KINETICS OF FREE RADICAL POLYMERIZATION OF STYRENE TO COMPLETE CONVERSION

ΒY

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A Thesis

Submitted to the School of Graduate Studies In Partial Fulfilment of the Requirements

For the Degree

Doctor of Philosophy

McMaster University September 1970

DOCTOR OF PHILOSOPHY (1970) (Chemical Engineering)

McMASTER UNIVERSITY Hamilton, Ontario.

TITLE	:	Kinetics of Free Radical Polymerization of Styrene to Complete Conversion
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NUMBER OF PAGES	: '	xii, 239.
SCOPE AND CONTENTS	•	

Polymerization of bulk styrene initiated thermally as well as with di-tertiary-butyl peroxide was studied in isothermal batch reactors. Thermal polymerization was carried out at 100, 140, 170 and 200°C while polymerization with di-tertiary butyl peroxide was at 100 and 140°C. A kinetic model was derived therefrom accounting for initiation reactions from a first order decomposition of catalyst and a second order reaction between two monomer molecules to form two monoradicals, propagation, chain transfer to monomer and termination by combination only. Gel effect was allowed by the variation of rate constants with conversion. Both the thermal initiation rate constant and the first order decomposition rate constant of di-tertiary butyl peroxide were found to agree with literature values with the present values slightly higher. The initial rate constants for propagation, chain transfer to

monomer, and termination were extrapolated to the range, 100-200°C using literature data. This kinetic model was used in the simulation of polymer reactor systems studying the effect of recycle and operating conditions on the molecular weight distribution and rate of production of polymer products.

The main body of this thesis reports the polymerization study and the development of the kinetic model. The details of the kinetic equations and methods of solution, experimental techniques involved, and the simulation of polymer reactor systems are reported in the Appendices.

ACKNOW LEDGEMENTS

The author wishes to express his gratitude to those who contributed to this work. He is particularly indebted to:

His research director, Dr. A.E. Hamielec, for his enthusiasm, interest and guidance throughout the course of this study. The members of the Ph.D. Supervisory Committee, Dr. J.W. Hodgins and Dr. W.K. Lu for their advice in this study and in the final write-up of the thesis.

Dr. S.P. Sood of the University of Hawaii for his helpful discussions in high vacuum technology.

Dr. L.H. Tung, S.T. Balke for providing computer programs, reports for their methods of resolution and skewing corrections in the gel permeation chromatograph.

J.D. Wilson, R.H.C. Cheng and P. Crickmore for their experimental assistance.

The Chemical Engineering Department, McMaster University, for providing financial assistance as a form of scholarship. Mrs. Ora Orbach for her careful and conscientious work in typing this dissertation.

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I. INTRODUCTION

The objectives of the present study were to obtain experimental data, such as the variation of conversion, molecular weight averages with reaction time, for styrene polymerization over the range of conditions involved in industrial processes; and to develop a kinetic model capable of predicting the behaviour of important variables such as the conversion of monomer and the molecular weights of polymer product in styrene polymerization. Both of the kinetic data and the model should find use in the design, operation and optimization of commercial polymer reactors. Such information has not been reported in the literature.

The experimental study requires the measurement of conversion and at least two molecular weight averages. This is conveniently done with gravimetrical techniques, spectrophotometry and gel permeation chromatography. The development of a model may be based on a proposed kinetic scheme which describes elementary reactions involved in the polymerization process. This approach of kinetic model has been chosen in the prosent study with the hope of promoting the understanding of polymerization reactions. In this case, the development of a kinetic model involves the selection of a useful kinetic scheme and the estimation of the corresponding rate constants from the observed data. The mechanism of free radical polymerization has been studied extensively. The general kinetic scheme includes ^[1] the initiation of free radicals thermally and by the decomposition of an initiator, the propagation reaction or the reaction of radicals with monomer molecules leading to the chain growth of radicals, chain transfer reactions or the reaction of radicals with other molecules with the termination of radical species to form dead polymer and the formation of a radical from the reactant molecule, and termination reactions or the reaction of two radicals to form dead polymer consuming the reactive radicals in the system.

The kinetic scheme is complicated and simplifying assumptions are generally introduced to make the solution easier. These assumptions include:

a) The reactivity of radicals are independent of their chain length and environment, for example, a single velocity constant will characterize all the propagation steps at all times in the reaction process.

b) The average chain length is large.

c) No volume change throughout polymerization - that is, no change in density.

d) All free radical concentrations are at stationary or steadystate.

These assumptions have been used widely as reported in literature for styrene and other vinyl polymerizations at low conversions with good agreement with experimental data [5, 6, 7].

The validity of these assumptions, however, becomes questionable towards higher conversion. The main concern of the present study is to extend low conversion kinetics to complete conversion. It appears that the first assumption above is a doubtful one based on the theory of diffusion controlled reaction and the well-known phenomena of gel-effect reported by many workers [3, 6, 19]. The second assumption is acceptable for styrene polymerization where the molecular weight of the polymer is high. The third assumption is not valid at high conversions and variation of density with polymerization will be accounted for in the present study. The validity of the steady state assumption at high conversion was also investigated in this study.

Other reactions such as transfer to polymer, second order thermal initiation, autocatalytic decomposition of catalyst etc. were reported as possible reactions for styrene polymerization. The importance of these reactions is also evaluated in order to explore the truth of the mechanisms of polymerization. However, it should be mentioned here that the kinetic model resulting from the present study is by no means a proof to the mechanisms of reaction, although every effort is tried to make the kinetic model as close to the truth as possible.

In the experimental study, styrene was polymerized in bulk, using the initiator di-t-butyl peroxide (DTBP) as well as thermal initiation, isothermally at temperatures of 100-200°C in vacuum sealed ampoules up to essentially complete conversion. The temperature of polymerization

encountered here is high enough to give fast rate of polymerization of the order used industrially. The rate constants reported in literature were mostly obtained from initial rate studies at temperatures well below 100°C. It is not certain whether extrapolation of low temperature data to temperatures as high as 200°C is valid. The aim of the present study is to obtain also kinetic data at moderately high temperature and to essentially complete conversion.

2. LITERATURE REVIEWS AND THEORETICAL BACKGROUND

The main features of this study involves the free radical polymerization of styrene to high conversion, at moderately high temperature, initiated thermally and with di-tertiary-butyl peroxide. These features will be introduced briefly in this section. For a complete review of the literature of free radical polymerization, the recent review articles by Lenz [13], Eastmond [12], North [3] and the M.Eng. Thesis of Hui [6] may be consulted.

2.1 High Conversion Kinetics

The term "high conversion kinetics" is used here to emphasize that classical polymerization kinetics do not apply at high conversions. The deviation of polymerization phenomena from classical kinetics was reported in 1947 by Trommsdorff et.al. ^[15]. It was observed that the rate of polymerization of methyl methacrylate initiated with benzoyl peroxide started to deviate from theoretical at about 20% conversion, and increased rapidly, eventually reached a maximum at about 70% conversion. Similar phenomena were also observed for other polymer systems, e.g. styrene, acrylates etc. and they were generally referred to as the "auto-acceleration effect" or "gel effect". It has become an accepted fact ^[3, 6] that for the free radical polymerization of many monomers, such as styrene, methyl methacrylate etc., kinetic schemes and rate constants obtained from the polymerization at low conversion (10% or lower)

cannot be used with confidence at higher conversion.

A large amount of work was done late in the '50's and early in the '60's in the area of high conversion kinetics or polymerization in viscous media $\begin{bmatrix} 15-26 \end{bmatrix}$. It may be summarised by introducing the concept of "diffusion controlled" reactions.

For any bimolecular reaction in a condensed phase, the stages of reaction may be represented by the following scheme [3]:-

$$\begin{array}{c} k_{1} \\ A+B \stackrel{1}{\leftarrow} A:B \\ k_{2} \\ A:B \stackrel{k_{3}}{\rightarrow} Products \end{array}$$

where A and B represent reactant molecules in the condensed phase which are not nearest neighbours, and A:B represents the "encounter" when the reactants are nearest neighbours undergoing repeated collisions. In general, the rate of formation of A:B will equal the rate of disappearance of such collision pairs, so that

$$\frac{d[Products]}{dt} = \frac{k_1 k_3}{k_2 + k_3} [A][B] = k[A][B]$$
(2-1)

For very rapid diffusion of reactants and slow chemical reaction, i.e., $k_2^{>>k_3}$, the overall rate constant becomes

$$k = \frac{k_1 k_3}{k_2}$$
 (2--2)

In the extreme case of very slow diffusion or for very rapid chemical reaction, $k_2^{<< k_3}$, the overall rate constant is given by

$$k = k$$
 (2-3)

Since the rate constant k₁ is independent of the chemical nature of the reactants, under this extreme condition, the reaction is referred to as being "diffusion controlled". In the case of macromolecular reactions, the diffusive processes are of a complicated nature, and may involve quite a large "diffusion activation energy", and tend to become "diffusion controlled" if the chemical reaction between the macromolecules is reasonably fast.

Benson and North ^[18] considered the diffusion process in a bimacromolecular reaction as a two stage process. The first stage was the translational diffusion of the centres of gravity of the two reacting macroradicals to a distance such that chemical reaction was possible without alteration in the separation of the active centres. This was followed by the segmental diffusion of the active centres on the macromolecular chains to within the separation distance for chemical reaction.

The dependence of the diffusion-controlled rate constant upon parameters such as solution viscosity and chain length was given in an approximate form by the Smolouchowski equation ^[19]. In general, it could be related as

$$k \alpha R_{E}(D_{A} + D_{B})$$
 (2-4)

where D_A , D_B were the diffusion coefficients of polymeric reactants A and B respectively, and R_F was the distance at which reaction is possible.

It was shown that if the reaction was diffusion controlled by translational diffusion ^[3],

$$k \alpha T \{(1 + N_A/N_B)^{\frac{1}{2}} + (1 + N_B/N_A)^{\frac{1}{2}}\}$$
 (2-5)

and by segmental diffusion,

$$k \alpha T (N_A^{-\frac{1}{2}} + N_B^{-\frac{1}{2}})$$
 (2-6)

where N_A and N_B are the chain length of reacting species A,B. Calculations indicated the overall rate constant k was significantly chain length dependent for the case of segmental diffusion controlling, and much less dependent on chain length in the case of translational diffusion controlling.

North and coworkers ^[20-22] studied the polymerization of alkyl acrylates, and low temperature polymerization of methyl methacrylate and detected the strong dominance of segmental diffusion over translational diffusion.

The idea of chain length dependence of diffusion controlled reactions was carried further by Benson and North ^[19]. A kinetic scheme was proposed taking into consideration the effect of chain length. The solution of the proposed scheme was not worked out, however, due to the complexities of mathematics. Recently, the concept of chain length dependence was rejected by Ito ^[34, 35]. Theoretical derivation showed that segmental diffusion was the controlling step and its rate constant does not depend on the mojecular weight of the reacting polymeric radicals.

Khanukayeva and Kolesnikov ^[31] studied the styrene polymerization in viscous media. Polymerization was carried out thermally and initiated with benzoyl peroxide for pure styrene and for 15%, 30% solutions of bulk polystyrene in styrene at temperatures 75, 85, 95°C. Results indicated that a 500-fold rise in viscosity of the polymerizing medium has practically no effect on the rate of polymerization, except to increase the molecular weights of the resulting polymer. This was explained by the decrease in catalyst efficiency and termination rate constant with the rise of viscosity. It appeared that the effect of viscosity upon styrene polymerization was not very significant as compared to systems such as methyl methacrylate.

Horie et al ^[32] studied the bulk polymerization of methyl methacrylate and styrene up to complete conversion by the technique of differential scanning calorimeter (DSC). It was observed that when methyl methacrylate polymerized below the glass transition temperature, the final conversion stopped short of complete conversion, the final conversion being higher with higher temperature as the glass transition temperature is approached. It was concluded that the diffusion-controlled polymerization reactions ceased at a conversion when the diffusion processes were suppressed because of the transition of the polymer-monomer system from a viscous liquid to a glassy state. No attempt was made, however, to develop the complete polymerization kinetics for either system.

2.2 <u>Thermal Degradation and Depolymerization</u> of Styrene Polymers

The effect of temperature on the stability of polymers has been of interest to the polymer chemist for the last few decades. Studies on the thermal behaviour of polymers, particularly on thermal degradation, are of prime importance from a practical point of view. It has been noted that most polymers decompose or degrade at elevated temperatures giving off volatile material with decrease in molecular weight in the remaining polymer. For the detailed review of the subject, the works of Jellinek ^[39], Grassie ^[38], Madorsky ^[40] and Dainton et.al. ^[43] may be consulted.

It was observed ^[40] that polystyrene under careful exclusion of oxygen has a greater thermal stability than in the presence of oxygen; polystyrenes prepared with rigorous exclusion of oxygen started to degrade at temperatures above 150°C depending on the molecular weight of the polymer and its method of preparation. Degradation was even more severe at temperatures beyond 280°C with monomer, dimer, trimer, benzene, toluene, ethylene etc. appearing as degradation products depending on the temperature of pyrolysis. In general, the molecular weight dropped abruptly during the first few percent loss of weight of sample to about 80,000. Beyond this the drop was gradual.

The process of thermal degradation or depolymerization has been considered as the reversal of a corresponding polymerization process ^[39]. The simplest polymerization process is composed of three reactions: initiation, propagation and termination. Similarly, the simplest

depolymerization process has an initiation (random or chain-end initiation), a depropagation and a termination reaction. An example of a simple kinetic scheme is given below:-

Random chain-scission initiation

 $P_r \rightarrow R_{r-n}^{\circ} + R_n^{\circ}$

Chain-end initiation

$$P_r \rightarrow R_{r-1}^{\circ} + R_1^{\circ}$$

 $R_r^{\circ} \rightarrow R_{r-1}^{\circ} + M$

Depropagation

Termination

$$R_{r}^{\circ} + R_{s}^{\circ} \rightarrow P_{r+s}$$
$$R_{r}^{\circ} + R_{s}^{\circ} \rightarrow P_{r} + P_{s}$$

For the polymerization at high temperature, both the forward polymerization and the reverse depolymerization processes have to be considered. The significance of depolymerization will be dependent on temperature. For styrene-polystyrene system, it has been indicated that the rate of depolymerization is not significant below 150°C, but increases with increase temperature, until the ceiling temperature is reached at which the rates of polymerization and depolymerization become equal. The ceiling temperature may be defined as the temperature at which the free energy of polymerization (for long-chain polymers) passes from a negative to a positive value during the rise in temperature, ie.

$$T_{c} = \Delta H_{p} / \Delta S_{p}, \qquad (2-7)$$

where ΔH_p and ΔS_p are heat and entropy changes, and T_c is the ceiling temperature.

Jessup ^[42] calculated the heat and free energy of polymerization of ethylene from available thermochemical and thermodynamic data. Results indicated a strong dependence of heat and free energy upon chain length, both being proportional to the chain length of the polymer. In other words, chemical equilibrium favours the low molecular weight polymer. At a certain elevated temperature, there exists a chain length n_{max} beyond which the change of free energy of polymerization becomes zero and positive ($\Delta F \ge 0$), and formation of polymer of chain length greater than n_{max} will not be possible. A rise in temperature is nearly always thermodynamically unfavourable towards polymerization equilibrium.

2.3 Thermal Polymerization of Styrene

Thermal polymerization of styrene was reported as early as in 1937 ^[46, 49, 50]. Since then many workers studied the thermal polymerization of styrene with various theories being proposed. Flory ^[50] proposed that the thermal initiation step was based on the formation of a diradical. First order, second order and third order dependence of the rate of polymerization on monomer were also suggested ^[47]. However, later workers ^[48] tended to favour the theory of the second order rate of thermal initiation to form two monoradicals, i.e.,

 $M + M \rightarrow 2M^{\circ}$

Thermal polymerization data before 1952 are compiled by Boundy and Boyer ^[46]. Other data can be found in references ^[47, 53-56]. The data reported were in the temperature range, 50-150°C most of them obtained from initial rate measurements. Results indicated the rate of thermal polymerization followed the Arrhenius type relationship with temperature, and that the molecular weight of polymer decreases significantly with rise of reaction temperature ^[46].

The contribution of thermal polymerization in the catalysed polymerization of styrene was accounted for by Duerksen, Hui ^[7, 6] assuming the rates of initiation thermally and from the decomposition of catalyst were additive, i.e.

$$I = I_{th} + I_{cat}$$
(2-8)

where I was the rates of formation of primary radicals in the initiation steps. Calculation indicated that the contribution of thermal polymerization were not significant for temperatures 85°C and lower using azobisisobutyronitrile as catalyst. In these cases, the rate of initiation from catalyst was far greater than the thermal initiation rate.

It has been widely known that the rate of polymerization of styrene is very sensitive to the presence of impurities as well as atmospheric oxygen. This is a result of the low initiation rates found with thermal initiation at moderate temperatures. The effect of inhibition caused by minute impurities may be overcome by the high rate of initiation. Thermal polymerization of styrene at high temperature

may not be as sensitive to impurities. The significance of thermal polymerization in catalysed polymerization is believed to be dependent on the relative contribution of rates of initiation, which in turn depends on the monomer and the initiator under consideration.

2.4 Catalysed Initiation with Di-t-butyl Peroxide (DTBP)

The decomposition of organic peroxides is widely used in polymerization processes as a source of free radicals. The decomposition products are often complex and vary markedly with changes in the external environment. The chemistry of various peroxides can be found in references ^[58-60]. Di-tertiary-butyl peroxide (DTBP) has been chosen for the present study because of its importance in the commercial production of polystyrene. DTBP is a stable, safe chemical at room temperature and is widely used as a high temperature initiator in the polymerization of styrene.

The decomposition of DTBP in gas phase, liquid phase and in various solvents was investigated by many workers [58, 70]. Various decomposition schemes were proposed with rates of decomposition differing depending on the conditions. The polymerization of styrene with DTBP was also reported. Offenbach and Tobolsky [62] reported a decomposition rate constant of

 $k_d = 2.8 \times 10^{14} EXP(-35 \text{ kcal},/\text{RT})$ (2-9)

from results measured in styrene, and in three other solvents. DTBP with a labelled c^{14} atom was also studied in styrene polymerization ^[64, 69]. Pryor ^[69] considered the transfer reaction to catalyst and reported a decomposition rate constant in agreement with other measurements in gas phase and in various solvents. An activation energy of 37 kcal was reported for a temperature range of 60 - 350°C. The agreement between rates of decomposition in the gas phase and in solution led to the belief that the catalyst efficiency was 100%.

Shaw and Pritchard ^[70] studied the thermal decomposition of DTBP in the presence of carbon dioxide at pressures from 0.05 to 15 atmosphere and temperatures from 90 - 130°C. It was observed that the first order rate of decomposition was independent of pressure. It was suggested that variations in the rate of decomposition were due to chemical reactions of DTBP with surrounding material or to the presence of trace quantities of impurities. Results of their measurements were in excellent agreement with a number of workers, and the decomposition rate constant of

$$k_d = 6.31 \times 10^{15} EXP(-37780/RT)$$
 (2-10)

was reported for a temperature range of 90 - 350°C.

The recombination of primary radicals to form waste products is generally accounted for by the use of the term "catalyst or initiator efficiency". The efficiency of initiation is defined as ^[1]

$$f = \frac{\text{rate of initiation of polymerization chain}}{2 \times (\text{rate of decomposition of catalyst})}$$
(2-11)

and that

f <u><</u> I

The decomposition of azobisisobutyronitrile (AIBN) in viscous media was investigated ^[29, 30]. DeSchrijver and Smets ^[29] studied the

decomposition of AIBN in polystyrene solution using labelled carbon (C^{14}) initiator, and reported a 50% decrease of catalyst efficiency over 20 poise viscosity range. Ye Messerle and Gladyshev ^[30] measured the catalyst efficiency from the induction period in the presence of iodine, and the rate of decomposition from the liberation of nitrogen; it was observed that the efficiency decreased, first rapidly with a relatively small increase of viscosity (up to about 200 centipoise), and then slowly, and finally remained practically constant at very large viscosities (10^4-10^5 cp.). The rate of decomposition also decreased with increase in viscosity probably due to the recombination of primary radicals and the regeneration of AIBN molecules. For styrene polymerization with DTBP as initiator, it would be expected that a similar decrease in catalyst efficiency would follow with the increase of viscosity and conversion.

Anisimov et.al. ^[67] studied the cause of branching in the styrene polymerization initiated by diacyl peroxides. Benzoyl peroxide, lauroyl peroxide and butyrl peroxide were used as sources of free acyl radicals, and the number of end groups in polystyrene was measured by infra red spectroscopy. Results indicated branching existed for the polymer initiated by lauroyl peroxide and butyrl peroxide, but not benzoyl peroxide. Reaction of polymer with lauroyl peroxide in benzene solution with the absence of monomer was also observed showing increased initiator end groups with reaction time. It was concluded that branching was due to the reaction between initiator radicals and polymer molecules, i.e.

 $R_c^{\circ} + P_r \rightarrow R_r^{\circ}$

at the advanced stages of conversion.

3. EXPERIMENTAL

3.1 Reagents and Analytical Techniques

Uninhibited styrene was obtained from Polymer Corporation Limited, Sarnia, Ontario. It was used for all polymerization reactions without further purification. The analysis provided by Polymer Corporation is given in Table 3-1 below. The same source of styrene was used previously [6, 7], no significant difference in experimental results was found between the further purified and the uninhibited styrene from Polymer Corporation.

TABLE 3-1 ANALYSIS OF STYRENE MONOMER

Components	Weight Percent
Styrene	99.73
Benzaldehyde	0.0034
Peroxide	0.0002
Sulphur	<0.0001
Chloride	0.0004
Polymer	0.0005
Water	remaining
Apha Color	7

The initiator di-tertiary-butyl peroxide (DTBP), manufactured by Lucidol Division, Wallace and Tiernan Inc., Buffalo, N.Y., was purchased from Harchem Limited, Toronto, Ontario. The gas chromatographic analysis [73, 74] of this initiator indicated a purity of 99% DTBP. The Lucidol DTBP (being from a major world peroxide producer) has been well accepted

by the polymer industry, and it was used here directly without further purification. All the solvents used in the courses of various analyses were purchased and were again used directly without further purification. They are listed in Table 3-2.

TABLE 3-2 SOLVENTS USED IN THE ANALYSES

Solvents	Grade	Used in	
Methanol	Fisher Certified	Gravimetric det. conversion	
I.4 Dioxane	Fisher Purified	11	
Methanol	Reagent	Spectrophotometry	
Chloroform	Reagen†	Spectrophotometry	
Toluene	Reagen†	Osmometry	
Tetrahydro- furan	Fisher Purified	GPC	

For conversions of styrene monomer up to about 95%, the determination of conversion was done gravimetrically. In this case, the polymer sample was weighed, dissolved in 1.4 dioxane, and was poured very slowly into at least a ten-fold excess of methanol, precipitating the polymer. The mixture was filtered on a sintered glass crucible and the precipitated polymer was dried under vacuum at 50°C for 24 hours. The amount of dried polymer, expressed as a percentage in the total weight of polymer sample, gave the percent conversion.

Ultraviolet spectrophotometry was employed in the determination of conversions above 95%, having an accuracy of better than 0.1%. The details of the method are reported in Appendix 9-D. The number average molecular weights of the dried polymers were measured by means of membrane osmometry, and both number and weight average molecular weights and MWD were measured via gel permeation chromatography. The details of these analyses are reported in Appendices 9-C and 9-B, respectively.

3.2 Apparatus and Procedures

All polymerization reactions were carried out in sealed Pyrex glass ampoules. Four sizes of ampoules were used. They were made of standard Pyrex glass tubings of 5, 7, 8 and 9 mm O.D., corresponding to 3.4, 5, 6, 7 mm. I.D. respectively. The geometry of these ampoules is shown in Fig. 3-1.

A test was made to determine the validity of isothermal conditions necessary in the present kinetic study. The reaction temperature was measured continuously using a thermocouple in close contact with the reaction mixture. Styrene was polymerized in an 8 mm. O.D. ampoule using I percent by weight of azobisisobutyronitrile as initiator. The reaction temperature was controlled at $80^{\circ} \pm 0.2^{\circ}$ C under which the reaction mixture solidified in three hours reaching a conversion of about 85%. The maintenance of uniform temperature was indicated from the continuous temperature indictor on a chart recorder. The variation of temperature was beyond the sensitivity of the chromel-alumel thermocouple measured in a 5 mv span recorder, i.e. the maximum temperature rise throughout the course of polymerization was less than 0.2°C. The time required for the reactants in the glass ampoule to reach the reaction temperature, in this case, was about one and a half minutes.



The reactant, consisting of styrene monomer (and di-tertiary-buty) peroxide for the case of catalysed polymerization), was prepared and introduced into the glass ampoules. They were sealed after being degassed under vacuum to the order of 10^{-6} mm.Hg. They were then stored at dry ice temperature for no more than 24 hours before the start of polymerization. An oil bath capable of maintaining a constant temperature up to 250°C controllable to \pm 0.5°C was used. The prepared reaction ampoules were transferred into the oil bath for predetermined reaction times, and were cooled in an ice bath immediately after the removal from the oil bath. They were opened and the reaction mixture transferred to pre-weighed weighing bottles containing hydroquinone as inhibitor. Conversions and molecular weight averages were then determined as described in Section 3.1.

Because oxygen is a free radical scavenger, it is necessary to degas all of the reactant samples by vacuum treatment. The vacuum line required for the degassing operation was a standard high vacuum apparatus. It consisted of a rotary backing pump, a mercury diffusion pump, a McLeod gauge, a cold trap and ten valved standard taper joints of size B14/23. The schematic diagram is shown in Figure 3-2. The complete degassing procedure follows:-

 The filled reaction ampoule was connected to the vacuum manifold, and immersed in liquid nitrogen.

2) Fifteen minutes later, the value connecting the ampoule to the vacuum line was open and the reactant ampoule was evacuated


for 15 minutes with only the rotary backing pump in operation.

3) The valve was then closed, liquid nitrogen removed, allowing the frozen sample to warm up to room temperature during which the dissolved gases escaped from the reactant. Cracking of the glass ampoule due to expansion of reactant was prevented by warming the frozen ampoule quickly with warm water immediately after the removal of the surrounding liquid nitrogen.

4) The flask of liquid nitrogen was put back again to freeze the sample ampoule.

5) Fifteen minutes later, the value to the vacuum line was open again. The ampoule was evacuated for 5 minute with only the rotary pump in operation, and then 15 minutes with both the rotary pump and the mercury diffusion pump in operation having also the McLeod gauge connected to the vacuum system.

6) The pressure of the system was tested with the McLeod gauge making sure that a vacuum of the order of 10^{-6} mmHg was attained.

7) Liquid nitrogen was removed and the ampoule sealed off using a gas-oxygen torch.

8) The sealed ampoule was warmed with warm water and stored in a dry ice-methanol mixture ready for polymerization at pre-determined temperature.

3.3 Experimental Conditions and Conversion Results

Bulk styrene was polymerized thermally and with di-tertiary-butyl peroxide (DTBP) at temperatures of 100 - 200°C. The experimental conditions are given in Table 3-3 below.

TABLE	3-3	EXPERIMENTAL	CONDITIONS

Temperature °C	100		140		170	200
DTDD	0.0	* (IA)	0.0	(2C)	0.0 (3D)	0.0 (4D)
DTBP (w/w %)	.0.085	(5C)	0.085	(6C)		-
	0.84	(7B)	0.17	(8D)	-	

* The integer refers to experiment number, and the letter indicates the size of glass ampoule used: A - 9 mm., B - 8 mm., C - 7 mm., D - 5 mm. O.D.

The reproducibility of experimental results was investigated by repeating one typical experiment twelve times, for each analyzing for conversion, number and weight average molecular weight. The variation of these measurements allowed the estimation of the overall experimental error accumulated from all successive experimental procedures including the variations in ampoule preparation, reaction temperature and time, weighing, precipitation as well as instrumental errors in the gel permeation chromatograph. Experiment number 5 (Table 3-3) having a DTBP content of 0.085% with a reaction temperature of 100°C and reaction time of 17 hours was chosen for reproducibility studies. This condition resulted a moderate rate of polymerization and molecular weights among all the

the experimental conditions in this study. The standard deviations of measurements among the twelve repeated runs was 1.02% for conversion, 5.8%for $\overline{M}n$ and 4.2% for $\overline{M}w$. The results of the twelve repeats are given in Table 9E-1 (Appendix 9-E). The results for conversions are given in Tables 3-4 and 3-5, and the results for molecular weight averages $\overline{M}n$ and $\overline{M}w$ are given in Table 9B5-4 (Appendix 9-B). The predicted results are calculated from the kinetic model which is presented in the next section.

Sample	Time	Conve	rsion	Sample	Time	Conve	rsion
Code	(hr.)	Measured	Predicted	Code	(hr.)	Measured	Predicted
+ -A	2	0.063	0.062	+ 2-DI	0.5	0.192	0.192
I-A2	3	0.092	0.092	2-D2	1.0	0.336	0.343
1-A3	4	0.124	0.121	2-D3	1.5	0.459	0.466
I-A4	5	0.149	0.149	2-D4	2.0	0.564	0.566
I-A5	6	0.170	0.176	2-D5	2.5	0.653	0.647
I-A6	8	0.226	0.228	2- D6	3.0	0.721	0.711
I-A7	10	0.272	0.277	2-D7	3.5	0.775	0.761
I-A8	12	0.322	0.324	2-D22	4	0.804	0.800
I-A9	14	0.380	0.369	2-D23	6	0.883	0.890
I-A12	20	0.485	0.493	2-D24	8	0.922*	0.928
I-A13	22	0.526	0.531	2-D25	10	0.934*	0.948
I-A14	24	0.551	0.567	2- D26	12	0.945*	0.960
I-A15	26	0.611	0.601	2-D27	15	0.956*	0.970
I-A16	28	0.647	0.633	2-D28	20	0.969*	0.980
I-A17	30	0.672	0.664	2-D29	25	0.947*	0.984
I-A21	46	0.845	0.834	2-D30	35	0.980*	0.990
1-A18	53	0.873	0.875				
I-A23	70	0.916	0.929				
I-A24	85	0.937	0.951				
I-A25	100	0.948	0.963				

TABLE 3-4 CONVERSION RESULTS FOR THERMAL POLYMERIZATION

* Conversions were measured by means of UV-spectrophotometry (Appendix 9-D).

+ Expt. I - Thermal polymerization at 100°C. Expt. 2 - Thermal polymerization at 140°C.

TABLE 3-4 CONT'ED

Sample Code	Time (min)	Conve Measured	rsion Predicted	Sample Code	Time (min)	Conve Measured	rsion Predicted
+ 3-R6/18	10	0.254	0.263	4-H1	I	0.110	0.111
3-R6/19	20	0.446	0.447	4-H2	10	0.627	0.621
3-R6/20	30	0.590	0.581	4-H3	15	0.728	0.730
3-R6/11	45	0.722	0.716	4 - H4	20	0.799	0.794
3-R6/13	60	0.813	0.800	4-H5	25	0.837	0.837
3-R6/14	90	0.880*	0.883	4-H6	30	0.863	0.865
3-R6/16	150	0.922	0.942	4-H7	35	0.879	0.886
3-R6/17	180	0.940*	0.955	4 - H8	40	0.891	0.901
3-R6/12	225	0.955 [*]	0.966	4-H9	50	0.909	0.923
3-R9/11	270	0.962	0.973	4-HI0	60	0.936	0.937
3-R9/13	350	0.965	0.980	4-HII	75	0.959	0.951
3- R9/14	460	0.968	0.986	4-HI2	90	0.970	0.959
3-R9/15	585	0.980*	0.989	4-HI3	120	0.980	0.970
				4-H!4	180	0.990	0.981
ć				4-H15	240	0.992	0.986
				4- HI6	360	0.992	0,991
				4-H17	480	0.993*	0.993

+ Expt. 3 - Thermal polymerization at 170°C Expt. 4 - Thermal polymerization at 200°C

Sample	Time	Conve	rsion	Sample	Time	Conve	rsion
Code	(hr.)	Measured	Predicted	Code	(hr.)	Measured	Predicted
⁺ 5-ЕТ		0.044	0.041	6-F1	0.25	0.176	0.165
5-E2	2	0.088	0.081	6-F2	0.5	0.315	0.315
5-E3	3	0.122	0.121	6-F3	0.75	0.458	0.454
5 - E4	4	0.165	0.161	6-F4	1.0	0.592	0.586
5-E5	6	0.228	0.242	6-F5	1.25	0.699	0.706
5 - E6	8	0.314	0.323	6-F6	1.5	0.806	0.810
5-E7	10	0.380	0.407	6 - F7	1.75	0.896	0.889
5-E8	12	0.491	0.492	6-F8	2.0	0.947	0.942
5-E9	14	0.586	0.585	6F9	2.5	0,969	0.987
5-E10	16	0.680	0.678	6-F10	3.0	0.987	0.997
5-EII	18	0.791	0.772	6-F11	3.5	0.991	0.999
5-E12	20	0.872	0.858	6-F12	4.0	0.994*	1.000
5-E 3	22	0.912	0.924				
5-E14	24	0.950*	0.965				
5-EI5	[.] 26	0.974	0.986				

TABLE 3-5 CONVERSION RESULTS FOR POLYMERIZATION WITH DTBP

* Conversions were measured by means of UV-spectrophotometry (Appendix 9-D).

0.998

+ Expt. 5 - Polymerization at 100°C with 0.085% DTBP Expt. 6 - Polymerization at 140°C with 0.085% DTBP.

0.978*

5-E16

30

TABLE 3-5 CONT'ED

Sample	Time	Conve	rsion	Sample	Time	Conve	rsion
Code	(hr.)	Measured	Predicted	Code	(min)	Measured	Predicted
+ 7-B1	0.5	0.044	0.041	8–G1	5	0.074	0.072
7B2	1.0	0.082	0.081	8-G2	10	0.146	0.140
7-B3	1.5	0.122	0.121	8-G3	15	0.199	0.205
7 - B4	2.0	0.153	0.160	8-G4	20	0.265	0.267
7 - 85	2.5	0.193	0.198	8-G5	25	0.338	0.327
7- B6	4.0	0.301	0.315	8G6	30	0.389	0.386
7 - B7	5	0.381	0.398	8–G7	37.5	0.484	0.471
7 - B8	б	0.469	0.487	8-G8	45	0.531	0,553
7- B9	7	0.583	0.586	8-G9	52,5	0.589	0.633
7-BI0	8	0.711	0.700	8-GI0	60	0.680	0.709
7-B11	10	0.943	0.944	8-G11	75	0.891	0.842
7- B12	12	0.982	0.999	8-G12	90	0.953	0.933
				8-G13	105	0.983*	0.977
				8-GI 4	120	0.989*	0.993
				8-G15	150	0.994*	0.999
				8-GI6	210	n 998 [*]	1.0

+ Expt. 7 - Polymerization at 100°C with 0.84% DTBP Expt. 8 - Polymerization at 140°C with 0.17% DTBP.

4. INTERPRETATION OF DATA AND RESULTS

The interpretation of experimental data was carried out as follows. A model was first proposed and its applicability tested by the goodness of fit between the experimental and predicted values. For each kinetic model being considered the parameters or rate constants were searched to give the best fit based on the Bayesian criterion (Appendix 9-E).

Various kinetic models have been tried (Appendix 9-E). The final accepted kinetic model involved a second order thermal initiation of monomer to form two monoradicals and a first order catalyst decomposition of di-tert-butyl peroxide (DTBP), propagation, transfer to monomer and termination by combination only. i.e.,

Initiation

M +	М	÷	2R <mark>°</mark>	k ¹
	С	→	2R <mark>°</mark> ·	k _d

Propagation

$$R^{\circ}r + M \rightarrow R^{\circ}r+I \qquad k_{p}$$

Transfer to Monomer

$$R_{r}^{\circ} + M \rightarrow P_{r} + R_{l}^{\circ}$$
 k_{fm}

Termination by Combination

$$\begin{array}{cccc} R^{\circ} + R^{\circ} \rightarrow P & k \\ r & s & r+s & k \end{array}$$

A considerable volume shrinkage was observed in the course of polymerization. Volume change was allowed with the use of the variablevolume rate equation assuming that the volume of reaction mixture is linear with conversion (Appendix 9A). The density data of styrene monomer and polymer reported by Patnode and Scheiber ^[57] were used, i.e.,

$$\rho_{\rm m} = 924 - 0.918 (T-273.1) \qquad (4-1)$$

$$\rho_{\rm p} = 1084.8 - 0.605 (T-273.1) \qquad (4-2)$$

where p was density in grams per litre and T was absolute temperature in degrees Kelvin.

The density of styrene monomer beyond its boiling point (B.P. 145°C) was assumed to follow the same relationship extrapolated from pure liquid data. The density of polymer ^[57] was obtained from the measurement of polystyrene produced by thermal polymerization at 100 - 150°C similar to some of the conditions carried out in the present study.

The method of moments was used in the solution of rate equations and the calculation of molecular weight averages. The validity of the steady-state assumption for free radicals was considered. It was found that the steady-state assumption was valid up to very high conversion (about 80%) with only small error encountered near complete conversion as indicated in Appendix 9A-3. The final equations for the proposed kinetic model using the steady-state assumption for free radicals were:

$$R_{p} = -\frac{dM}{dt} = \left(\frac{I}{k_{t}/k_{p}^{2}}\right)^{\frac{1}{2}} M(M_{o} + \epsilon M)/M_{o}$$
(4-3)

$$\frac{d(MP)_{o}}{dt} = \phi_{3} \left[\frac{k_{fm}}{k_{p}} + \frac{\phi_{3}}{2M^{2}} \left(\frac{k_{t}}{k_{p}^{2}} \right) \right] - \frac{(MP)_{o}}{v} \frac{dv}{dt}$$
(4-4)

$$\frac{d(MP)_{|}}{dt} = \frac{\phi_{3}}{1-\phi_{|}} \left[\frac{k_{fm}}{k_{p}} + \frac{\phi_{3}}{M^{2}} \left(\frac{k_{t}}{k_{p}^{2}} \right) \right] - \frac{(MP)_{|}}{v} \frac{dv}{dt}$$
(4-5)

$$\frac{d(MP)_2}{dt} = \frac{\phi_3}{(1-\phi_1)^2} \left[\frac{k_{fm}}{k_p}(1+\phi_1) + \frac{\phi_3}{M^2}(\frac{k_t}{k_p^2})(2+\phi_1)\right] - \frac{\phi_3}{M^2} \left[\frac{k_{fm}}{k_p^2}(1+\phi_1) + \frac{\phi_3}{M^2}(\frac{k_{fm}}{k_p^2})(2+\phi_1)\right] - \frac{\phi_3}{M^2} \left[\frac{k_{fm}}{k_p^2}(1+\phi_1) + \frac{\phi_3}{M^2}(1+\phi_1) + \frac{\phi_3}{M^2}(1+\phi_1)\right] - \frac{\phi_3}{M^2} \left[\frac{k_{fm}}{k_p^2}(1+\phi_1) + \frac{\phi_3}$$

$$\frac{(MP)}{v} \frac{dv}{dt} \qquad (4-6)$$

where

 $\phi_{1} = \frac{1}{1 + \frac{k_{fm}}{k_{p}} + R_{p}(\frac{k_{+}}{k_{p}^{2}}) \frac{M_{o}}{M^{2}(M_{o} + \varepsilon M)} + \frac{\varepsilon R^{o}}{M_{o}}}$ $\phi_{2} = I + R_{p}(\frac{k_{fm}}{k_{p}}) \frac{M_{o}}{M_{o} + \varepsilon M}}$ $\phi_{3} = \frac{\phi_{1}\phi_{2}}{1 - \phi_{1}}$

$$I = 2 k_1 M^2 + 2k_d f C_0 EXP(-k_d+)$$

The details of equation derivation are given in Appendix 9A-1. The solutions of equations (4-3) to (4-6) led to the predicted conversion x, number and weight molecular weight averages $\overline{M}n$ and $\overline{M}w$. In other words, measurements of x, $\overline{M}n$ and $\overline{M}w$ permitted the evaluation of k_{fm}/k_p , k_{t}/k_p^2 and

the rate of radical initiation. The transfer reaction to catalyst was not included as the effect of transfer to DTBP was found to be insignificant.

4.1 Thermal Polymerization of Styrene

For the thermal polymerization alone, equation (4-3) becomes

$$R_{p} = -\frac{dM}{dt} = A M^{2}(M_{o} + \epsilon M)/M_{o}$$
 (4-7)

 $A = \left[(2k_{1})^{\frac{1}{2}} / (k_{1}^{2}/k_{p}^{2}) \right]^{\frac{1}{2}}$ (4-8)

The group of rate constants A directly related to the experimental conversions. A was assumed to vary with conversion as

$$A = A_{0} E_{xp}(A_{1}x + A_{2}x^{2} + A_{3}x^{3})$$
(4-9)

where A_o corresponded to the rate constants at zero conversion. Conversion data were fitted based on equation (4-7) searching for the parameters A_o , A_1 , A_2 and A_3 . The rate constants k_i and (k_t/k_p^2) were then separated using the literature value of $(k_t/k_p^2)_o$ ^[8] for zero conversion and assuming k_i remained constant while allowing (k_t/k_p^2) to vary with conversion dictated by equation (4-9). (k_{fm}/k_p) was estimated from the combined fit of x, Mn and Mw using the values of k_i and k_t/k_p^2 found from conversion

$$k_{fm}/k_p = (k_{fm}/k_p) + A_4 x$$
 (4-10)

The literature values ^[6, 8] of rate constants, in litre/gm-mole.

$$(k_{+})_{o} = 1.255 \times 10^{9} \text{ Exp}(-844/T)$$

 $(k_{p})_{o} = 1.051 \times 10^{7} \text{ Exp}(-3557/T)$ (4-11)
 $(k_{fm})_{o} = 2.31 \times 10^{6} \text{ Exp}(-6377/T)$

The parameters obtained from the search are given in Table 4-1. The temperature dependence of k_i is shown in Figure 4-1, and the variation of (k_{+}/k_{p}^{2}) and (k_{fm}/k_{p}) with conversion are given in Figure 4-2 and 4-3 respectively. Experimental and predicted results of x, Mn, Mw are compared in Figures 4-4 to 4-11. Measured and predicted molecular weight distributions at low and high conversions are shown in Figures 4-12, 4-13.

TABLE 4-1 PARAMETERS FOUND FOR THERMAL POLYMERIZATION

Т°К	Ao	A	A ₂	A ₃	A ₄	^k i
373.1	1.15×10 ⁻⁶	4.229×10 ⁻¹	2.034	1.789×10 ⁻¹	2.48 ×10 ⁻⁴	1.493×10 ⁻¹⁰
413.1	1.61×10 ⁻⁵	3.164×10 ⁻¹	1.447	1.444×10 ⁻²	3.47 ×10 ⁻⁴	5.751×10 ⁻⁹
443.1	7.35×10 ⁻⁵	1.99 ×10 ⁻¹	1.30	0.0	5.61 ×10 ⁻⁴	4.289×10 ⁻⁸
473.1	2.88×10 ⁻⁴	3.119×10 ⁻¹	0.365	0.0	3.686×10 ⁻³	2.685×10 ⁻⁷



FIGURE 4-1 ARRHENIUS RELATIONSHIP OF THERMAL INITIATION RATE CONSTANT K







FIGURE 4-4 CONVERSION - TIME DATA FOR THERMAL POLYMERIZATION

FIGURE 4-5 CONVERSION - TIME DATA FOR THERMAL POLYMERIZATION فتتنك 1.0 0 0 0.8 -0.6 -0.4 140 °C AT T Ó 40 5 20 15 0 Pearting





FIGURE 4-7 CONVERSION - TIME DATA FOR THERMAL POLYMERIZATION









12 FIGURE 4-12 MEASURED AND PREDICTED MOLECULAR WEIGHT DISTRIBUTION (THERMAL) 10-MEASURED PREDICTED 8 6 ×103 4 TEMPERATURE 100 °C. REACTION TIME 2 hr. \overline{M}_n Mw Х 2 391000 703000 MEASURED 0.063 PREDICTED 0.063 416000 737000 4 10² 10³ 104 105 CHAIN LENGTH

FIGURE 4-13 MEASURED AND PREDICTED MOLECULAR 12 WEIGHT DISTRIBUTION (THERMAL) 10 MEASURED 8 PREDICTED × 10⁴ 6 Wr TEMPERATURE 200 °C. 4 REACTION TIME 1.25 hr. Mn $\overline{\mathsf{M}}_{\mathsf{W}}$ X MEASURED 35500 71200 0.959 2 PREDICTED 0.951 34300 70600 48 10² 10³ 104 :0 CHAIN LENGTH



The results shown thus far have demonstrated the possibility of predicting the course of thermal polymerization of styrene to complete conversion with reasonable accuracy employing a simple kinetic scheme accounting for mono-radical initiation, propagation, chain transfer to monomer and termination by combination. The model employs initial values $(k_p)_o$, $(k_{fm})_o$, $(k_{t})_o$ taken from the literature and allows (k_t/k_p^2) and (k_{fm}/k_p) to vary with conversion. The thermal initiation rate constant k, is assumed to depend on temperature alone, and its values so obtained agree well with literature values as shown in Figure 4.1. There is an indication of k, falling off the straight line at 200°C. This effect will be discussed shortly. Industrial uninhibited styrene has been used for the present study without sophisticated purification procedures. The good agreement of k, from Figure 4-1 indicated that variations in polymerization due to trace amount of impurities can be tolerated by the kinetic model in the temperature range, 100 - 200°C, and that the parameters found in this study may therefore be of interest for the design or optimization of industrial polystyrene reactors.

Figure 4-2 shows the change of (k_{+}/k_{p}^{2}) with conversion which is a useful measure of the significance of the viscosity effect. It indicates a very slight viscosity effect at 200°C but with more significance towards the lower temperatures. It is shown in Appendix 9-A that only groups of rate constants can be found from experimental x, \overline{M}_{n} , \overline{M}_{w} and the determination of all individual rate constants is not possible from these measurements

However, the literature reported constants (k_t) and (k_p) and (k_{fm}) alone. are used in the model, the isolation of individual rate constants is possible if we assume that $\mathbf{k}_{\rm fm}$ does not change with conversion. This seems to be a reasonable assumption as k_{fm} is much smaller (8x10⁻² to 3) compared to k_{t} and k_{p} , and is therefore not likely to be appreciably affected by physical limitations due to the gel effect. The ordinate of Figure 4-3, $(k_{fm}/k_p)_o/k_{p}$ (k_{fm}/k_p) is the same as $k_p/(k_p)_0$ when $k_{fm} = (k_{fm})_0$. $(k_+)/(k_+)_0$ can then be calculated and is plotted in Figure 4-14. From Figure 4-3, we see that the relative significance of $k_{\rm D}$ decreases from 100-140°C but increases to a large extent towards 200°C. In other words, the viscosity effect upon k_n decreases from 100-140°C but increases very much towards 200°C, with no significant change from 140°C to 170°C. This strange behaviour may be explained as follows: (1) The proposed kinetic model is completely erroneous; (2) The effect of viscosity depends on both rates of diffusion and chemical reaction, which are strongly depended on temperature. At 100°C being very close to the glass transition temperature of polystyrene there is a large diffusion effect but the magnitude of k_{p} (760) is not large. At temperature as high as 200°C the diffusion effect is much less while k_{n} (5700) is much higher. k_{n} has reached a large value and the actual rate of propagation is reduced significantly by the diffusion step; (3) Temperature affects the equilibrium of the propagation and de-propagation reaction. At the temperature of 200°C, the influence of de-propagation starts to show its effect although the overall reaction is still much favoured to

the right. It has been observed that ^[40] polystyrene prepared with rigorous exclusion of oxygen started to degrade at temperatures above 150°C depending on the molecular weight of the polymer and its method of preparation. Severe degradation was encountered at or above 280°C.

The author tends to favour the last explanation for the strange behaviour of k_p at high temperature. This is also reflected by the slight decrease of k_i from the Arrhenius temperature relationship at 200°C as shown in Figure 4-1. Results from the present study favours completely the monoradical initiation over the di-radical initiation. Di-radical initiation will result in the formation of polymer with a broader distribution of polydispersity of 2 and higher ^[1, 124]

The abnormal behaviour of $(k_{t})/(k_{t})_{o}$ (Figure 4-14) at 200°C may be explained by the variation of k_{fm} . The assumption of k_{fm} being constant tends to underestimate the decrease of k_{p} from (k_{fm}/k_{p}) . A slight underestimation of the rate of decrease of k_{p} with conversion tends to have a more significant effect on k_{t} calculated from $k_{t} = (k_{t}/k_{p}^{2}) \times k_{p}^{2}$. It should also be noted that the extension of literature values to 200°C may also be a source of error in the analysis.

4.2 <u>Catalysed Polymerization of Styrene with</u> <u>Di-tert-butyl Peroxide (DTBP)</u>

For catalysed polymerization allowing for the contribution of thermal polymerization, the rate of polymerization is given by

 $I = 2k_1 M^2 + 2k_d f C_0 EXP(-k_d^{\dagger})$

$$R_{\rm P} = -\frac{dM}{dt} = A^{\dagger}M(M_{\rm O} + \epsilon M)/M_{\rm O} \qquad (4-12)$$

$$A' = [I/(k_{1}^{2}/k_{p}^{2})]^{\frac{1}{2}}$$
(4-13)

where

Again, the group A' is related to conversion directly and can be estimated from conversion data. Thus, A' was assumed to vary with conversion similar to that of thermal polymerization as

$$A' = A'_{o} EXP(A'_{i}X + A'_{2}X^{2} + A'_{3}X^{3})$$
 4-15)

where A_0^1 corresponded to the rate constants at zero conversion, e.g.

$$A_{0}^{\prime} = (2k_{1}M_{0}^{2} + 2k_{d}C_{0})^{\frac{1}{2}}/(k_{1}^{\prime}/k_{p}^{2})^{\frac{1}{2}}$$
(4-16)

The decomposition rate constant of catalyst, k_d , was calculated from initial rate data based on k_i found from thermal polymerization and $(k_t/k_p^2)_o$ from literature (equations 4-11), using equation (4-16). The parameters A'_o , A'_1 , A'_2 and A'_3 were estimated from conversion data as in thermal polymerization.

In the calculation of molecular weight averages \overline{M}_n , \overline{M}_w , the rate constants k_i and k_d were assumed constant while allowing the catalyst efficiency f to vary with conversion as

(4 - |4)

$$f = EXP(f|X)$$
(4-17)

Similar exponential function was reported for the catalyst efficiency leading to good agreements of molecular weights ^[6, 7]. k_{fm}/k_{p} was assumed to followed to same relationship from thermal polymerization. The transfer reaction to catalyst did not appear to be significant and it was not considered here.

The parameters obtained from the experimental data are given in Table 4-2. The variation of $(k_{\rm t}/k_{\rm p}^2)$, and f with conversion are given in Figures 4-15 and 4-16 respectively. Experimental and predicted results of X, $\bar{M}_{\rm n}$ and $\bar{M}_{\rm w}$ are shown in Figures 4-17 to 4-24. Examples of measured and predicted molecular weight distributions are shown in Figures 4-25 to 4-27.

The results of styrene polymerization with di-tert-butyl peroxide (DTBP) as initiator were treated in a similar fashion taking into consideration thermal polymerization. The significance of thermal polymerization at temperatures of 100 and 140°C may be seen in Table 4-3. In all cases, the contribution of thermal initiation is significant compared to the catalysed initiation rates. The decomposition rate constants (k_d) of DTBP obtained from the difference of the overall rate of initiation (from the rate of polymerization) and thermal initiation are given in Table 4-2, along with the literature values. The rate constant k_d found here, and the values reported by Mageli ^[71] and Tobolsky ^[63] all indicated a one-hundred fold difference from 100° to 140°C.

TABLE 4-2 PARAMETERS FOUND FOR POLYMERIZATION WITH DTBP

	С	f.	A' f	rom equa	ition (4	-15)		sec ⁻¹)			
TEMP.	gm-mole/2		A'	A	A;	A'3	Present	Mageli ^[71]	Tobolsky ^[63]	Shaw ^[70]	
100°C	0.00485	-1.782	1.147	0.6016	1.868	0.0	1.1	0.964	0.743	0.389	
			× 10 ⁻⁵	•							
	0.048	-3.175	2.35	0.0171	3.189	0.0073					
•			× 10 ⁻⁵	;					•		
140°C	0.00463	-0.631	1.97	0.088	1.432	0.001	113.5	96.4	72,5	55.0	
			× 10 ⁻⁴	ļ							
	0.00926	-1.078	2.50	0.0	1.384	0.328					
			× 10 ⁻⁴	Ļ				•			





FIGURE 4-17 CONVERSION - TIME DATA FOR EXPT. 5



FIGURE 4-18 CONVERSION-TIME DATA FOR EXPT. 6


















FIGURE 4-25 MEASURED AND PREDICTED DIFFERENTIAL MOLECULAR WEIGHT DISTRIBUTION

MEASURED AND PREDICTED DIFFERENTIAL MOLECULAR FIGURE 4-26 WEIGHT DISTRIBUTION





FIGURE 4-27 MEASURED AND PREDICTED DIFFERENTIAL MOLECULAR

The values of k_d found in this work is perhaps a little bit too high. Industrial grade DTBP of 99% pure was used directly without purification. Impurity such as tert-butyl hydroperoxide is normally present in commercial DTBP. These two peroxides are reported to affect each other synergistically [71] and may be responsible for the slightly higher k_d . This raises an interesting point that the purity of DTBP is very important for industrial polymerization processes and also that the literature reported k_d value based on super-pure DTBP may not be used faithfully for industrial grade initiator.

	° C	$I_{0} \times 10^{6}$ gm-mole/l.sec.		
Temperature	gm-mole/l.	Thermal	Catalysed	Total
100°C	0.00485	0.0191	0.0107	0.0304
	0.048	0.0191	0.1056	0.1247
I 40°C	0.00463	0.67	1.05	1.72
	0.00926	0.67	2.10	2.77

TABLE 4-3 INITIATION RATES THERMALLY AND FROM DTBP

The significance of gel effect in polymerization may be observed from the variation of $(k_{t}^{\prime}/k_{p}^{2})/(k_{t}^{\prime}/k_{p}^{2})$ and f with conversion (Figures 4-15 and 4-16). It is shown that both $(k_{+}/k_{p}^{2})/(k_{+}/k_{p}^{2})$ and f decrease with conversion to a lesser degree at a higher temperature of 140°C indicating a lesser degree gel effect as expected. It is interesting to note that gel effect also depends on the rate of initiation. Gel effect is sometimes referred to as autoacceleration effect which has been reported as the phenomenon of the abnormal increase of rate of polymerization and molecular weight of polymer product. The general explanation is that of the decrease of \boldsymbol{k}_{+} causing the surge of free radical concentration and high rate of polymerization. Higher molecular weight polymer is due to the increasing significance of k_{n} over the decreasing k_{+} . It appears that autoacceleration effect requires a high level of initiation rate as well as the environmental effect on the diffusion of free radicals. A slight S-shape conversion-time curve is shown in Figure 4-19 having a highest rate of initiation compared to Figures 4-17 and 4-4 of the same temperature where autoacceleration is much less prominent. The decrease of $(k_t/k_p^2)/(k_t/k_p^2)$ is more for the case of highest rate of initiation for the same reaction temperature being consistent with the above explanation. The difference in $(k_{+}/k_{D}^{2})/(k_{+}/k_{D}^{2})$ between thermal and catalysed polymerization (Figure 4-15) is, however, too much and cannot be explained by the difference in rates of initiation (Table 4-3).

The behaviour of catalyst efficiency f is quite obvious (Figure 4-16) as the efficiency is lower for a higher catalyst level which has a high probability of recombination to form waste products.

5. DISCUSSIONS

The bulk polymerization of styrene has been studied at temperatures of 100-200°C being close to and higher than the glass transition temperature of polystyrene. The glass transition temperature of polystyrene is about 100°C^[4] depending on molecular weight. Horie et al ^[32] studied the bulk polymerization of methyl methacrylate and styrene to complete conversion and concluded that the final conversion stopped short of complete conversion for polymerization below the glass transition temperature. The present conversion data showed that polymerization at 100°C was very slow near complete conversion. The rate of polymerization near complete conversion (beyond 95%) is much faster at higher temperature. This is in agreement with the finding of Horie et al. The gel effect, as indicated by the variation of $(k_{+}/k_{p}^{2})/(k_{+}/k_{p}^{2})$ with conversion and the conversion-time plots, was also the strongest for the lowest temperature of 100°C as expected. The model, in general, gave a poor fit of the 100°C data. This reflected the complexities of polymerization at 100°C near the glass transition temperature, and perhaps the inadequacy of the present kinetic model.

The rates of polymerization in the present kinetic model assumes a second order dependence with monomer for thermal polymerization and a first order dependence with monomer for catalysed polymerization. This

leads to the prediction of a smaller rate of polymerization near complete conversion for thermal polymerization which is supported by the conversiontime data.

Conversion has been the major variable under consideration for the correction of gel effect. The groups (k_{t}^{2}/k_{p}^{2}) , (k_{fm}^{2}/k_{p}) and f are allowed to vary with conversion leading to good fit of experimental X, \bar{M}_n and \bar{M}_w . The chain length dependence of free radical reactivity [19] has not been considered here and it is doubtful that the reactivity of free radicals do, Ito [34, 35] recently reported on in fact, depend on their chain length. the theory of diffusion controlled radical polymerization and concluded that segmental diffusion is the controlling step and that rate of bimolecular termination in radical polymerization is independent of the molecular weight or chain length of the polymeric free radical. The termination rate constant is also reported to be dependent on conversion, but not the viscosity of the reacting medium. The present treatment of not accounting for the chain-length dependence of rate constant are supported by Ito. However, Ito ignores the influence of initiation rate or radical concentration upon k_{+} and postulates that k_{+} depends on temperature and conversion only. This is in disagreement with Figure 4-15 from the present treatment. The effect of viscosity was not investigated due to experimental difficulty of viscosity measurement.

6. CONCLUSIONS AND RECOMMENDATIONS

Polymerization of bulk styrene was carried out thermally and with di-t-butyl peroxide as initiator to complete conversion in isothermal batch reactors. A kinetic model was developed based on thermal and catalysed initiations, propagation, transfer to monomer and termination reaction by combination. The model gave good agreement with experimental data while at the same time had all the initial rate constants agreed with literature For the range of experimental conditions investigated, gel effect was values. found to be moderate with more significance towards the low temperature of 100°C. The rates of thermal polymerization were high and its contribution in catalysed polymerization with DTBP could not be disregarded. Generally high rates of polymerization have been encountered producing polymer with moderate molecular weights. These experimental data and the kinetic model may be of industrial interests in relation to the large scale production of polystyrene. The usefulness of the model is demonstrated in Appendix 9F3-2where continuous polymerization is simulated using ideal continuous stirred tank and plug flow reactors.

The method of moments was shown to be an efficient method to the solution of polymerization kinetics leading to average molecular weights. Molecular weight distribution may be calculated, when necessary, by the

solution of dead polymer key species. Key species of no more than fifty were found to be sufficient if they were spaced at an equal $\Delta(\log r)$ interval with the minimum and maximum calculated chain length selected depending on the molecular weight of the polymer. The Bayesian criterion of parameter estimation was used in the development of the kinetic model. It was an useful and convenient tool in estimating rate constants from experimental data allowing for experimental errors.

The present study has been the first attempt to develop polymerization kinetics to complete conversion despite the vast number of literature dealing with diffusion controlled polymerization kinetics. The kinetic model obtained in this study is rather primitive and lacks generality required for interpolation and extrapolation purposes. The ultimate goal of the kinetic study is to develop a general model capable of predicting, accurately, the conversions, molecular weights and molecular weight distributions over a wide range of conditions of interest. To achieve this end, additional measurements of free radical concentrations by electron spin resonance (ESR) and rotating sector method are recommended. Such additional information will enable us to isolate all the rate constants possibly leading to the better understanding of the polymerization process. More accurate measurement of molecular weights is also desirable. Difficulties in the measurement of high molecular weight polymer with gel permeation chromatography (GPC) were encountered. High molecular weight polymers tended to give skewed GPC

chromatograms and required large skewing corrections. In addition very high porosity column packing material was required for high molecular weight polymers. This high porosity packing (styragel) was comparatively weak in structure and could subject to compression under repeated operations under high pressure. The method of skewing correction by Balke and Hamielec was the best method available. This method depends on the skewing factor sk which is extremely sensitive to experimental variation. The correlation of sk with peak elution volume based on mono-disperse polymer standard is also subject to question. Further work in chromatogram skewing is being studied by my colleague T. Ishige. Accurate GPC molecular weight measurements require improvement of column packing material as well as the improvement in the correction of the skewing phenomena.

7. NOMENCLATURE			
a	- a constant related to slope of GPC calibration curve equation 984-25		
а	- absorptivity in spectrophotometry, equation 9DI-I		
A	- absorbance in spectrophotometry, equation 9DI-3		
A, A _i	- a parameter related to the concentration of species in the GPC analysis, equations 9B4-1, 2		
A, A, A,A4	- coefficients for thermal polymerization, equations 4-8, 9, 10		
A', A', A', A'z	- coefficients for catalysed polymerization, equations 4-15, 16		
b	- thickness of absorbing sample, equation 9D1-1		
^B ₁ , ^B ₂	- parameters defined in equations 9AI-18, 19		
с.	- concentration		
С	- catalyst molecule or catalyst concentration gm-mole/l.		
C	- initial catalyst concentration gm-mole/l		
c ₁ , c ₂	- constants of GPC calibration curve, equation 9B3-1		
CSTR	- continuous stirred tank reactor		
Cov	- covariance, equation 9E-6		
D _A , D _B	- diffusion coefficient of molecules A, B		
D ₁ , D ₂	- constants of GPC calibration curve, equation 9B3-2		
DMWD	- differential molecular weight distribution		

DTBP	- di-tertiary-butyl peroxide
e	- random error, equations 9E-1, 2
E	- activation energy in Arrhenius equation
E	- expected value of, equation 9E-2
EXP	- exponential of
f	- catalyst efficiency
f	- coefficient in equation 4-17
fi	- response function, equation 9E-1
F	- bilateral Laplace transform of F(v), equation 9B4-14
F(v)	- GPC response or chromatogram, equation 9B4-1
g, gm	- measurement of mass, gram.
G	- moment generating function, equation 9AI-1
GR	- moment generating function for radical species
GP	- moment generating function for dead polymer species
GPC	- gel permeation chromatography
h, h	- resolution factor in GPC
H p	- enthalpy at constant pressure
I	- rate of initiation gm-mole/l.sec.
I	- initial rate of initiation at zero conversion
k	- rate constant, its type defined by subscript
k	- number of responses, equation 9E-1
k	- number of moments of average molecular weight, equation 9B4-11

L	- volume measure, litre
Μ	- monomer molecule, molecular weight or monomer concentration gm-mole/ $\ensuremath{\mathfrak{l}}$
Mo	- initial monomer concentration
M°	- radical resulted from monomer molecule
M _n	- number average molecular weight
м _w	- weight average molecular weight
M rms	- root mean square average molecular weight
Mk	- k th average molecular weight, k = !, 2,
MP	- moment of dead polymer species
MR	- moment of free radical species
MWD	- molecular weight distribution
N _A , N _B	- chain length of reacting species, A, B, equation 2-6
N _i ·	- mole of component i, equation 9A-1
р	- coefficient in polynomial, equation 9B4-10
P, P _o	- radiant power in spectrophotometry, equation 9DI-1
Р	- parameter in GPC, equation 9B4-27
Ρ	- total dead polymer species concentration, equation 9A-12
P'	 dead polymer species concentration, being function of chain length r and reaction time t
Pf	- pclymer weight fraction
Pr	- dead polymer species of chain length r
PFTR	- plug flow tank reactor

q	- number of independent variables, equation 9E-1
q .	- coefficient of polynomial, equation 9B4-9
Q	- mass flow of exit stream, gm/sec.
Q _k	- k th moment, equation 9B4-20
r	- chain length of polymeric species
r	- rate of reaction of component i
r _n	- number average chain length
r _w	- weight average chain length
R	- ideal gas law constant
R°	- total radical concentration, equation 9A-12
R!	- free radical species, being function of chain length r and reaction time t
R° _c	- free radical resulted from the decomposition of a catalyst
R _E	 distance between two reacting molecules at which reaction is possible
Rp	- rate of polymerization, equation 9A-18
R	- total polymer concentration in reactor gm/l.
R° r	- free radical species of chain length r
R(r)	- same as R ¹
R _i	- coefficients in polynomial, equation 9B4-10
S	- dummy variable in generating function
S	- dummy variable in Laplace transform
s _{ij}	- estimates of variance and covariance, equation 9E-10

s ^{ij}	- elements of the inverse of matrix s
sk	- skewing factor in GPC, equation 9B4-24
S	- solvent concentration, gm-mole/%.
S P	- entropy at constant pressure
+	- reaction time
†	- refers to the true value in GPC
Т	- absolute temperature in degrees Kelvin
Т	- transmittance in spectrophotometry
т _с	- ceiling temperature
U,	- coefficient in polynomial, equation 9B4-9
v	- elution volume in GPC
vo	- peak elution volume in GPC
∨ _{ij}	- defined by equation 9E-4
V .	- reactor volume or volume of reaction mixture
Vo	- initial volume at zero reaction time
V _q	- volumetric flow rate at exit of reactor l/sec.
V _{ij}	- co-factor of v _{ij} , equation 9E-5
W	- weight fraction of polymer
Ŵ	- bilateral Laplace transform of W
W _r	- weight fraction of polymer species of chain length r
×	- conversion of monomer, equations 9A-5, 6
×iu	- independent variable, equation 9E-1

- dummy variable for elution volume in GPC y - observations or measured values, equation 9E-1 Уiu - objective functions defined in equations 9E-3, 11, 5 z, z', z Greek Symbols - parameter in equation 9A2-12 α - fractional change in volume on reaction, equation 9A-4 ε - unknown parameters, equation 9E-1 Θ \$1, \$7, \$z - defined in equations 9A-28, 31 and 9A1-28 - density in gm/l ρ - covariance, equation 9E-7 σil σij - element of the inverse of matrix σ_{ii} - osmotic pressure π - viscosity in centipoise μ Subscripts of Rate Constant k d - decomposition of catalyst diff - defined by equation 9E-13 - depropagation reaction dp - transfer reaction to catalyst fc - transfer reaction to monomer fm - transfer reaction to dead polymer fp - second order thermal initiation i - propagation reaction p

t, tc	- termination reaction by combination		
†d.	- termination reaction by disproportionation		
Other Subscripts			
0	- refers to initial value of zero time		
0	- (superscript) indicate a free radical		
0, 1, 2	- refers to the order of moments		
A, B	- refers to molecular species A, B		

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9. APPENDICES

9A. Methods of Solution of the Equations of Free Radical Polymerization

The following general reaction mechanism and kinetic rate equations derived therefrom will now be considered. According to existing theories for the bulk polymerization of styrene, the following elementary chemical reactions may be used to describe free radical polymerization initiated thermally or with an initiator ^[1].

Initiation

	M + M →	2R <mark>°</mark>	κ _i
	C →	2R°	k _d
Propagation			
	R <mark>°</mark> + M →	R° r+l	k _D
Depropagation			r
	R°r+I →	R <mark>°</mark> + M	k dp
Chain Transfer		•	
	R <mark>°</mark> + M →	Pr + R ^o M	k fm
	R°+C →	P _r + C°	k _{fc}
	R° + P →	P _r + R ^o _s	k _{fp}
Termination			
	$R_r^{\circ} + R_s^{\circ} \rightarrow r$	P r+s	k _{tc}
	R° + R° →	Pr + Ps	k _{td}
Other possible reactions, such as termination reaction between primary radicals, depolymerization of dead polymer etc. are not included here. From the theory of diffusion controlled free radical polymerization $[^{3}]$, the rate constants may vary with the viscosity of the reaction medium which is in turn depends on the polymer concentration and molecular weight averages of polymer in the system. They may be depended also on the chain length of the reacting species.

There is a considerable change of volume, i.e., shrinkage, during the course of styrene polymerization ^[46]. Strickly speaking, the volume of the reacting mixture cannot be regarded as constant. In describing the rate equations for a variable-volume reaction system, the rate of change of component i (r_i) is given ^[117],

$$r_{i} = \frac{I}{V} \frac{dN_{i}}{dt} = \frac{I}{V} \frac{d(C_{i}V)}{dt}$$

or

 $r_{i} = \frac{dC_{i}}{dt} + \frac{C_{i}}{V} \frac{dV}{dt}$ (9A-1)

If the volume of reacting mixture varies linearly with conversion of monomer.

 $V = V_{0} (1 + \varepsilon x)$ $\frac{dV}{dt} = V_{0}\varepsilon \frac{dx}{dt}$ $\frac{1}{V} \frac{dV}{dt} = \frac{\varepsilon}{(1+\varepsilon x)} \frac{dx}{dt}$ (9A-3)

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where $\boldsymbol{\epsilon}$ is defined as

$$\epsilon = \frac{V_{x=1} - V_{x=0}}{V_{x=0}}$$
 (9A-4)

being the fractional change in volume of the system between zero conversion and complete conversion. Conversion is defined as the fractional weight of monomer converted and it can be written as

$$c = \frac{M_{o}V_{o} - MV}{M_{o}V_{o}}$$
(9A-5)

which combines with equation (9A-2) to give

>

$$x = \frac{M_{o} - M}{M_{o} + M\epsilon}$$
(9A-6)
$$M = \frac{M_{o}(1-x)}{1 + \epsilon x}$$

or

Now if the assumptions, that all free radicals have the same reactivity and that the free radicals R_M^o , R_C^o and C^o are considered as R_l^o , are made, the rate equations for the described kinetic scheme are:-

$$\frac{dR_{1}^{\circ}}{dt} = I + k_{dp}R_{2}^{\circ} + (k_{fm}M + k_{fc}C) R^{\circ} - R_{1}^{\circ}[k_{p}M + k_{fm}M + k_{fc}C + k_{fp}P + (k_{tc} + k_{td})R^{\circ} + \frac{1}{V}\frac{dV}{dt}] \quad (9A-7)$$

$$\frac{dR_{2}^{\circ}}{dt} = k_{p}M(R_{1}^{\circ} - R_{2}^{\circ}) + k_{dp}(R_{3}^{\circ} - R_{2}^{\circ}) + k_{fp}R^{\circ}P_{2} - R_{2}^{\circ}[k_{fm}M + k_{fc}C + k_{fp}P + (k_{tc} + k_{td})R^{\circ} + \frac{1}{V}\frac{dV}{dt}] \quad (9A-8)$$

$$\frac{dR_{r}^{\circ}}{dt} = k_{p}M(R_{r-1}^{\circ}-R_{r}^{\circ}) + k_{dp}(R_{r+1}^{\circ}-R_{r}^{\circ}) + k_{fp}R^{\circ}P_{r}$$

$$- R_{r}^{\circ}[k_{fm}M + k_{fc}C + k_{fp}P + (k_{tc} + k_{td})R^{\circ} + \frac{1}{V}\frac{dV}{dt}]$$
where r > 2 (9A-9)

Summation of equations (9A-7) to (9A-9) gives

$$\frac{dR^{\circ}}{dt} = I - (k_{tc} + k_{td}) R^{\circ} - \frac{R^{\circ}}{V} \frac{dV}{dt}$$
(9A-10)

where

$$I = 2k_{i}M^{2} + 2k_{d}f C$$
 (9A-11)

$$R^{\circ} = \sum_{r=1}^{\infty} R_{r}^{\circ}$$
, $P = \sum_{r=1}^{\infty} P_{r}$ (9A-12)

Similarly for dead polymer species,

$$\frac{dP_r}{dt} = (k_{fm}M + k_{fc}C + k_{fp}P + k_{td}R^\circ)R_r^\circ - P_r(k_{fp}R^\circ + \frac{1}{V}\frac{dV}{dt}) + k_{tc}\sum_{n=1}^{r/2} R_n^\circ R_{r-n}^\circ$$
(9A-13)

where $r \ge 2$, and the summation in the last term of equation (9A-13) is from 1 to r/2, r/2 being truncated to a integer, e.g., r/2 = 2, when r=4 or 5.

The last term in equation (9A-13) represents the contribution or formation of dead polymer species of chain length r by termination by combination, and is usually given as $\begin{bmatrix} I \end{bmatrix}$,

 $\frac{1}{2} k_{tc} \sum_{n=1}^{r-1} R_n^{\circ} R_{r-n}^{\circ}$

The difference between the two representations is small for large r. One encounters virtually no significant error for styrene kinetics.

There has been a great deal of confusion in the definition of the termination rate constants k_{tc} and k_{td} . The confusion occurs when two of the same size radical terminates, i.e.,

$$R_i^\circ + R_i^\circ \xrightarrow{k_+} P_{2i}$$

Strictly speaking, k_{\dagger} should be defined such that when the disappearance of radical R^{o}_{i} is considered,

$$\frac{dR_i^{\circ}}{dt} = -2k_t [R_i^{\circ}]^2 \qquad (9A-14)$$

and when the formation of dead polymer P_{2i} is considered,

$$\frac{dP_{2i}}{dt} = k_{t} [R_{i}^{\circ}]^{2}$$
(9A-15)

with this convention, equation (9A-10) should be

$$\frac{dR^{\circ}}{dt} = I - (k_{tc} + k_{td})[R^{\circ 2} + \sum_{i=1}^{\infty} R^{\circ 2}_{i}] - \frac{R^{\circ}}{V} \frac{dV}{dt}$$
(9A-10)

The error in equation (9A-10) caused by $\Sigma R_i^{o^2}$ is extremely small and is normally neglected. Equation (9A-13) for dead polymer species follows the same convention as described here.

The rate equations of monomer and catalyst are

$$\frac{dM}{dt} = k_{dp}R^{\circ} - I - (k_{p} + k_{fm})MR^{\circ} - \frac{M}{V}\frac{dV}{dt}$$
(9A-16)

$$\frac{dC}{dt} = -C(k_d + k_{fc}R^{\circ} + \frac{1}{V}\frac{dV}{dt})$$
(9A-17)

Normally, the first two terms in equation (9A-16) are very small compared to the other two terms, and are neglected. Further simplifications lead to

$$R_{p} = -\frac{dM}{dt} = (k_{p} + k_{fm})MR^{\circ}(M_{o} + \epsilon M)/M_{o} \qquad (9A-18)$$

$$\frac{1}{V}\frac{dV}{dt} = -\frac{\varepsilon}{(M_{o} + \varepsilon M)}\frac{dM}{dt} = (k_{p} + k_{fm})\varepsilon R^{\circ}M/M_{o} \qquad (9A-19)$$

Equations (9A-6) to (9A-13) and (9A-17) to (9A-19) completely describe the polymerization system. The molecular weight distribution, and molecular weight averages may be obtained from

$$W_{r} = \frac{rP_{r} + rR_{r}^{\circ}}{M_{o}x}$$
(9A-20)

 $\bar{r}_{n} = \frac{\Sigma r P_{r} + \Sigma r R^{\circ}_{r}}{P + R^{\circ}}$ (9A-21)

$$\bar{r}_{w} = \frac{\Sigma r^{2} P_{r} + \Sigma r^{2} R^{\circ}_{r}}{\Sigma r P_{r} + \Sigma r R^{\circ}_{r}}$$
(9A-22)

where W_r is the weight fraction of dead polymer of chain length r, and \bar{r}_n and \bar{r}_w are number and weight average chain length respectively. The free radical concentrations are much smaller than the dead polymer species concentrations, and they are normally omitted in equations (9A-20) to (9A-22).

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The methods of solution of the kinetic rate equations up to 1958 are summarized by Bamford et al [1]. It was shown that analytical solutions could be obtained for a few kinetic schemes using the steady state assumption for free radicals. The statistical approach and Laplace transformation were shown to be the powerful tools. For complicated kinetic schemes where no analytical solution can be found, numerical solution of these equations may prove to be useful.

Liu and Amundson ^[12] solved the complete set of rate equations numerically for some hypothetical polymer systems. The same method was used by Tebbens ^[5] and Hui ^[6] for the styrene polymerization kinetics. The method, however, is not efficient. It requires much computation time and computer storage being uneconomical for routine calculations.

It should be noted that the rate equations for free radical species are of the type,

$$\frac{dR_{r}^{\circ}}{dt} = D_{1}(t) - D_{2}(t) R_{r}^{\circ}$$
(9A-23)

For some kinetic systems, e.g. styrene, both the positive and negative terms on the right hand side of equation (9A-23) are extremely small. Very small time step is required in the numerical integration routine. Fortunately the numerical solution for styrene kinetics approves the validity of the steady-state assumption for the polymerization of styrene (Appendix 9A3), and the solution of the differential equation (9A-23) is not necessary. For some polymer system where the steady-state assumption

cannot be made, solution of free radical rate equations appears to be stable and straight forward.

For the case where $k_{dp} = k_{fp} = k_{td} = 0$, $k_{t} = k_{tc}$, and that the steady-state assumption for free radicals is valid, it may be shown from equations (9A-7, 8, 9, 13) that,

$$R_{r}^{o} = \phi_{l}R_{r-l}^{o} = \phi_{l}^{r-l}R_{l}^{o}$$
 (9A-24)

$$R_{1}^{o} = \frac{I + (k_{fm}^{M} + k_{fc}^{C})R^{o}}{k_{p}^{M} + k_{fm}^{M} + k_{fc}^{C} + k_{t}^{R}R^{o} + \frac{1}{V}\frac{dV}{dt}}$$
(9A-25)

where

$$\phi_{1} = \frac{k_{p}M}{k_{p}M + k_{fm}M + k_{fc}C + k_{t}R^{\circ} + \frac{1}{V}\frac{dV}{dt}}$$
(9A-26)

 $\frac{dP_{r}}{dt} = \phi_{l}^{r-l} R_{l}^{\circ} \left[k_{fm}^{M} + k_{fc}^{C} + \frac{r k_{t}^{R}}{2\phi_{l}} \right] - \frac{P_{r}}{V} \frac{dV}{dt}$ (9A-27)

Dividing both numerator and denominator of equation (9A-26) by k M and p combining equation (9A-18, 19) leads to

 $\phi_{1} = \frac{1}{1 + \frac{k_{fm}}{k_{p}} + \frac{k_{fc}C}{k_{p}M} + \frac{k_{p}}{k_{p}}(\frac{k_{t}}{k_{p}^{2}}) \frac{M_{o}}{M^{2}(M_{o} + M)} + \frac{\epsilon R^{o}}{M_{o}}}$ (9A-28)

$$R_{1}^{o} = \phi_{1}\phi_{2}/k_{p}M \qquad (9A-29)$$

and

Then,

$$\frac{dP_{r}}{dt} = \phi_{l}^{r} \phi_{2} \left[\frac{k_{fm}}{k_{p}} + \frac{k_{fc}C}{k_{p}M} + \frac{r\phi_{2}}{2M^{2}} \left(\frac{k_{t}}{k_{p}^{2}} \right) \right] - \frac{P_{r}}{V} \frac{dV}{dt} \qquad (9A-30)$$

$$\phi_2 = \mathbf{I} + \left(\frac{k_{fm}}{k_p} + \frac{k_{fc}C}{k_pM}\right) \underset{p}{\mathsf{R}} \left(\frac{M_o}{M_o + \varepsilon M}\right)$$
(9A-31)

The term $\epsilon R^{\circ}/M_{o}$ in equation (9A-28) is very small compared to all other terms in the denominator and may be neglected. Then, all dead polymer species concentrations Pr, depends on I, $(k_{fm}/k_p + k_{fc}C/k_pM)$ and (k_t/k_p^2) only. Molecular weight averages and distributions derived from Pr will also depend on these parameters. The significance of this will be further discussed in the next section.

Equation (9A-27) also indicates that dead polymer species concentration Pr of any chain length r may be calculated directly. Solution of only 20-50 dead polymer species will be sufficient to describe the complete molecular weight distribution and molecular weight averages. Differential molecular weight distribution (DMWD) of polymer are usually measured with the use of gel permeation chromatograph (GPC). Experience with the GPC indicates a requirement of about 30 data points with equal Δv increments to give DMWD of sufficient accuracy. Similar number of dead polymer species concentrations with equal interval of $\Delta(\log r)$ will be needed for the calculation of predicted DMWD and \overline{M}_n , \overline{M}_w . The number of Pr's required, however, should be depended on the complexity of the distribution but not on the maximum or average molecular weights.

9A.1 Method of Moments

The method of moments was proposed by Liu and Amundson [122] as a fast method of calculating molecular weight distribution. It was later used by Ray [123] to obtain number and weight average molecular weight for the optimization of a series of continuous polymer reactors. The method makes use of the moment generating function which is defined as

$$G(s, t) = \sum_{l}^{\infty} s^{l}C^{l} \qquad (9Al-1)$$

The moment generating function for active and dead polymer species may be formed by first, multiplying the species concentration by s^{r} corresponding to the r^{th} chain length for each species and then summing up for all species, i.e.,

$$GR(s,t) = \sum_{n=1}^{\infty} s^{r}R_{r}^{\circ}, \quad GR(1,t) = \Sigma R_{r}^{\circ} = R^{\circ} \qquad (9A1-2)$$

$$GP(s,t) = \sum_{n=1}^{\infty} s^{r}P_{r}, \quad GP(1,t) = \Sigma P_{r} = P \qquad (9A1-3)$$

Solution for these two moment generating functions will allow one to directly calculate the molecular weight averages of polymer in the system.

For the kinetic scheme described above, the rate equations for the radical and polymer moment generating functions may be obtained from equations (9A-7, 9) and (9A-13), i.e.

$$\frac{d GR(s,t)}{dt} = s(I + k_{fm}MR^{\circ} + k_{fc}CR^{\circ}) + k_{fp}R^{\circ}GP(s,t) + GR(s,t)\{k_{p}M(s-1) + k_{dp}(\frac{1}{s} - 1) - k_{fm}M - k_{fc}C - k_{fp}P - (k_{tc}+k_{td})R^{\circ} - \frac{1}{V}\frac{dV}{dt}\}$$
(9A1-4)

$$\frac{d GP(s,t)}{dt} = GR(s,t) \{k_{fm}M + k_{fc}C + k_{fp}P + k_{td}R^{\circ}\} + \frac{1}{2} k_{tc}[GR(s,t)]^{2} - GP(s,t) \{k_{fp}R^{\circ} + \frac{1}{V}\frac{dV}{dt}\}$$
(9A1-5)

It is interesting to note that when $s \rightarrow I$, equation (9AI-4) becomes

$$\frac{d GR(I, t)}{dt} = I - (k_{tc} + k_{td})R^{\circ 2} - \frac{R^{\circ}}{V}\frac{dV}{dt}$$

which is identical to equation (9A-10).

Ideally, solutions of equations (9A-17, 18 and 9A1-4, 5) simultaneously would give M,C, GR(s,t), GP(s,t). Combining with equations (9A-21, 22) gives,

$$\bar{r}_{n} = \frac{d}{ds} \{ ln[GR(s,t) + GP(s,t)] \}_{s=1}$$
 (9A1-6)

$$\bar{r}_{w} = 1 + \frac{d^{2}}{ds^{2}} [GR(s, +) + GP(s, +)]_{s=1} / \frac{d}{ds} [GR(s, +) + GP(s, +)]_{s=1}$$
(9A1-7)

Equations (9AI-4, 5) cannot be solved analytically, in general, except for the special case of steady-state operation. However, they can be broken down to equations for each moment by making use of the properties of moment generating function, i.e.

zero moment (MR)_o = GR(1,t) = R^o_r = R^o (9A1-8)
1st moment (MR)₁ =
$$\frac{\partial}{\partial s} \left[(GR(s,t)]_{s=1} = \Sigma rs^{r-1}R^o_r \right]_{s=1} = \Sigma rR^o_r (9A1-9)$$

2nd moment (MR)₂ =
$$\frac{\partial^{-}}{\partial s^{2}} [GR(s, +)]_{s=1} + (MR)_{1}$$
 (9A1-10)

3rd moment
$$(MR)_3 = \frac{\partial^2}{\partial s^3} [GR(s,t)]_{s=1} + 3(MR)_2 - 2(MR)_1$$
 (9A1-11)

and so on. These lead to the equations of individual moments, i.e.,

$$\frac{d(MR)}{dt} = \frac{dR^{\circ}}{dt} = I - (k_{tc} + k_{td})R^{\circ 2} - \frac{R}{V}\frac{dV}{dt}$$
(9AI-12)
$$\frac{d(MR)}{dt} = I + R^{\circ}[k_{p}M - k_{dp} + k_{fm}M + k_{fc}C + k_{fp}(MP)]$$

$$\frac{d(MR)_2}{dt} = k_{fp}(MR)_0[(MP)_2 - (MP)_1] + 2k_{dp}(MR)_0 + 2(k_pM - k_{dp})(MR)_1 + B_1(MR)_1 + \frac{d(MR)_1}{dt} - B_1(MR)_2$$
(9A1-14)

$$\frac{d(MP)_{o}}{dt} = B_{2}(MR)_{o} + \frac{1}{2} k_{tc}(MR)_{o}^{2} - [k_{fp}(MR)_{o} + \frac{1}{V} \frac{dV}{dt}](MP)_{o} \quad (9A1-15)$$

$$\frac{d(MP)_{I}}{dt} = (MR)_{I} \begin{bmatrix} B_{2} + k_{tc}(MR)_{o} \end{bmatrix} - \begin{bmatrix} k_{fp}(MR)_{o} + \frac{1}{V} \frac{dV}{dt} \end{bmatrix} (MP)_{I} \qquad (9AI-16)$$

$$\frac{d(MP)_{2}}{dt} = (MR)_{2} [B_{2} + k_{tc}(MR)_{0}] + k_{tc}(MR)_{1}^{2} - [k_{fp}(MR)_{0} + \frac{1}{V} \frac{dV}{dt}](MP)_{2}$$
(9A1-17)

and so cn, where

$$B_{I} = k_{fm}M + k_{fc}C + k_{fp}(MP)_{o} + (k_{tc} + k_{td})(MR)_{o} + \frac{1}{V}\frac{dV}{dt} \quad (9AI-18)$$

$$B_{2} = k_{fm}M + k_{fc}C + k_{fp}(MP)_{o} + k_{td}(MR)_{o} \quad (9AI-19)$$

MR = radical moments

MP = dead polymer moments

Equations (9A-17, 18 and 9A1-12 to 17), eight in all, were solved numerically for styrene polymerization allowing the rate constants to vary with time. There is a significant saving of computation time using this method as compared to the direct solution described previously. The method of moments is completely general, and does not depend on the validity of the steady-state assumption for free radicals. It should be pointed out, however, that the equations for radical moments are similar to the type of equation for free radical species (equation 9A-23) and tend to be unstable for styrene kinetics requiring a very small step size in time in the numerical integration solution. This difficulty may be eliminated if the steady-state assumption for free radicals can be made.

For the specific case of conventional styrene kinetics, simplifications can be made if $k_{dp} = k_{fp} = k_{td} = 0$, and $k_t = k_{tc}$. The equations for the radical and polymer moments become.

$$\frac{dGR(s,t)}{dt} = s(I + k_{fm}MR^{\circ} + k_{fc}CR^{\circ}) -GR(s,t)[k_{p}M(I-s) + k_{fm}M + k_{fc}C + k_{t}R + \frac{1}{V}\frac{dV}{dt}] \quad (9AI-20)$$

$$\frac{dGP(s,t)}{dt} = GR(s,t)(k_{fm}M + k_{fc}C) + \frac{1}{2}k_{t}GR^{2}(s,t) - \frac{GP(s,t)}{V}\frac{dV}{dt} \quad (9AI-21)$$

The steady-state assumption for free radicals leads to

$$GR(s,t) = \frac{s(I + k_{fm}MR^{\circ} + k_{fc}CR^{\circ})}{k_{p}M(I-s) + k_{fm}M + k_{fc}C + k_{t}R^{\circ} + \frac{1}{V}\frac{dV}{dt}}$$
(9A1-22)

Dividing the right hand side of equation (9AI-22) top and bottom by

$$(k_{p}M + k_{fm}M + k_{fc}C + k_{t}R^{\circ} + \frac{1}{V}\frac{dV}{dt})$$

$$GR(s,t) = \frac{s}{1-\phi_{1}s} \left[\frac{I + k_{fm}MR^{\circ} + k_{fc}CR^{\circ}}{k_{p}M+k_{fm}M+k_{fc}C+k_{t}R^{\circ} + \frac{1}{V}\frac{dV}{dt}} \right]$$

$$(9AI-23)$$

Further simplification leads to

$$GR(s,t) = \frac{\phi_{1}\phi_{2}s}{k_{D}M(1-\phi_{1}s)}$$
(9A1-24)

where ϕ_1 and ϕ_2 are described in equations (9A-26, 28, 31).

The equations for individual polymer moments may be obtained from equation (9AI-21) and from the properties of moment generating function described in equations (9AI-8 to 11), i.e.,

$$\frac{d(MP)}{dt} = \phi_3 \left[\frac{k_{fm}}{k_p} + \frac{k_{fc}C}{k_pM} + \frac{\phi_3}{2} \left(\frac{k_t}{k_p^2} \right) \frac{1}{M^2} \right] - \frac{(MP)}{V} \frac{dV}{dt}$$
(9A1-25)

$$\frac{d(MP)}{dt} = \frac{\phi_3}{1-\phi_1} \left[\frac{k_{fm}}{k_p} + \frac{k_{fc}C}{k_pM} + (\frac{k_t}{k_p^2}) \frac{\phi_3}{M^2} \right] - \frac{(MP)}{V} \frac{dV}{dt}$$
(9A1-26)

$$\frac{d(MP)_{2}}{dt} = \frac{\phi_{3}}{[1-\phi_{1}]^{2}} \left[(1+\phi_{1}) (\frac{k_{fm}}{k_{p}} + \frac{k_{fc}C}{k_{p}M}) \right]$$
(9A1-27)

+
$$(2+\phi_1)$$
 $(\frac{k_+}{k_p^2}) \frac{\phi_3}{M^2}] - \frac{(MP)_2}{V} \frac{dV}{dt}$ etc.

where

$$=\frac{\phi_1\phi_2}{1-\phi_1} \tag{9A1-28}$$

All the moments of dead polymer species depends only on I, R_p , $(k_{fm}/k_p + k_{fc}C/k_{fm}M)$ and k_t/k_p^2 . This is also true for the molecular weight averages of resulting polymer in the system as the concentration of free radicals is extremely small at all conversions. It may then be said that molecular weight averages can be calculated knowing the relationsips of R_p , I, k_{fm}/k_p , $k_{fc}C/k_pM$, k_t/k_p^2 , C, M with time. The individual values of k_{fm} , k_p , k_{fc} and k_t are not required. This also means that individual rate constants cannot be obtained from experimental measurements of conversion and molecular weight averages. Additional measurement of the total free radical concentration (R°) will be required to uncouple the groups of rate constants.

¢3

Further simplifications can be obtained for the limiting case of zero time or initial rate where the number and weight average chain length can be calculated directly from,

$$\bar{r}_{n} = \frac{(MP)}{(MP)_{0}} = \frac{1}{1-\phi_{1}} \frac{\frac{k_{fm}}{k_{p}} + \frac{k_{fc}C}{k_{M}} + \frac{\phi_{3}}{M^{2}} (\frac{k_{1}}{k_{p}})}{\frac{k_{p}}{k_{p}} + \frac{k_{fc}C}{k_{p}} + \frac{\phi_{3}}{2M^{2}} (\frac{k_{1}}{k_{p}})}{\frac{k_{p}}{k_{p}}}$$
(9AI-29)
$$\bar{r}_{w} = \frac{(MP)_{2}}{(MP)_{1}} = \frac{1+\phi_{1}}{1-\phi_{1}} \frac{\frac{k_{fm}}{k_{p}} + \frac{k_{fc}C}{k_{p}} + \frac{\phi_{3}}{M^{2}} (\frac{k_{1}}{k_{p}}) (\frac{2+\phi_{1}}{1+\phi_{1}})}{\frac{k_{fm}}{k_{p}} + \frac{k_{fc}C}{k_{p}} + \frac{\phi_{3}}{M^{2}} (\frac{k_{1}}{k_{p}}) (\frac{2+\phi_{1}}{1+\phi_{1}})}{(9AI-30)}$$
(9AI-30)

Making use of the fact that at zero time, $\phi_1 = 1$, further manipulation leads to

$$\frac{k_{fm}}{k_{p}} + \frac{k_{fc}C}{k_{p}M} = \frac{2C-1}{(C-1)\bar{r}_{n}}$$
(9A1-31)

$$\frac{k_{p}^{2}}{k_{t}} = \frac{R_{p}}{2M^{2}(\frac{1}{r_{n}} - \frac{k_{fm}}{k_{p}} - \frac{k_{fc}C}{k_{p}M})}$$
(9A1-32)
$$I = \frac{R_{p}^{2}}{(k_{p}^{2}/k_{t}^{2})M^{2}}$$
(9A1-33)

where

 $C = (I - \bar{r}_{w}/2\bar{r}_{n})^{\frac{1}{2}}$, $R_{p} = k_{p}MR^{\circ} = \phi_{3}$

That is to say that the groups $(\frac{k_{fm}}{k_p} + \frac{k_{fc}C}{k_pM})$, k_p^2/k_t and I may be calculated directly from the initial rate data of R_p , \bar{r}_n and \bar{r}_w . This agrees with the results given by Macosko and Weale ^[37] who arrived the same relation-ship from the equation of dead polymer (dP_r/dt).

The usefulness of the method of moments is again demonstrated for the simplified case of styrene kinetics. The interdependence of moment equations dictates the maximum information obtainable from \bar{r}_n and \bar{r}_w . Measurements of higher moments or molecular weight averages will not uncouple the groups of rate constants except to provide more constraints to the values of group constants. Molecular weight distribution (MND) may be calculated from moments via Laguerre polynomials [1, 124]. The accuracy is, however, rather poor unless a large number of moments are available. In general, calculation of MWD is not very efficient from moments unless based on analytical solutions. Molecular weight distribution, differential or cumulative, may be calculated easily from the solution of dead polymer species from equation (9A-13).

It should be pointed out that the method of moments depends entirely on the radical and polymer moment generating functions from the kinetic scheme. The chain length dependence of rate constants will render the derivation of the moment generating functions impossible using any direct addition procedure. It may be said that the method of moments is not suitable when chain length dependence of rate constants must be considered in the kinetic scheme.

The numerical integration of the rate equations may be carried out by any of the conventional methods. The method by Adam-Moulton-Shell [118, 119] was used here. It is a type of predictor-corrector method which allows the calculation of error and adjustment of step-size in the numerical integration. It is a versatile method capable of solution of very unstable solution.

9A.2 Method of Continuous Variable

Zeman and Amundson ^[125-127] solved the equations of polymerization kinetics for continuous and batch reactors using the polymer chain length as a continuous variable. In a continuous stirred tank reactor, an infinite set of mass balance equations for polymer species was reduced to one ordinary differential equation, whereas for a batch reactor, an infinite set of ordinary differential equations was reduced to one partial differential equation. It was demonstrated that the method was general and could be applied to many practical and rather complicated kinetic mechanisms.

The method is based on the Taylor series expansion for a continuous variable. Consider the free radical concentration R is a function of chain length γ , Taylor series expansion gives

$$R(r + \Delta r) = R(r) + \frac{dR(r)}{dr} \Delta r + \frac{1}{2} \frac{d^2 R(r)}{dr^2} (\Delta r)^2 + -- \qquad (9A2-1)$$

if $\Delta r=1$,

$$R(r+1)-R(r) = \frac{dR(r)}{dr} + \frac{1}{2} \frac{d^2R(r)}{dr^2} + --$$
(9A2-2)

or
$$\Delta r = -1$$
, $R(r-1) - r(r) = -\frac{dR(r)}{dr} + \frac{1}{2}\frac{d^2R(r)}{dr^2} ---$ (9A2-3)

Zeman and Amundson ^[126] applied the 1st derivative model considering only the first derivative on the right hand side of equation (9A2-1), and the 2nd derivative model considering both the 1st and 2nd derivatives. It was concluded that the first derivative model is faster and provides sufficient accuracy, especially if the chain length is large and radical concentrations were monotonically decreasing. The second derivative model provided more accurate solutions, but required excessive computation time.

Applying the first derivative model to the same kinetic equations (9A-9) and (9A-13) becomes

$$\frac{\partial R'}{\partial t} = -k_{p}M \frac{\partial R'}{\partial r} + k_{dp} \frac{\partial R'}{\partial r} - R'[k_{fm}M + k_{fc}C + k_{fp}P + (k_{tc} + k_{td}) R^{\circ} + \frac{1}{V} \frac{dV}{dt}] + k_{fp}P'R^{\circ}$$
(9A2-4)

$$\frac{\partial P'}{\partial t} = (k_{fm}M + k_{fc}C + k_{fp}P + k_{td}R^{\circ})R' - P'(k_{fp}R^{\circ} + \frac{1}{V}\frac{dV}{dt}) + k_{tc} \int_{1}^{r/2} R'(\epsilon)r'(r-\epsilon) d\epsilon \qquad (9A2-5)$$

where R' and P' are functions of chain length r and time t.

Equation (9A2-4) can be solved numerically by the method of characteristics $^{\left[116\right]}$, i.e.

$$\left(\frac{dR'}{ds}\right)_{\phi} = \left(\frac{dt}{ds}\right)_{\phi} \frac{\partial R'}{\partial t} + \left(\frac{dr}{ds}\right)_{\phi} \frac{\partial R'}{\partial r}$$
(9A2-6)

where $\left(\frac{dR'}{ds}\right)_{\phi}$ is the directional derivative of R'(r,t) along a set of curves ϕ in the (r,t) plane. Comparing equations (9A2-4) and (9A2-5) leads to

$$\left(\frac{dt}{ds}\right)_{\phi} = 1 \tag{9A2-7}$$

$$\left(\frac{dr}{ds}\right)_{\phi} = \left(\frac{dr}{dt}\right)_{\phi} = k_{dp} - k_{p}M \qquad (9A2-8)$$

equation (9A2-4) becomes

$$(\frac{dR'}{dt})_{\phi} = P'k_{fp}R^{\circ} - R'[k_{fm}M+k_{fc}C+k_{fp}P+(k_{tc}+k_{td})R^{\circ} + \frac{1}{V}\frac{dV}{dt}]$$
 (9A2-9)
Solution of equations (9A2-6, 8, 9) with adjustment of the right time to-
gether will lead to R'(r,t), and P'(r,t). The manipulation, however, is
not straight forward due to the complication in the kinetic scheme [116, 126]

For kinetics which are not easy to solve by the method of characteristics, the partial differential equation (9A2-4) can be solved directly by various finite difference techniques [120], or can be converted back to a series of ordinary differential equations, e.g.

$$\frac{dR'(r)}{dt} = -k_p M \frac{\left[R'(r) - R'(r - \Delta r)\right]}{\Delta r} + k_{dp} \frac{\left[R'(r + \Delta r) - R(r')\right]}{\Delta r}$$
$$-R'(r) \left[k_{fm}^{M+k} c^{C+k} p^{P+(k} + c^{+k} + d)R^{\circ} + \frac{1}{V} \frac{dV}{dt}\right] + P'(r) k_{fp}^{\circ}R^{\circ}$$
(9A2-10)

where $\Delta r \ge 1$. The number of ordinary differential equations (9A-9) is reduced by a factor of Δr . The magnitude of Δr does not cause instability as in the solution, but accuracy will suffer if too large a Δr is used. The method of key species equation is an improvement over the direct solution of all rate equation mentioned earlier and is the most versatile being good for very complex and nonlinear kinetics, but still quite inefficient compared to the method of moments in terms of computation time. A significant simplication may be obtained if the transfer reaction to polymer is not important, $k_{fp} = 0$, and the steady-state assumption for free radicals is valid. Equation (9A2-10) becomes,

$$R(r) = \frac{\left[k_{p}^{MR(r-\Delta r)} + k_{dp}^{R(r+\Delta r)}\right]/\Delta r}{(k_{p}^{M-k}_{dp})/\Delta r + k_{fm}^{M+k}_{fc} C + (k_{tc}^{+k}_{td})R^{\circ} + \frac{1}{V}\frac{dV}{dt}}$$
(9A2-11)

However, if k_{dp} depends on the chain length of reacting radical species, the application of the first derivative model leads to

$$\frac{\partial}{\partial r} \left[(k_{dp}(r) - k_{p}M)R' \right] - \alpha R' = I \qquad (9A2-12)$$
$$= k_{fm}M + k_{fc}C + (k_{tc} + k_{td})R^{\circ} + \frac{1}{V}\frac{dV}{dt}$$

where

Integration from I to r leads to,

α

$$R(r) = \left[\frac{k_{dp}(1) - k_{p}M}{k_{dp}(r) - k_{p}M}\right] R(1) EXP\left\{\int_{1}^{r} \frac{\alpha dy}{k_{dp}(y) - k_{p}M}\right\}$$
(9A2-13)

Further assumption that $k_{dp}(r) = k_{dp}(I)EXP[E(r-I)]$ gives

$$R(r) = \left[\frac{k_{dp}(1) - k_{p}M}{k_{dp}(r) - k_{p}M}\right] R(1) EXP\{D\}$$
(9A2-14)

where

$$D = -\frac{\alpha}{k_{p}M} \{(r-1) - \frac{1}{E} \ln \left[\frac{k_{dp}(r) - k_{p}M}{k_{dp}(1) - k_{p}M}\right]\}$$
(9A2-15)

If k_{dp} does not depend on chain length, on the other hand, the solution for free radical species becomes,

$$R(r) = R(1)EXP[\alpha(r-1)/(k_{dp} - k_{p}M)]$$
(9A2-16)

Solution of R(r) with equation (9A2-5) will lead to the molecular weight distribution and molecular weight averages therefrom.

In summary, the method of continuous variable is a very powerful tool in the solution of polymer kinetics. It is flexible and can be used to account for extremely complicated kinetics including the chain length dependence of rate constants, and it is specially useful when molecular weight distribution of polymer is required.

9A.3 <u>Criterion for Justification of the Steady-State</u> Assumption for Free Radicals

The steady-state for free radicals refers to the state of reaction in which the net rate of change of concentration of radical intermediates is very much less than both their rate of production and their rate of consumption. The equation for total radical (9A-10) ignoring volume change is $dR^{\circ} = -2$

$$\frac{dR^{\circ}}{dt} = I - k_t R^{\circ 2}$$
(9A3-1)

Mathematically, steady-state for free radicals means dR°/dt = 0.

$$R_{ss}^{o} = (I/k_{+})^{\frac{1}{2}}$$
(9A3-2)

If we consider only the early part of polymerization where the rate of initiation (I) is practically constant, equation (9A3-1) can be solved analytically to give

$$R^{\circ} = (I/k_{+})^{\frac{1}{2}} \left[\frac{\exp(2I^{\frac{1}{2}}k_{+}^{\frac{1}{2}}) - I}{\exp(2I^{\frac{1}{2}}k_{+}^{\frac{1}{2}}) + I} \right]$$

$$R^{\circ} = (I/k_{+})^{\frac{1}{2}} \tanh[I^{\frac{1}{2}}k_{+}^{\frac{1}{2}} + 1] \qquad (9A3-3)$$

$$\frac{R^{\circ}}{R^{\circ}} = \tanh[I^{\frac{1}{2}}k_{+}^{\frac{1}{2}} + 1] \qquad (9A3-4)$$

or

 $\frac{R^{\circ}}{R^{\circ}} = \tanh \left[I^{\frac{1}{2}} k_{\dagger}^{\frac{1}{2}} t \right]$ (9A3-4)

The steady-state assumption is justified if $tanh[I^{\frac{1}{2}}k_{\dagger}^{\frac{1}{2}}t]$ equal to or very close to unity. Noting that

tanh (2) = 0.96403
tanh (3) = 0.99505
tanh (6) = 0.99999

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The steady-state assumption will be satisfied if

$$I_{k_{+}}^{1_{2}} + \geq 3$$
 (9A3-5)

for the thermal polymerization of styrene at 100°C,

 $k_{+} = 1.3 \times 10^{8} \text{ lgm-mole.sec}$

The rate of thermal initiation is $I_0 = 1.91 \times 10^{-8}$ gm-mole/l.sec,

$$. I_0^{\frac{1}{2}} k_{\frac{1}{2}}^{\frac{1}{2}} t = 2.5 t$$

It can be said that the total free radical concentration R° reaches steadystate in about two seconds, and the steady-state assumption introduces virtually no error whatsoever. Numerical solution of equation (9A3-1) allowing for variation of initiation rate also led to the same conclusion.

For the bulk polymerization of styrene or methyl methacrylate leading to complete conversion, one would expect all reactions to slow down and stop completely at 100% conversion. In these situations of extremely high conversion, it is natural to suspect the validity of the steady-state assumption, i.e., $(Ik_{+})^{\frac{1}{2}}$ + will be very much less than 1 near 100% conversion.

Calculations of $(Ik_{+})^{\frac{1}{2}}$ were carried out for all the experiments based on the kinetic models described in Section 4, assuming that k_{fm} was independent of conversion. The results for thermal polymerization are given in Figure (9A3-1) and for polymerization initiated with di-tert-butyl peroxide (DTBP) in Figure (9A3-2). The values of $(Ik_{+})^{\frac{1}{2}}$ are seen to be decreasing with conversion as expected. The magnitude of $(Ik_{+})^{\frac{1}{2}}$ is strongly dependent on





temperature being smallest for the lowest temperature of 100°C. The justification of the steady-state assumption as stated by equation (9A3-5) will not be satisfied for the experiments at high conversion. The validity of the steady-state assumption is, however, relative to the time scale and directly related to the rate of polymerization. The rate of polymerization is the highest at the beginning of polymerization where $(Ik_{+})^{\frac{1}{2}}$ is high. At high conversion, the value of $(Ik_{+})^{\frac{1}{2}}$ is smaller indicating a longer time for free radicals to reach steady-state, but the significance of the time scale is reduced by the slower rate of polymerization. Calculations of molecular weight averages with and without the steady state assumption were carried out for all the experiments. There is virtually no difference in the calculated x, \overline{M}_n and \overline{M}_w up to about 50% conversion, and that the maximum error encountered is about 1% towards complete conversion. It may be said that, for practical purposes, the steady state assumption is valid for the bulk polymerization of styrene at conditions encountered in the present study.

9B. <u>Gel Permeation Chromatography (GPC) for the Measurements of</u> Molecular Weight Averages and Molecular Weight Distributions (MWD)

9B.I Introduction

Gel permeation chromatography (GPC) is based on physical separations according to size in porous media, such as cross-linked polystyrene gel or porous glass etc. The characteristic features of the GPC are: (1) separation occurs in liquid phase; (2) molecules are separated by size with the larger molecule eluting first; (3) separation takes place in a limited volume of column packing and depends largely on the size and available pores of the packing material. Because of its ease of operation and success in a large range of molecular separations, GPC has gained guick and wide acceptance by polymer chemists in many fields. The commercial GPC was first introduced by Waters Associates Incorporated in 1963. Many publications have since appeared in the literature dealing with the theories of separation, variables of operations and methods of trace interpretation etc. They are best summed up by Moore ^[77], Altgelt ^[76], Duerksen ^[78] and others ^[75]. In this section, only the interpretation of the GPC trace for linear homopolymer will be discussed. GPC was used mainly as an analytical tool for the measurements of molecular weight averages and molecular weight distributions (MWD) of linear polystyrene.

9B.2 Brief Description of Apparatus and Procedures

The Waters Model-100 gel permeation chromatograph (GPC) was used in the present study. It consisted, of a solvent system for steady flow of carrier solvent, a series of columns for the separation process, a sample injection valve for the input of test samples, an output detection system using a differential refractometer as detector and recording the measurement to a strip chart recorder. A digital translator was also installed to enhance fast handling of output data. Thus, a test sample started going into the instrument through the sample injection device, being separated by the columns, its final concentration detected by the differential refractometer with the signal recorded directly on a strip chart recorder. In addition, the analog signal was digitized through the digital translator and the digital output was punched onto a paper tape as well as printed with a teletype. Solvent was eluted at a constant rate so that retention time of samples was directly related to the amount of solvent eluted. The eluted solvent flowed continuously into the syphon (Figure 9B2-1). The discharge of the syphon triggered an electric signal causing an elution mark on the chart recorder. Each elution mark or count indicated a volume of 5 ml solvent eluted. The analysis time for each measurement varied depending on solvent flow rate and the number of columns used. For normal operation with solvent flow rate of I ml/min. with five 4 foot styragel columns, the complete output response took about 4 hours (about 1 hour for four 4 ft styragel columns at



FIGURE 982-1 GEL PERMEATION CHROMATOGRAPH ASSEMBLY

3 ml/min.), less time was required when overlapping of sample was permissible.

The Waters 3-channel Digital Translator came as an extra separate unit. It provided an option of read-out interval of 20-240 seconds and three different output formats. The twelve 4-digit words with spacing (12 words per line) with no sequence number (and x-off switch at off position) was adapted. These four digits were coded number: the first digit identified the type of result and the last three digits referred to the corresponding magnitude of signal. The first digit must be either 0, 1, 4 or 7. They are referred to as:-

- 0 height of GPC trace
- I heading number for the identification of sample
- 4 injection of sample with the last three digits for time in 1/100 of a read-out interval
- 7 elution marker or counts with the last three digits for time in 1/100 of a read-out interval.

The resulting digital words were then decoded, through the use of a computer program. The digitizer was designed to convert the output of 3 GPC instruments simultaneously to a single typewritten and punched tape record.

The paper tape was the standard I" wide eight channel tape used in the Teletype Model-33. The punched tape output was first converted to binary cards via the IBM Tape to Card Punch Model-46. The binary cards were converted to digital cards via the use of a Macro-Assembly-Program (MAP) for the IBM-7040 computer. The digital cards were then used as input data for decoding and calculation of molecular weights and MWD. An example of the punched tape output and binary card is shown in Figure 9B2-2. The circuit board for the tape to card operation required in the IBM-46 key punch is shown in Figure 9B2-3. In order to start the tape to card operation, the tape must be started from the line return marker (Figure 9B2-2) and the first and second columns of the first card must be punched with both seven and nine. The press of the start button then initiated the operation automatically. FIGURE 9B2-2 DATA OUTPUT OF PAPER TAPE AND BINARY CARD





9B.3 Basic Relationships in the Separation Processes

or

The principle operation of a GPC is the separation of molecules by size. There is a definite relationship between the molecular weights (or hydrodynamic radius) of molecules and its retention time (or elution volume). Experimentally, it is often observed that the peak elution volume is inversely proportional to the logarithm of molecular weight, i.e.

$$= C_1 - C_2 \log_{10} M C_1, C_2 > 0$$
 (9B3-1)

 $M = D_{1} EXP(-D_{2} v) \qquad D_{1}, D_{2} > 0 \qquad (9B3-2)$

A linear calibration curve is often resulted on a semi-log plot of log M vs. v. Linearity for the calibration curve is convenient but not essential.

Molecular weight distributions may be calculated from GPC chromatograms based on the known molecular weight-elution volume relationship or the calibration curve. Strictly speaking, only monodispersed polymer $(\bar{M}_n = \bar{M}_w = \bar{M}_z = --)$ of the same kind may be used for calibration purpose. However, truly mono-disperse standards are as yet unavailable. The root mean square (r.m.s.) average and peak values are normally used [78], i.e.

$$\overline{M}_{r.m.s.} = \sqrt{\overline{M}_{r.m.w}}$$
 (9B3-3)

Many polystyrene standards were available commercially. The polydispersity (\bar{M}_w/\bar{M}_n) of these standards were narrow and usually less than I.I.

Molecular weight distributions (MWD) may be represented in various forms. The ordinate is usually chosen to be the weight fraction of polymer species per unit abscissa. The abscissa may be elution volume v, chain

length r, molecular weight M as well as log M. The normalised version of all these forms follow $\begin{bmatrix} 84 \end{bmatrix}$

$$\int_{0}^{\infty} W(v) dv = \int_{0}^{\infty} W(r) dr = \int_{0}^{\infty} W(M) dM = \int_{0}^{\infty} W(\log M) d(\log M) = 1 \quad (9B3-4)$$

or $W(v)dv = W(r)dr = W(M)dM = W(\log M)d(\log M)$ (9B3-5)

The various forms of MWD may be interchanged easily. The ordinate of weight fraction requires adjustment however, whenever the abscissa is changed. For example, the transformation of MWD from an abscissa of v to M requires the transformation of the abscissa from v to M, and the ordinate from W(v) to W(M) with

$$W(M) = W(v) \quad \frac{dv}{dM} \quad (9B3-6)$$

Similar relationship for the transformation of the ordinates may be obtained from equation (9B3-5). The derivative term, e.g. dv/dM may be obtained from the calibration equation (9B3-1 or 2). A detailed procedure of calculating MWD is given by Yau and Fleming ^[90] for the specific case of logM as abscissa.

The resolution of the GPC is not unlimited as a rule. The response of a single compound appears not as a straight line but mostly as a bellshape Gaussian curve, the width of which depends on the resolution of the columns. In general, two types of correction may be necessary in obtaining the true MWD from GPC Chromatograms: these are the correction for symmetrical axial dispersion and the correction for unsymmetrical skewing. The methods for corrections will be discussed in the following.

9B.4 Methods of Chromatogram Interpretation

9B.4.1 Symmetrical Axial Dispersion

The response of single polymer species is normally assumed to be symmetrical and Gaussian (normally distributed). This may be represented by by ^[84]

$$F(v) = A \sqrt{h / \pi} EXP[-h(v-v_0)^2]$$
 (9B4-1)

where v is the peak elution volume

A is a constant related to the concentration of the species

h is the resolution factor

For a polydispersed sample the chromatogram is a composite of all its components.

$$F(v) = \sum_{i} A_{i} \sqrt{h_{i}/\pi} EXP[-h_{i}(v-v_{o}^{i})^{2}]$$
(9B4-2)

A distribution function W(y) may be used to denote the distribution of components in the system,

$$F(v) = \int_{v_{a}}^{v_{b}} W(y) \sqrt{h/\pi} EXP[-h(v-y)^{2}] dy \qquad (9B4-3)$$

where v_{a} is the initial elution volume and v_{b} the final elution volume of the chromatogram.

The problem of correction for symmetrical axial disperse becomes the solution of Tung's integral equation (9B4-3). The corrected distribution W(y) or W(v) is to be solved given the GPC chromatogram F(v). There have been many methods proposed to solve Tung's integral equation, namely:
(1) Tung's solution by Gaussian Quadrature with linear programming $[^{84}]$; (2) Tung's Hermite polynomial expansion method $[^{84}]$; (3) Method by Smith $[^{87}]$; Fourier transform method by (4) Pierce and Armonas $[^{89}]$ and (5) by Tung $[^{91}]$; (6) the improved polynomial method by Tung $[^{91}]$; (7) analytical solution by Hamielec and Ray $[^{81}]$; (8) point-to-point fitting by Chang and Huang $[^{92}]$.

The methods (2), (3) have been evaluated thoroughly by Duerksen ^[78], method (4) by Balke ^[82], methods (5), (6), and (7) will be discussed below. Tung's Fourier Transform Method ^[91]

Tung's integral dispersion equation can be stated generally as

$$F(v) = \int_{-\infty}^{\infty} g(v-y)w(y) dy \qquad (9B4-4)$$

where the parameters of the instrumental spreading function g(v-y) are independent of molecular weight (or eluent volume). If the instrument spreading can be expressed by Gaussian distribution

$$g(v) = \sqrt{h/\pi} EXP(-hv^2)$$
 (9B4-5)

the solution of equation (9B4-4) by Fourier transform gives

$$w(v) = \left(\frac{1}{2\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} EXP(k^{2}/4h) \{F_{r}(k)\cos(kv) + k_{i}(k)\sin(kv)\} dk \quad (9B4-6)$$

where

$$F_{r}(k) = \left(\frac{1}{2\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} F(v) \cos(kv) dv$$
 (9B4-7)

$$F_{i}(k) = (\frac{1}{2\pi})^{\frac{1}{2}} \int_{-\infty}^{\infty} F(v) \sin(kv) dv$$
 (9B4-8)

The integration in equations (9B4-6, 7, 8) may be carried out numerically. It was pointed out [91] that a variable resolution factor h could also be used although h was considered constant over the entire elution volume range in the derivation. The errors associated in variable h was said to be insignificant.

Tung's Polynomial Method [91]

This method involves the fitting of the chromatogram with a Hermite polynomial, i.e.,

$$F(v) = EXP[-q^{2}(v-v_{0})^{2}] \sum_{i=0}^{4} U_{i}(v-v_{0})^{i}$$
(9B4-9)

where q, v_0 and U_i are adjustable coefficients of a 4th degree of the polynomial. The true or corrected chromatogram is represented by a similar polynomial

$$W(y) = EXP[-p^{2}(v-v_{0})^{2}] \sum_{i=0}^{4} R_{i}(y-v_{0})^{i}$$
(9B4-10)

In this method, only nine data points on the chromatogram were fitted at each time which was different from the previous Hermite polynomial expansion method where the entire chromatogram was fitted altogether. The adjustable coefficients were evaluated by method of least square from the nine data points. The fit was carried out using every point from the GPC Chromatogram as a center point except for the first and the last three points whose values of W were calculated from the polynomials using the 4^{th} and the $(n-4)^{th}$ points as the center points. Variable h can also be used similar to the Fourier method.

Analytical Solution by Hamielec and Ray [81]

When the chain length is assumed to be a continuous variable, the molecular weight averages may be expressed by

$$\frac{M_{k}(h)}{M_{k}(\infty)} = \frac{\int_{v_{a}}^{v_{b}} W(v) M(v)^{k-1} dv / \int_{v_{a}}^{v_{b}} W(v)M(v)^{k-2} dv}{\int_{v_{a}}^{v_{b}} F(v) M(v)^{k-1} dv / \int_{v_{a}}^{v_{b}} F(v) M(v)^{k-2} dv}$$
(9B4-11)

where $M_{\mu}(h)$ = dispersion corrected average molecular weight $M_{L}(\infty)$ = uncorrected average molecular weight W(v) = corrected normalised chromatogram F(v) = un-corrected normalised chromatogramM(v) = molecular weight from the calibration relation = initial elution volume va v_h = final elution volume.

Equation (9B4-11) combining with the calibration equation (9B3-2)

gives

$$\frac{M_{1}(h)}{M_{1}(\infty)} = \frac{\int_{-\infty}^{\infty} F(v) EXP(D_{2}v) dv}{\int_{-\infty}^{\infty} W(v) EXP(D_{2}v) dv} = \frac{\overline{F}(-D_{2})}{\overline{W}(-D_{2})}$$
(9B4-12)

$$\frac{M_{2}(h)}{M_{2}(\infty)} = \frac{\int_{-\infty}^{\infty} W(v) EXP(-D_{2}v) dv}{\int_{-\infty}^{\infty} F(v) EXP(-D_{2}v) dv} = \frac{\overline{W}(D_{2})}{\overline{F}(D_{2})}$$
(9B4-13)

and so on. \bar{F} and \bar{W} are the bilateral Laplace transform of F and W respectively. In general

$$\tilde{F}(s) = \int_{-\infty}^{\infty} F(v) EXP(-sv) dv \qquad (9B4-14)$$

with Tung's integral equation,

$$\overline{F}(s) = (h/\pi)^{\frac{1}{2}} \int_{-\infty}^{\infty} \int_{\infty}^{\infty} W(\gamma) EXP(-h(\nu-\gamma)^2) EXP(-s\nu) d\nu$$
$$= (h/\pi)^{\frac{1}{2}} \overline{W}(s) \int_{-\infty}^{\infty} EXP(-h\nu^2) EXP(-s\nu) d\nu$$

$$= \overline{W}(s) EXP(s^2/4h)$$
 (9B4-15)

Thus, the analytical solutions are,

$$\frac{M_{1}(h)}{M_{1}(\infty)} = EXP(D_{2}^{2}/4h)$$
(9B4-16)

$$\frac{M_2(h)}{M_2(\infty)} = EXP(-D_2^2/4h)$$
(9B4-17)

$$\frac{M_{k}(h)}{M_{k}(\infty)} = EXP\{(3-2k)D_{2}^{2}/4h\}$$
(9B4-18)
k = 1, 2, ---

The ratics of the corrected to uncorrected moments may be expressed as

$$\frac{Q_{k}(h)}{Q_{k}(\infty)} = EXP(-D_{2}^{2}/4h) \frac{k-1}{\pi} EXP\{(3-2(k-j))D_{2}^{2}/4h\}$$
(9B4-19)

where Q_k is the k_{th} moment,

$$Q_{k} = \sum_{r=1}^{\infty} P_{r} r^{k}$$
(9B4-20)

where P_r is the concentration of species of chain length r in gm-mole/litre.

The ratio $D_2^2/4h$ relates directly to the amount of correction required for the number and weight average molecular weight. The instrumental spreading is less if the slope of the calibration curve is small and with a large h-factor (i.e. good column separation). This is not usually achievable, however, if the columns are to be useful for a large range of molecular weight. The columns are usually chosen so that the separation power and the range are compromised for the desirable application. The resolution factor h on the other hand depends largely on the physical state of the column packings.

Evaluation of Tung's Fourier and Polynomial Methods of Correction

The same fictitious two-peak distribution as Tung's ^[91] was used here to test the two methods,

$$w(y) = \frac{100}{\sqrt{\pi}} \left[0.6 \text{ EXP} \{ -0.105625(y-25)^2 \} + 0.4 \text{EXP} \{ -0.105625(y-31)^2 \} \right]$$
(9B4-21)

The uncorrected chromatogram for equation (9B4-21) was,

$$F(v) = 100 \sqrt{\frac{h}{(0.1056+h)\pi}} [0.6EXP\{-0.10562h(y-25)^{2}/(0.1056+h)\} + 0.4EXP\{-0.105625h(y-31)^{2}/(0.1056+h)\}]$$
(9B4-22)

The initial and final elution volumes were chosen at 12 and 44 counts respectively using 65 data point with an interval of 0.5 counts. An arbitrary calibration curve

or

$$V = 56.793 - 4.666 \log_{10} M$$

was used. The corrected \overline{M}_n , \overline{M}_w and \overline{M}_z by both methods were compared with Hamielec's analytical solutions. The results are given in Table 9B4-1, and the corrected distributions W(y) are shown in Figure 9B4-1, with h = 0.1 $\operatorname{count}^{-2}$.

Results showed that the Fourier, polynomial and the analytical solution all gave the same corrected \bar{M}_n , \bar{M}_w and \bar{M}_z for the resolution factor h of 5 and higher. The distribution did not give any observable oscillation in the MWD. As h decreased, however, the results from the Fourier method started to oscillate and become extremely unstable at h = 0.1. At the same h of 0.1, the polynomial method still gave stable MWD and acceptable \bar{M}_n , \bar{M}_w . The short-comings of Fourier method may be overcome by extending the limits of integration ^[91].

In the comparison of the two methods, it is clear that polynomial is superior to the Fourier method. It may be said that Tung's new polynomial method is the best method, at the time of this writing for the correction of symmetrical spreading. The program was relatively simple, using only 9 seconds in a CDC6400 computer for the calculation of 4 curves. The Fourier

TABLE 984-1	COMPARISON	OF	CORRECTED	M _n ,	Μ _w	and	Μz	
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h	Correc	cted Mn >	< 10 ⁻⁵	Corre	ected \bar{M}_{w}	× 10 ⁻⁶	Corre	ected \bar{M}_z	× 10 ⁻⁷
(Count) ⁻²	a*	b*	c*	а	b	· c	а	b	с
5	4.397	4.398	4.398	7.198	7.198	7.198	3,583	3,568	3,569
1	4.397	4.397	4.398	7.198	7.199	7.198	3.583	3,565	3.568
0.25	4.373	4.390	4.398	7.224	7.223	.7.198	4.433	3.558	3.544
0.1	2.316	4.408	4.411	1.198	7.281	7.169	103.9	3.862	3.087

- *a refers to the result by Fourier method
- b refers to the result by Polynomial method
- c refers to the result by Analytical solution



method was equally fast in terms of computer time but had a higher tendency to oscillate. When only \overline{M}_n , \overline{M}_w , \overline{M}_z are required, the analytical solution is of course the best of all.

It should be mentioned that the analytical solution of Hamielec and Ray ^[81] was derived assuming the calibration curve is linear. However, it may be extended for non-linear calibration curve without too much difficulties ^[83].

9B.4.2 Unsymmetrical Axial Dispersion

Excessive axial dispersion in the columns could possibly lead to unsymmetrical chromatograms. Chromatograms predicted by a plug-flow dispersion model for various Peclet numbers are shown in Figure 9B4-2. Other factors such as high polymer molecular weight, high sample concentration and long sample injection time were also reported as causes for skewing chromatogram. Chromatogram skewing have been known for some time, and there have been a few methods proposed for the correction of unsymmetrical axial dispersion.

Hess and Kratz ^[86] were the first to propose a method of correcting for unsymmetrical axial dispersion. Their method was based on a plug-flow dispersion model for a closed vessel. Pickett, Cantow and Johnson ^[88] proposed a method for correction of skewing based on the actual measured shape of narrow standards. Smith ^[87] suggested a log-normal distribution in his analysis. These methods were evaluated and reported by Duerksen ^[78]. The method of Hess and Kratz did not always work out because of occasional

FIGURE 9B4-2 SINGLE SPECIES CHROMATOGRAMS - UNSYMMETRICAL DISTRIBUTIONS PREDICTED BY PLUG-FLOW DISPERSION MODEL



ill-condition of the matrix involved. The two methods by Smith and Pickett et. al. were only partially successful. Smith's log-normal distribution and two-Gaussian halves were proven to be inadequate to account for skewing. The method of Pickett et. al. appeared to over correct for skewing and to introduce severe oscillations in the MWD. The most promising method so far has been the method of Balke and Hamielec ^[82].

Method by Balke and Hamielec

This method follows the analytical solution of Hamielec and Ray that for symmetrical axial dispersion alone,

$$\frac{M_{n}(h)}{M_{n}(\infty)} + \frac{M_{w}(h)}{M_{w}(\infty)} = \exp(D_{2}^{2}/4h) + \exp(-D_{2}^{2}/4h) = 2$$
(9B4-23)

This was observed experimentally by Duerksen and Hamielec ^[79] to be true when the chromatograms were symmetrical. A skewing factor is introduced as the correction factor for the deviation from symmetrical spreading as

$$sk = \frac{M_{n}(+)}{M_{n}(\infty)} + \frac{M_{w}(+)}{M_{w}(\infty)} - (e^{-a/h} + e^{a/h})$$
(9B4-24)

The letter t replaces h and stands for the true value, and

$$a = D_2^2 / 4 = (2.303)^2 / 4 C_2^2$$
 (9B4-25)

Assuming skewing is caused by a shifting of the calibration curve leads to

$$M_{n}(t) = M_{n}(\infty)(1 + \frac{1}{2} \text{ sk})\exp(a/h)$$
(9B4-26)
$$M_{w}(t) = M_{n}(\infty)(1 + \frac{1}{2} \text{ sk})\exp(-a/h)$$

and in general, $M_k(t) = M_k(\infty) (1 + \frac{1}{2} \text{ sk}) \exp((3-2k)a/h)$ k = 1, 2, --the resolution factor h is given by

> $h = 2a/(ln P(\infty) - lnP(t))$ (9B4-27) $P(\infty) = M_{w}(\infty)/M_{n}(\infty)$ $P(t) = M_{w}(t)/M_{n}(t)$

The resolution factor may be calculated directly from equation (9B4-27) from standards with known $M_n(t)$ and $M_w(t)$.

The procedures of correction for both symmetrical and unsymmetrical dispersions are as follows:

a) Both sk and h are obtained over the range of molecular weight under investigation from various standards of known $M_{n}(t)$ and $M_{w}(t)$.

b) The corrected molecular weight averages $M_n(t)$ and $M_w(t)$, for unknown samples are then calculated by equations (9B4-26) using sk and h from known polymer standards.

c) When MWD's of the unknown samples are required, an approximated MWD can be calculated from the original GPC chromatogram F(v) and $M_n(t)$, $M_w(t)$. An effective calibration curve is searched for such that F(v) operated on the new effective calibration curve gives the molecular weights at infinite resolution agree with the calculated true molecular weights. The MWD generated by using the effective calibration curve will approximate the true MWD. It is proved ^[77] that the MWD is exact if F(v) is Gaussian. For simple distributions of F(v), this method of generating MWD is believed to

where

be sufficiently accurate. It is difficult to judge exactly how good is this method of generating MWD for experimental chromatograms because of the difficulty of getting absolute MWD for comparison purposes.

An alternative way of calculation of MWD is to separate the symmetrical and unsymmetrical correction into two parts. The correction for skewing is basically the shifting of the original calibration curve while maintaining the same slope. The calibration curve correcting for skewing is given as

$$M(v) = D_1(sk)EXP(-D_2V)$$
 (9B4-28)

where

$$D_{l}(sk) = D_{l}[l + sk/(exp(-a/h) + exp(a/h))]$$

Now the correction for symmetrical spreading can be applied with Tung's new polynomial method with the corrected calibration curve (equation 9B4-28).

9B.5 Experimental and Results

The number and weight average molecular weights \bar{M}_n , \bar{M}_w of polystyrene samples were measured as well as molecular weight distributions (MWD). The molecular weights of these samples ranged from 40-500 thousands for \bar{M}_n and 80-800 thousands for \bar{M}_w . Significant skewing was observed especially for high molecular weight polymer samples as indicated by mono-disperse polystyrene standards with known \bar{M}_n and \bar{M}_w .

Attempts were made to use commercial Porasil glass columns for high molecular weight polymers with limited success. The plate-counts, which is a measured of the power of column separation, of the two Porasil glass columns of 20-100 microns were 130 and 150 plates per foot using trichlorobenzene. The highly skewed GPC chromatograms with poor resolution resulted from these columns rendered it unsuitable for the purpose required in the present study. The commercial Styragel (cross-linked polystyrene) columns appeared to be still the best at the time of analyses. A similar version of the Waters GPC was reported appearing in the Japanese market recently with their own column packing material. The performance of columns with new packing material has not been investigated.

The polymer samples were analysed with three sets of Styragel columns designated as code 18, 22 and 24. The details of the column combinations are given in Table 985-1. Code 22 was in operation only for a short period of time due to the plugging of column at the end fittings. The results derived from using the three set of columns were cross-checked

using the same narrow and broad polystyrene samples as well as a few independent measurements of \bar{M}_n by membrane osmometry.

The calibration curves for each set of column were obtained using the same narrow polystyrene standards of known \overline{M}_n and \overline{M}_w purchased from Pressure Chemical Company and Waters Associates. The molecular weights of these standards are given in Table 9B5-2. All samples were analysed at a tetrahydrofuran flow rate of 3 ml/min. with a solvent volume of 4.95 ml. to a count. The operating temperature was controlled to 24 \pm 2°C. The results of polystyrene standards are given in Table 9B5.3 and the calibration curves are shown in Figures 9B5-1, 2, 3 for code 18, 22 and 24 respectively.

All polymer samples in the kinetic study were corrected for axial dispersion and skewing using the method of Balke and Hamielec ^[82]. The corrected molecular weight averages were calculated with equation (9B4-26), i.e.,

$$M_{n}(t) = M_{n}(\infty)(1 + \frac{1}{2} \text{ sk}) \text{ EXP}(a/h)$$
$$M_{w}(t) = M_{w}(\infty)(1 + \frac{1}{2} \text{ sk}) \text{ EXP}(-a/h)$$

The values of sk and h were obtained from narrow polystyrene standards. They are plotted against the peak elution volume and shown in Figures 985-4, 5, 6. The results of molecular weight averages of all the polymer samples are given in Table 985-4. The sample is designated by two code numbers. The first number refers to the experiment number of which the conditions are given in Table 3-3. The second number describes the sample of which the corresponding reaction time and conversion may be found in

TABLE 985-1 DESCRIPTION OF COLUMN ARRANGEMENTS AND CONDITIONS

GPC Code	Sample Conc.	Column combination, Maximum rated porosities in Angstroms	Amount Injected	THF Flow rate
18	0.1%	7×10^{6} , 10^{5} , 10^{4} , 900, 800	2 ml	3 ml/min
22	0.5%	>5 × 10 ⁶ , 10 ⁵ , 10 ⁴ , 900	l me	3 ml/min
24	0.5%	7 × 10 ⁶ , 10 ⁵ , 10 ⁴ , 900	l ml	3 ml/min

TABLE 985-2 POLYSTYRENE STANDARDS USED FOR CALIBRATION PURPOSES

Standard	Average	Peak or Av.	Given	M.W.
Designation	used	M×10 ⁻³	$M_{n} \times 10^{-3}$	M _w ×10 ⁻³
SI2a	M	2.03	2.07	2.2
Slla	Nominal	4.8	4.8	4.8
S8a	Peak	10.3	9.7	10.3
\$419 0039	Peak	19.75	19.65	19.85
S7a	Peak	50	49.	51
S4a	Peak	97.2	96.2	98.2
S41984	Peak	171	164	173
S108	M	257	247	267
\$3a	Peak	402	392	411
\$4190038	M	830	773	86.7
S61970	M rms	1987	1780	214.5
NBS706			136.5	257.8
COOPA			116	304

Code Number	P.S. Standards	Peak E.V.	sk	h
18	S12a	40.84	0.2	0.40
	S11a	39.76	0.73	0.39
	S8a	37.57	-0.05	0.42
	S4190039	36.01	-0.30	0.42
	S7a	34.00	-0.39	0.35
	S41984	31.93	-0.18	0.39
	S4190038	29.10	0.02	0.46
	S61970	27.64	1.07	0.24
22	SIIa	34.13	0.32	1.12
	S4190039	32.45	0.05	1.05
	S7a	31.13	-0.04	0.72
	S4a	30.50	-0.10	1.52
	S108	29.38	0.51	0.51
	S3a	28.79	0.25	0.64
	S4190038	27.73	0.10	0.66
	S61970	26.98	1.23	0.51
24*	SIIa	33.64	-0.47	0.25
	S8a	32.20	-0.54	0.28
	S4I90039	31.00	-0.56	0.27
	S7a	29.33	-0.49	0.31
	S4a	28.19	-0.38	0.33
	S41984	27.13	-0.22	0.33
	SI08	26.59	-0.19	0.29
	S3a	25.68	-0.14	0.31
	S4I90038	24.65	-0.13	0.90
	S6I970	23.37	1.30	0.27

TABLE 985-3 RESULTS FOR POLYSTYRENE STANDARDS













TABLE 985-4 RESULTS FOR MOLECULAR WEIGHT AVERAGES

Sample	GPC 🐧	Perfect F	Resolution	Correcte	d Results	Predicted	Results*
Designation	Code	• M _n ×10 ⁻⁵	M _w ×10 ⁻⁵	M _n ×10 ⁻⁵	M _w ×10 ⁻⁵	M _n ×10 ^{−5}	M _w ×10 ⁻⁵
I-A I	18	3.29	8.94	3.91	7.03	4.16	7.37
I-A2	18	3.44	8.63	4.07	6.76	4.12	7.23
I-A3	18	3.47	8.12	4.10	6.36	4.08	7.28
I-A4	18	3.17	8.18	3.74	6.41	4.05	7.24
I-A5	18	3.21	8.45	3.80	6.62	4.02	7.21
I-A6	18	3,68	8.06	4.35	6.31	3.97	7.16
I-A7	18	3.25	8.13	3.84	6.37	3.92	7.12
I-A8	18	3.40	8.29	4.02	6.49	3.88	7.08
I-A9	18	3.41	8.37	4.05	6.57	3.85	7.05
1-A12	18	3.12	8.30	3.69	6.51	3.77	6.99
I-A12	24	3.23	8.81	3.67	6.34	3.77	6.99
I-A13	18	3.19	8.27	3.77	6.48	3.74	6.97
I-AI4	18	3.13	8.22	3.70	6.44	3.72	6,95
I-A15	18	3.17	8.34	3.75	6.56	3.70	6.93
I-A16	18	3.21	8.61	3.81	6.76	3.68	6.91
I-A17	18	2.71	8.26	3.22	6.49	3.66	6.89
I-A21	18	4.07	10.04	4.87	7.97	3.55	6.77
1-A 8	18	3.19	8.82	3.80	6.94	3.52	6.74
I-A18	24	3.58	9.37	4.08	6.78	3.52	6.74

×

Predicted results are calculated from the kinetic model reported in Section 4.

TABLE 985-4 Cont'ed

Sample	GPC	Perfect	Resolution	Corrected	d Results	Predicted	Results*
Designation	Code	M _n ×10 ⁻⁵	M×10	M _n ×10 ⁻⁵	M×10	M _n ×10 ⁻⁵	M_×10 5
2-D1	24	1.41	3.88	1.51	2.64	1.70	2.97
2-D2	18	1.30	4.28	1.48	3.22	1.69	2.98
2-D3	18	1.58	4.76	1.80	3.59	1.68	3.00
2-D4	18	1.57	4.59	1.82	3.54	1.68	3.02
2-D21	24	1.68	4.45	1.82	3.06	1.68	3.02
2-D5	18	1.72	4.93	1.96	3.73	1.68	3.04
2 - D6	18	1.70	4.84	1.94	3.65	1.68	3.06
2-D7	18	1.49	4.26	1.69	3.21	1.68	3.07
2-D22	24	1.57	4.15	1.69	2.83	1.68	3.08
2-D23	24	1.53	4.44	1.65	3.04	I.68	3.10
2-D24	24	1.55	4.58	1.68	3.16	1.67	3.11
2- D25	24	1.48	4.38	1.60	3.01	1.67	3.11
2 - D26	24	1.38	4.14	1.49	2.83	1.67	3.11
2-D27	24	1.27	3.91	1.36	2.67	1.67	3.11
2-D28	24	1.42	4.36	1.54	3.00	1.67	3.11
2-D29	24	1.31	4.22	1.42	2.91	1.67	3.11
2-D30	24	1.35	4.26	1.45	2.92	1.67	3.11
3-R6/18	22	0.75	2.10	1.06	1.80	1.04	1.81
3- R6/20		0.78	2.18	1.10	1.87	1.02	1.83
3-R6/13		0.72	2.14	1.03	I.80	1.01	1.85
3-R6/16		0.70	2.18	1.01	1.83	1.01	1.86
3-R6/12		0.69	2.20	1.00	1.85	1.01	1.87
3-R9/11		0.67	2.26	0.97	1.90	1.01	1.87
3-R9/13		0.63	2.27	0.91	1.91	1.01	1.87

TABLE 985-4 Contied

Sample	GPC	Perfect F	Resolution	Correcte	d Results	Predicte	d Results*
Designation	Code	M ×10	W XIO W	n ×10 n	M ×10 W	n×10	M ×10
4- H I	24	.547	1.48	.543	.931	.618	1.09
4 - H2		.418	1.20	.404	.731	.414	.810
4-H3		.440	1.22	.432	.761	.387	.771
4- H4		. 394	1.17	.385	.725	.373	.751
4 - H5		.400	1.21	.391	.753	.364	.738
4- H6		.373	1.23	.364	.762	.359	.729
4-H7		.387	1.17	.373	.717	.355	.724
4- H8		.365	1.14	.356	.708	.352	.719
4-H9		.334	1.11	.324	.686	.348	.713
4-HI0		.364	1.19	. 354	.732	.345	.710
4-H11		.364	1.15	.355	.712	.343	.706
4-H12		.328	1.08	.319	.666	.341	.704
4-HI3		. 323	1.13	.315	.698	.339	.701
4-114		.339	1.12	. 330	.695	.337	.698
4-HI5		.331	1.13	.323	.700	.337	.697
4-H16		.344	1.23	.353	.763	.336	.695
4-HI 7		.325	1.15	.318	.716	.335	.695

TABLE 985 -4 Contied

Sample Designation	GPC Code	Perfect F M _n ×10 ⁻⁵	Resolution M _w ×10 ⁻⁵	Corrected M _n ×10 ⁻⁵	Results M _w ×10 ⁻⁵	Predicted M _n ×10 ⁻⁵	Results* M _w ×10 ⁻⁵
5-E I	24	3.18	8.03	3.55	5.70	3.76	6.54
5-E2		2.91	7.37	3.26	5.24	3.76	6.57
5-E3		2.95	7.73	3.32	5.53	3.76	6.61
5- E4		2.91	7.51	3.27	5.35	3.76	6.66
5-E5		3.05	7.63	3.43	5.45	3.77	6.74
5- E6		3.05	7.87	3.44	5.64	3.76	6.89
5-E18		2,99	7.56	3.38	5.42	3.76	6.89
5-E8		3.17	8.21	3.59	5.90	3.75	6.94
5-E9		3.45	8.80	3.92	6.34	3.72	6.96
5-EIO		3.69	9.61	4.20	6.95	3.68	6.95
. 5- ETT		3.79	10.09	4.32	7.32	3.63	6.90
5-E12		3.84	10.36	4.34	7.44	3.58	6.84
5-EI3		3.63	10.48	4.15	7.60	3.52	6.77
5-E14		3.70	10.84	4.23	7.88	3.49	6.72
5-E15		3.70	10.56	4.24	7.67	3.46	6,69
5-E16		3.79	10.76	4.36	7.87	3.44	6,66

	TABLE	9B5-4	Cont'	ed
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Sample	GPC	Perfect F	Resolution	Corrected	d Results	Predicte	d Results*
Designation	Code	M _n ×10 ⁻⁵	M _w ×10 ⁻⁵	M _n ×10 ⁻⁵	M _w ×10 ⁻⁵	$\overline{M}_{n} \times 10^{-5}$	M _w ×10 ⁻⁵
6-F1	24	1.16	3.04	1.22	2.03	1.29	2.16
6-F2		1.17	3.21	1.23	2.15	1.30	2.22
6-F3		1.30	3.45	1.38	2.32	1.33	2.29
6-F4		1.25	3.33	1.32	2.23	1.34	2.35
6-F5		1.25	3.44	1.32	2.32	1.36	2.40
6-F6	•	1.35	3.68	1.44	2.49	1.37	2.44
6-F7		1.23	3.59	1.30	2.42	1.36	2.44
6-F8		1.24	3.61	1.33	2.44	1.35	2.43
6-F9		1.20	3.53	1.28	2.38	1.32	2.40
6-F10		1.19	3.61	1.27	2.44	1.29	2,38
.6-F11		1.18	3.70	1.25	2,50	1.26	2.37
6-F12		1.19	3.73	1.27	2.53	1.24	2.37
6-FI 3	•	1.18	3.67	1.26	2.48	1.24	2.37
6-F14		1.12	3,53	1.20	2.39	1.24	2.37
6-F15		1.17	3.58	1.25	2.42	1.24	2.37
6-F16		1.16	3.59	1.24	2.43	1.24	2.37

TABLE 9B5-4 Contled

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	Sample	GPC	Perfect I	Resolution	Corrected	d Results	Predicted	d Results
D	esignation	Code	M_×10 ⁻⁵	M _w ×10 ^{−5}	M_×10 ⁻⁵	M _w ×10 ⁻⁵	m _n ×10 ^{−5}	M _w ×10 ^{−5}
	7-B1	18	2.18	5.04	2.51	3.84	2.37	3.90
	7- B2	24	2.12	5.33	2.32	3.71	2.37	3.90
	7-B2	18	1.90	5.14	2.17	3.89	2.42	4.01
	7 - B3	18	1.93	5.26	2.22	4.00	2.47	4.12
	7 - B4	18	2.02	4.87	2.31	3.69	2.52	4.24
	7 - B5	18	2.04	4.86	2.34	3.69	2.57	4.36
	7- B6	18	1.86	4.96	2.14	3.78	2.72	4. 75
	7-B7	18	1.83	5.17	2.11	3.94	2.82	5.02
	7- B8	18	2.28	5.71	2.65	4.39	2.91	5.29
	7-B9	18	2.16	6.18	2.51	4.76	2.99	5.54
	7-BI0	18	2.72	7.58	3.20	5.90	3.05	5.74
	7-BII	18	3.25	9.82	3.87	7.73	3.07	5.87
	7-B12	18	3.15	10.04	3.75	7.91	3.04	5.84
	7- B12	24	2.86	9.44	3.24	6.78	3.04	5.84
	COOPA	18	1.03	4.42	1.15	3.27		
	NBS-706	18	1.57	4.18	1.78	3.14		
	COOPA	24	1.02	4.15	1.08	2.79		•
	NBS-706	24	1.27	3.88	1.36	2.64		

TABLE 985-4 Cont'ed

Sample	GPC	Perfect	Resolution	Correcte	d Resuits	Predicte	d Results
Designation	Code	M _n ×10 ⁻⁵	M _w ×10	M _n ×10 ⁻⁵	M _w ×10 ⁻⁵	$\overline{M}_{n} \times 10^{-5}$	M _w ×10 ⁻⁵
8-GI	24	1.06	2.79	1.11	1.85	1.09	1.78
8-G2		1.06	2.72	1.10	1.80	1.09	1.80
8 - G3		1.05	2.71	1.10	1.79	1.10	1.82
8 - G4		1.02	2.63	1.06	1.74	1.11	1.85
8-G5		1.13	2.88	1.18	1.91	1.12	1.88
8-G6	•	1.07	2.81	1.11	1.81	1.14	1.91
8-G7		1.08	2.85	1.13	1.88	1.15	1.96
8-G8		1.12	3.03	1.17	2.02	1.17	2.01
8-69		1.19	3.18	1.25	2.13	1.19	2.06
8-GI0		1.19	3.22	1.25	2.15	1.21	2.11
8-GII		1.14	3.30	1.19	2.20	1.22	2.17
8-G12		1.18	3.42	1.24	2.30	1.22	2.18
8-G13		1.12	3.32	1.19	2.23	1.21	2.16
8-GI4		.958	3.32	1.01	2.23	1.19	2.14
8-G15		.917	3.28	.967	2.20	1.15	2.13
8-GI6		.885	3.17	.926	2.11	1.15	2,13
8-G18		.881	2.94	.921	1.95	1.15	2.13
8-G17		.923	3.05	.968	2,03	1.15	2.13

table 3-4 and 3-5. The predicted results in Table 9B5-4 are calculated from the kinetic model as reported in Section 4. The comparison of the corrected and predicted \overline{M}_n and \overline{M}_w is also shown in Figures 4-8, 9, 10, 11 and Figures 4-21, 22, 23, 24.

Corrections of both symmetrical and unsymmetrical dispersions are necessary to obtain the corrected molecular weights, as indicated from the results of broad and narrow polymer standards. The method of Balke and Hamielec ^[82] is chosen here because it is the best method available to-date accounting for both symmetrical and unsymmetrical spreading and be able to give reasonably good results.

The major difficulty of this method is to chose the right values of skewing factor sk. sk is very sensitive to many operating variables. It is extremely sensitive to any inaccuracies that may occur in the calibration curve, and in the values of $M_n(t)$ and $M_w(t)$ for the standards used. At present, sk is assumed to be dependent on peak elution volume alone. Other variables such as polydispersity may also be significant, and may contribute to the scatter of sk values. The molecular weight averages obtained from the different column combinations were cross checked with broad polystyrene standards COOPA and NBS706 and with a few polymer samples. The number average molecular weights of a few polymer samples were also determined by means of membrane osmometry and their results are given in Table 9C-1. The results of the twelve polymer samples obtained from the twelve repeated runs in the polymerization are given in Table 9E-1.

The actual experimental error will be higher because of additional error in sk. The large variations are believed to be contributed to the general poor resolution (h < 0.5 in most cases) and significant skewing effect from the columns. The method of Balke and Hamielec provides a means to overcome these difficulties, however, the ability of the GPC as an analytical tool for the measurement of molecular weights still lies on the process of separation. Accurate measurements call for the need of a better and more stable column packing material.

9C. Measurements of Number Average Molecular Weights (M) by Membrane Osmometry

9C.1 Introduction

Membrane osmometry is one of the most widely used methods for the measurement of molecular weights of high polymer. It is an absolute method and its results are sometimes used as standard references, e.g., for the calibration of other methods such as viscometry and gel permeation chromatography. Membrane osmometry may be used easily to obtain accurate molecular weights for well fractionated polymer samples with \overline{M}_n that are not too low, or for unfractionated samples containing only negligible amount of low molecular weight polymer ^[94].

When a solution is separated from the pure solvent, at the same temperature, by means of a membrane permeable only to the solvent molecules, the osmotic pressure of the solution is defined as the excess pressure which must be placed on it in order to prevent any diffusion of solvent through the membrane. The cause of osmosis is diffusion which arises from a difference in chemical potential; at the same temperature and pressure the solvent substance is at a lower chemical potential in the solution than in its own pure liquid, and there is a tendency for it to pass through the membrane in the direction pure solvent to solution.

Bsed on the thermodynamics of ideal solution, it can be shown that ^[94]

$$\pi_{c=0} = CRT/\overline{M}_{n}$$

$$(9C-1)$$

$$(\pi/c)_{c=0} = RT/\overline{M}_{n}$$

where $\pi_{c=0}$ is the osmotic pressure at infinite dilution.

or

 \overline{M}_n is the number average molecular weight of the solute. Notice that equation (9C-1) is of the same form as the ideal gas law. In general, the osmotic pressure can be expressed as

$$\pi = RT(a_1c + a_2c^2 + a_3c^3 + ---)$$

$$\pi/c = RT(1/M_n + a_2c + a_3c^2 + ---) \qquad (9C-2)$$

where a_1 's are the osmotic virial coefficients. A plot of π/c versus c extrapolated to zero concentration is the conventional method of determination for \tilde{M}_n .

In the present study, number average molecular weights of a few polystyrene samples were measured via osmometry to provide results as reference to the results obtained via gel permeation chromatography.

9C.2 Apparatus and Procedures

The Hewlett-Packard/Mechrolab Model 502 high-speed membrane osmometer was used in the present study. This instrument is claimed to provide a rapid means for measuring osmotic pressure from the indicated hydrostatic head. This is accomplished automatically using a photocell/ electric-servo system. The osmotic pressure is presented on a four digit odometer type readout as well as on a strip-chart recorder. This instrument has a temperature range of ambient to 130°C. Number-average molecular weights in the range of 20,000 to 1,000,000 can be determined with a minimum sample volume of 1 ml per measurement. The Hewlett-Packard/ Mechrolab osmometer was recently evaluated with the two other modern commercial osmometers comparing designs and operating limitations ^[96]. All the commercial instruments being evaluated are of modern design capable of measuring osmotic pressure accurately and rapid enough for routine analysis.

The number-average molecular weights (\overline{M}_n) of all polystyrene samples were measured at 30°C with toluene as solvent using the Hewlett-Packard type 0-8 membrane. About 0.2-0.25 grams of polystyrene were weighed accurately to prepare a 25 ml solution in toluene (8-9 gm/l). Three other solutions at 80, 50 and 25 percent full strength were then prepared by dilution with reagent grade toluene. All dilutions were carried out at 20°C using volumetric flasks. The four polymer solutions and pure toluene were warmed to about 31°C before measurements were carried out. For each polymer sample, four measurements for sample pressure and two for solvent pressure

were made. The result of ($\pi/c)$ was then plotted vs. c and \bar{M}_n was calculated from the intercept.

9C.3 Results and Discussion

The instrument was first used for the measurements of polystyrene standard samples with known \overline{M}_n to ensure that the desired accuracy of measurements were attained. The \overline{M}_n of unknown polystyrene samples were then measured. The results are given in Table 9C-1. The results for polystyrene standards agree well with the known values of \overline{M}_n and the results for polymer samples checked well with the results obtained by the gel permeation chromatography.

It was observed that the experimental error varied with the magnitude of M_n . For very high molecular weights, the osmotic pressures are small resulting more error to the intercept $(\pi/c)_{c=0}$. Higher concentration would give a larger osmotic pressure but may affect the linearity of the plot. In general, \overline{M}_n near 10⁶ and higher are difficult to measure accurately. \overline{M}_n lower than 10,000, on the other hand, tends to go through the membrane. The instrument does not have provision for flushing on the solvent side and measurement of very low molecular weight may cause a positive error in subsequent measurements. For broad polymer samples with significantly low molecular weight tails, apparently high value of \overline{M}_n (low osmotic pressure) will result. There was only one polymer sample (#4-H4) of which \overline{M}_n =46,200 was relatively low. This is only 10% higher than the results given by gel permeation chromatography.
Sample	Conc. (c) gm/l	Sample Press. P (cm.)	Solv. Press. P(cm.)	(PP)/c or π/c	(π/c) _{c=0}	M _n
PS Standard 4A	9.996 7.992	21.82	17.11	0.473	0.283	104,500
	4.998 2.499	19.00	17.12	0.378 0.328		(97,600*)
PS Standard 3A	8.720 6.976	18.73 18.15	16.99 16.99	0.1995 0.1662	0.075	394,000
	4.360 2.180	17.22	16.99	0.1055		(392,000*)
PS Standard 6a	8.892 7.1136 4.446	18.54 18.04	17.15 17.15	0.1575 0.125 0.092	C.04	740,000
	2.223	.17.31	17.16	0.067		(735,000*)
PS Standard NBS 706	10.160 8.128 5.080	20.87 19.89 18.65	17.18 17.18 17.19	0.363 0.330 0.290	0.227	130,400
	2.540	17.85	17.19	0.260		(136,000*)
! - A1	7.900 6.320 3.950	8.45 7.98 7.47 7.2	17.01 17.01 17.02 17.02	0.182 0.153 0.116 0.0912	0.065	416,000

TABLE 9C-1 RESULTS ON OSMOMETRY MEASUREMENTS

* Values of \overline{M}_n supplied by manufacturer.

TABLE 9C-1 Contied

Sample	Conc. (c) gm/l	Sample Press. P.(cm.)	Solv. Press. P _o (cm.)	(PP)/c or π/c	(π/c) _{C=0}	м _п
2-D21	8.620 6.465 4.310 2.155	19.72 18.78 18.07 17.53	17.16 17.16 17.15 17.13	0.297 0.25 0.218 0.185	0.155	190,000
3-R6/18	9.540 7.155 4.770 2.385	21.63 20.17 18.96 17.99	17.18 17.18 17.17 17.17	0.467 0.418 0.376 0.344	0.296	100,000
4 - H4	8.808 6.606 4.404 2.202	24.31 22.30 20.57 18.95	17.46 17.46 17.46 17.47	0.78 0.735 0.707 0.673	0.64	46, 200
5-E3	7.412 5.930 1.853	18.03 17.61 16.84	16.65 16.65 16.65	0.186 0.162 0.1025	0.075	395, 000
6-F2	9.116 6.837 4.558 2.279	20.77 19.64 18.71 17.98	17.40 17.40 17.39 17.39	0.370 0.328 0.29 0.259	0.22	135,000
7 - B2	6.340 4.755 3.170 1.585	18.57 18.06 17.71 17.41	17.22 17.21 17.21 17.21	0.213 0.177 0.158 0.126	0.097	305,000
8-66	8.620 6.460 4.310 2.155	20.64 19.56 18.63 17.83	17.23 17.23 17.23 17.23	0.396 0.3605 0.325 0.278	0.25	118,000

In summary, measurement of number average molecular weight (M_n) by membrane osmometry gave reliable results with accuracy better than 10%. The results are also complementary to those measured via GPC. There is a positive error of about 1% due to the preparation of sample solutions at 20°C and measured at 30°C, caused by thermal expansion of toluene. The error is, however, small compared to the accuracy of the instrument and method of analysis.

9D. Spectrophotometric Determinations of Conversion Beyond 95%

9D.1 Introduction

The determinations of conversion by gravimetric method in the reproducibility study (Appendix 9E) indicated an overall variance of 6.6067 x 10⁻⁵, or a standard deviation of 0.0078 or 0.78%. This represented the overall experimental error incurred throughout all stages of operations from variations of preparation, reaction temperature, precipitation etc. Measurements over 98% conversion showed inconsistency in the results. It was indicated that the accuracy of gravimetric measurement was not sufficient to distinguish the difference of conversions of about 0.5% and under. For the application of polystyrene in food packaging, it is desirable to convert all unreacted monomer and a minimum conversion of 99.9% of monomer is required. A more accurate method of determination is needed at extremely high conversion.

Spectrophotometric measurements of residue monomer styrene in polystyrene were reported by Newell, and Eisenbrand et. al. [101, 100] who claimed an accuracy of $\pm 0.02\%$. The method was based on the absorption of ultraviolet at the region of 245-280 mu by the double bond in the styrene molecule. It has been widely used in industries for the detection of residual monomer in polymer.

Spectroscopy is a common analytical tool and is discussed in most standard textbooks of analytical chemistry ^[106]. It's ability for

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quantitative analysis is based on Beer-Lambert law as

$$\log_{10} P/P_{o} = -abc \qquad (9DI-I)$$

where P is the radiant power of the beam striking the sample

P is the radiant power of the beam transmitted by the sample

b is the thickness of absorbing sample

- c is the concentration of the absorbing constituent of the sample
- a is the absorptivity which depends on condition of measurement. Absorbance A and transmittance T are defined as

$$T = P/P_{O}$$
(9DI-2)

$$A = -\log_{10} T = -\log(P/P_0) = abc$$
 (9DI-3)

Absorbance is directly proportional to concentration of the absorbing constituent. The concentration of an unknown solution can be calculated from the measured absorbance or transmittance provided the calibration relationship between absorbance and concentration is known.

It should be mentioned here that the photometric error in concentration resulted from the instrumental error of the absorbance measurement follows a regular pattern adheres rigidly to Beer's law, i.e.

$$\frac{dc}{dT} = -\frac{0.4343}{abT}$$
 (9DI-4)

and

$$\frac{\Delta c/c}{\Delta T} = \frac{0.4343}{T \log_{10} T}$$
(9DI-5)

 ΔT represents the absolute error in the transmittance and is referred as absolute photometric error. ΔT is usually found to be between 0.002 and 0.01 corresponding to absolute photometric errors of 0.2% and 1% in the transmittance. The variations of the relative error in concentration ($\Delta c/c$) in relation with transmittance (T) is shown in Table 9DI-1 ^[126].

TABLE 9DI-I	VARIATION OF $\frac{\Delta c/c}{\Delta T}$ IN	RELATION TO T
Т	$-\frac{\Delta c/c}{\Delta T}$	- Δc/c (ΔT=0.01)
0.95	20.5	0.205
0.90	10.6	0.106
0.80	5.6	0.056
0.60	3.3	0.033
0.40	2.7	0.027
0.20	3.1	0.031
0.10	4.3	0.043
0.05	6.7	0.067
0.02	12.8	0.128
0.01	43.4	0.434

The error analysis above indicates that one should always adjust the concentration of the sample solution such that its transmittance falls between 0.1 to 0.7 (corresponding to absorbance values between 1 and 0.15)

9D.2 Apparatus and Procedures

A Beckman model DK-1 spectrophotometer was used in the analysis. This is a double-beam photoelectric ratio recording instrument. It is claimed to record linearly in percent transmittance, absorbance or energy versus wavelength continuously over a range from 185 to 3500 millimicrons (mµ) with negligible stray light. The sample and reference cells were l-cm silica rectangular cells with thickness of l cm. The operating procedures for this instruments are described clearly in the Beckman instruction manual and will not be repeated here.

The method of Eisenbrand and Eich [100] was chosen for the analyses of conversion. The weighed sample was dissolved in chloroform, and polystyrene precipitated in methanol. The clear filtrate containing unreacted styrene was used for the measurement of absorbance at 245 µm by the spectrophotometer. Percentage conversion was then calculated from the calibration curve of absorbance vs. styrene concentration. The complete procedures in details are listed below:-

a) About 0.1 gram of polymer sample was weighed and transferred
 into a 50 ml volumetric flask containing about 30 ml reagent grade chloroform.
 The resulting solution was left standing until all polymer was dissolved.
 It was then made up to volume with addition of chloroform.

b) 10 ml of this polymer solution in chloroform was added slowly into 90 ml. of reagent grade methanol in a 125 ml Erlenmeyer flask to allow the precipitation of polymer. c) The resulting mixture was filtered through a course sinteredglass crucible. The filtrate was the sample solution ready for measurement.

d) The reference solution was prepared by adding 10 ml of reagent grade chloroform into 90 ml of reagent grade methanol, similar to the preparation of sample solution.

e) Both transmittance and absorbance were measured at 245 mµ for the sample solution. The concentration of styrene (c mg/100 ml) in the sample solution was read off from the calibration curve at the given absorbance.

f) Calculations

Weight of styrene in sample = 5c (mg)

Percent of styrene in sample = $\frac{5c}{\text{weight of sample (mg)}} \times 100$ Percent of polymer in sample = % conversion

= 100 - Percent of styrene in sample.

9D.3 Results and Discussion

The calibration curve is shown in Figure 9D3-1, which was obtained by the measurements of absorbance of known amounts of freshly distilled styrene in the chloroform-methanol solution. Results agree very well with the data by Eisenbrand and Eich [100].

The results on polymer samples are given in Table 9D3-1. Most of the absorbance-transmittance values lie within the desirable range (absorbance 0.15 to 1.0). One draw back on this method of conversion measurement is that the desirable range of the measured concentration is very narrow. One has to know the conversion quite accurately in order to have the solution made up to the desirable concentration.

The minimum error for concentrations ($\Delta c/c$) occurs at an absorbance of 0.37 (or transmittance of 0.43) as indicated in Table 9DI-I. This is corresponding to a styrene concentration (from Figure 9D3-I) of 0.3 mg/100 ml. The weights of polymer samples at various conversions corresponds to the optimum absorbance (or transmittance) are given in Table 9D3-2.

There is a thousand-fold difference in the polymer sample weight between 10-99.9% conversion to give absorbance of 0.37 with minimum instrumental error. Measurements of conversion for absolutely unknown sample would require trial and error to obtain an acceptable concentration. In general, the UV-spectrophotometry is not suitable for low conversion measurement as it requires too small amount of sample. Conversions beyond



Sample #	Wt. of sample (gram)	Absorbance A	Transmittance T	% (from A)	Conversion (from T)	Average
2-D24	0.0172	0.395	0.418	92.06	92.30	92.18
2-D25	0.0264	0.517	0.310	93.18	93.66	93.42
2- D26	0.03469	0.546	0.295	94.51	94.65	94.58
2- D28	0.0340	0.300	0.515	96.91	97.06	96.98
2-D29	0.0626	0.471	0.350	97.41	97.44	97.42
2- D30	0.0765	0.440	0.362	98.01	98.04	98.02
3-6/13	0:0081	0.43		81.25		81.25
3-6/14	0.0200	0.69		88.00		88.00
3-6/16	0.0206	0.45	•	92.23		92.23
3-6/17	0.0774	1.33		93,99		93.99
3-6/12	0.0330	0.43		95.45		95.45
3-9/11	0.0107	0.11	0.745	96.50	95.79	96.15
3-9/13	0.0283	0.240	0.561	97.17	96.91	96.54
3-9/14	0.0436	0.335	0.488	97.36	96.79	96.83
3-9/15	0.0474	0.268	0.530	98.05	97.94	98.00
4-HI0	0.0205	0.38	0.41	93.68	93.48	93.58
4-H11	0.0128	0.15	0.72	95.90	96.10	96.00
4-HI5	0.0184	0.04	0.88	99.18	99.00	99.09
4-HI6	0.0182	0.04	0.92	99.18	99.37	99.27
4-H17	0.0251	0.05	0.89	99.30	99.20	99.25

TABLE 9D3-1 RESULTS ON SPECTROPHOTOMETRIC MEASUREMENTS

	TABLE	9D3-1	Cont'ed
--	-------	-------	---------

Sample	Wt. of Sample	Absorbance	Transmittance	%	Conversion	
#	(gram)	А	Т	(from A)	(from T)	Average
5-E12	0.0315	1.16	0.07	87.14	87.20	87.17
5-E13	0.0327	0.81	0.17	90.60	91.82	91.21
5-EI4	0.0230	0.33	0.46	95.00	94.90	94.95
5-EI5	0.0230	0.18	0.68	97.28	97.50	97.39
5-E16	0.0500	0.32	0.47	97.75	97.74	97.75
5-EI7	0.0722	0.07	0.83	99.65	99.62	99.63
6-F11	0.0934	0.242	0.564	99.12	99.09	99.80
6-F12	0.1233	0.232	0.612	99.35	99.43	99.39
6-F13	0.2058	0.236	0.575	99.60	99.35	99.48
6-FI4	0.2400	0.274	0.549	99.60	99.62	99.61
6-F15	0.3051	0.171	0.662	99.81	99.79	99.80
6-F16	0.2018	0.071	0.860	99.89	99.89	99.89
8-G12	0.0233	0.311	0.480	· 95.39	95.28	95.34
8-G13	0.1117	0.565	0.285	98.24	98.28	98.26
8-G14	0.0757	0.238	0.571	98,92	98.90	98.91
8-G15	0.0951	0.170	0.710	99.40	99.47	99.43
8-GI6	0.1870	0.115	0.742	99.77	99.76	99.76
8-G17	0.2039	0.060	0.893	99.90	99.91	99.91
8-G18	0.1359	0.028	0.930	99.93	99.93	99.93

99.9% will not be very accurate as they require too high a polymer concentration. Analysis by gas chromatography may be more accurate for this extremely high conversion polymer.

In summary, the UV-spectrophotometric method was used for the measurement of conversion beyond 95% with an accuracy of better than 0.1%. It is an accurate and convenient method for measurements at high conversion if the conversion of sample is known to lie $\frac{1}{2}$.

TABLE 9D3-2 RECOMMENDED WEIGHTS OF POLYMER SAMPLE* AT VARIOUS CONVERSIONS BASED ON STYRENE AT 0.3 mg/100 ml.

¢	Conversion	% styrene	wt. of sample	% conversion	% styrene	wt. of sample
	10	90	1.67 mg	. 95.0	5.0	30 mg
	20	80	1.88 mg	98.0	2.0	75 mg
	50	50	3.0 mg	99.0	1.0	150 mg
	70.0	30	5.0 mg	99.5	0.5	300 mg
	90.0	10	15.0 mg	99.9	0.1	1500 mg

* method of preparation follows procedures described in this section.

9E. Statistical Approach for the Analysis of the Kinetic Data

The objective of the present study has been the development of a kinetic model from experimental conversions x, number and weight average molecular weights \overline{M}_n , \overline{M}_w . The kinetic model must be able to give a good fit of all experimental data, and at the same time does not contradict to the basic knowledge in the field of free radical polymerization. In fact a kinetic model, which follows the true mechanism of reactions and gives exact fit of all data, is the ultimate goal and is most desirable. However most real systems are highly complex , search for the true mechanism and the perfect kinetic model becomes a lengthy, if not an impossible task. An engineering approach to the problem is to place the goodness of fit as the most important criterion, while at the same time to try to develop a model consistent with our understanding of the phenomena encountered. This section concerns the mathematical techniques of model fitting.

Statistical analysis for experimental design, model descrimination and parameter estimation for single and multiple response situations have been reported recently [107-114]. For the present study, the kinetic model is to be derived from the three measured variables x, \overline{M}_n and \overline{M}_w , and the problem encountered is of multi-response. The treatment here follows directly the work of Box and Draper [108] entitled "The Bayesion Estimation of Common Parameters from Several Responses".

Defining y_{iu} (i = 1, 2, ---k; u = 1, 2, --- n) as n sets of observations on each of k responses, and x_{iu}^q (i = 1, 2, ---k; u = 1, 2 --- n, q = 1, 2, --- r) as r independent variables corresponding to the n sets of observations on each of k responses, the model can be represented by

$$y_{iu} = f_i(x_{iu}^q, \Theta_h) + e_{iu}$$
(9E-1)

where f_i are response functions of known form, and Θ_h (h = 1, 2, --- m) are m unknown parameters to be estimated. e_{iu} represent random errors which are assumed to be normally distributed with mean zero, i.e.

$$\begin{split} & \mathsf{E}(\mathsf{e}_{\mathsf{i}\mathsf{u}}) = 0 \text{ all } \mathsf{i}, \, \mathsf{u}; \, \mathsf{E}(\mathsf{e}_{\mathsf{i}\mathsf{u}}, \, \mathsf{e}_{\mathsf{j}\mathsf{v}}) = 0 \text{ all } \mathsf{i}, \, \mathsf{j}, \, \mathsf{u} \neq \mathsf{v}; \qquad (9\mathsf{E}-2) \\ & \mathsf{E}(\mathsf{e}_{\mathsf{i}\mathsf{u}}^2) = \sigma_{\mathsf{i}\mathsf{i}}; \, \mathsf{E}(\mathsf{e}_{\mathsf{i}\mathsf{u}}, \mathsf{e}_{\mathsf{j}\mathsf{u}}) = \sigma_{\mathsf{i}\mathsf{j}}, \, \mathsf{i} \neq \mathsf{j} \text{ for all } \mathsf{u}. \end{split}$$

where E() means the expectation of, and σ_{ij} are variances and covariances. In general, a function of quadratic form z may be formulated

$$z = \sum_{i=1}^{k} \sum_{j=1}^{k} \sigma^{ij} v_{ij}$$
(9E-3)

where σ^{ij} are elements obtained from the inverse of the covariance matrix and v_{ij} is defined as

$$v_{ij} = \sum_{u=1}^{n} \{y_{iu} - f_i(x_{iu}^q, \underline{\Theta})\} \{y_{ju} - f_j(x_{ju}^q, \underline{\Theta})\}$$
(9E-4)

which are the sums of squares and sums of products of the deviations of the observed values y_{iu} 's from their respective responses.

The problem of estimating parameters $\underline{\Theta}$ is to choose a set of $\underline{\Theta}$ such that z is a minimum. This is normally referred to as the generalised least square method. The minimization of z is the same as the minimization of error weighed by σ^{ij} 's.

When σ^{ij} 's are unknown, the Bayesian criterion of estimation may be used. In this case, the parameter $\underline{\Theta}$ is selected until the determinant of matrix v_{ij} is at a minimum,

$$z_{o} = |v_{ij}| = \sum_{i=1}^{k} v_{ij} = \sum_{i=1}^{k} \sum_{j=1}^{k} v_{ij} |v_{ij}|^{k}$$
(9E-5)

where V_{ij} is the co-factor of $|v_{ij}|$.

The covariance matrix refers to the matrix whose elements are covariances and variances of two or more random variables, i.e.

$$Cov(\underline{y}) = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \cdots & \sigma_{1k} \\ \sigma_{21} & & & \\ \sigma_{k1} & \sigma_{k1} & \cdots & \sigma_{kk} \end{bmatrix}$$
(9E-6)

and the covariance σ_{ii} is defined as

$$\sigma_{ij} = E[(\gamma_i - E(\gamma_i))(\gamma_j - E(\gamma_j))]$$
(9E-7)

$$\sigma_{ij} = E[(\gamma_i - \overline{\gamma}_i)(\gamma_j - \overline{\gamma}_j)]$$

$$\sigma_{ii} = E[(\gamma_i - \overline{\gamma}_i)^2] = \sigma_i^2$$
 (9E-8)

|f i = j,

)

or

$$\sigma_{11} = \sigma_{1}^{2} = \int_{-\infty}^{\infty} (\gamma_{1} - \overline{\gamma}_{1})^{2} f(\gamma_{1}) d\gamma_{1}$$

The variance σ_{ii} may be estimated from a random sample of size n using the unbiased estimator [115]

$$s_{ii} = \frac{1}{n-1} \sum_{u=1}^{n} (y_{iu} - \overline{y}_{i})^2$$
 (9E-9)

In general,

$$s_{ij} = \frac{1}{n-1} \sum_{u=1}^{n} (y_{iu} - \bar{y}_{i})(y_{ju} - \bar{y}_{j})$$
 (9E-10)

In the present study, three variables (x, \bar{M}_n , \bar{M}_w) were measured and the number of responses was k=3. For the twelve repeated observations as tabulated in Table 9E-1, the number of observations was n=12. Using the unbiased estimator (equation 9E-10) for variance and covariances, the estimate for the covariance matrix was

$$\begin{bmatrix} s_{ij} \end{bmatrix} = \begin{bmatrix} 6.067 \times 10^{-5} & 1.345 \times 10^{2} & 6.485 \times 10^{1} \\ 1.345 \times 10^{2} & 5.13 \times 10^{8} & 3.552 \times 10^{8} \\ 6.485 \times 10 & 3.553 \times 10^{8} & 9.341 \times 10^{8} \end{bmatrix}$$

and inverse $[s_{ij}]^{-1} = [s^{ij}]$ was

	1	- 3.373×10 ⁴	-9.804×10 ⁻³	1.386×10 ⁻³ -	ľ
[s ^{ij}]	=	-9.804×10 ⁻³	5.495×10 ⁻⁹	-1.409×10 ⁻⁹	
	i	1.386×10 ⁻³	-1.409×10 ⁻⁹	1.510×10 ⁻⁹ -	1

Sample Designation	Conversion	Perfect M _n ×10 ⁻⁵	Resolution M _w ×10 ⁻⁵	Corrected M _n ×10 ⁻⁵	Results M _w ×10 ⁻⁵
5-E22	0.7560	3.40	9.50	3.87	6.88
5- E24	0.7593	3.43	10.04	3.92	7.29
5-E26	0.7478	3.34	10.23	3.82	7.42
5-E27	0.7474	3.37	9.64	3.83	6.95
5-E28	0.7516	3.18	9.74	3.62	7.05
5- E29	0.7504	3.24	10.66	3.72	7.77
5-E30	0.7515	3.65	10.73	4.18	7.80
5-E33	0.7584	3.47	10.36	3.98	7.53
5-E34	0.7705	3.84	10.52	4.39	7.63
5ЕЗ5	0.7649	3.52	10.19	4.01	7.38
5- E36	0.7566	3.48	10.02	3.98	7.27
5- E37	0.7686	3.74	10.42	4.29	7.60
Mean	0.7569			3.97	7.38
Standard deviation	0.0078			0.23	0.31

TABLE 9E-1 RESULTS OF THE TWELVE REPEATED POLYMERIZATIONS

The criteria of estimation becomes the choice of $\underline{0}$ (which is the kinetic rate constants in this case) such that

 $z' = \sum_{i=1}^{3} \sum_{j=1}^{3} i_{j} v_{ij}$ (9E-11)

is at the minimum. The resulting set of parameters $\underline{0}$ will be the best estimates for the given kinetic model under consideration, provided the estimated covariance matrix is the true representative of all the errors involved. However, it is doubtful that the covariance matrix estimated from twelve repeats at only one polymerization condition can represent the experimental errors for all other conditions. In fact the experimental errors in the molecular weight measurements were higher due to the error involved in the sk factors (Appendix 9B-5). The Bayesian criterion (equation 9E-5) was used in the final estimations of parameters.

The function of the twelve repeats served to give an indication of the experimental errors involved in the repeated measurements.

Various kinetic models have been tried in order to arrive at the most satisfactory model. The types of models considered in this study were:

A general model where rate constants remained constant. This was the simplest model similar to the conventional low conversion kinetics.
 It was intended to have only one set of rate constants to fit all thermal and catalysed polymerization experiments.

2) A general model for thermal polymerization where all rate constants were allowed to vary.

In this model, all rate constants were corrected for gel effect following,

$$k = \frac{k_{diff} k_{o}}{k_{diff} + k_{o}}$$
(9E-12)

where

$$k_{diff} = k_1 EXP(k_2)$$
 (9E-13)

$$k_2 = f(T, x, \bar{r}_n)$$
 (9E-14)

and k_o was the initial value of the rate constant at zero conversion where $k_{diff} >> k_o$. The variation of k_{diff} affects all rate constants with strongest effect for the largest rate constant.

3) A model fitted each experiment separately, allowing the rate constants to vary with conversion.

In this model, the variation of $I/(k_{+}/k_{p}^{2})$ was allowed to fit the conversion data. $I_{+}(k_{+}/k_{p}^{2})$ and $(k_{fm}/k_{p} + k_{fc}C/k_{p}M)$ were then estimated from the combined x, \overline{M}_{p} , \overline{M}_{w} data.

Various models were discriminated based on either the weighed least square criterion (equation 9E-11) or the Bayesian criterion (equation 9E-5). The model having the least least square function (z^{\dagger}) or the least Bayesian function (z_0) were considered as the best model under consideration. The first and second model types gave reasonably good fit for the most part of experimental data, but had difficulty in fitting either high or low conversion accurately. Thermal polymerization at 200°C did not fit well in the general models. The third model type gave the best fit of overall data and was accepted as the final model in the present study. The model, however, lacks the generality desired for interpolation and extrapolation purposes. A summary of all models attempted are given in Table 9E-2. It should be pointed out that the success of the weighed least square and/or Bayesian method depends largely on the type of response surface. All the available multi-variable search techniques to-date apply strictly to unimodal responses. The search becomes increasing slow when the number of variables are more than three and that the search for the true minimum will be much more difficult because of the high probability of having a multi-modal response surface.

TABLE 9E-2 SUMMARY OF MODELS ATTEMPTED

Model Type	Description	Least Square z'	Bayesian ^Z o	Remarks
1	general model for all expts.			All rate constants are of Arrhenius type
·	search for k _i k _{fc} =k _{td} =0, k _d from [70] k _p ,k _{fm} ,k _{tc} from [8]	2.3×10 ⁵	3.5×10 ²³	
	search for k _i ,k _p ,k _{fm} k _{fc} =k _{td} =0, k _d from [70] k _{tc} from [8]	1.5×10 ⁵	2.2×10 ²³	
	search for k _p ,k _{fm} ,k _{fc} k _i =1.96x10 ⁴ exp(-11980/T) k _{td} =0, k _{tc} from [8], k _d from [70]	1.85×10 ⁵	2.7×10 ²³	good fit of all expt. data not obtainable
	search for k _i ,k _d ,k _p ,k _{tc} ,k _{td} ,k _{fm} k _{fc} =0	8.2×10 ⁴	1.6×10 ²³	· · · · · · · · · · · · · · · · · · ·

TABLE 9E-2 (CONT'ED)

Least Square Bayesian Model Description Remarks Type z '. z_o 2 all rate constants general model for thermal polym. 9.9×10³ are of Arrhenius search for k, kdp, kdiff type type k_p, k_{fm}, k_{tc}, k_{td} from [8] 8.0×10³ search for k_i, k_{fc}, k_{td}, k_{diff} good fit of all expt. data not k_p, k_{fm}, k_{tc} from [8] obtainable 3 Independent fit for each expt. one objective function for each expt. good fit for all expt. based on Bayesian criterion $I/(k_{+}/k_{p}^{2})=A_{0}+A_{1}x+A_{2}x^{2}+A_{3}x^{3}$ Catalysed polym. accounts for the contribution of thermal polym. $I/(k_{+}/k_{p}^{2}) = A_{p}EXP(A_{+}x+A_{2}x^{2}+A_{3}x^{3})$ exponential form slightly better than polynomial. details in section 4 of this thesis.

9F. Simulation of Polymer Reactor Systems

9F.1 Introduction

Kinetics of free radical initiated styrene polymerization has been developed for high and complete conversions based on polymerization studies in batch reactors [6, this thesis]. They can be used directly to predict the behaviour of batch polymerization of styrene. The batch process is still used in polymer industry, but with emphasis being shifted towards the continuous process. In one batch process ^[36], bulk styrene is polymerized to about 30% conversion in a batch reactor. The resultant syrup is then poured into molds where the reaction is finished. Because of the relatively poor heat transfer in the finishing trays, hot spots exist resulting in a broadening of the molecular weight distribution. The batch process requires excessive material handling giving relatively small rate of production. On the other hand, the continuous mass polymerization may be set up to handle a high rate of production with good control of the polymer product. In one continuous process ^[36], the prepolymerization is carried out in two kettles in the same fashion as in the batch process. The syrup is then passed into a continuous finishing tower with temperature controlled to increase from top to bottom. The finished polymer melt at 200°C flows into a vented two-stage extruder in which the residual monomer dissolved in the polystyrene is removed and recycled to the prepolymerization tanks, while the polymer is extruded into strands which are then cooled and

chopped to produce the finished product. Continuous bulk polymerization of styrene with capacities up to 5000 lb/hr., has been reported. Continuous mass polymerization is gaining importance in polymer industry, and the study of continuous polymerization may be of industrial interest. The aim of this section is to use the batch kinetics to investigate the behaviour of continuous polymer reactor systems, and the role of viscosity and recycle upon molecular weight distribution of product polymer.

9F.2 Theoretical Development

A continuous stirred tank reactor (CSTR) model may be derived from the mass balance for each component around the reactor, i.e.,

Rate of accumulation = Rate in - Rate out

- Rate of loss by reaction (9F2-1)

If the reaction mixture is homogeneous with perfect mixing in the reactor, the isothermal batch kinetics may be used to account for the change of the components by chemical reactions. For the kinetics described in Section 4 or section 9A where $k_{dp} = k_{fp} = k_{fs} = k_{td} = 0$, and $k_t = k_{tc}$, the mass balance equations for all the components are,

$$V \frac{dR_{1}^{\circ}}{dt} = (flow in) - R_{1}^{\circ}V_{q} + [I + (k_{fm}M + k_{fc}C) R^{\circ} - R_{1}^{\circ}(k_{p}M + k_{fm}M + k_{fc}C + k_{t}R^{\circ})]V \qquad (9F2-2)$$

$$V \frac{dR_{r}^{\circ}}{dt} = (flow in) - R_{r}^{\circ}V + [k_{p}M R_{r-1}^{\circ} - R_{r}^{\circ}(k_{p}M + k_{fm}M + k_{fc}C + k_{t}R^{\circ})]V \qquad (9F2-3)$$

$$V \frac{dR^{\circ}}{dt} = (flow in) - R^{\circ}V_{q} + [I - k_{t} R^{\circ}] V \qquad (9F2-4)$$

$$V \frac{dP}{dt} = (flow in) - P_r V_q + [(k_{fm}M + k_{fc}C) R_r^\circ]$$

$$+\frac{1}{2}k_{+}\sum_{n=1}^{\Sigma}R_{n}^{o}R_{r=n}^{o}]$$
(9F2-5)

$$V \frac{dM}{dt} = (flow in) - MV_q - [I + (k_p + k_m) MR^o] V \qquad (9F2-6)$$

$$V \frac{dC}{dt} = (flow in) - C V_q - k_d CV$$
 (9F2-7)

$$V \frac{dS}{dt} = (flow in) - S V_q \qquad (9F2-8)$$

$$V = \frac{d R_{poly}}{dt} = (flow in) - R_{poly} V + [I+(k_p+k_fm)MR^{\circ}]V W_{m} \qquad (9F2-9)$$

$$P_{f} = R_{poly} V_{q}/Q \qquad (9F2-10)$$

where V

is the volume of the reactor, l

V is the volumetric flow rate of effluent stream, l/sec Q is the mass flow rate of effluent stream gm/sec.

W is the molecular weight of monomer

 $R_{\rm poly}$ is the total polymer in the reactor, gm/2.

 P_{f} is the polymer weight fraction in the reactor.

If no density change is involved in the reaction, the mass and volumetric flow rates will be the same at inlet and outlet at all time. If however,

density change is significant and is linear with conversion (Appendix 9A), then [117]

$$V_{q} = V_{qi} (1 + \epsilon x')$$
 (9F2-11)
 $x' = \frac{M'_{0} - M}{M'_{0} + \epsilon M}$ (9F2-12)

where V is the volumetric flow rate at inlet of reactor

x' is the conversion of monomer based on the initial and outlet monomer concentration and may not necessarily be equal to the polymer weight fraction P_{f} .

M' is the initial monomer concentration in the reactor as a result of mixing only.

M is the monomer concentration in the reactor

 ε is defined by equation (9A-4).

The transient continuous stirred tank reactor (TCSTR) model may be obtained directly from equations (9F2-2 to 12). Solution of these differential equations will lead to the transient behaviour of the polymer reactor concerned. Steady-state operation of the continuous stirred tank reactor (CSTR) may also be derived from the same equations (9F2-2 to 12) with all the rate equations (or accumulation terms) set equal to zero. The resulting CSTR model is simple and involves algebraic equations only. Further simplifications may be obtained by making the steady-state assumption (no more an assumption for steady-state operation) and ignoring the flow in and out of free radicals. This has been shown to be valid for styrene polymerization [135] where the time for free radicals to reach steady-state is much less than the residence time of the reactor. In this case, the equations for free radicals and dead polymer species becomes,

$$R_{r}^{o} = \phi_{l}^{r-l} R_{l}^{o}$$
(9A-24)

$$V \frac{dP_{r}}{dt} = (flow in) - P_{r}V_{q} + \phi_{l}^{r}\phi_{2} \left[\frac{k_{fm}}{k_{p}} + \frac{k_{fc}C}{k_{p}M} + \frac{r\phi_{2}}{2M^{2}}\left(\frac{k_{+}}{k_{p}^{2}}\right)\right]$$
(9F2-13)

where ϕ_1 and ϕ_2 are defined in equations (9A-28, 31). The molecular weight distribution and molecular weight averages may be calculated using no more than 50 key dead polymer species in an equal interval of $\Delta(\log r)$.

A plug flow tubular reactor (PFTR) model may be derived from mass balances over a small element of the reactor and integrated over the length of the reactor ^[117]. Alternatively, it may be approximated by a series of CSTR's. The performance of n equal-sized CSTR in series is shown to approach that of a PFTR of the same total reactor volume when the number of CSTR's (n) approaches to infinity ^[117]. In practice, n \geq 15 would lead to PFTR performance with sufficient accuracy ^[136]. In the present study, a PFTR model is developed based on n CSTR in series. This model is simple and is also useful in replacing the more complicated batch reactor (BSTR) model which involves the solution of differential equations rather than the algebraic equations in the steady-state CSTR.

9F3. Simulation of Polymer Reactor Systems

The transient and steady-state behaviour of a system of reactors was simulated using the TCSTR, CSTR and PFTR models in a book-keeping executive program MACSIM (McMaster Sizer and Simulator) which is an advanced version of the program, PACER, developed by P.T. Shannon and H. Mosler at Purdue University. The basic strategy of the executive system ^[133] is that the simulation models will receive information on all process streams entering the unit and information on how it is operated. Using this information, the simulation model must generate all information about the process streams leaving the equipments.

The executive system accepts case studies in coded form. It consists of a process matrix, lists of equipment and stream parameter data. They are described below.

1) Information Flow Diagram and Process Matrix

An example of the information flow diagram for the system of reactors simulated is given in Figure 9F3-1. The process matrix for steady-state operation of the three reactors follows:



FIGURE 9F3-1 INFORMATION FLOW DIAGRAM OF THE REACTOR SYSTEM IN THE SIMULATION STUDY

PROCESS MATRIX

Equip Number	oment Name	S†r	eam Nu	Imbers
ļ	CSTR	I	5	-2
2	CSTR	2	7	-3
3	CSTR	3	-4	
4	JUNCIO	4	-5	-6

2) Stream List (SN(I,J) where I is the stream number and J is the element in the stream list)

- I. Stream number
- 2. Stream flag
- 3. Monomer flow in gm/sec
- 4. Catalyst flow in gm/sec
- 5. Solvent flow in gm/sec
- 6. Total mass flow in gm/sec
- 7-56. Dead polymer flow in gm moles/sec

3) Equipment Parameters List (EN(I,J) where I is the equipment number

and J is the element of the equipment parameters list)

I. Equipment number

1 1

1 15.

2. Reactor temperature in °K

- 3. Reactor volume in litre
- 4.

Frequency factors and activation energies

- 16. Monomer molecular weight
- 17. Catalyst molecular weight
- 18. Solvent molecular weight

19. Number of key species to be calculated

- 20. Minimum chain length
- 21. Maximum chain length
- 22. Output streams splitting fraction

23. Time step size for solution of transient reactor equation

24. Number of time intervals per printout
25.
Constants for correlations of
viscosity, termination rate constant, and
catalyst efficiency
38.

Further computer storages may be assigned to the equipment control vector (ENC) and stream control vector (SNC) if required. Options on the control of program printout, specification of convergent tolerance, calculation order etc. are also provided to enable the flexibility of the system. Complete details of the executive routine are given by Crowe et. al. ^[133].

The executive program is designed originally for steady-state simulation. Calculation proceeds consecutively around each loop until the solution converges so that the results between two consecutive loops are less than the prescribed tolerance. For the simulation of transient polymer reactor, however, the transient equations are solved only one increment (Δ t) at a time. The number of loops of calculation indicates the number of time increments of the system. For three reactors in series, an error of 3 x Δ t involved will not be significant for small Δ t. This error may also be removed by the modifications in the executive program [135].

The simulation study of polymer reactor systems will be divided into two parts. The first part employs the kinetics of solution polymerization developed for intermediate conversion [6, 136]. The second part uses the kinetics of polymerization of bulk styrene reported in Section 4 of this thesis.

9F3.1 Solution Polymerization of Styrene

This part reports the results of a computer study of the transient and steady-state behavior of a system of isothermal, backmixed reactors which interact via recycle streams containing dead polymer. Reactor configurations included:

- A) Three reactors in series at steady-state with recycle and no intermediate feed
- B) Three reactors in series at steady-state with recycle and intermediate feed
- C) One to twelve reactors in series at steady-state with no recycle and no intermediate feed
- D) Three reactors in series under transient conditions with no recycle and no intermediate feed
- E) Transient mixing model for a single reactor

Kinetics of solution polymerization of styrene was used in the reactor model accounting for a reduction in the rates of initiation and termination with increase in reactor viscosity

Empirical correlations which are used to account for the effect of reactor viscosity on rates of termination and initiation follow:

$$\log_{10}(\mu) = 17.66 - 0.311 \log_{10}(1+S) - 7.72 \log_{10}(T)$$

- 10.23 $\log_{10}(1-P_f) - 11.82 [\log_{10}(1-P_f)]^2$
- 11.22 $[\log_{10}(1-P_f)]^3 + 0.839 \log_{10}(\bar{r}_n)$

200

(9F3-1)

$$\log_{10}(k_{+}/k_{+0}) = -0.133 \log_{10}(1+\mu) - 0.0777 [\log_{10}(1+\mu)]^2$$
(9F3-2)

$$\log_{10}(f/f_{o}) = -0.133 \log_{10}(1+\mu)$$
(9F3-3)

where $\mu \equiv$ reactor viscosity in centipoise.

The system of reactors simulated is given by the information flow diagram in Figure 9F3-1. Equipments 1, 2, and 3 are continuous stirred-tank reactors and equipment 4 is a junction splitter which controls the recycle ratio (ratio of mass flow rates of dead polymer in recycle stream to dead polymer in effluent stream from the third reactor) and the composition of the recycle stream. For case studies A, B, C, and D, all the reactors are of equal volume at 5000 liters and are maintained isothermally at 70°C. The feed stream parameters are given in Table 9F3-1.

20.1

TABLE 9F3-I FEED STREAM PARAMETERS

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Case Study	Feed Stream	Monomer g./sec.	Solvent g./sec.	Catalyst g./sec.	Temperature °C
A	Primary Intermediate	400	90 -	10	70
В	Primary Intermediate	240 160	54 36	6 4	70 70
С	Primary Intermediate	. 400	90 -	10	70
D	Primary Intermediate	400	90 . -	10	70

* Refer to information flow diagram in Figure 9F3-1.

Case Study A - Effect of Recycle on Steady-State Operations, No Intermediate Feed.

The effect of recycle was studied for two conditions: first, the recycle of all components - i.e., the composition of recycle stream was the same as effluent from the third reactor - and second, the recycle of dead polymer only - i.e., unreacted catalyst, monomer, and solvent were not present in the recycle stream. Compositions for both kinetic schemes, with and without viscosity corrections, are also presented. The results are tabulated in Tables 9F3-2, 3, 4 and shown graphically in Figures 9F3-2, 3, 4 and 5.

Conversion of monomer is significantly increased by connecting CSTR's in series and as the recycle ratio approaches unity the behavior of these three backmixed reactors approaches the behavior of a single CSTR of the same total volume (Table 9F3-2). These are not unexpected results.

It is more interesting to observe the effect of viscosity on polymer production rate and molecular weight averages. There is a significant increase in polymerization rate and in molecular weights as a result of the correction of rates of termination and initiation for viscosity. In fact, conventional kinetics (no viscosity correction) predict a slight decrease in molecular weight averages, whereas in fact there is a rather large increase. The benefit of recycle on polymer production is not apparent when monomer, solvent, and catalyst are recycled along with dead polymer. If a small reduction in polymer production rate can be tolerated and if a higher
TABLE 9F3-2 EFFECT OF RECYCLE ON STEADY-STATE OPERATION - CASE STUDY A No intermediate feed, composition of recycle stream is the same as effluent from last reactor

KINETIC CORRECTED FOR VISCOSITY

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Rervcle								1.1.1					
Ratio		0.0			0.25			0.50			0.75		1.0
Reactor No.	1	2	3	1	2	3	1	2	3	1	2	3	1,2,3
r _n	206.	225.	243.	239.	248.	260.	269.	271.	278.	292.	293.	295.	307.
ř,	311.	344.	380.	367.	379.	401.	410.	414.	424.	443.	444.	447.	464.
rw/rn	1.51	1.53	1.56	1.53	1.53	1.54	1.53	1.52	1.53	1.52	1.52	1.52	1.51
Conversion	.350	.605	.789	.434	.622	.768	.521	.644	.747	.610	. 670	.724	.679
Polymer Fraction <	.280	.487	.638	.348	.501	.621	.420	.520	.605	.493	.542	.587	.543
Polymer Production Rate gm/sec	-	-	319.	-	-	310.	. - '	• •	302.		-	294.	271.

TABLE 9F3-3 EFFECT OF RECYCLE ON STEADY-STATE OPERATION - CASE STUDY A

No intermediate feed, composition of recycle stream

is the same as effluent from last reactor

KINETICS NOT CORRECTED FOR VISCOSITY

Recycle Ratio	0.0			0.25				0.50			1.0		
Reactor No.	1	2	3	1	2	3	1	2	3	1	2	3	1,2,3
r _n	134.	123.	115.	123.	119.	114.	117.	116.	113.	113.	113.	112.	113.
ŕw	202.	186.	175.	187.	180.	773.	176.	174.	171.	170.	169.	168.	169.
r̃ _w ∕r̃n	1.50	1.51	1.53	1.51	1.51	1.52	1.51	1.51	1.51	1.50	1.50	1.50	1.50
Conversion	.325	.539	.657	.381	.532	.636	.439	.537	.612	.498	.546	.587	.542
Polymer Fraction <	.260	.425	.532	.306	.429	.514	. 353	.434	.496	.403	.442	.476	.433
Polymer Production Rate gm/sec	-	-	266.	-	-	257.	-	-	248.	-	-	238.	216.

TABLE 9F3-4 EFFECT OF RECYCLE ON STEADY-STATE OPERATION

Case study A, no intermediate feed, recycle of dead polymer only

KINETICS CORRECTED FOR VISCOSITY

Recycle Ratio		0.0			0.25		0.50*
Reactor No.	1	2	3	1	2	3	1 3 3
r _n	206.	225.	243.	313.	331.	358.	223 295 197
r _w	311.	344.	380.	495.	519.	577.	1023 1180 1126
r _₩ /r _n	1.51	1.53	1.56	1.58	1.57	1.61	4.58 4.00 5.72
Conversion	.350	.605	.789	.485	.696	.882	0.654 0.998 1.0
Polymer Fraction	.280	.487	.638	.406	.586	.744	0.582 0.890 0.893
Mass flow rate gm/sec.	500.	500.	500.	615	615	615	904. 904. 904.
Polymer Production Rate gm/sec.	•	-	319.	•••	-	343.	400.

* Viscosity probably beyond the range of kinetic model







molecular weight is desired, recycle of this composition might be employed.

Recycling dead polymer free of monomer, catalyst, and solvent can actually increase the polymer production rate as well as the molecular weight averages. Recycle ratios greater than 0.50 were not investigated. The viscosity correlations may not be applicable when the reactor viscosity exceeds 100 poises. The results for a recycle of 0.50 are therefore open to guestion.

The operation of a train of backmixed reactors at these elevated viscosities may be beneficial. Other types of reactors, such as those involving suspension polymerization, might also benefit from an application of the viscosity effect - for example, monomer, catalyst, and dead polymer might be premixed before suspension as droplets to achieve both higher polymer production rates and molecular weight averages. Case Study B - Effect of Recycle on Steady-State Operation, Intermediate Feed.

To show the advantages of an intermediate feed with regard to polymer production rate, total monomer, catalyst, and solvent feed rates (primary feed plus intermediate feed) were set equal to the primary feed rates used in case study A; 40% of these total rates entered as intermediate feed and 60% as primary feed. The concentrations of both feeds were identical to that used for the primary feed in case study A (Table 9F3-1). The results are tabulated in Tables 9F3-5, 6 and Figures 9F3-5, 6.

The use of intermediate feed for the case of zero recycle ratio reduces the production significantly and allows only a small increase in molecular weight (Tables 9F3-2 and 9F3-5). The effect of intermediate feed is to lower the primary feed rate, increasing the residence time and molecular weight averages produced in reactor 1. The effect of residence time on molecular weights for a single CSTR is shown in Table 9F3-7. These results were obtained by varying reactor volume, keeping reactor temperature, feed flow, and composition constant. Conventional kinetics (no viscosity correction) predict a decrease in molecular weight with increase in residence time. Accounting for viscosity gives a marked increase in molecular weight with increase in residence time. These results suggest that a large residence time in the first reactor of a series would give higher molecular weights in the product stream. The use of an intermediate feed in fact does result in significantly higher molecular weights (Tables 9F3-5, 6 and Figure 9F3-6).

TABLE 9F3-5 EFFECT OF RECYCLE ON STEADY-STATE OPERATION - CASE STUDY B

With intermediate feed, composition of recycle stream

is the same as effluent from last reactor

			1										
Recycle Ratio	0.0			0.10			0.25			0.40			
Reactor No.	1	2	3	1	2	3	1	2	3	1	2	3	
r _n	237.	245.	262.	251.	254.	268.	268.	267.	277.	281.	279.	286.	
r _w	358.	371.	402.	381.	385.	410.	406.	405.	422.	426.	423.	434.	
r _w /r _n	1.51	1.51	1.54	1.52	- 1.51	1.53	1.52	1.52	1.52	1.52	1.52	1.52	
Conversion	.489	.565	.762	.519	.575	.756	.560	.591	.746	0.596	0.610	0.737	
Polymer Fraction	.391	.454	.616	.416	.463	.611	.450	.476	.603	0.481	0.492	0,596	
Mass Flow Rate gm/sec	300.	500.	500.	355.	556.	556.	467.	667.	667.	633.	833.	833.	
Polymer Production Rate gm/sec	-	_	308.	-		306.	-	-	302.	-	-	298.	212

KINETICS CORRECTED FOR VISCOSITY

TABLE 9F3-6 EFFECT OF RECYCLE ON STEADY-STATE OPERATION - CASE STUDY B

With intermediate feed, recycle of dead polymer only

KINETICS CORRECTED FOR VISCOSITY

Recycle Ratio	0.0			÷	0.10		0.25			0.40*			
Reactor No.	1	2	3	1	2	3	1	2	3	1	2	3	
rn	237.	245.	262.	288.	288.	306.	449.	433.	455.	419.	459.	333.	
r _w	358.	371.	402.	438.	436.	491.	686.	661.	701.	1036.	1034.	1006.	
r _w /r _n	1.51	1.51	1.54	1.52	1.52	1.54	1.53	1.53	1.54	2.47	2.25	3.02	
Conversion	.489	.565	.762	•553	.603	.795	.677	.695	.901	0.999	0.995	1.00	
Pol <i>y</i> mer Fraction	.391	.454	.616	.454	.493	.652	.580	•584	.760	0.894	0.868	0.874	
Mass Flow Rate gm/sec	300.	500.	500.	335	535 .	535.	417.	617.	617.	570.	770.	770.	
Polymer Production Rate gm/sec	-	-	308.	-	•	314.	-	—	352.	-	••	400.	2

* Viscosity probably beyond the range of kinetic model

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TABLE 9F3-7 EFFECT OF RESIDENCE TIME ON STEADY-STATE OPERATION CASE STUDY B - SINGLE REACTOR

Residence Time(Sec)	r _n		r _w		Polymer Fraction
	a	b	a	þ	a b
873.	183.	165.	275.	248.	.042 .041
2180.	183.	157.	276.	237.	.095 .094
2620.	184.	155.	277.	233.	.111 .109
2910.	184.	154.	278.	231.	.122 .119
4360.	188.	147.	283.	221.	.169 .163
8730.	206.	134.	311.	200.	.280 .260
17500.	254.	119.	384.	178.	.436 .370
26200.	307.	113.	464.	168.	.543 .433

Monomer flow = 400 gm/sec Azocatalyst = 10 gm/sec Toluene = 90 gm/sec 90 gm/sec Temperature = $70^{\circ}C$

a - refers to results obtained with viscosity correctionb - refers to results obtained without viscosity correction.





Case Study C - Simulation of Steady-State CSTR Train, No Recycle and No Intermediate Feed.

For this set of computer trials the reactor configuration shown in Figure 9F3-1 was used with zero intermediate feed and zero recycle. Simulations were obtained for one, three, six, nine, and 12 CSTR reactors in series using kinetics both with and without viscosity correction to show the approach to PFTR or batch reactor behavior. The total reactor volume was maintained at 15,000 liters and all reactors operated at 70°C (Table 9F3-1). The results are tabulated in Table 9F3-8.

The molecular weight averages fall significantly as the number of reactors in series increases when the viscosity correction is applied. Conventional kinetics predict a negligible change in molecular weight. When designing a train of CSTR's in series, one would have to account for this significant reduction in molecular weight averages.

TABLE 9F3-8 SIMULATION OF A STEADY-STATE CSTR TRAIN - CASE STUDY C

no recycle, no intermediate feed, results for product stream

Number of Reactors	7		3		6		9		12	
Reactor vol (liter)	15,	15,000		000	25	00	1(667	1	250
Viscosity Corr.	YES	NO	YES	NO	YES	NO	YES	NO	YES	NO
r _n	308.	113.	243.	114.	230.	114.	226.	114.	224.	115
r _w	465.	168.	380.	174.	361.	177.	356.	178.	353.	179.
r _w ∕r _n	1.51	1.50	1.56	1.53	1.57	1.55	1.57	1.56	1.57	1.56
Conversion	.679	.542	.789	.657	.829	.696	.844	.710	.852	.718
Polymer Fraction	.543	.433	.638	.532	.672	.564	.685	.576	.692	.583
Polymer Production Rate gm/Sec	272.	216.	319.	266.	336.	282.	342.	288.	346.	291.

<u>Case Study D</u> - Simulation of a Transient CSTR Train, No Recycle and No Intermediate Feed.

The three reactors are full of monomer, solvent, and catalyst of composition equal to the feed composition. The feed composition and flow rate are constant with time. At time zero the reaction rates are all zero.

The transient is initiated with a step change in reactor temperature to 70°C for each reactor.

This computer program is very versatile and would allow the following cases to be readily investigated:

- Changes in flow with time of any component in the feed (primary or intermediate).

- Changes in temperature with time of any reactor in the system.

- Reactor configuration varied almost at will.

The results for these trials are shown graphically in Figures 9F3-7, 8, 9, and 10.

An interesting feature of Figures 9F3-7, 8, 9, and 10 is the very extensive period required for the train of reactors to reach steady state when the kinetics are corrected for viscosity. This is particularly apparent for the molecular weight averages. An even longer time would be required to reach steady state when recycle is employed. The residence time per reactor is approximately 3 hours. The transient approach to steady state of \bar{r}_n and \bar{r}_w predicted by conventional kinetics is shown in Figure 9F3-10. The molecular weight averages fall with time, the largest values being in reactor 1. This is opposite to the behavior predicted by kinetics corrected for viscosity, where the molecular weights increase with time and are largest in reactor 3.









Case Study E - Transient CSTR Mixing Model

The information flow diagram used for the mixing model is shown in Figure 9F3-11.

Equipment I splits the feed stream into three, with 10% of the flow bypassing both active and dead volumes, 85% going to the active volume, and 5% going to the dead volume. The nonideal reactor which is being simulated has a volume of 5000 liters. This real reactor is represented by a model which has an active volume (equipment 2 in Figure 9F3-11) of 4250 liters and a so-called dead volume of 750 liters. The feed stream splitting ratio and active and dead volumes are chosen so that the residence time in the active volume is identical to the residence time in the real reactor. This choice means that the composition of stream 5 leaving the active volume is identical to that which the real reactor would have produced if it were perfectly mixed with no segregated flow. The effect of imperfect mixing can be evaluated by comparing the compositions of streams 5 and 7. The splitting fractions used in equipment I would probably depend on feed flow rate, r.p.m. of the stirrer in the reactor, and reactor viscosity. The configurations for a mixing model are limited only by one's imagination. Many models which give the same residence time distribution as the plant reactor can be found. To find the best model one should compare predicted and measured values of conversion and molecular weight distribution. Such a model might account for deviations from maximum mixedness.



MIXING MODEL

FIGURE 9F3-11 INFORMATION FLOW DIAGRAM FOR THE MIXING MODEL USED IN CASE STUDY E

Results for one set of splitting fractions are shown graphically in Figures 9F3-12, 13, and 14. In this case imperfect mixing has reduced capacity and increased \bar{r}_n and \bar{r}_w with a negligible change in the dispersion index. The dispersion index can be increased significantly by adjusting the splitting fractions. This has been demonstrated for steady-state operation ^[10]. An interesting result of the transient simulation is the excessively long time required for the dead volume to reach steady-state conditions. This suggests that the time to reach steady state is much greater for the non-ideal reactor. Focusing attention on the reactor effluent, one would observe a very gradual change over a very long period of time.







9F3.2 Bulk Polymerization of Styrene

This part reports the results of a computer study of polymer reactor systems based on the polymerization kinetics of bulk styrene reported in Section 4 of this thesis. Complete homogeneity and isothermal conditions were again assumed. Reactor configurations included:

F) Three CSTR's in series at steady-state with recycle.

G) One CSTR followed by two PFTR's in series at steady-state with no recycle.

Case Study F - Effect of Recycle on Steady-State CSTR

In this case, the reactor configuration was the same as Case Study A and is shown in Figure 9F3-1. The three reactors were 5000 liters in volume maintained at 140°C. Both the recycle of all components and the recycle of dead polymer alone were considered. Only the primary feed stream was allowed having a monomer flow of 4996 g/sec. and a flow of DTBP as catalyst of 4.25 g./sec. corresponding to 0.085% of total feed. The results are tabulated in Table 9F3-9, 10 and shown graphically in Figures 9F3-15, 16.

The effect of recycle was similar to that demonstrated in case study A. Recycle of all stream components resulted in decrease of conversion as expected, and recycle of dead polymer alone raised the polymer production rate taking the advantage of gel effect. TABLE 9F3-9 EFFECT OF RECYCLE ON STEADY-STATE OPERATION - CASE STUDY F

Composition of recycle stream is the same as effluent from last reactor

Recycle Ratio		0.0			0.25			0.50			0.75		1.0
Reactor No.	I	2	3	1	2	3	l	2	3	I.	2	3	1,2,3
r _n	1257	1276	1297	1288	1294	1306	1309	1311	1315	1324	1324	1325	1336
r _w	2108	2165	2228	2203	2219	2253	2263	2267	2281	2305	2306	2310	2341
rw/rn	1.68	1.70	1.72	1.71	1.72	1.73	1.73	1.73	1.73	1.74	1.74	1.74	1.75
Pf	0.145	0.282	0.415	0.208	0.310	0.410	0.272	0.340	0.406	0.336	0.370	0.404	0.401
Polymer Production(gm/sec)	-		2075	- -	-	2050	_	_	2030 [.]	-	-	2020	2005

Recycle Ratio		0.0			0.25			0.50			0.75			0.90	x
Reactor No.	1	2	3	ł	2	. 3		2	3	t.	2	3	1	2	3
r _n	1257	1276	1297	1328	1335	1348	1419	421	1425	1525	1526	1526	1561	1562	1563
r _w	2108	2165	2228	2294	2314	· 2353	2526	2532	2548	2811	2814	2816	2924	2927	2928
r _w /r _n	1.68	1.70	1.72	1.73	1.73	1.75	1.78	1.78	1.79	1.84	1.84	1.85	1.87	1.87	1.87
P _f	0.145	0.282	0.415	0.242	0.360	0.476	0.379	0.473	0.565	0,583	0.642	0.698	0.747	0.777	0.806
Polymer Production(gm/sec)	-	-	2075		-	2380	_	_	2825	_	-	3490	-		4030

Recycle of dead polymer only

TABLE 9F3-10 EFFECT OF RECYCLE ON STEADY-STATE OPERATION - CASE STUDY F





<u>Case Study G</u> - Simulation of Continuous Thermal Polymerization of Styrene

Continuous thermal polymerization was simulated by three steadystate reactors in series. Styrene was to be polymerized in a CSTR up to intermediate conversion. The resulting syrup was directed to the top of a polymerization tower (PFTR) and then into an extruder (PFTR) where polymer was extruded into strands which were then cooled and chopped to produce the finished polymer.

In this computer exercise, bulk styrene was fed to the first reactor (CSTR) of 5000 liters in volume, at a rate of 500 g./sec., and maintained at a temperature of 140°C. Two sets of conditions in the next two reactors (PFTR) were chosen. The 1st set of conditions (G1) involved a reactor volume of 5000 litres and temperature of 170 and 200°C for the second and third (PFTR) reactors respectively. The second set of conditions (G2) involved a reactor volume of 5000 litres for the 2nd reactor (PFTR) and 1000 litre for the 3rd reactor (PFTR). The two PFTR's had the same temperature of 200°C. The results of simulation is given in Table 9F3-11, and the differential molecular weight distribution (DMWD) of the polymer product at the exit of the last reactor is shown in Figure 9F3-17. It is interesting to note that the molecular weight distributions (MWD) of polymer product are strongly dependent on the reaction temperature throughout the polymerization process. Very broad MWD is results for a large temperature range.

TABLE 9F3-11 SIMULATION OF CONTINUOUS POLYMERIZATION - CASE STUDY G

Conditions		GI			G2	
Reactor Number	!	2	3	I	2	3
Туре	CSTR	PFTR	PFTR	CSTR	PFTR	PFTR
Volume (litre)	5000	5000	5000	5000	5000	1000
Temperatu re (°C)	140	170	200	140	200	200
r _n	1614	1237	1079	1614	472	470
r _w	2949	2431	2361	2949	1764	1757
r _w /r _n	1.83	1.97	2.19	1.83	3.73	3.74
Pf	0.506	0.951	0.985	0.506	0.976	0.980



9F.4 Summary

The simulation of polymer reactor systems has been carried out for styrene polymerization assuming that the system is homogeneous and isothermal. Gel effect is corrected for based on kinetics obtained from polymerization studies. The roles of certain system parameters such as recycle and intermediate feed have been evaluated. It is found that recycle of dead polymer may be used to increase polymer production rate and to control the molecular weight distribution of product polymer. The use of conventional low conversion kinetics may lead to serious errors in predicting the conversion and molecular weight of polymer formed. It should be pointed out that the assumption of homogeneity and isothermal are far from correct for most industrial polymer reactors. In addition, the kinetic model employed in solution polymerization (9F3-1) is valid up to about 60% conversion. These limitations will certainly affect the accuracy of the results. The effect of mixing and segregated flow may also be incorporated if necessary by a suitable mixing model. In summary, the results of the present simulation studies has demonstrated the possibility of polymer kinetic models to be used in predicting the performance of polymer reactor systems.