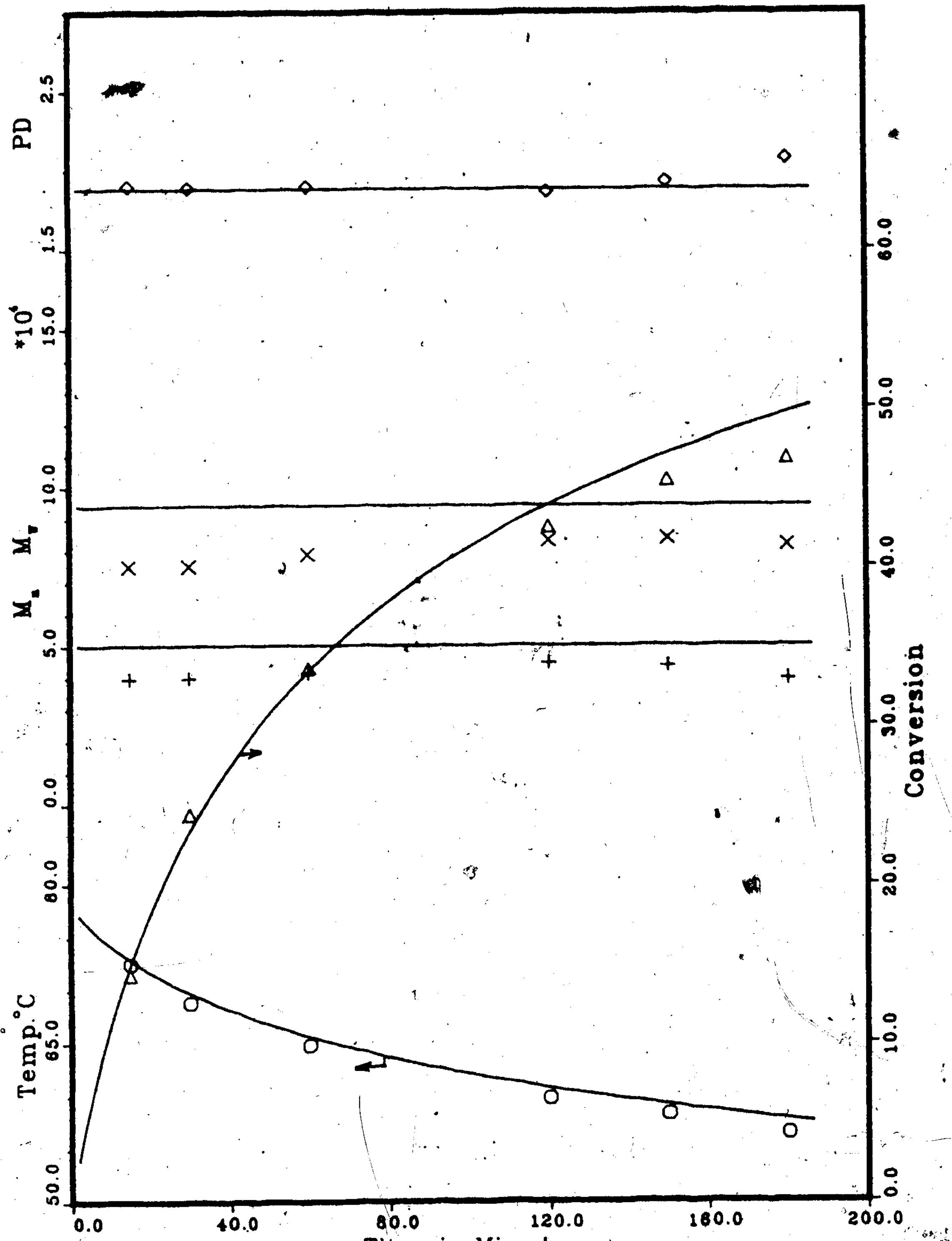

Fig. 6.12 Experimental Results of Minimum Polydispersity Policy-I
Desired x=0.5 Desired M_n=50000 Φ_s=0.6 I_0=0.075 mol/l

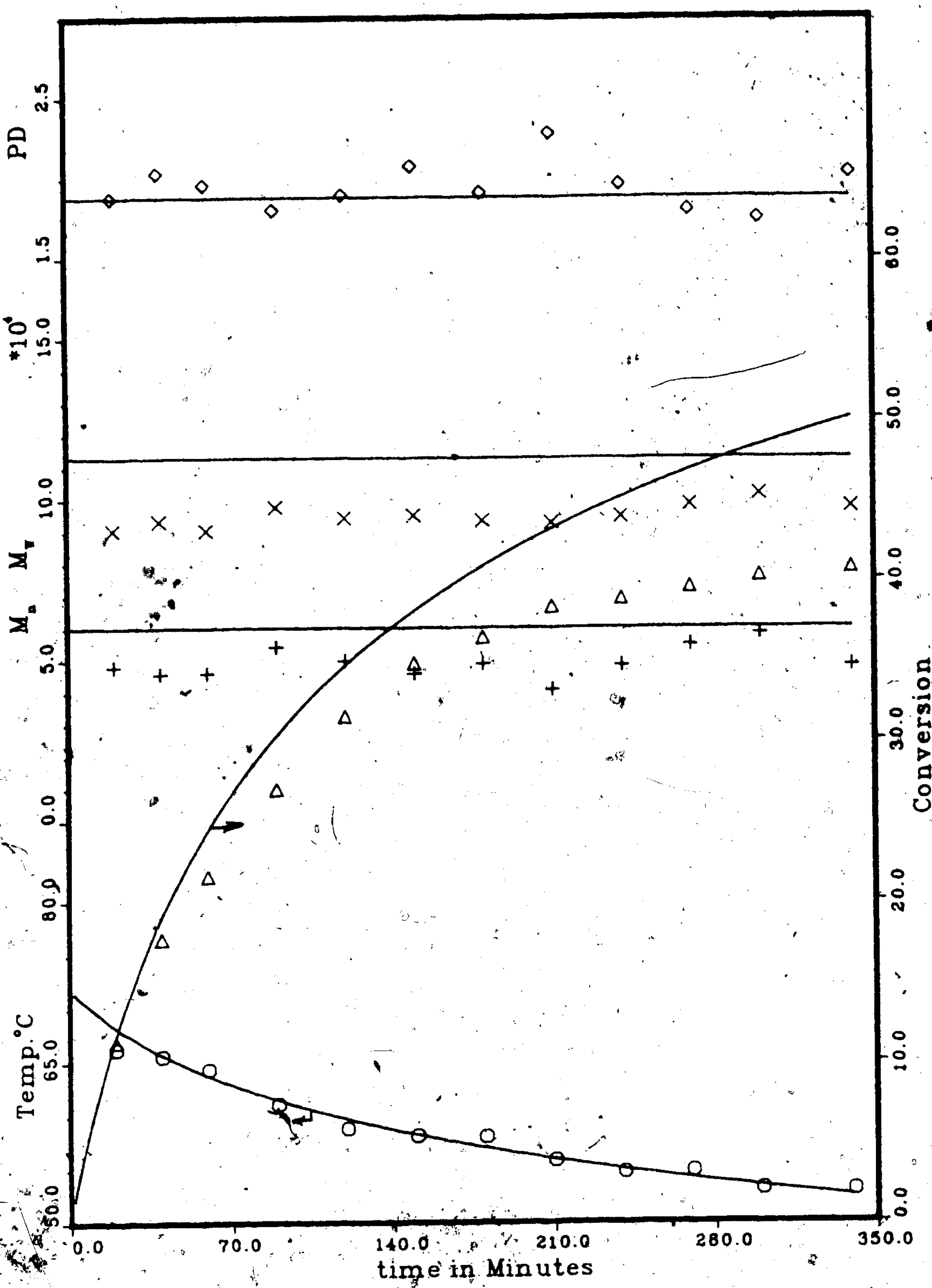

Fig. 6.13 Experimental Results of Minimum Polydispersity Policy - II

Desired x=0.5 Desired M_n=60000 Φ_s=0.6 I_0=0.075 mol/l by about 20 percent whereas the weight average molecular weight values are smaller by about 20-30 percent. However, though systematic error is observed, the experimental molecular weight averages follow the trend predicted by the model in all cases.

For estimation of the parameters of the model the molecular weight averages were measured using only two columns at a flowrate of 2 mL/min. At the time of open loop control studies some columns were replaced with new columns and an extra column was added to obtain better resolution. Also the flowrate was increased to 3mL/min so as to achieve the SEC analysis in about 10 minutes. All these changes could have contributed to a different resolving power of the column set compared to the original set used and ~~hence~~ a systematic error could have crept into the SEC analysis.

Also errors in the calculation of M_n and Mw may have resulted due to the following reasons. We assumed a semi-logarithmic relationship of the SEC calibration curve for the molecular weights less than 45000. The dispersion correction was based on the variance of the SEC chromatograms of the narrow standards. The variance contribution due to the polydispersity of the narrow standards was not taken into account.

Recently some investigators have reported experimental verification of the model results in polymerization reactor systems. Chen and Huang(1981) implemented optimal initiator policies on a batch solution polymerization of styrene.

Their experimental conversion results agreed very well with the theoretical results whereas their experimental M_n and Mw values were in error with the theoretical predictions by about 20 percent. Cutter and Drexler(1982) carried out experimental studies to verify their simulation results in large scale polymerization reactors. Their experimental conversion values differed from model conversions by as much as 15 percent. The experimental M_n and Mw values were in error with model results upto 25 percent.

Pittman-Berger(1982) reported errors of as much as 150 percent between experimental and predicted values of number average and weight average molecular weights in batch copolymerization of styrene and MMA. Hamer(1983) carried out model verification studies in solution polymerization of vinylacetate in a pilot scale tubular reactor. His experimental number and weight average molecular weights were in error with model results to the extent of 35 percent. Both of the authors attributed the discrepancy to the poor values of kinetic constants used in their models.

From the above studies it can be concluded that the reported errors between the experimental and predicted number and weight average molecular weights fall in the range of 25-50 percent. The errors observed in this study which is 25-30 percent is at the bottom end of the range. The error reported in this study could have been improved if the same conditions for the SEC analysis could have been maintained.

6.9 Conclusions

In this chapter optimal control theory has been applied to the mathematical model of the batch polymerization reactor to derive open loop control policies. Four different control problems were formulated and solved.

Some of the optimal control policies corresponding to the minimum time temperature policies and minimum polydispersity temperature policies were implemented on the experimental polymerization reactor system. The experimental conversion results agreed very well with theoretical predictions whereas errors in the range of 20-30 percent were observed between experimental and theoretical molecular weight averages. These errors are well within the range of errors reported by other investigators who carried out model verification studies in polymerization processes.

7. CLOSED LOOP CONTROL STUDIES

7.1 Introduction

In chapter six open loop control policies were developed by the application of optimal control theory to the model of the batch reactor. These policies were implemented on the experimental reactor system with no provision for feedback control as corrective action in the event of process upsets or disturbances or process-model mismatch. A more suitable mode of control is to carry out closed loop optimal control i.e. to monitor polymer properties on-line and then take necessary corrective action should they deviate from the optimal trajectories. In this chapter we will develop and evaluate by simulation the feedback control policies by the application of linear regulator theory to the model of the batch reactor.

7.2 Previous Work

MacGregor et al.(1983) have reviewed the application of on-line control of different polymer properties in polymerization reactor control. Zeeman and Adams(1967) have presented an on-line control scheme which included on-line measurement of MWD and a digital computer. Roquemore and Eddy(1961) developed a discrete deterministic model and implemented feedback control schemes to regulate final conversion in a series of 9 to 12 continuous SBR emulsion polymerization reactors by manipulating temperature and the number of reactors in the reactor chain. Fellows(1969) studied theoretically the regulator control of conversion and molecular weight in continuous SBR reactors where the feedback was subjected to random disturbances.

Jo and Bankoff(1976) studied experimentally the on-line estimation of states in the solution polymerization of vinylacetate in a CSTR using various forms of Kalman filter to be used for the control of the process. Hyun and Bankoff(1976) used a semiempirical model of the kinetics of a vinyl polymerization reactor to obtain estimates of the performance of a linearized Kalman filter in early detection of on-line process drifts.

Ahlberg and Cheyne(1977) implemented a computer control scheme on a full scale continuous solution polymerization for the production of rubber. Some process model parameters were updated by using extended Kalman filter and the control action was based on the solution of the Riccati equation.

Kiparissides(1978) solved a regulator problem of a continuous latex reactor. He derived suboptimal stochastic control policies by solving a linear quadratic optimal control problem and concluded that the control algorithm can be used to achieve better performance of the reactor. Kiparissides and Ponnuswamy(1981) applied the linear regulator theory to control conversion in a train of three CSTR-s. By using a locally linear state space model of the reactor, they obtained optimal temperature profile that brought the monomer conversions to the desired values over the reactor train.

Cluett et al.(1982) used a globally stable Adaptive Predictive Control System(APCS) for setpoint tracking and constant reaction rate control of a simulated PVC batch reactor. They obtained good, robust control despite nonlinear dynamics of the system. Kiparissides and Shah(1983) evaluated two types of adaptive controllers and a PID controller to a simulated batch suspension PVC reactor. They found that despite the time varying and nonlinear characteristics of the reactor, excellent control was obtained using either one of the two adaptive controllers. Both adaptive techniques proved to be very robust and outperformed a well-tuned PID controller under noisy conditions and time-varying parameters.

Timm et al.(1982) studied feedback control of the molecular weight and production rate of polymer using the model of the styrene polymerization reactor and reported that PID controller worked well in tracking the setpoint changes in production rate and molecular weight. Schuler(1980) used a Luenberger observer and a Kalman filter to estimate non-measurable states in a simulated polymerization reactor. He also described how SEC measurement can be used to estimate the states that can be used for feedback control.

However there have been only a few experimental evaluation studies with respect to on-line measurements and control of polymerization reactors. Meira et al.(1979)

studied the control of MWD of the polymer product in free radical solution polymerization of MMA in a CSTR. They varied the feed flowrate of monomer and initiator in a feedforward manner and measured the effects of these variables on MWD of the polymer product and reported considerable success in controlling the MWD of the polymer product.

In the following sections we will describe the development of optimal feedback control policies using the mathematical model of the free radical solution polymerization of MMA in a batch reactor.

7.3 Development of Feedback Policies

From previous experimental studies (chapter four) we know that temperature and initiator concentration affect conversion and molecular weight averages in the free radical solution polymerization in the batch reactor. The nonlinear model developed in chapter five can not be directly used to develop feedback control policies as the discrete linear regulator theory can be applied only to discrete linear systems. Hence it is necessary to linearize and then discretize the nonlinear model of the reactor.

7.3.1 Linearization and Discretization

There are two methods available for the linearization of nonlinear models. The first one, called apparent linearization, was proposed by Pearson(1962) and later successfully used by Weber and Lapidus(1971) and McGreavy and Vago(1975). In this scheme the state equations are recast in a form that appears [illegible] linear. The local values of the state variables are used [illegible] the coefficients of the linearized equat[illegible]des(1978) used this method to linearize the non-linear model derived for the case of emulsion polymerization of vinylacetate in a CSTR. This method is useful in situations where the steady states around which linearization is done is not known in advanced and is useful for batch processes where the operations values always change with respect to time.

The second method uses the truncated Taylor series approximations of the nonlinear terms. The linearization is done around known steady state variables of the system. The objective in this feedback control problem is to follow the nominal trajectories of state variables as closely as possible. The nominal trajectories are obtained by solution of open loop control problem as described in chapter six. Since the nominal values of state and control variables are known in advance, the linearization using Taylor series could be used for this problem. Sage(1968) dealt with the procedure of linearizing around the nominal trajectories. In the following the Taylor series approximation is used to linearize the model of the batch reactor. The simplified model equations as shown in Appendix C are:

$$\frac{dI}{dt} = -k_d I \qquad (7.1)$$

$$\frac{dM}{dt} = -k_1 M\sqrt{I} \qquad (7.2)$$

$$\frac{d\mu_0}{dt} = Ck_d I + k_2 M\sqrt{I} + k_3 S\sqrt{I} \qquad (7.3)$$

$$\frac{d\mu_2}{dt} = \frac{k_4 S M^2}{\sqrt{I}} + \frac{k_5 M^3}{\sqrt{I}} + k_6 M^2 \qquad (7.4)$$

Let I_s, M_s, μ_{0s} and μ_{2s} refer to the nominal values of trajectories of initiator, monomer, zeroth moment and second moment of dead polymer concentrations respectively. Let T_s be the nominal temperature profile. Linearizing the Equations (7.1)-(7.4) around the nominal trajectories in terms of deviation variables as denoted by Δ gives the following state-space model in a vector-matrix form as shown in Equation(7.5) given in the next page. Equation(7.5) can be compactly written in the standard state-space form as:

$$\frac{d\Delta Y}{dt} = A\Delta Y + B\Delta u + W\Delta I \qquad (7.6)$$

where

$$\Delta Y = (\Delta M\ ,\ \Delta\mu_0,\ \Delta\mu_2)^t \qquad (7.7)$$

$$\left|\begin{array}{c} \frac{d\Delta M}{dt} \\ \\ \frac{d\Delta \mu_0}{dt} \\ \\ \frac{d\Delta \mu_2}{dt} \end{array}\right| = \left|\begin{array}{ccc} -k_{1s}\sqrt{I_s} & 0 & 0 \\ \\ k_{2s}\sqrt{I_s} & 0 & 0 \\ \\ \frac{2Sk_{4s}M_s}{\sqrt{I_s}} + \frac{3k_{5s}M_s^2}{\sqrt{I_s}} + 2k_{6s}M_s & 0 & 0 \end{array}\right| \left|\begin{array}{c} \Delta M \\ \\ \Delta \mu_0 \\ \\ \Delta \mu_2 \end{array}\right|$$

$$+ \left|\begin{array}{c} \cancel{-\frac{M_s\sqrt{I_s}k_{1s}E_1}{RT_s^2}} \\ \\ \frac{CE_d k_{ds} I_s}{RT_s^2} + \frac{E_2 k_{2s} M_s \sqrt{I_s}}{RT_s^2} + \frac{Sk_{3s}E_3\sqrt{I_s}}{RT_s^2} \\ \\ \frac{Sk_{4s}M_s^2E_4}{RT_s^2\sqrt{I_s}} + \frac{k_{5s}M_s^2E_5}{RT_s^2\sqrt{I_s}} + \frac{k_{6s}M_s^2E_6}{RT_s^2} \end{array}\right| \Delta T$$

$$+ \left|\begin{array}{c} -\frac{k_{1s}M_s}{2\sqrt{I_s}} \\ \\ Ck_{ds} + \frac{k_{2s}M_s}{2\sqrt{I_s}} + \frac{k_{3s}}{2\sqrt{I_s}} \\ \\ -\frac{Sk_{4s}M_s^2}{2I_s^{1.5}} - \frac{k_{5s}M_s^3}{2I_s^{1.5}} \end{array}\right| \Delta I$$

(7.5)

$$\Delta u = \Delta T \qquad (7.8)$$

Matrices **A** and the vectors **B** and **W** can be identified easily from Equation(7.5). The elements of **A**, **B** and **W** are dependent on the nominal values of state of the system and hence are time varying.

For the purpose of digital control of the process, it is necessary to discretize the linearized model of the reactor. Discretization of the continuous differential equations has been treated by many authors (Ogata(1967), Franklin and Powell(1980)).

After discretization the continuous linearized Equation(7.6) can be written in the standard form as:

$$\Delta \mathbf{Y}_{k+1} = \mathbf{F}\,\Delta \mathbf{Y}_k + \mathbf{G}\,\Delta u_k + \mathbf{H}\,\Delta I_k \qquad (7.9)$$

where the discrete state-space coefficient matrices **F**, **G**, and **H** are given by:

$$\mathbf{F} = \exp(\mathbf{A}t) \qquad (7.10)$$

$$\mathbf{G} = \int_0^t \exp(\mathbf{A}\tau)\mathbf{B}\,d\tau \qquad (7.11)$$

$$\mathbf{H} = \int_0^t \exp(\mathbf{A}\tau)\,\mathbf{W}\,d\tau \qquad (7.12)$$

and t = sampling time

To check the validity of the linearization and discretization procedure, the responses of the linearized and discretized models were compared to the response of the original nonlinear model when disturbances in the initiator concentration from the nominal values are introduced. The nominal values obtained from the open loop optimal temperature policy developed in section 6.4 has been used. The discretization is done based on a sampling time of five minutes which is the expected SEC analysis time when efficient and fast columns are used.

First an increase in the initial initiator concentration by 0.025 mol/L from the nominal value (0.05 mol/L) is introduced. The conversion and number average molecular weight responses to the initiator changes predicted by the nonlinear, linear and discrete models along with the nominal responses are presented in Figure 7.1. It can be observed that conversion and number average molecular weight responses almost coincide for the linearized and discretized models whereas a small discrepancy exists between the nonlinear model response and the other two model responses. These results confirm that the linearized and discretized model represent the nonlinear model quite well. In Figure 7.2 the conversion and number average molecular weight responses are given for the case where the initial initiator concentration is decreased by 0.025 mol/L from its nominal value (0.05 mol/L). Again the responses confirm that the linearization and discretization procedure represents

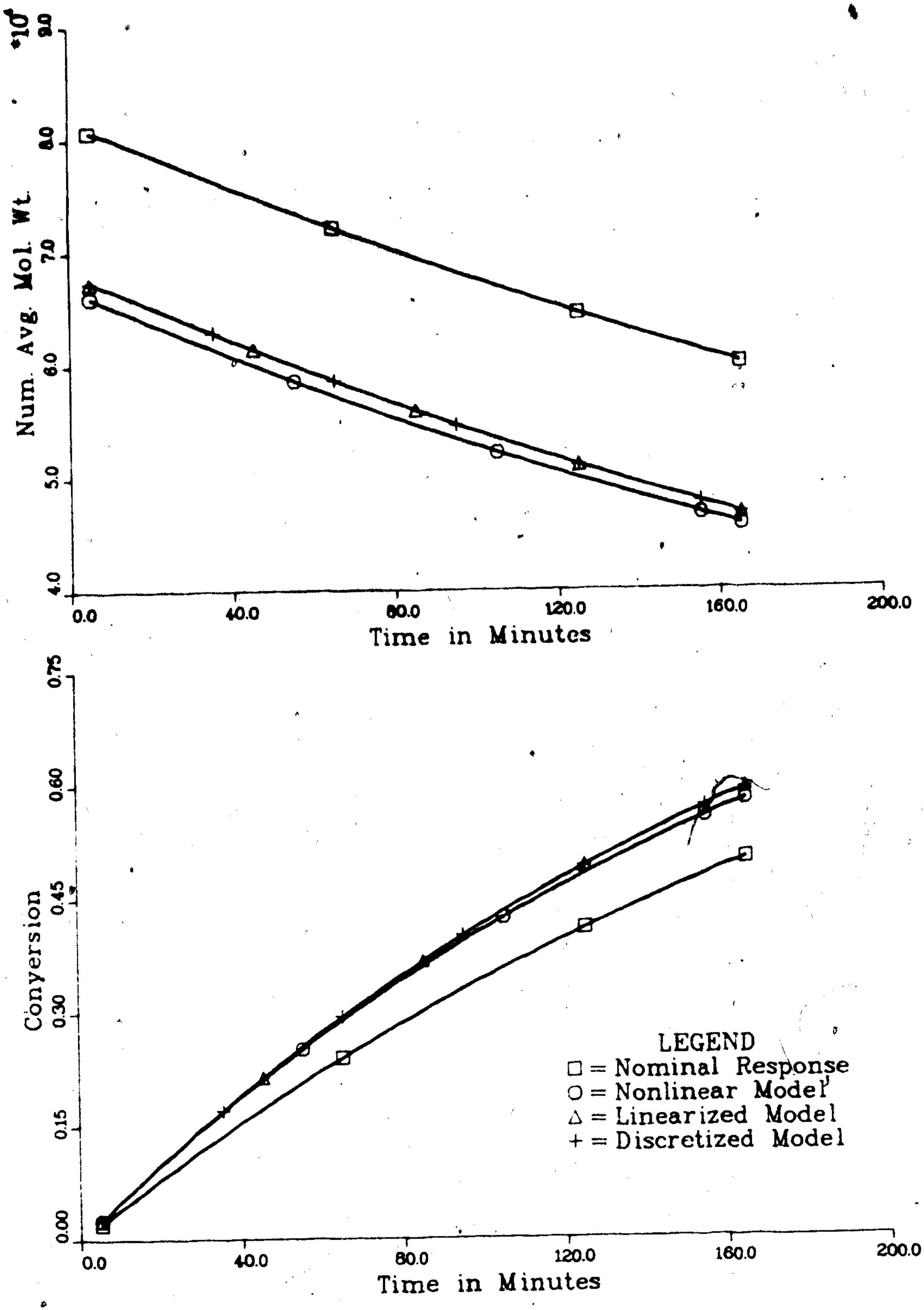

Fig. 7.1 Comparison of Responses of Different Models - I
Initiator Concentration Change=+0.025 Mol/l

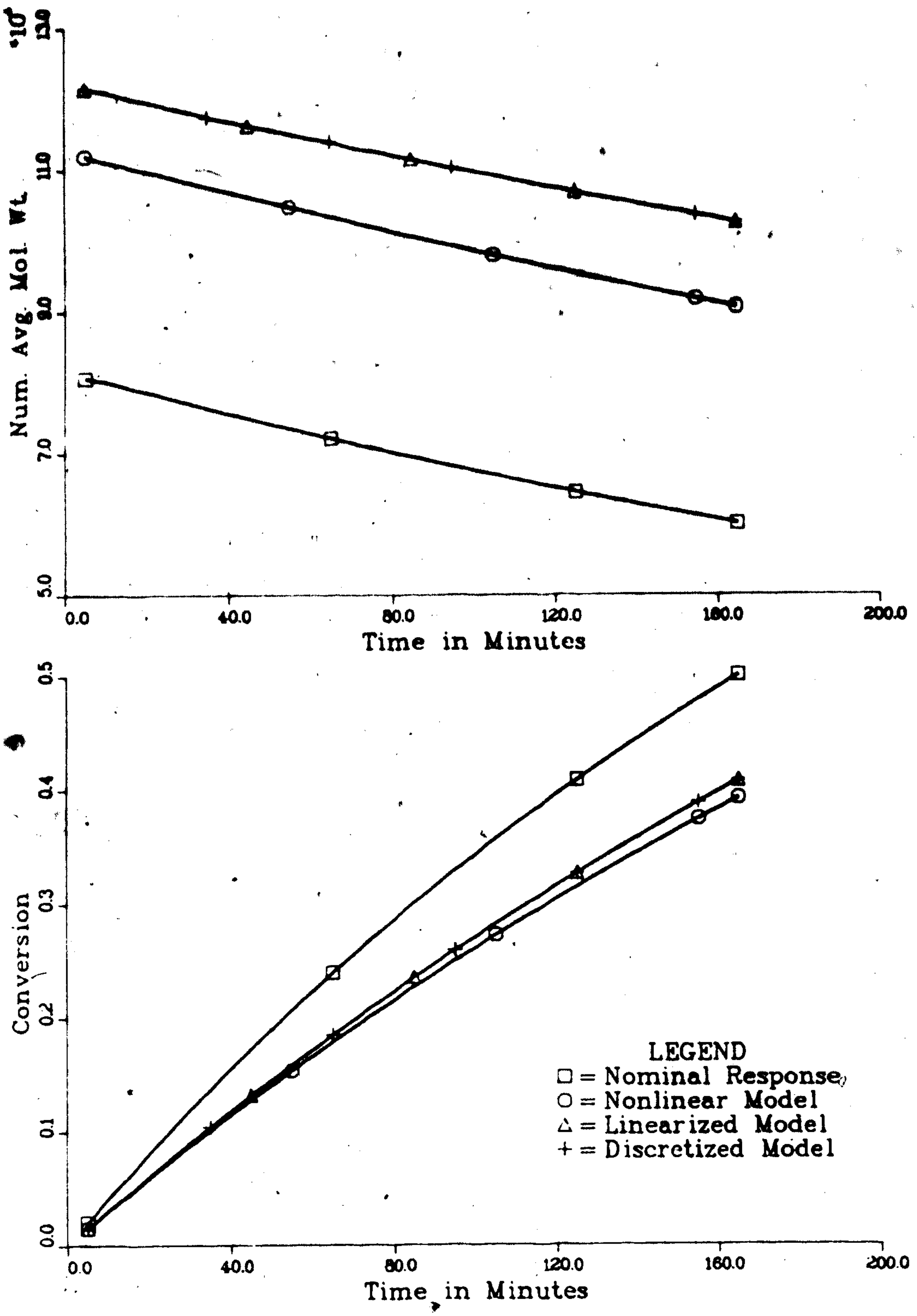

Fig. 7.2 Comparison of Responses of Different Models - II
Initiator Concentration Change=–0.025 Mol/l

the nonlinear model quite well.

7.3.2 Control Law Design

Our objective is to design a feedback controller for the batch polymerization reactor so that the states of the reactor track the nominal trajectories of states despite process upsets, disturbances, process model mismatch etc. The nominal trajectories were previously obtained by solving the open loop minimum time or minimum polydispersity problem as described in chapter six.

One can formulate a quadratic objective function for the closed loop control as:

$$\min J = \Delta Y_n^t Z \Delta Y_n + \sum_{k=0}^{n-1} (\Delta Y_k^t Q \Delta Y_k + R\, \Delta u_k^2) \qquad (7.13)$$

The following physical interpretation can be given to the objective function (Kirk(1970)). It is desired to maintain the state vector close to the nominal or desired values without excessive expenditure of control effort. The weighting function matrices **Z** and **Q** are positive semidefinite and **R** is positive definite. If **R** is singular, the control effort would become infinite.

The above is a well studied problem in discrete linear-regulator theory. The control law that results from the minimization of J with respect to u_k is: (Sage(1968), Franklin and Powell(1980)):

$$\Delta u_k = K \Delta Y_k \tag{7.14}$$

where

$$K = R^{-1} G^t (F^t)^{-1} (P_k - Q) \tag{7.15}$$

$$P_k = Q + F^t P_{k+1} (I + GR^{-1}G^t Pk+1)F \tag{7.16}$$

$$P_n = Z \tag{7.17}$$

The elements of **K** which are time varying gains of the feedback controller can be computed from Equation (7.15). The elements of the 3x3 matrix P_k in Equation (7.16) can be obtained by solving the discrete-time matrix-Ricati Equation (7.16) using the boundary condition given in Equation (7.17). It can be observed that the gain matrix **K** can be calculated off-line by using only the nominal trajectories of the states. These time varying gains can be stored in a computer and then used to implement the feedback control after measuring the values of the state variables as shown in Figure 7.3.

7.3.3 Simulation Results

Closed loop control policies were derived using the discretized model of the reactor. For all the cases the nominal control and state variables corresponding to the minimum time policy developed in chapter six was chosen. Although initiator concentration could have been chosen as another control variable, in this study it is treated as a disturbance. Temperature is treated as the control variable.

In Figure 7.4 a disturbance in the form of increase in the initiator concentration has been introduced. It is known that in free radical polymerizations, increases in initiator concentration reduces the molecular weight of the polymer and increase the rate of polymerization. These effects can be observed in the responses of the uncontrolled reactor in figure 7.4. When the reactor is put under feedback control, the control variable temperature decreases from its nominal values to counteract the effect of the disturbances. It can be clearly observed in Figure 7.4, that the conversion and number average molecular weight responses move towards the nominal responses.

Figure 7.5 presents the results when a disturbance in the form of decrease in initiator concentration is introduced. Again it can be observed that the feedback controller brings the responses to the nominal desired values. In Figure 7.6 the feedback control results are given for the case where initiator disturbance is introduced 20 minutes after the start of reaction. Results similar to the previous cases can be observed.

In all of the feedback control results it can be observed that there are offsets between the nominal values and the controlled responses. From Equation (7.14) and Figure 7.3 it can be seen that the optimal feedback controller has the structure of proportional controller. Since integral action is absent, the offset is not entirely

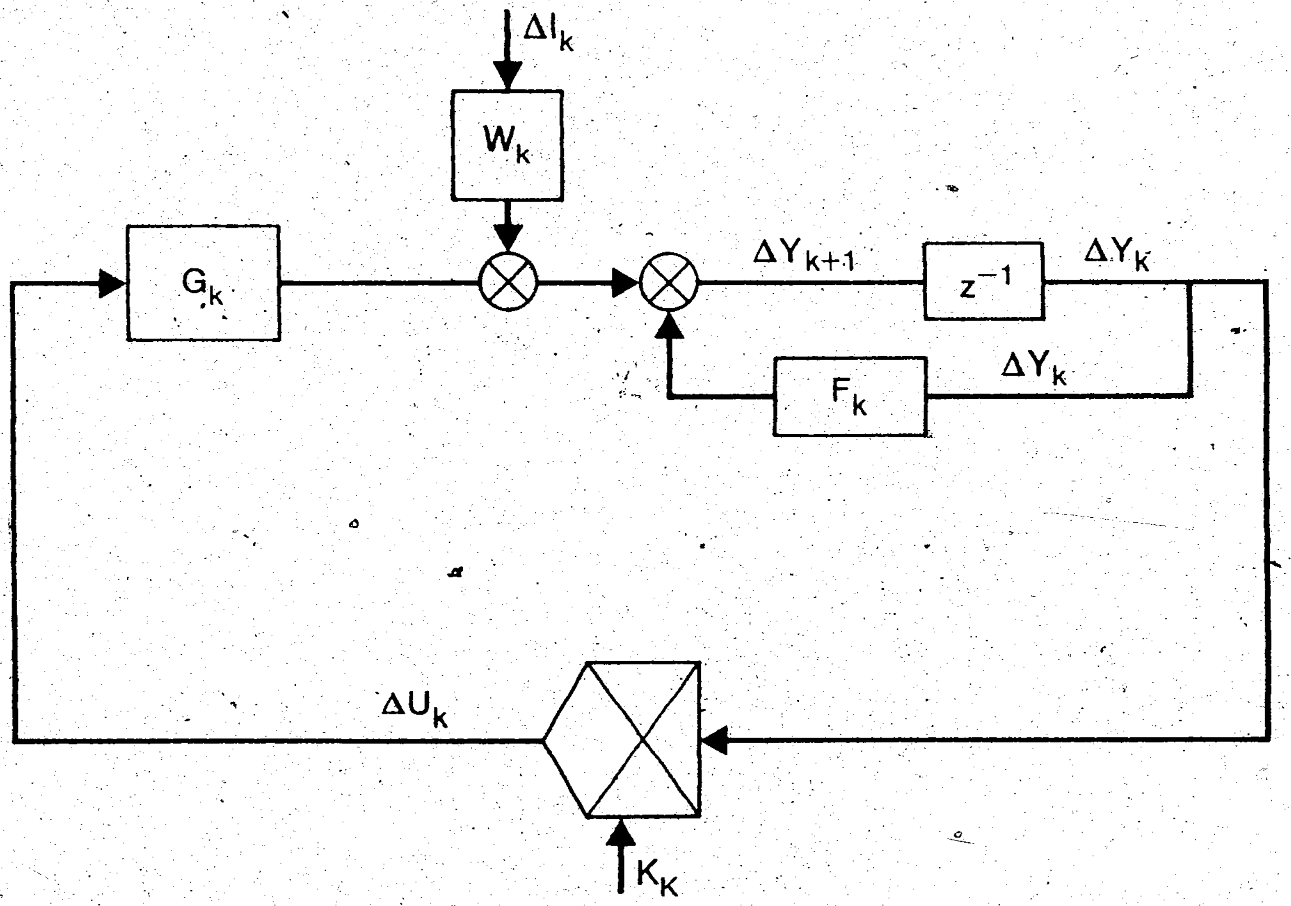

FIG. 7.3. BLOCK DIAGRAM OF OPTIMAL CLOSED LOOP CONTROLLER.

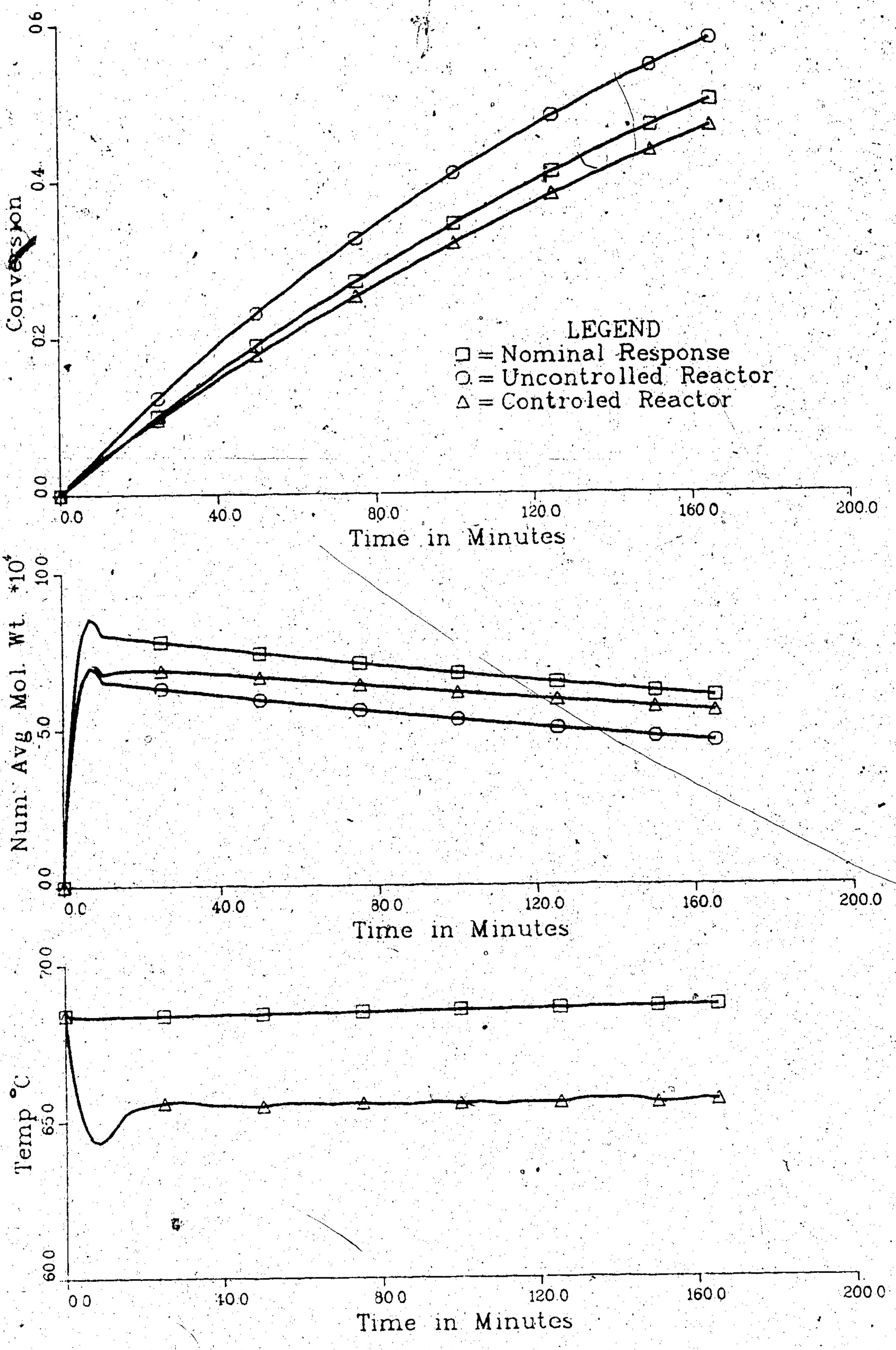

Fig. 7.4 Closed Loop Control of Polymerization Reactor-I
Increase in Initiator Level=0.025 Mol/l

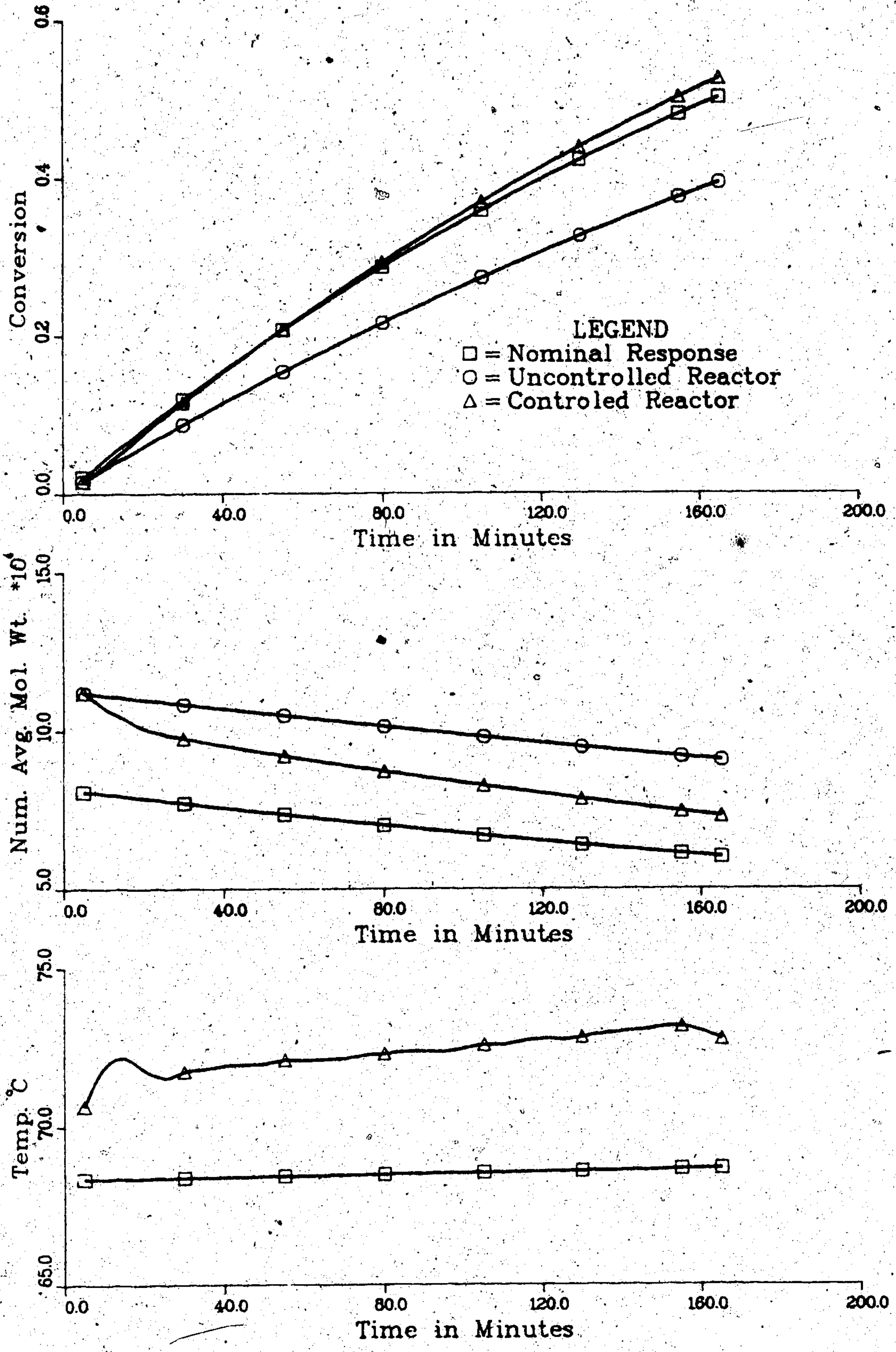

Fig. 7.5 Closed Loop Control of Polymerization Reactor - II
Decrease in Initiator Level=0.025 Mol/l

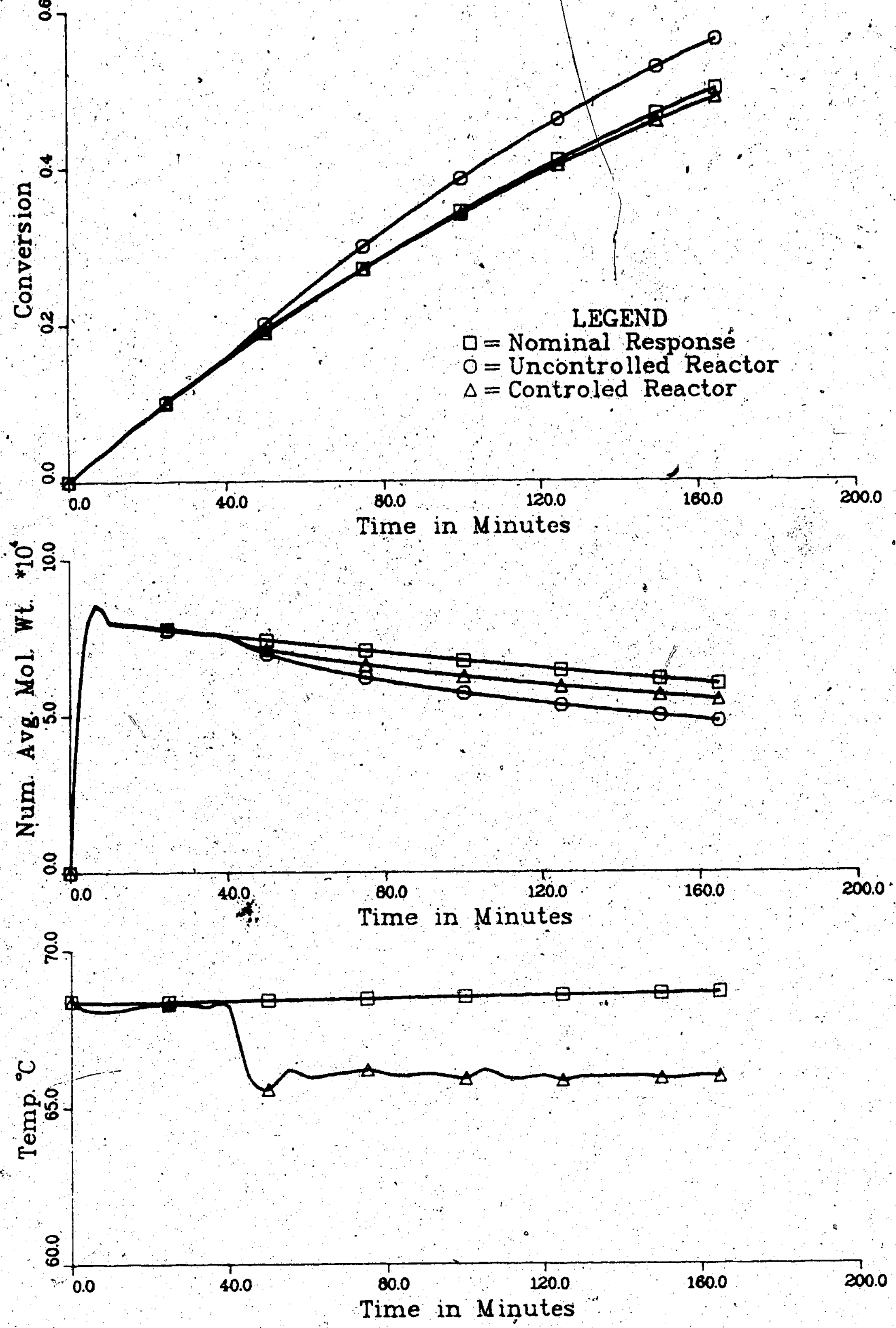

Fig. 7.6 Closed Loop Control of Polymerization Reactor-III
Increase in Initiator Level=0.025 Mol/l

eliminated by the proportional controller. However, integral action by introducing additional state variables can be easily incorporated to remove this offset.

7.3.4 The choice of Q and R

Q is a 3x3 matrix and was chosen as a diagonal matrix. The q_{33} term was set equal to zero to indicate that we did not wish to explicitly control deviations of Mw (weight average molecular weight) from nominal values. The remaining diagonal terms q_{11} and q_{22} terms were chosen after numerical experimentation. They also show the relative importance given to the deviations of monomer concentration and zeroth moment from nominal values. Final values chosen were $q_{11}=1.0$ $q_{22}=10^5$, and $q_{33}=0$. In the proposed run **R** is a scalar. The value of **R** decides the magnitude of control action. A zero value of **R** results in large control action and drives the controller to the limits of saturation. In our case we used a value of $R=10^{-5}$.

Stochastic Estimation and Control:

Even though we developed control strategies only for the case of deterministic model of the reactor, a realistic model would be stochastic in nature. The model prediction of states and the measurement of states could be used to design a Kalman filter. The state Estimation and regulator theory could be used realistically to design the feedback control of the reactors.

7.4 Conclusions

In this chapter the nonlinear model of the reactor was linearized around the nominal trajectories obtained from open loop control policies. The linearized model was further discretized and the optimal regulator theory was used to derive the feedback control policies. The simulation results show that the feedback control counteracts the effects of disturbances and brings the conversion and number average molecular weight back to the nominal values.

8. CONCLUSIONS

The on-line measurement and computer control problems associated with the solution polymerization of MMA in a batch reactor have been studied in detail in this thesis. An experimental batch polymerization reactor with facilities for on-line measurements of density, viscosity, torque on the stirrer and molecular weight of the polymer was built. All these measurements were interfaced to a HP/1000 process control computer. An automatic sampling system was designed to collect samples of the polymerization mixture periodically from the reactor and to automatically inject them into the size exclusion chromatograph (SEC) after dilution with a solvent. Computer programs were developed for automatic acquisition of SEC data and processing of these data to obtain molecular weight averages of the polymer.

Conversion measurements were made using three different techniques: gravimetry, gas chromatography and densimetry. The analysis of the results showed that gravimetry showed appreciable error in conversion measurement particularly for high conversion samples that are viscous. The densimetry results agreed very well with the GC results that were shown to be more accurate than the gravimetric results. It is recommended that on-line densimetry be used to monitor monomer conversion during the course of polymerization. The analysis of the SEC results showed that the number and weight average molecular weights could be measured with reasonable accuracy during the course of polymerization.

A mathematical model of the solution polymerization of MMA in a batch reactor has been derived. Since the parameters available in the literature did not predict the experimental results well, these model parameters were re-estimated using our own experimental data. Verification of the model (with the re-estimated parameters) was demonstrated to be excellent by comparing it with the experimental data.

Optimal control theory was applied to the reactor model to derive optimal temperature and initiator concentration policies for four different problems. The optimum policies corresponding to minimum time and minimum polydispersity temperature profiles were implemented on the experimental reactor. The comparison of model and experimental results showed that conversion results followed the model results very well whereas discrepancies of the order of 25-30 percent were observed in the number and weight average molecular results. These errors are well within the range of model prediction errors reported by other investigators in this research area.

Linear regulator theory was also applied to the linearized model of the reactor for the design of closed loop optimal policies. Implementation of these policies on the simulated reactor showed that the feedback controller was able to track the nominal trajectories of conversion and number average molecular weight in the presence of disturbances due to initiator concentration changes.

As an overall conclusion this study demonstrated that with a proper choice of on-line measurement instruments it is possible to do advanced control of a polymerization reactor.

Future Work: This project was started to provide the necessary groundwork for a series of application studies in the area of on-line measurements and computer control of polymerization reactors. Though closed loop control was studied only on a simulation basis, computer implementation and verification of these policies are recommended for future work. An energy balance of the reactor can be performed from the measurements of hot water and cold water flow rates and their temperatures. This energy balance information could be used to predict and control the reaction rate during the course of polymerization. The experimental system can be easily modified to study continuous polymerization reactions. Also the reactor system can be used to study on-line measurements and control problems associated with emulsion and suspension polymerization reactions.

In this study only optimal control theory has been applied to optimize the operation of the polymerization reactor. Since the polymerization reactor is highly nonlinear and contains time varying parameters, adaptive control techniques such as self-tuning regulators (STR) and self-tuning controllers (STC) could be applied to study the control problems.

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APPENDIX A: EQUIPMENT AND INSTRUMENTS REQUIRED

Reactor System

1. Five litre cylindrical jacketted glass reactor.

2. Hot water tank.(25 litres capacity, 1500 Watts)
Blue M Electric Company, Blue Island, Illinois, USA

3. Hot water circulating pump (centrifugal)
115 Volts, 120 Watts, 3000 rpm.
Little Giant pump Co, Oklohama city, OK, US.

4. Rotameter (Hot water flowrate)
0-2 gallons per minute
Brooks Instrument Division

5. EMF Converter (millivolts to 10-50ma signal)
118 volts, 60 cycles, 9 watts.
Foxboro Company, Mass., US.

6. Foxboro M/62 Controller.(Model 621-5L)
Input(10-50ma) -Output(10-50ma)
Foxboro Company, Mass., US.

7. Electro Pneumatic Transducer(10-50ma to 3-15psi)
Foxboro Company, Mass., US.

8. Control Valve (for cooling water)
Research Meter Inc, Tulsa, OK, US.

9. D/P Cell(To measure cooling water flowrate)
Foxboro Company, Mass., US.

10 Densitometer(DMA 45)
Anton Paar Ltd, Austria
Distributed by Mettler Ltd, USA.

11. Stirrer-Motor Assembly.
130 volts, 1.0 Amp 1/8 h.p.
G.K. Heller Corporation, Floral Park, New york.

12. Liquid Chromatograph (Size Exclusion Chromatograph)
Model 244.
Waters Associates, Mass., US.

13. Gas Chromatograph (Model 5710A)
Hewlet-Packard C

14. Viscometer(Model M8B)

Norcross corporation, Newton, Mass., US.

15. Reciprocating-Revolving Pump.
Fluid Metering Inc., N.Y., US.

Automatic Sampling

1. 50 ml conical flask

2. Solenoid Valves.
Skinner Valves, CT, US.

3. FMI Pumps(See Item 15 Reactor System)

4. Magnetic stirrer

5. Automatic Sample Injection Valve
Valco Instruments Co., Houston, Texas, US.

6. Programmable Sequence Timer.
Potter and Brumfield, Guelph, Ontario, Canada.

Computer System

1. HP/1000 Minicomputer
2. LSI 11/03 as I/0 subsystem
3. HP Plotter
4. Terminals

APPENDIX B: SEC DISPERSION CORRECTION

Let $Mw(v)$ and $M_n(v)$ be the weight and the number average molecular weight respectively of the polymer within an infinitesimal fraction at elution volume, v.

If there were no column dispersion i.e at infinite resolution the weight concentration and the molecular weight at any SEC elution volume, y, are $W(y)$ and $M_t(y)$ respectively, where $M_t(y)$ is the true calibration relationship. If we let a Gaussian function $G(v-y)$ describe the fraction of species at y which gets spread over to v, we can consider the molecular weight mixture at any v to be made up by species coming from all different y elution volumes. The molecular weight of these species are $M_t(y)$ and their weight concentrations detected at v are $W(y)G(v-y)$.

By definition of the weight average molecular weight, we can write the Mw of the mixture at v as follows:

$$Mw(v) = \frac{\int_{-\infty}^{+\infty} W(y)G(v-y)M_t(y)dy}{\int_{-\infty}^{+\infty} W(y)G(v-y)dy} \tag{B.1}$$

where

$$G(v-y) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[- \frac{(v-y)^2}{2\sigma^2} \right] \tag{B.2}$$

and

$$M_t(y) = D_1\exp(-D_2y) \qquad (B.3)$$

In Equation (B.2) σ is the peak standard deviation of the assumed Gaussian distribution. In Equation (B.3) D_1 and D_2 are constants of the true molecular weight calibration. The denominator of Equation (B.1) gives the overall weight concentration detected at elution volume, v, which is F(v). Hence F(v) can be obtained by the following equation:

$$F(v) = \int_{-\infty}^{+\infty} W(y)G(v-y)dy \qquad (B.4)$$

Let us now evaluate the numerator of Equation (B.1). Substituting for G(v-y) from Equation (B.2) and for $M_t(y)$ from Equation (B.3), the numerator of Equation (B.1) can be written as:

$$N = \int_{-\infty}^{+\infty} W(y)\left(\frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(v-y)^2}{2\pi^2}\right]\right)D_1\exp(-D_2y)\ dy$$

After considerable manipulation the above equation can be evaluated as:

$$N = M_t(v)\exp\{(D_2\sigma)^2/2\}\ F(v-D_2\sigma^2) \qquad (B.5)$$

substituting Equations (B.4) and (B.5) into Equation (B.1) we obtain:

$$M_w(v) = \frac{F(v-D_2\sigma^2)}{F(v)} \exp\{\frac{(D_2\sigma)^2}{2}\} M_t(v) \qquad (B.6)$$

By using the definition of the number average molecular weight, the number average molecular weight of the polymer sample eluting at the elution volume, v, can be given as:

$$M_n(v) = \frac{\int_{-\infty}^{+\infty} W(y)G(v-y)dy}{\int_{-\infty}^{+\infty} \{W(y)/M_t(y)\}G(v-y)dy} \qquad (B.7)$$

The denominator of Equation (B.7) can be evaluted by substituting for $M_t(y)$ and $G(v-y)$ from Equations (B.3) and (B.2) respectively. Let denominator of Equation (B.7) be D. Then

$$D = \int_{-\infty}^{+\infty} \frac{W(y)\exp(-\frac{(v-y)^2}{\sigma\sqrt{2\pi}})}{\sigma\sqrt{2\pi}\ D_1\exp(-D_2y)} dy$$

The above equation can be evaluated as:

$$D = \frac{1}{M_t(v)} \exp[\frac{(-D_2\sigma)^2}{2}] F(v+D_2\sigma^2) \qquad (B.8)$$

Substituting Equations (B.8) and (B.4) in Equation (B.7) the instantaneous number average molecular weight at the elution volume, v, is given as:

$$M_n(v) = \frac{F(v)}{F(v+D_2\sigma)} \exp\{ \frac{(D_2\sigma)^2}{2} \} M_t(v) \qquad (B.9)$$

Since F(v) is the weight fraction eluting at elution volume v, and $M_n(v)$ and Mw(v) are the number average and weight average molecular weights respectively at elution volume, v, the overall number and weight average molecular weights can be obtained by the following relations:

$$Mw = \frac{\int_{-\infty}^{+\infty} F(v)Mw(v)dv}{\int_{-\infty}^{+\infty} F(v)dv} \qquad (B.10)$$

$$M_n = \frac{\int_{-\infty}^{+\infty} F(v)dv}{\int_{-\infty}^{+\infty} \{F(v)/M_n(v)\}dv} \qquad (B.11)$$

Equations (B.10) and (B.11) give the number and weight average molecular weights after the dispersion correction. These corrections are implemented in the computer program developed for the analysis of SEC data.

For constant σ^2, Equations (B.10) and (B.11) can be integrated analytically and simplified further.

Let $M_n(uc)$ and $Mw(uc)$ be the number average and weight average molecular weights of the uncorrected chromatograms, respectively. Then, Equations (B.10) and (B.11) can be rewritten as

$$Mw = Mw(uc)\exp\{-(D_2\sigma)^2/2\} \tag{B.12}$$

$$M_n = M_n(uc)\exp\{(D_2\sigma)^2/2)\} \tag{B.13}$$

where

$$Mw(uc) = \frac{\int_{-\infty}^{\infty} F(v)M_t(v)dv}{\int_{-\infty}^{\infty} F(v)dv} \tag{B.14}$$

$$M_n(uc) = \frac{\int_{-\infty}^{\infty} F(v)dv}{\int_{-\infty}^{\infty} \{F(v)/M_t(v)\}dv} \tag{B.15}$$

Equations (B.12) to (B.15) could be used to correct for the dispersion effect.

APPENDIX C: SIMPLIFICATION OF REACTOR MODEL

The mathematical model of the solution polymerization of MMA in a batch reactor has been derived in chapter five and is given as follows:

$$dI/dt = -k_d I \qquad (C.1)$$

$$dM/dt = -k_1 M\sqrt{I} \qquad (C.2)$$

$$d\mu_0/dt = (k_s S+k_m M)\lambda_0+(k_{td}+k_{tc}/2)\lambda_0^2 \qquad (C.3)$$

$$d\mu_2/dt = (k_s S + k_m M)\lambda_2 + k_t\lambda_0\lambda_2 + k_{tc}\lambda_1^2 \qquad (C.4)$$

where

$$\lambda_0 = \sqrt{2fk_d I/k_t} \qquad (C.5)$$

$$\lambda_1 = \frac{2fk_d I + (kpM+k_m M + k_s S)\lambda_0}{(k_m M + k_s S + k_t\lambda_0)} \qquad (C.6)$$

$$\lambda_2 = \lambda_1 + 2kpM\lambda_1/(k_m M + k_s S + k_t\lambda_0) \qquad (C.7)$$

Thomas(1981) carried out an order of magnitude study for the terms appearing in Equations (C.6) and (C.7). In Equation (C.6) it was shown that the term $(2fk_d I)$ is negligible compared to $(kpM\lambda_0)$. Neglecting the rate constants for transfer reactions, the following expression for λ_1 is obtained:

$$\lambda_1 = kpM/k_t \qquad (C.8)$$

Similarly an expression for λ_2 can be obtained as:

$$\lambda_2 = \frac{2kp^2M^2}{k_t\lambda_0} \qquad \text{(C.9)}$$

Substitution of Equations (C.5), (C.8) and (C.9) into Equations (C.2) through (C.4), the model is simplified to the following set of equations.

$$\frac{dI}{dt} = -k_dI \qquad \text{(C.10)}$$

$$\frac{dM}{dt} = -k_1M\sqrt{I} \qquad \text{(C.11)}$$

$$\frac{d\mu_0}{dt} = Ck_dI + k_2M\sqrt{I} + k_3S\sqrt{I} \qquad \text{(C.12)}$$

$$\frac{d\mu_2}{dt} = \frac{k_4SM^2}{\sqrt{I}} + \frac{k_5M^3}{\sqrt{I}} + k_6M^2 \qquad \text{(C.13)}$$

where

$$k_1 = kp\sqrt{2fk_d/k_t} = A_1\exp(-E_1/RT) \qquad \text{(C.14)}$$

$$k_2 = k_m\sqrt{2fk_d/k_t} = A_2\exp(-E_2/RT) \qquad \text{(C.15)}$$

$$k_3 = k_s'\sqrt{2fk_d/k_t} = A_3\exp(-E_3/RT) \qquad \text{(C.16)}$$

$$k_4 = \frac{2kp^2k_s}{\sqrt{2fk_d}\,k_t^{1.5}} = A_4\exp(-E_4/RT) \qquad \text{(C.17)}$$

$$k_5 = \frac{2kp^2k_m}{\sqrt{2fk_d}k_t^{1.5}} = A_5\exp(-E_5/RT) \qquad (C.18)$$

$$k_6 = \frac{(2+\nu)kp^2}{k_t} = A_6\exp(-E_6/RT) \qquad (C.19)$$

$$C = 2f(1-\nu/2) \qquad \nu = k_{tc}/k_t \qquad (C.20)$$

The above simplified equations were derived by the order of magnitude study on the terms occuring in the expressions for λ_1 and λ_2.

Further simplifications of the model equations can be achieved if the transfer reactions are neglected in the model in which case the terms k_2, k_3, k_4 and k_5 become zero. Then the model equations are:

$$\frac{dI}{dt} = -kdI \qquad (C.21)$$

$$\frac{dM}{dt} = -k_1\sqrt{IM} \qquad (C.22)$$

$$\frac{d\mu_0}{dt} = Ck_dI \qquad (C.23)$$

$$\frac{d\mu_2}{dt} = k_6M^2 \qquad (C.24)$$

These models are used to derive the open loop and control policies in chapter six and also the Appendices D, E and F.

APPENDIX D: MINIMUM TIME TEMPERATURE POLICY

The objectiveis to find the optimal temperature policy for a given initial initiator concentration to produce a polymer product with desired conversion and number average molecular weight in minimum time.

The simplified model equations have been derived in Appendix C. They are:

$$\frac{dI}{dt} = -k_d I \tag{D.1}$$

$$\frac{dM}{dt} = -k_1 M\sqrt{I} \tag{D.2}$$

$$\frac{d\mu_0}{dt} = Ck_d I + k_2 M\sqrt{I} + k_3 S\sqrt{I} \tag{D.3}$$

$$\frac{d\mu_2}{dt} = \frac{k_4 SM^2}{\sqrt{I}} + \frac{k_5 M^3}{\sqrt{I}} + k_6 M^2 \tag{D.4}$$

The desired conversion X^* and desired number average molecular weight $M_n{}^*$ can be expressed in terms of desired monomer concentration (M^*) and desired zeroth moment of the polymer($\mu_0{}^*$) as:

$$M^* = M_0(1-X^*) \tag{D.5}$$

$$\mu_0{}^* = M_0 X^* \, MW/M_n{}^* \tag{D.6}$$

where MW is the molecular weight of the monomer and M_0 is the initial monomer concentration. If tf is the final time and $M(tf)$ and $\mu_0(tf)$ are monomer and zeroth moment of polymer concentration respectively at the final time, the following objective function can be formulated.

$$\min J = w_1\{M(tf)-M^*\}^2 + w_2\{\mu_0(tf)-\mu_{0*}\}^2 + \int_0^{tf} 1 \cdot dt \qquad (D.7)$$

where w_1 and w_2 are weights.

The Hamiltonian for the above optimization problem can be written as follows:

$$H = 1 - P_1 k_d I - P_2 k_1 M\sqrt{I} + P_3\{C k_d M\sqrt{I} + k_3 S\sqrt{I}\} \qquad (D.8)$$

In Equation (D.8) P_1, P_2, P_3 are co-state variables which must satisfy the following canonical equations.

$$\frac{dP_1}{dt} = -\frac{\partial H}{\partial I} = k_d P_1 + \frac{1}{2}\,\frac{P_2 k_1 M}{\sqrt{I}} - P_3\left(C k_d + \frac{1}{2}\,\frac{k_2 M}{\sqrt{I}} + \frac{1}{}\,\frac{k_3 S}{\sqrt{I}}\right) \qquad (D.9)$$

$$\frac{dP_2}{dt} = -\frac{\partial H}{\partial M} = k_1 P_2\sqrt{I} - k_2 P_3\sqrt{I} \qquad (D.10)$$

$$\frac{dP_3}{dt} = -\frac{\partial H}{d\mu_0} = 0 \qquad (D.11)$$

The co-state variables will also satisfy the following transversality conditions:

$$P_1(tf) = 0. \qquad (D.12)$$

$$P_2(tf) = \left.\frac{\partial J}{\partial M}\right|_{tf} = 2w_1\{M(tf)-M^*\} \qquad (D.13)$$

$$P_3(tf) = \left.\frac{\partial J}{\partial \mu_0}\right|_{tf} = 2w_2\{\mu_0(tf)-\mu_0{}^*\} \qquad (D.14)$$

The initial and final conditions for the state and co-state variables for the above problem can be written as:

variable	t=0	t=tf
I	I_0	free
M	M_0	free
μ_0	free	
P_1	free	0
P_2	free	$2w_1\ (M(tf)-M^*)$
P_3	free	$2w_2\ (\mu_0(tf)-\mu_0{}^*$

If the temperature is constrained, the optimality conditions that must be satisfied by the optimal policy are:

$$H = 0$$

$$\partial H/\partial t < 0 \qquad T = T^*$$

$$\partial H/\partial T > 0 \qquad T = T_*$$

$$\partial H/\partial T = 0 \qquad T \text{ is in the interior} \qquad (D.15)$$

where T^* and T_* are upper and lower limits of the temperature

A two point boundary value has to be solved with the simultaneous satisfaction of the optimality conditions to obtain the optimal temperature profile.

A discrete control method algorithm (Thomas(1981)), Thomas and Kiparissides(1984) is used to solve the above problem. It should be pointed out that the minimum time problem is not directly solved in this method. First a series of fixed terminal time problems are solved and then the smallest time for which convergence is possible, is selected as the minimum time.

The essential steps of the discrete control method are given under:

1. Select a fixed time.
2. Guess a piecewise constant temperature profile T(t).
3. Using T(t), integrate state equations forward.
4. Compute $P_1(tf)$, $P_2(tf)$ and $P_3(tf)$ from Equations (D.12) to (D.14) and integrate the co-state equations backward; simultaneously compute $g(t)=\partial H/\partial T$
5. If the final conditions of state variables are satisfied within a tolerance limit, stop.
6. Otherwise compute new temperature history using the following equation

$$T(t)_{new}=T(t)_{old} - \alpha g(t)$$

where α is selected after some numerical experimentation. A small value of α would lead to long computing times before reaching the solution and a large value can lead to oscillations or even divergence from the solution.

APPENDIX E: MINIMUM TIME TEMPERATURE POLICY SIMPLIFIED MODEL

As given in Appendix D, the objective in this problem is to find the optimal temperature profile at a given initial initiator concentration to produce a polymer with desired final conversion and number average molecular weight in minimum time.

In this development the simplified mathematical obtained by neglecting the transfer reactions are used. (see Appendix C) The simplified model equations are:

$$\frac{dI}{dt} = -k_d I \qquad (E.1)$$

$$\frac{dM}{dt} = -k_1 M\sqrt{I} \qquad (E.2)$$

$$\frac{d\mu_0}{dt} = C k_d I \qquad (E.3)$$

The objective function of this problem is:

$$\min tf = \max \int_0^{tf} -dt \qquad (E.4)$$

The Hamiltonian for the above problem can be written as:

$$H = -1-P_1 k_d I-P_2 k_1 M\sqrt{I}+P_3 C k_d I \qquad (E.5)$$

In Equation (E.5) P_1, P_2, and P_3 are costate variables which satisfy the following equations.

$$\frac{dP_1}{dt} = -\frac{\partial H}{\partial M} = P_1 k_d + \frac{P_2}{2}\frac{k_1 M}{\sqrt{I}} P_3 C k_d \qquad (E.6)$$

$$\frac{dP_2}{dt} = -\frac{\partial H}{\partial M} = P_2 k_1 \sqrt{I} \qquad (E.7)$$

$$\frac{dP_3}{dt} = -\frac{\partial H}{d\mu_0} = 0 \qquad (E.8)$$

The optimality conditions assuming no constraint on the temperature are given by:

$$H=0 \qquad (E.9)$$

$$\frac{\partial H}{dT} = \left\{\frac{P_1 E_d k_d I - P_2 E_1 k_1 M\sqrt{I} + P_3 C E_d k_d}{RT^2}\right\} = 0 \qquad (E.10)$$

From Equations(E.2) and (E.7) we obtain

$$\frac{dM}{M} + \frac{dP_2}{P_2} = 0 \qquad (E.11)$$

From Equation(E.11) the following equation is easily obtained.

$$P_2 M = \text{constant} = a \qquad (E.12)$$

From Equation(E.10), Equation(13) can be derived.

$$P_3 C E_d k_d = P_1 E_d k_d I + P_2 E_1 k_1 M\sqrt{I} \qquad (E.13)$$

Substituting (E.13) in (E.9) we get:

$$P_2 M\sqrt{I} k_1 (E_1 - E_d) - E_d = 0 \qquad (E.14)$$

From Equation (E.12) and (E.14) we get:

$$k_1\sqrt{I} = \frac{E_d}{(E_1 - E_d)} \frac{1}{a} \qquad (E.15)$$

Equation (E.15) can be used to get the optimal temperature. The optimal temperature can be obtained by the following procedure.

4. Guess the value of P_2 at time t=0
5. Calculate $a = P_2 M$ = constant at time t=0
6. Calculate the temperature T from Equation(E.15)
7. Integrate Equations (E.1)-(E.4) forward and at each step calculate temperature T. Proceed until the desired conversion is reached.
8. When conversion has reached the desired value, compare the number average molecular weight with the desired value.
9. If they are within the tolerance value, stop
10. Otherwise go to step 1 and adjust the value of P_2 at time t=0

A bisection method is used to iterate upon the initial values of P_2 in this program. Computer programs have been developed to solve the above problem. The results are presented in Section 6.6.

APPENDIX F: TEMPERATURE POLICY FOR MINIMUM POLYDISPERSITY

This Appendix solves the problem 4 described in section 6.3. The objective is to produce a polymer product with desired conversion (x^*) and number average molecular weight and having minimum polydispersity.

The model equations required after neglecting the transfer reactions (see Appendix C) are:

$$\frac{dI}{dt} = -k_d I \qquad (F.1)$$

$$\frac{dM}{dt} = -k_1 M\sqrt{I} \qquad (F.2)$$

$$\frac{d\mu_0}{dt} = Ck_d I \qquad (F.3)$$

$$\frac{d\mu_2}{dt} = k_6 M^2 \qquad (F.4)$$

Note Equations (F.1) and (F.3) are linearly dependent and hence μ_0 can be calculated from I.

The objective of the problem can be written as:

$$\min J = \mu_2(tf) \qquad (F.5)$$

The Hamiltonian for the above problem can be formed as:

$$H=-P_1 k_d I - P_2 k_1 M\sqrt{I} + P_3 k_6 M^2 \qquad (F.6)$$

In Equation (F.6) P_1, P_2 and P_3 are co-state variables which must satisfy the following equations:

$$\frac{dP_1}{dt} = -\frac{\partial H}{\partial I} = P_1 k_d + \frac{P_2 k_1 M}{2\sqrt{I}} \qquad (F.7)$$

$$\frac{dP_2}{dt} = -\frac{\partial H}{\partial M} = P_2 k_1 \sqrt{I} - 2P_3 k_6 M \qquad (F.8)$$

$$\frac{dP_3}{dt} = -\frac{\partial H}{\partial \mu_2} = 0 \qquad (F.9)$$

The initial and boundary conditions of the problem can be written as follows: Boundary Conditions:

Variable	t=0	t=tf
I	I_0	$I_0 - M_0 x^* MW/CM_n^*$
M	M_0	$M_0(1-x^*)$
μ_2	0	free
P_1	free	free
P_2	free	free
P_3	-1	-1

(F.10)

Along the optimal path the following two equations will hold good.

$$\frac{\partial H}{\partial T} = \frac{1}{RT^2}\left(-P_1E_dk_dI - P_2E_1k_1M\sqrt{I} + P_3E_6k_6M^2 \right\} = 0 \qquad (F.11)$$

$$H = -P_1k_dI - P_2k_1M\sqrt{I} + P_3k_6M^2 = 0 \qquad (F.12)$$

Substituting $P_3 = -1$ and Equation (F.12) in Equation (F.11) and rearranging we get:

$$P_2k_1M\sqrt{I}\{E_d - E_1\} - k_6M^2\{E_6 - E_d\} = 0 \qquad (F.13)$$

But we know that:

$$k_6 = (2+\nu)kp^2/k_t = A_6\exp(-E_6/RT) \qquad (F.14)$$

$$k_1 = kp\sqrt{2fk_d/k_t} = A_1\exp(-E_1/RT) \qquad (F.15)$$

With a value of f=0.5, from Equations (F.14) and (F.15) we get:

$$(E_6 - E_d) = -2(E_d - E_1) \qquad (F.16)$$

$$k_6 = (2+\nu)k_1^2/k_t \qquad (F.17)$$

Substituing Equation (F.17) in Equation (F.12) and rearranging we get:

$$\frac{k_1}{k_6} = -\frac{2M}{P_2\sqrt{I}} \tag{F.18}$$

From Equations (F.14), (F.15) and (F.18), the optimal temperature T can be obtained as:

$$T = \frac{(E_6-E_1)}{R\ln\left(\frac{-2A_6M}{A_1P_2\sqrt{I}}\right)} \tag{F.19}$$

The optimal temperature profile can be calculated by the following procedure.

1. Assume $P_2(0)$
2. Calculate T from Equation (F.19)
3. Integrate Equations (F.1), (F.2) and (F.3) until desired conversion x^* is reached.
4. Check if M_n has reached the desired value.
5. If M_n has not reached the desired value go to step 1 and adjust $P_2(0)$.

By using the simplified model, we avoid the solution of the two point boundary value problem. We have to iterate only on the initial value of the co-state variable P_2.

APPENDIX G: EXPERIMENTAL RESULTS

EXPERIMENT NO= 1

TIME IN MIN	CONVERSION PERCENT GC	CONVERSION PERCENT GRAVIMETRY	VISCOSITY CP	DENSITY g/mL
20.	7.2	4.5	-	-
40.	11.9	9.8	-	-
60.	17.6	15.6	-	-
80.	21.7	21.0	-	-
100.	26.1	25.7	-	-
125.	31.3	31.8	-	-
150.	36.4	38.1	-	-
175.	40.9	43.8	-	-
200.	45.4	47.6	-	-
225.	48.7	53.6	-	-
250.	52.3	58.3	-	-
275.	56.1	63.1	-	-
300.	59.4	66.2	-	-

TEMPERATURE= 65.°C

SOLVENT RATIO= 0.6

INITIAL INITIATOR CONCENTRATION= 0.05MOL/L

EXPERIMENT NO= 2

TIME IN MIN	CONVERSION PERCENT GC	CONVERSION PERCENT GRAVIMETRY	VISCOSITY CP	DENSITY g/mL
20.	11.0	7.9	-	-
40.	17.8	18.2	-	-
60.	26.5	24.1	-	-
80.	31.1	31.1	-	-
100.	37.2	37.8	-	-
120.	42.4	45.2	-	-
140.	46.2	49.8	-	-
160.	51.2	56.3	-	-
180.	54.9	60.5	-	-
200.	59.1	65.4	-	-
220.	62.4	70.5	-	-
240.	66.8	73.9	-	-
270.	67.4	81.1	-	-

TEMPERATURE= 65. °C

SOLVENT RATIO= 0.6

INITIAL INITIATOR CONCENTRATION= 0.10MOL/L

EXPERIMENT NO= 3

TIME IN MIN	CONVERSION PERCENT GC	CONVERSION PERCENT GRAVIMETRY	VISCOSITY CP	DENSITY g/mL
20.	19.7	17.0	1.6	0.8954
40.	31.4	31.2	3.3	0.9075
60.	42.2	44.3	6.8	0.9188
80.	50.3	55.4	13.4	0.9283
100.	56.8	63.9	19.8	0.9372
120.	66.1	71.6	26.5	0.9433
140.	72.1	76.2	46.7	0.9495
160.	75.8	80.3	57.3	0.9540
180.	79.1	85.1	76.5	0.9578

TEMPERATURE= 75. °C

SOLVENT RATIO= 0.6

INITIAL INITIATOR CONCENTRATION= 0.05MOL/L

EXPERIMENT NO= 4

TIME IN MIN	CONVERSION PERCENT GC	CONVERSION PERCENT GRAVIMETRY	VISCOSITY CP	DENSITY g/mL
15.	19.1	16.9	1.6	0.8996
30.	34.9	35.1	3.2	0.9137
45.	45.5	48.3	5.8	0.9234
60.	55.2	59.4	10.4	0.9345
75.	62.6	67.4	16.0	0.9416
90.	69.5	74.7	18.0	0.9484
105.	73.6	80.5	25.2	0.9558
120.	78.7	86.2	33.7	0.9575

TEMPERATURE= 75. C

SOLVENT RATIO= 0.6

INITIAL INITIATOR CONCENTRATION= 0.10MOL/L

EXPERIMENT NO= 5

TIME IN MIN	CONVERSION PERCENT GC	CONVERSION PERCENT GRAVIMETRY	VISCOSITY CP	DENSITY g/mL
15.	7.0	2.6	0.0	0.8976
30.	9.1	7.3	0.0	0.9021
45.	13.8	11.3	0.0	0.9073
60.	17.0	15.3	0.0	0.9123
80.	21.3	21.3	6.5	0.9200
100.	24.5	25.8	11.0	0.9256
120.	29.5	32.1	21.8	0.9300
145.	35.4	38.8	56.5	0.9421
170.	40.4	48.1	120.2	0.9513
200.	40.4	57.2	-	0.9623

TEMPERATURE= 65. °C

SOLVENT RATIO= 0.4

INITIAL INITIATOR CONCENTRATION= 0.05MOL/L

EXPERIMENT NO= 6

TIME IN MIN	CONVERSION PERCENT GC	CONVERSION PERCENT GRAVIMETRY	VISCOSITY CP	DENSITY g/mL
20.	10.5	6.2	2.1	0.9083
40.	17.5	15.7	4.6	0.9200
60.	27.4	25.3	12.1	0.9319
80.	33.7	35.2	22.7	0.9428
100.	40.4	44.1	62.0	0.9542
120.	46.3	56.4	195.0	0.9641
140.	51.9	61.8	-	0.9734
160.	-	67.2	-	0.9865

TEMPERATURE= 65. °C

SOLVENT RATIO= 0.4

INITIAL INITIATOR CONCENTRATION= 0.05MOL/L

EXPERIMENT NO= 7

TIME IN MIN	CONVERSION PERCENT GC	CONVERSION PERCENT GRAVIMETRY	VISCOSITY CP	DENSITY g/mL
15	13.5	9.8	2.2	0.9083
30	23.0	20.5	6.2	0.9230
45	32.8	33.2	19.4	0.9376
60	42.5	41.6	55.0	0.9517
75	48.2	54.2	131.5	0.9636
90	-	61.8	-	0.9740
105	-	67.2	-	0.9880

TEMPERATURE= 75 °C

SOLVENT RATIO= 0.4

INITIAL INITIATOR CONCENTRATION= 0.05MOL/L

EXPERIMENT NO= 8

TIME MIN	CONVERSION PER CENT	VISCOSITY CP	DENSITY g/mL	NUM.AVG.MW	WT.AVG.MW	POLYDISPERSITY
30.	6.0	1.3	0.8833	85400.	148000.	1.74
60.	13.7	2.6	0.8910	83100.	145000.	1.74
90.	22.1	4.3	0.9000	82100.	139000.	1.70
120.	28.7	7.0	0.9061	76900.	134000.	1.74
150.	36.6	12.6	0.9131	74200.	130000.	1.75
180.	43.7	19.7	0.9204	77700.	132000.	1.69
210.	49.4	25.0	0.9251	74500.	127000.	1.70
240.	55.1	48.0	0.9321	70700.	122000.	1.72
270.	60.5	70.0	0.9360	60700.	111000.	1.82

TEMPERATURE= 65. C

SOLVENT RATIO= 0.6

INITIAL INITIATOR CONCENTRATION= 0.05 MOL/L

EXPERIMENT NO= 9

TIME MIN	CONVERSION PER CENT	VISCOSITY CP	DENSITY g/mL	NUM.AVG.MW	WT.AVG.MW	POLYDISPERSITY
30.	9.0	1.6	0.8904	76900.	125000.	1.62
60.	18.9	2.9	0.9011	58900.	106000.	1.79
90.	28.6	4.8	0.9092	51900.	97200.	1.87
120.	36.9	7.6	0.9165	54800.	97900.	1.79
150.	45.0	13.0	0.9247	45700.	88900.	1.94
180.	51.7	19.4	0.9303	49200.	88800.	1.80
210.	57.7	26.7	0.9372	44800.	86200.	1.92
240.	64.5	42.0	0.9433	41900.	83900.	2.00
270.	68.6	60.5	0.9507	40600.	83300.	2.05

TEMPERATURE= 65. C

SOLVENT RATIO= 0.6

INITIAL INITIATOR CONCENTRATION= 0.10 MOL/L

EXPERIMENT NO=10

TIME MIN	CONVERSION PER CENT	VISCOSITY CP	DENSITY g/mL	NUM.AVG.MW	WT.AVG.MW	POLYDISPERSITY
20.	10.8	1.8	0.8886	76400.	126000.	1.64
40.	19.7	3.4	0.8971	73400.	123000	1.68
60.	28.5	5.5	0.9051	64832.	111980.	1.73
80.	35.9	10.0	0.9126	63861.	112284.	1.76
105.	44.5	16.4	0.9207	66900.	111000.	1.66
120.	48.0	20.4	0.9252	65200.	110000.	1.68
140.	53.4	23.8	0.9323	62100.	107000.	1.72
160.	57.8	38.7	0.9371	59500.	102000.	1.71
180.	61.7	55.0	0.9431	52800.	95000.	1.80

TEMPERATURE= 70. C

SOLVENT RATIO= 0.6

INITIAL INITIATOR CONCENTRATION= 0.05 MOL/L

EXPERIMENT NO=11

TIME MIN	CONVERSION PER CENT	VISCOSITY CP	DENSITY g/mL	NUM.AVG.MW	WT.AVG.MW	POLYDISPERSITY
20.	13.4	1.9	0.8952	57900.	95500.	1.65
40.	24.9	2.8	0.9068	46000.	78100.	1.70
60.	37.4	4.8	0.9166	43500.	75700.	1.74
80.	45.2	10.5	0.9258	42300.	71700.	1.70
100.	53.6	17.5	0.9346	39000.	69200.	1.77
120.	59.5	22.2	0.9414	38300.	67900.	1.77
140.	63.4	35.0	0.9494	34800.	64000.	1.84
160.	67.5	60.0	0.9557	34100.	61500.	1.80
180.	71.4	75.0	0.9567	33800.	62800.	1.86

TEMPERATURE= 70. °C

SOLVENT RATIO= 0.6

INITIAL INITIATOR CONCENTRATION= 0.10 MOL/L

EXPERIMENT NO=12

TIME MIN	CONVERSION PER CENT	VISCOSITY CP	DENSITY g/mL	NUM.AVG.MW	WT.AVG.MW	POLYDISPERSITY
20.	7.5	1.7	0.8881	80300.	124000.	1.54
40.	15.2	2.0	0.8954	72000.	116000.	1.61
60.	22.6	2.8	0.9020	60600.	109000.	1.80
80.	29.9	4.3	0.9088	58200.	103000.	1.77
100.	36.7	7.0	0.9153	54700.	98900.	1.81
130.	45.0	13.4	0.9247	57100.	94900.	1.66
160.	54.7	21.0	0.9325	47500.	89200.	1.87
190.	62.3	36.5	0.9389	42900.	81000.	1.89
220.	68.0	54.2	0.9456	43100.	81500.	1.89

TEMPERATURE= 70. °C

SOLVENT RATIO= 0.6

INITIAL INITIATOR CONCENTRATION= 0.05 MOL/L

EXPERIMENT NO=13

TIME MIN	CONVERSION PER CENT	VISCOSITY CP.	DENSITY g/mL	NUM.AVG.MW	WT.AVG.MW	POLYDISPERSITY
2[illegible]	13.5	1.9	0.8950	50700.	85700.	1.69
40.	26.3	2.8	0.9061	46100.	80300.	1.74
60.	35.1	4.8	0.9166	42800.	73300.	1.71
80.	45.8	9.1	0.9260	40200.	72600.	1.80
100.	54.3	16.6	0.9260	36300.	65000.	1.79
120.	59.7	20.5	0.9431	35900.	64600.	1.80
140.	66.3	30.5	0.9505	35200.	64800.	1.84
160.	73.3	46.5	0.9530	34200.	62800.	1.83
180.	76.1	60.5	0.9572	33700.	61800.	1.83

TEMPERATURE= 70. C

SOLVENT RATIO= 0.6

INITIAL INITIATOR CONCENTRATION= 0.10 MOL/L

EXPERIMENT NO=14

TIME MIN	CONVERSION PER CENT	VISCOSITY CP	DENSITY g/mL	NUM.AVG.MW	WT.AVG.MW	POLYDISPERSITY
20.	19.8	2.0	0.8918	65500.	105000.	1.60
40.	31.3	2.6	0.9024	54000.	93800.	1.74
60.	42.8	5.0	0.9131	48800.	86700.	1.78
80.	52.2	9.0	0.9254	46500.	82700.	1.78
100.	59.4	14.6	0.9303	45700.	81400.	1.78
120.	65.3	20.6	0.9420	43800.	78400.	1.79
140.	75.3	23.4	0.9437	34400.	64800.	1.88
160.	76.5	40.0	0.9500	36000.	68900.	1.91
180.	82.3	52.0	0.9523	32100.	63000.	1.96

TEMPERATURE= 75. C

SOLVENT RATIO= 0.6

INITIAL INITIATOR CONCENTRATION= 0.05 MOL/L

EXPERIMENT NO=15

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TIME     CONVERSION    VISCOSITY    DENSITY    NUM.AVG.MW    WT.AVG.MW   POLYDISPERSITY
MIN       PER CENT        CP          g/mL
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 15.        20.0          1.8        0.8993      44500.       75200.        1.69
 30.        32.5          3.2        0.9114      41000.       71400.        1.74
 45.        44.3          5.3        0.9190      40700.       69300.        1.70
 60.        52.5          8.4        0.9436      35100.       63000.        1.79
 75.        60.9         13.0        0.9360      35800.       64200.        1.80
 90.        67.5         18.7        0.9436      32600.       58700.        1.80
105.        74.8         23.0        0.9521      31900.       58400.        1.83
120.        78.0         30.0        0.9595      30500.       57500.        1.88
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TEMPERATURE= 75. C

SOLVENT RATIO= 0.6

INITIAL INITIATOR CONCENTRATION= 0.10 MOL/L
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