BULK THERMAL COPOLYMERIZATION OF STYRENE AND ACRYLIC ACID IN CONTINUOUS FLOW REACTORS

BULK THERMAL COPOLYMERIZATION OF STYRENE AND ACRYLIC ACID IN CONTINUOUS FLOW REACTORS

by

Steven W. Webb (B.A.Sc.)

A Thesis
Submitted to the
Faculty of Graduate Studies
in Partial Fulfilment
of the Requirements
for the Degree
Master of Engineering.
McMaster University
March, 1985

TO MY PARENTS

Master of Engineering (1985)
(Chemical Engineering)

McMaster University,
Hamilton, Ontario.

Title: Bulk,Thermal Copolymerization of Styrene and Acrylic Acid in Continuous Flow Reactors

Author: Steven W. Webb
B.A.Sc., Chemical Engineering
University of Waterloo, Waterloo, Ontario

Supervisor: Professors A.E. Hamielec and J.F. MacGregor
McMaster University, Hamilton, Ontario

Number of Pages: 143

ABSTRACT

This thesis contains two parts. The first involves the theoretical modelling of bulk, thermal, homo- and copolymerizations of styrene with another vinyl monomer in continuous flow stirred tank and tubular reactors. The second involves an experimental study of such polymer production in pilot plant scale reactors.

Kinetic modelling fundamentals, applicable assumptions and their implications are discussed.

Three series of experimental runs were performed in a 1.4 liter stirred tank reactor. The experimental conditions were in the range of 200 to 300 C with residence times of 15- 60 minutes. The first set was done with pure styrene to verify the current styrene kinetic model and provide more detail on the formation of oligomers. Two additional series of experiments were performed with two different comonomer compositions. The monomers were styrene and acrylic acid. Parameter estimation and model verification were attempted with all data.

The parameter estimation results are necessarily uncertain due to the low number of experiments possible with pilot plant work and the low variance of the responses obtained in experimentation on high temperature systems.

The kinetic mechanism describing styrene thermal initiation, oligomer formation and polymer production are supported in this work.

Trimer formation is suppressed in the copolymerization of styrene with acrylic acid. This is due to the reaction of acrylic acid monomer with the thermal initiation intermediate, thus preventing rearrangement to trimer species.

Trimer formation is accelerated by the addition of chlorine radical to the reaction. This radical reacts with the intermediate to produce chlorinated trimer species and prevents macroradical formation.

The addition of a tubular reactor was found to severely increase polymer oil fraction and decrease molecular weight, with only a minor productivity increase.

It is believed thermal degradation is very significant in determining molecular weights at temperatures greater than 280 C.

ACKNOWLEDGEMENTS

The author would like to thank those mentionned below f their assistance in the completion of this work.

1. The McMaster Institute for Polymer Production Technology and McMaster University (MIPPT)
2. Dr. A.E. Hamielec and Dr. J.F. MacGregor
3. Mr. D. Keller and Mrs. A. Vanderlaan

TABLE OF CONTENTS

1.0 Introduction

2.0 Kinetic Modelling

3.0 Experimental Plan and Equipment

4.0 Results

5.0 Conclusions

7.0 Appendix

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

A1,A3 === gel effect parameters (dimensionless)

As === Mark-Houwink "a" parameter for polystyrene (dim.

Ax === Mark-Houwink "a" parameter for sample (dim.)

B1,B2 === transfer to oligomer constants for monomer 1 and monomer 2 (mol/gram)

B3 === transfer to oligomer constant = kfO/kp (mol/gram)

C1,,C4 === GPC calibration coefficients (dim.)

C" === recorrected calibration coefficients (dim.)

C === polystyrene calibration coefficients (dim.)

cmonin === monomer feed density (grams/l)

conv(T) === final conversion at time T (wt.fr.)

D === diffusion rate parameter (cm**2/s)

D/uL === bulk, axial diffusion coefficient (dim.)

Den === monomer feed density at feed temperature (gram

dx === increment of conversion (wt.fr.)

dt === increment of time (s)

[dimer] === dimer concentration (mol/l)

e11,e12 === transfer ratios

e22,e21 === e11=kf11/kp11, e12 == kf12/kp12 etc. (dim.)

EV === elution volume (ml)

f1 === feed weight fraction styrene (wt.fr.)

F1 === copolymer composition (mol.fr.)

flow === volume flow rate (liter/s)

kdim === dimer kinetic constant (l/mol/s)

Kf === previously determined calibration factor between styrene and toluene (dim.)

kfO === transfer to oligomer constant (l/mol/s)

ki === thermal initiation rate constant (l/mol/s)

kp === pseudo propagation constant (l/mol/s)

kp22,kp12,=== propagation constants (l/mol/s)
kp11,kp21

ksc === scission kinetic constant (l/s)

kun === unzipping kinetic constant (l/s)

KSC === scission matrix (r:r) (dim.)

Ks === Mark-Houwink K parameter for polystyrene (g/cm

Kx === Mark-Houwink K parameter for sample (gram/cm/s

KUN === unzipping matrix (r:r) (dim.)

kt22,kt12,=== termination constants (l/mol/s)
kt11,kt21

ktrim === trimer kinetic constant (l/mol/s)

kto === copolymer average termination constant
=== kt11*F1**2 +2*phi*sqrt(kt11*kt22)*F1*F2 +kt22*F2**2 (l/mol/s)

[O] === oligomer concentration (mol/l)

l(seg) === mean length of segregated fluid (cm)

[M1] === concentration monomer 1 (mol/l)

[M2] === concentration monomer 2 (mol/l)
[M] === monomer concentration (mol/l)
monmw1 === molecular weight monomer 1 (gram/mol)
monmw2 === molecular weight monomer 2 (gram/mol)
Mw === fraction molecular weight (gram/mol)
mwdim === molecular weight of dimer fraction (gram/mol)
mwtrim === molecular weight of trimer fraction (gram/mol)
P === mol.wt. composition dispersity factor (gram/mo
PHI === cross-termination factor
=== kt12/sqrt(kt11*kt22) (dim.)
phi1,phi2 === radical fractions of type 1 and 2 (mol.fr.)
Q === composition mol.wt. dispersity factor (gram/mo
r === chain length (dim.)
r1 === reactivity ratio kp11/kp12 (dim.)
r2 === reactivity ratio kp22/kp21 (dim.)
[R1] === radical 1 concentration (mol/l)
[R2] === radical 2 concentration (mol/l)
rate1 === rate of consumption of monomer 1 (mol/l/s)
rate2 === rate of consumption of monomer 2 (mol/l/s)
resid === residual monomer (grams)
Rdim === rate of dimer formation (mol/l/s)
Rtrim === rate of trimer formation (mol/l/s)
Ri === rate of initiation (mol/l/s)
Rp === total rate of monomer consumption (mol/l/s)
sample === sample weight (grams)
tau(f) === mean residence time of tubular reactor (s)
tauo === original derivation of tau (mol/gram)
time === degradation time (s)
va,vb === refractive index increment for the a and b monomer in the solvent (dim.)
v === refractive index increment of the solution (cc
vf === free volume (cc)
Vh === hydrodynamic volume (cc)
vol === volume of reaction (liter)
w === vector of weight fraction polymer (length r) (
w^ === degraded vector of weight fraction polymer (r)
w(r,t) === weight fraction polymer of length r at time t
wmonin1 === flow rate of monomer 1 in (grams/s)
X === conversion (wt.fr.)

CHAPTER 1.0

1 INTRODUCTION

1.1 General Background

The work described in this report is in the area of high temperature polymerization and is aimed at the production technology for low molecular weight polymers. In particular, the manufacture of acrylic resins and vinyl-acrylic copolymers. These particular resins find uses as coating binders, pigment dispersants and adhesives.

The most notable property of acrylic resins is that they are soluble in basic aqueous solvents. There is no need to use expensive and hazardous organic solvent systems to solubilize the resin. Also, such coating resins can be easily removed in mild basic detergents, so that many re-applications are possible. The film properties of acrylic coatings are noted for their high gloss and clear finish. Copolymerization of appreciable amounts of a "hard" monomer such as styrene, enhances the film durability.

These resins are used in a variety of commercial materials such as finishing lacquer, metal paints, floor polishes, furniture wax, ink resins to name but a few. They are characterized by a number of properties.

- low solution viscosity permits easy application

- high solids (resin) content reduces application and curing time, while reducing volatile component
- excellent levelling and fixation flow properties result in smooth films
- excellent gloss retention and low water absorbance gives a hard, clear, easily painted film

Current designs for producing such resins are limited to low temperature bulk, continuous flow reactions with the use of appreciable amounts of transfer agents, inhibitors and initiators.

The main concern in the patented process for the production of lower molecular weight resins is control of the heat generation at high polymer concentrations. During this portion of the reaction, an increasing viscosity limits the heat removal capacity, while also limiting the diffusion rate of macroradicals. This causes a decrease in the rate of macroradical termination. This phenomena is referred to as the 'gel effect' portion of a polymerization and is specific to the monomer-process studied.

Gel effect causes the combined problems of accelerating rate of monomer consumption, with concurrent increase in heat generation rate, and reduced capacity to remove heat, due to the higher viscosities at high conversion. Temperature control becomes very difficult and polymer molecular weight dispersity increases. Generally, polymers with large polydispersities have more limited use.

Technology presented in U.S. Patent No. 3753958 (46) describes the current method for the production of low molecular weight acrylic copolymers. A two stage, stirred tank system is used with the following operating characteristics. A diagram of the existing technology is provided on Figure 1.1 .

- first reactor designed to get the conversion up to 70-90%, before the gel effect becomes important; this allows the use of a high rate and therefore a smaller reactor vessel
- second reactor is operated in the gel effect region and runs at a much lower rate; this is to allow the now reduced heat removal capacity to be effective in controlling the reaction temperature; a slightly higher temperature is used to attempt to increase the conversion
- fresh initiators are used in each reactor to control the rates in the respective reactors; up to 3% of total feed to the system is initiator
- inhibitor is added in the fresh feed to further aid in reaction rate control and to reduce geling at cold surfaces; it comprises up to 1% of the fresh feed
- molecular weight is controlled by addition of chain transfer agents in the fresh feed, in proportions of roughly 3% of feed monomers

The difficulty of running such a scheme is quite apparent. Up to 7 pounds of additional agents with each 100 pounds of fresh feed must be added to the reaction. These comprise 4 additional variables impacting on the reaction controllability and product quality. The derived complexity is enormous and its impact on the cost of such a scheme is obvious.

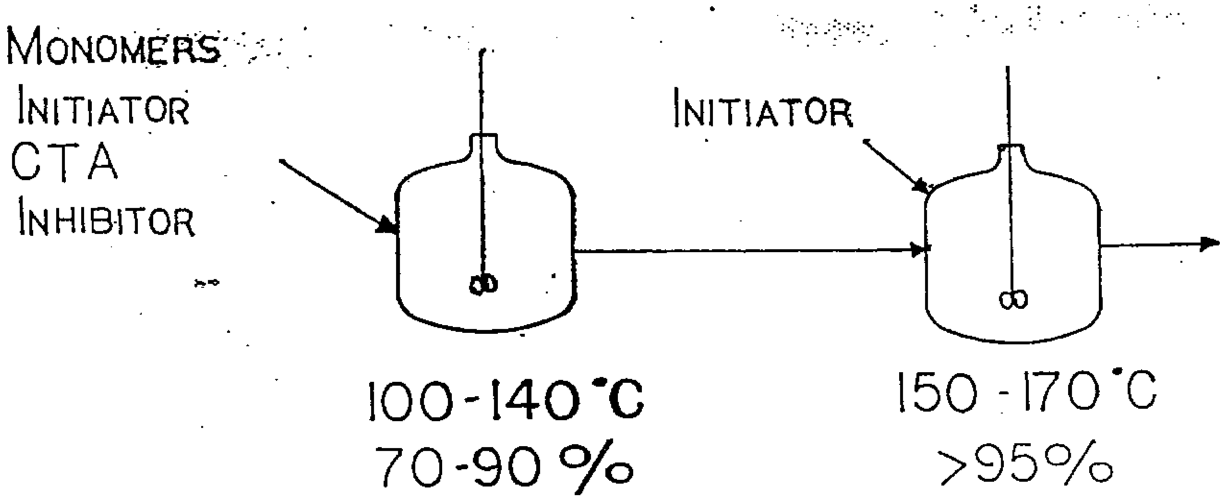


Figure 1.1
Conventional Low Molecular Weight Resin
Production Method

New technology has been developed to overcome this complexity and the resulting potential operating problems. This is technology current to 1983 in U.S. Patent 4414370 (47). It involves the production of acrylic and vinyl-acrylic resins by high temperature, bulk, thermally initiated polymerization in a continuous flow reactor.

The features of this scheme are its simplicity and ease of control. Both of these points make the process easier to operate, study, and understand. With understanding, it becomes possible to tighten polymer quality constraints and improve process efficiency.

Bulk polymerization is the most volume-efficient and therefore, the least capital intensive, means of producing polymers. The entire reactor volume is utilized in the consumption of monomer. There are no solvents or dispersants in the reactor that take up volume, or that must be removed by downstream equipment.

Thermal initiation is the cheapest form of radical generation available. No additional flows and chemicals are required. Temperature may be used directly to control rate of monomer consumption. Styrene monomer is particularly suited to thermal initiation schemes since it has a very appreciable rate of thermal radical generation.

The problems with this system are quite apparent to those familiar with polymer reactions. Bulk systems have very high viscosities and lines are prone to freezing and sticking if allowed to cool. Higher pressures are required to push the molten viscous resin through the process.

With all the benefits of such a polymerization reaction scheme, it is believed that this process is a viable method of producing low molecular weight resins, and is certainly worthy of continued study.

1.2 Scope And Purpose Of Work

The objectives of the study documented in this report include the generation of a deeper understanding of the thermal bulk process and explore possible improvements to the new technology through process experimentation and modelling.

There are two aspects under study in this report; one is the modelling of the kinetic phenomena associated with polymerization at high temperatures; the other, involves the experimentation of high temperature polymerizations in pilot plant equipment. Both aspects will then be joined in order to estimate fundamental kinetic parameters and thus, provide some understanding of the kinetics of the new polymerization process.

CHAPTER 2.0

2 KINETIC MODELLING

The purpose of this model development work is to develop a computer model that describes the kinetics of a bulk thermal copolymerization of styrene with another vinyl monomer. Enclosed in this chapter is the background study,literature review, theoretical development, model results, and example output of the computer simulation of this process.

As with all modelling work, the goal is to understand the system, equations and parameters that describe its important properties. In this attempt, certain limits in its scope are required. The most general limits of this model are provided below.

1. vinyl copolymerizations involving styrene and another vinyl monomer
2. linear chains
3. continuous,bulk, thermal initiation
4. ideal plug flow or stirred tank reactors
5. adiabatic or isothermal operation

2.1 Description And Development Of Model-Material Balances

The basic material balances for either the copolymer or the homopolymer model are given below. For monomers 1 and 2, the inflow outflow, accumulation and reaction terms become..

```
d([M1])/dt = wmonin1*(1-X)/vol/monmw1-rate1                     (1)
d([M2])/dt = wmonin2*(1-X)/vol/monmw2-rate2
```

This set of equations is solved numerically on a fixed interval basis by Runge-Kutta 4th order. Maximum accuracy is achieved by the selection of a small time interval in relation to the overall important time constants in the system. The choice of this interval is discussed in Section 2.8.5 . For a steady state solution (CSTR), equation(1) is set to zero and solved simutaneously.

2.1.1 Rate Of Polymerization -

Two copolymerization rate expressions are available with the model, to be used at the option of the user. The first, or conventional rate equation is suitable for use at low temperatures, when long chain lengths are expected. The expression is taken from Rudin(1) and is given below.

```
rate1  = (r1*[M1]**2 +[M1]*[M2])*sqrt(Ri)                   (2)
         -----------------------------------------
             sqrt(kto) * (r1*[M1] +r2*[M2] )
                          -------  ---------
                           kp11     kp22
rate2  = (r1*[M2]**2 +[M1]*[M2])*sqrt(Ri)                   (3)
         -----------------------------------------
             sqrt(kto) * (r1*[M1] +r2*[M2] )
                          -------  ---------
                           kp11     kp22

kto   = kt11*F1**2 +2*phi*sqrt(kt11*kt22)*F1*F2 +kt22*F2**2 (3a)
Rp    = rate1 + rate2
```

The second rate expression finds use at higher temperatures or when relatively short chain lengths are expected. Equation(4,5) is the fundamental rate definition and requires knowledge of radical concentrations.

```
rate1  = kp11*[R1]*[M1] + kp21*[R2]*[M1]                     (4)
rate2  = kp22*[R2]*[M2] + kp21*[R1]*[M2]                     (5)
```

The differences between the two rate expressions is described in Section 2.8.3. Radical concentrations are obtained by the solution of the radical mass balances, given below.

```
d( [R1])/dt = Ri1 + 0.5*Ri12 +kp21*[M1]*[R2]                   (6)
           -kp12*[R1]*[M2]-kt11*[R1]**2-kt12*[R1]*[R2]
           -kf12*[R1]*[M2]+kf21*[R2]*[M1]

d( [R2])/dt = Ri2 + 0.5*Ri12 + kp12*[M2]*[R1]                  (7)
           -kp21*[M1]*[R2]-kt22*[R2]**2-kt21*[R1]*[R2]
           -kf21*[M1]*[R2]+kf12*[M2]*[R1]

d([R] )/dt  = Ri -kt11*[R1]**2 -2*kt12*[R1]*[R2]               (8)
           -kt22*[R2]**2
```

Setting the last two equations equal to zero and solving the resulting two non-linear simultaneous equations for [R1] and [R2] in the interval allows the calculation of the rates of polymerization from equations (4,5) .

The effect of varying volume on rate of polymerization is accounted for by revising the rate expression with the following correction.

let N = number of moles of monomer

```
V*Rp = -dN/dt= -d([M]*V)/dt= -V*d[M]/dt-[M]*dV/dt
```

$$Rp = - d [M]/dt - [M]/V * dV/dt \qquad (9)$$

assuming contraction is linear with conversion and quantified as 'e' below...

$$V = Vo(1 + e*X) \qquad (10)$$

the derived rate correction factor becomes..

$$Rp = -d[M]/dt* (1 - (1-X)*e/(1+e*X)) \qquad (11)$$

Note that epsilon takes on negative values for shrinkage and produces an increase in the computed rate of polymerization. For styrenic systems volume shrinkage is significant.

The rate of initiation has been taken from Husain and Hamielec (2) as third order with respect to styrene monomer concentration.

$$Ri = ki * [M1]**3 \qquad (12)$$

2.1.2 Conversion -

Conversion is calculated as weight percent converted monomer based on total weight fresh monomer feed. It is calculated on an interval basis by keeping track of monomer concentration in weight per unit volume.

$$\text{conversion} = 1-\frac{(monmw1*[M1]+monmw2*[M2])}{Den1 + Den2} \qquad (13)$$

2.2 Polymer Property Equations

The polymer properties being modelled in this work are composition, molecular weight and oligomer fraction. Presented are the equations used to describe both instantaneous or cumulative properties.

2.2.1 Copolymer Composition -

All monomer which disappears in an interval is assumed to appear as polymer. This is fundamental to the long chain hypothesis (LCA). The composition of this polymer is given by the relative rates of disappearance of each monomer in that interval. This composition is expressed as mole fraction of either component bound in copolymer chains.

$$F1(t) = \mathrm{rate1}/Rp \qquad (14)$$

$$F1(T) = \int F1(\mathrm{conversion})*dx \;/\; \mathrm{conv}(T)$$

At high temperature, the LCA hypothesis is strained somewhat since molecular weights can become very low, and production of significant amounts of non-polymeric materials is also likely. This assumption will be discussed in detail in Section 2.8.3 .

2.2.2 Molecular Weight Distribution -

Basic polymer balances for linear polymers have been performed by Hamielec (11). These result in a convenient two parameter relation for weight distribution and associated averages. The distribution is calculated in each interval, summed at the close of the simulation and then normalized such that the distribution area is equal to 1.0. This is necessary to overcome the limitations of discretization of the distribution function.

Instantaneous Distribution and Averages

```
w(r,t) = (tau+beta)*(tau+beta/2*(tau+beta)*(r-1))        (15)
                           *exp (- (tau+beta) *r)

Mninst(t)=   monmw /  ( tau +beta/2 )                    (15a)
Mwinst(t)=   monmw * 2 * (tau +3/2*beta)/
                                 (tau+beta)**2
```

Cumulative Distribution and Averages

```
Mn(t)= Mn(t-1) + 1/2 * (1/mninst(t)                      (15b)
                        + 1/mninst(t-1))*dx
Mw(t)= Mw(t-1) + 1/2 * (mwinst(t)
                        +mwinst(t-1))*dx
```

$$w(r,T) = \int w(r,conversion)*\frac{dx}{conv(T)}$$

Tau and beta are kinetic parameters derived from the development of Hamielec (11). Tau represents the effect of chain transfer to small molecules in developing molecular weight. Beta represents the effect of chain termination in molecular weight. These parameters are given below.

$$tau = \frac{r2*e11*f1**2 + 2*r1*r2*f1*f2 + r1*e22*f2**2}{r2*f1**2 + 2*f1*f2 + r1*f2**2} \qquad (16)$$

$$beta= \frac{-Rp * kto * (kp22*r2*f1**2 + kp11*r1*f2**2)**2}{(r2*f1**2 + 2*f1*f2 + r1*f2**2)**2 \; kp11**2 * kp22**2 * [M]**2} \qquad (17)$$

An additional transfer reaction is included in the calculation of tau, as a molecular weight parameter. This is taken from Husain et.al. (2) and is used to model the transfer to oligomers.

$$tau= tauo + kfO/kp*[O]/[M] =tauo+B1*[O]/[M] \qquad (18)$$

Since oligomer concentration was not measured in Husain et.al. (2) he chose an empirical fit, given below.

$$tau = tauo + B3*conversion \qquad (19)$$

The parameter B1 is temperature dependent only. For the copolymer case, the generalized version of this equation can be given as the following (Chiantore et.al (36)).

$$tau = tauo+(B1*phi1+B2*phi2)*conversion \qquad (20)$$

2.2.3 Oligomer Development -

With polymerizations at high temperatures, production of extremely low molecular weight material is common. These are referred to as oligomers; cyclic dimers, cyclic trimers,pentamers etc. These are not included in the model in the polymer molecular weight distribution, but are given as weight fraction of polymer.

A considerable amount of interest is placed on these low molecular weight materials because they are difficult to separate from the product resin and they usually have a large effect on the final properties of the resin. Those properties most affected are colour, mechanical strength, fatigue, flow ability and processability. Generally, oligomeric elements are not desired in the final product.

The prediction of weight fraction and characterization of the two most significant oligomers ,namely dimers and trimers, is quite valuable. This involves the study of the mechanisms by which they are created and the kinetics governing these reactions.For this model, the kinetics of the production of dimers and trimers are taken from the work of Kirchner (37). His work was limited to temperatures of 137 and 180C and covered conversions up to 97 %. This work will extend these kinetics to higher temperatures and to the styrene-acrylic acid copolymer process. To allow comparison, the equations of Kirchner (37) will be used in the model. The outflow of oligomers in the continuous flow kinetic model is assumed to be negligible since oligomer concentrations are very low. The equations for dimer and trimer development are given below.

```
d[dimer]/dt  = kdim * [M1]**2                              (21)
d[trimer]/dt = ktrim * [M1]**2
```

Instantaneous Oligomer Fractions

$$\text{dimer fraction}(t) = \frac{d[\text{dimer}]/dt * \text{mwdim} * \text{volume}}{\text{conversion} * \text{wmonin}} \qquad (21a)$$

$$\text{trimer fraction}(t) = \frac{d[\text{trimer}]/dt * \text{mwtrim} * \text{volume}}{\text{conversion} * \text{wmonin}}$$

Cumulative Oligomer Fractions

$$\text{dimer fraction} = \int \frac{d[\text{dimer}]/dt*dt *\text{mwdim}}{\text{conv}(T)*\text{cmonin}} \qquad (21b)$$

$$\text{trimer fraction} = \int \frac{d[\text{trimer}]/dt*dt *\text{mwtrim}}{\text{conv}(T)*\text{cmonin}}$$

Oligomers are also formed by thermal degradation. Extensive work in the area of thermal degradation of polystyrene has already been done, (Ebert et.al. (12) ,DeSomer (32) ,Schroder et.al.(40)). It is found that deterioration in the molecular weight distribution occurs at temperatures in excess of 280C and times of several hours. This deterioration is characterized by a decrease in average chain length, narrowing of the polydispersity, and an increase in the oligomer fraction.

Schroder et. al.(40) have done detailed analyses of the oligomeric fraction of degraded polystyrene. He found that immediately after creation, large amounts of styrene (unconverted monomer), diphenylbutene (a dimer), triphenylhexene (a trimer),and diphenylpropane are present.

After advanced degradation, the oligomer fraction changes character to ethylbenzene, toluene and cumene, or generally more stable molecules. His results and methods will be used later in this work to characterize the oil fraction of high temperature polymers.

The complexity involved in modelling oligomers produced by conventional kinetics and thermal degradation is great, since the mechanisms of each are so different. No account for oligomers generated by thermal degradation is included in this model.

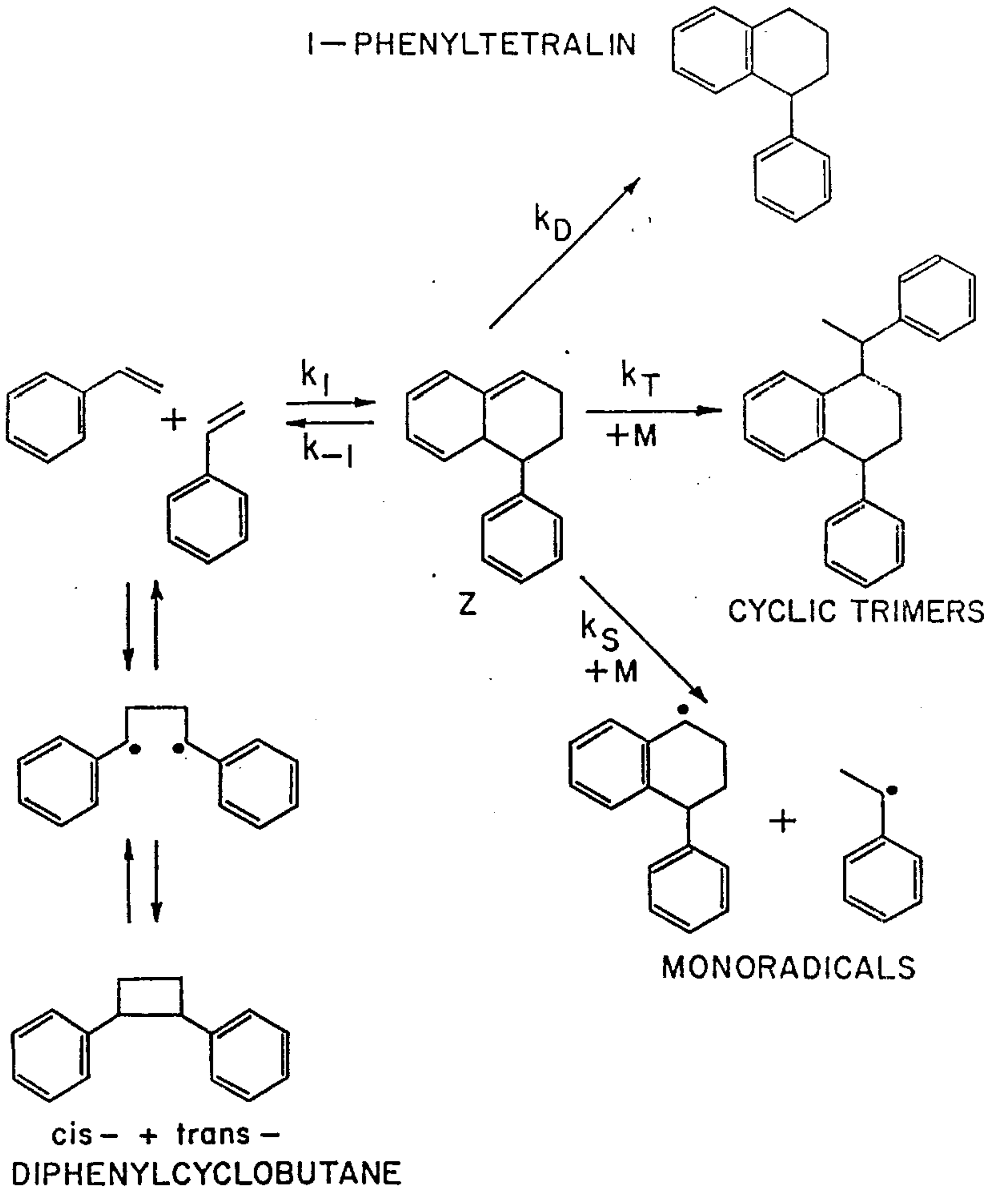
The nature of the kinetic process which creates such oligomers is believed to be due to the thermal initiation mechanism of styrene at high temperatures. A mechanism that is currently proposed is given on Figure 2.1, taken from Hamielec (11).

Trimers include up to 95 % phenyltetralin while dimers are up to 80 -95 % diphenylcyclobutane. Dimers are produced independently of the initiation scheme and are believed to be controlled by styrene monomer concentration and temperature. Trimers are the by-product of the thermal initiation intermediate and as such, are involved in the chain growth step. The mechanism by which oligomers are formed in styrene-acrylic copolymerizations will be investigated in this study.

FIGURE 2.1

POLYSTYRENE REACTOR MODELLING

THERMAL INITIATION AND OLIGOMER FORMATION



2.3 Degradation

The effect of thermal scission and unzipping was included in the model since it was felt that this may be significant at the higher operating temperatures. The equations are based on the scission and unzipping expressions developed by Ebert et.al. (12). The degradation matrices and parameters were taken from Ebert (12) as well.

$$w^{\wedge} = w * [\ ksc * KSC + kun * KUN\ ] * time \qquad (22)$$

The degradation calculation is performed only on the final product distribution from the CSTR or tube reactors. This is not entirely valid and the calculation should be performed every interval. The number of calculations would, however, be excessive.

A complete set of elemental reactions covered in the model is given on Table 2.1 .

2.4 Reactor Types

Most of what is described fits into the time dependent operation of batch reactors. The application of the model equations to simulate continuous tubular and stirred tank reactors is made by assumptions discussed later in this chapter. For the tubular reactor, it is assumed that ideal plug flow is maintained. With this assumption, the time differentials can be converted to space time for the tube.

TABLE 2.1

SUMMARY OF KINETIC REACTIONS IN THE MODEL

Reaction	Parameter
Initiation/Oligomerization	
M1 + M1 ==> dimer	kdim
M1 + M1 + M1 ==> intermediate	ki
intermediate ==> R(3,1)	
==> trimer	ktrim
Propagation	
M1 + R(r,1) ==> R(r+1,1)	kp11
M1 + R(r,2) ==> R(r+1,1)	kp12
M2 + R(r,1) ==> R(r+1,2)	kp21
M2 + R(r,2) ==> R(r+1,2)	kp22
Polymer Formation (by termination by combination)	
R(r,1) + R(s,1) ==> P(r+s)	kt11
R(r,1) + R(s,2) ==> P(r+s)	kt12,kt21
R(r,2) + R(s,2) ==> P(r+s)	kt22
Polymer Formation (by transfer to oligomers)	
R(r,1) + O ==> P(r) + R(1,1)	B1
R(r,2) + O ==> P(r) + R(1,1)	B2
Polymer Formation (by transfer to monomer)	
R(r,1) + M1 ==> P(r) + R(1,1)	kf11
R(r,1) + M2 ==> P(r) + R(1,2)	kf12
R(r,2) + M1 ==> P(r) + R(1,1)	kf21
R(r,2) + M2 ==> P(r) + R(1,2)	kf22
Thermal Degradation (by chain unzipping)	
P(r) ==> P(r-1) + M1	kun,KUN
==> P(r-1) + M2	
Thermal Degradation (by random chain scission)	
P(r) ==> P(m) + P(r-m)	ksc,KSC

Definitions

P(r) == polymer of chain length r
Mp == monomer type p
R(r,p)== radical of chain length r and type p
O == oligomer (dimer and trimer)

The modelling of the stirred tank involves the solution of the monomer mass balances given above. These are used as the steady state criterion. The units of these balances were chosen as grams per second. The solution technique is taken from a non-linear simultaneous solving routine of the IMSL package, called 'ZSCNT'.

2.5 Diffusion Control

To account for the gel effect, or the onset of diffusion controlled kinetics, the equation and parameters are taken from Husain and Hamielec (2).

```
kt =kto*exp(-A1*conversion- A2*conversion**2                 (23)
                            - A3*conversion**3 )

        A1 = 2.57 - 5.05E-03*temperature
        A2 = 9.56 - 1.76E-02*temperature
        A3 = -3.03 + 7.85E-03*temperature
```

Many other types of correlations have been used by workers to account for gel effect and references to these are included in Section 2.7.

For copolymerizations, the three chemical rate constants describing homo- and co-termination should also involve some sort of diffusion correlation similar to those developed for styrene. To date in the literature, no reference is found for this effect. It remains that considerable experimentation is required on the single monomer kinetics before the co-kinetics can be developed.

For this modelling work, only the styrene termination constant was corrected for gel effect by equation(24). No gel effect was assumed for acrylic acid.

2.6 Literature Review Summary

Although most of the modelling equations are based on first principle derivations, a literature review was undertaken to complete the study.

1. The kinetics of the bulk thermal polymerization of styrene were taken from the work of Husain et.al (2). Correlations and parameters are given in that paper that are used in the model. Thermal initiation equation(12), conversion dependent transfer ratio (defined as kfm/kp,) from equation(12)and conversion dependent termination rate in equation(24) are included for the bulk homopolymerization of styrene.

2. The rate equation(2,3) was chosen from Rudin et.al. (1), whose paper describes a comparison between conventional rate expressions, his own, and actual measured initial rates for the styrene/methyl methacrylate system at 60C .

3. Melville et.al.(3) provides one of the earliest treatments of copolymerization rate expressions. The equation was not used in the model. His definition of the transfer ratio kinetic parameter is used.

4. The book of Alfrey et.al.(4) provides an early study of copolymerization kinetics. The authors propose a heat of copolymerization expression which was considered for this model, but rejected for a much simpler relation given by Hamielec (11).

5. An expression for instantaneous composition was given by Wall (5) in a very early paper. For the purposes of modelling it is not useful.

6. A paper by Walling (7) considered the copolymerization of the styrene/MMA system. His study of the copolymerization rate expression actually is a pre- cursor to the work of Hamielec (11). Both papers are considered later in this report.

7. A book by Bamford (8) provides another study of copolymerization kinetics which was considered. Of most interest, was their discussion of experimental determination of the kinetic parameters and their sensitivities.

8. Barb et.al. (10) provides a consideration of cross initiation which, although not providing any actual parameters, did suggest ways of obtaining copolymerization kinetic parameters experimentally.

9. A set of recent notes by Marano (9) gives a general overview of modelling and the problems that may arise in particular with polymer models. These problems are discussed at length in Section 2.8 .

10. Wallis (19) performed solution styrene polymerizations in a pilot scale tubular reactor. He used the model correlations of Husain and Hamielec (2) for styrene kinetics up to 20 % conversion. He found that the fits were very good and could find no problem with the kinetics.

11. Khac-Tien (24) studied the bulk, thermal production of polystyrene in a tube reactor. He also found that the kinetics of Husain and Hamielec (2) fit his data quite well up to conversions of 50 % .

12. Extensive study of polymer modelling equations, assumptions and properties, may be found in Biesenberger(35). His method using the characteristic kinetic time constant applied to kinetic assumptions is used in this work.

13. Discussions of the effect of mixing in polymer reactors were found in Biesenberger(35) and Levenspiel(23). Single parameter, imperfect mixing correction routines were included in the model and are discussed in Appendix 7.4.

14. Atherton and North (34) present an early derivation of the copolymer rate expression and termination rate constant. Hamielec (11) presents an expression for copolymer termination rate constant, which was rejected for that of Rudin (1).

15. Diffusion control modelling has been studied extensively by workers such as Hui(26), Lord(27), Sacks et.al.(29), Beuche(33), and O'Driscoll et.al.(28). The expression selected for this model was taken from Hui(26) and is given in equation (24).

Some example output of the model is included in Figures 2.2 to 2.5.

2.7 Assumptions Involved In The Model Derivations

In building and understanding a kinetic model, one way of describing kinetic phenomena and their interrelationships is by the time constants which characterize them. By looking at these time representations, one can make logical assumptions regarding the significance of each, relative to the dynamic properties of interest. These assumptions are the foundation for the model and will be justified in detail in this section.

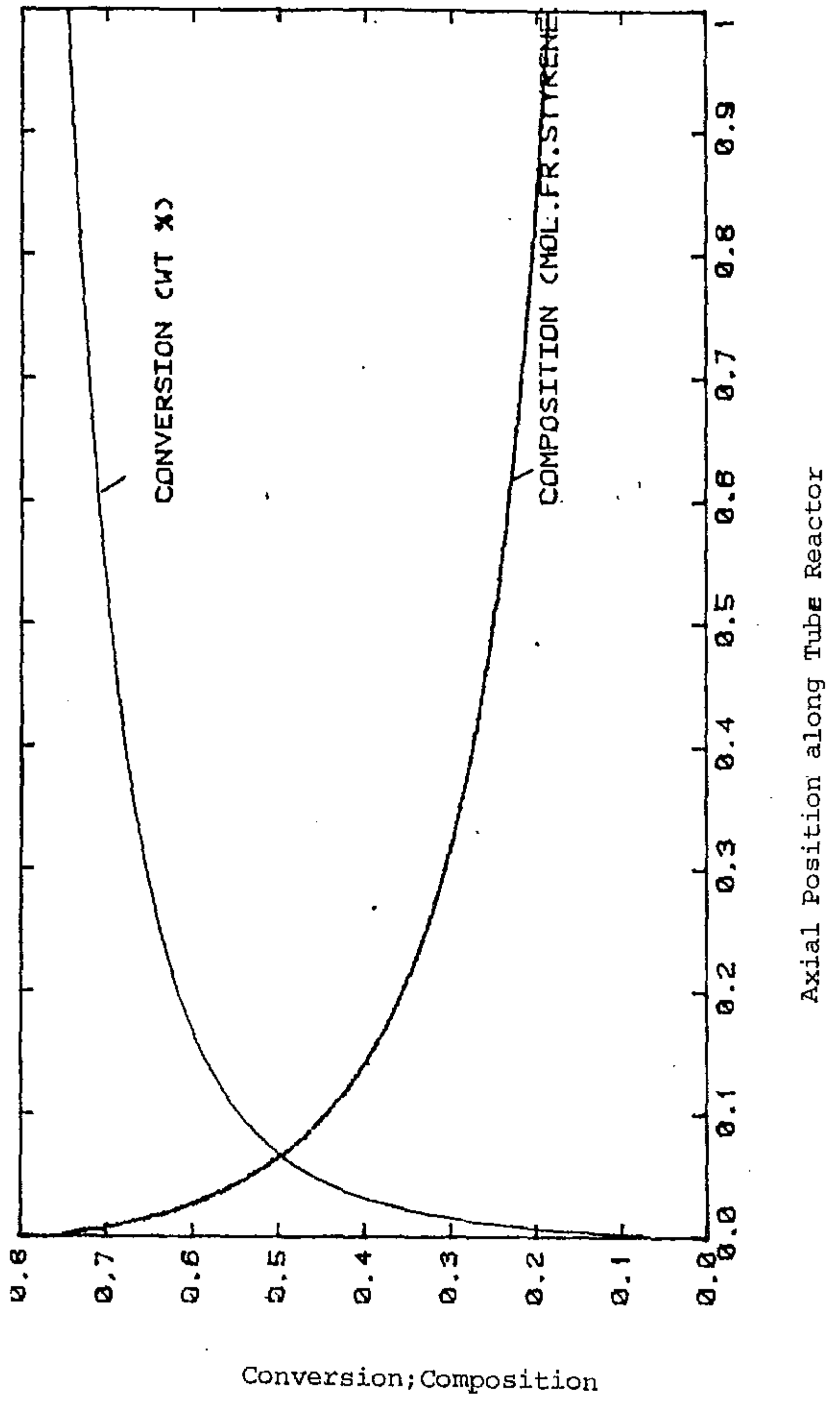


Figure 2.2
Model Predictions of Conversion and Composition for an Example Test Data Set; temperature=230C

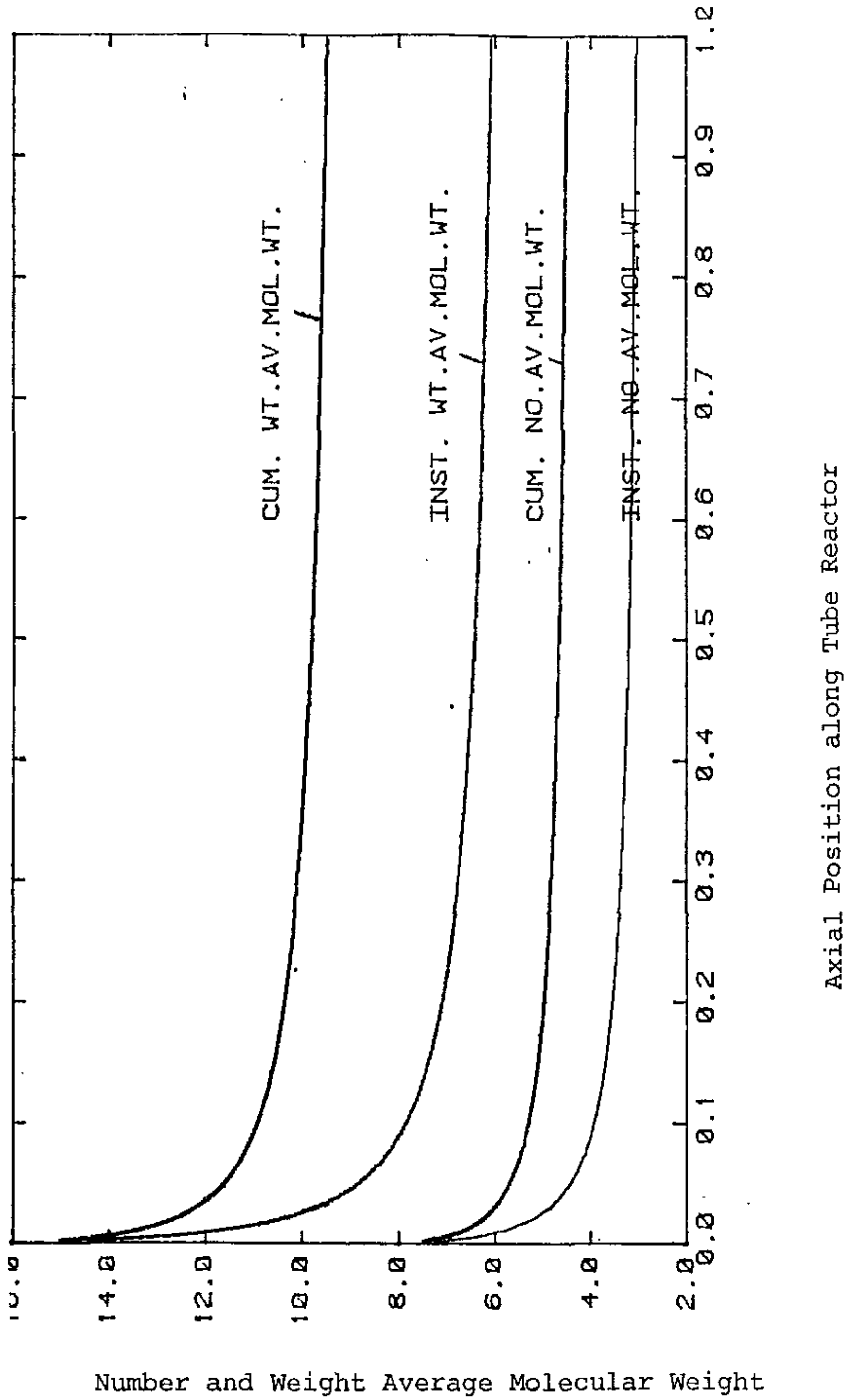


Figure 2.3
Instantaneous and Cumulative Molecular Weight
Averages for Example Data Set;temperature=230C

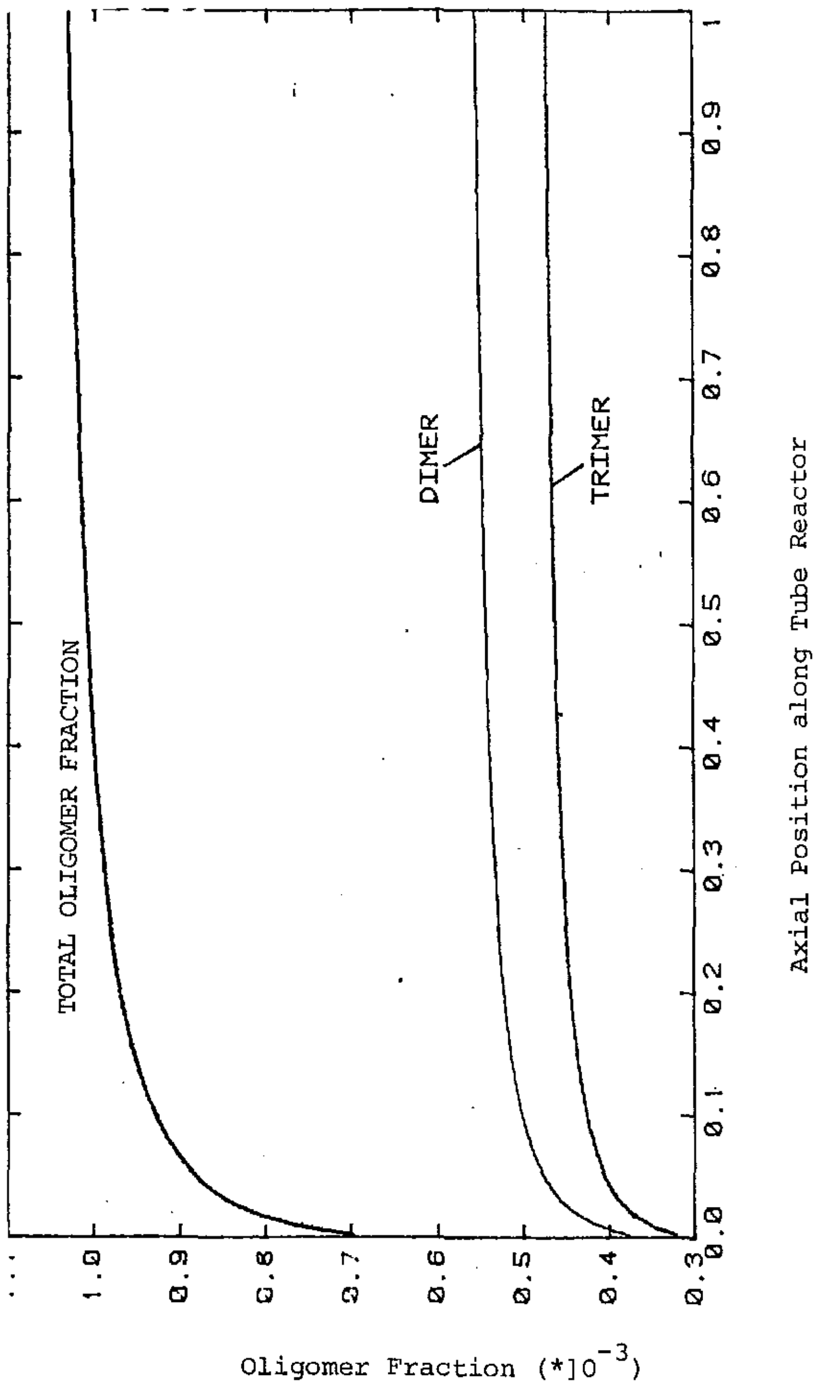


Figure 2.4
Oligomer Fraction Development along Tube Reactor Expressed as Weight Fraction of Polymer;temperature=230C;Test Data Set

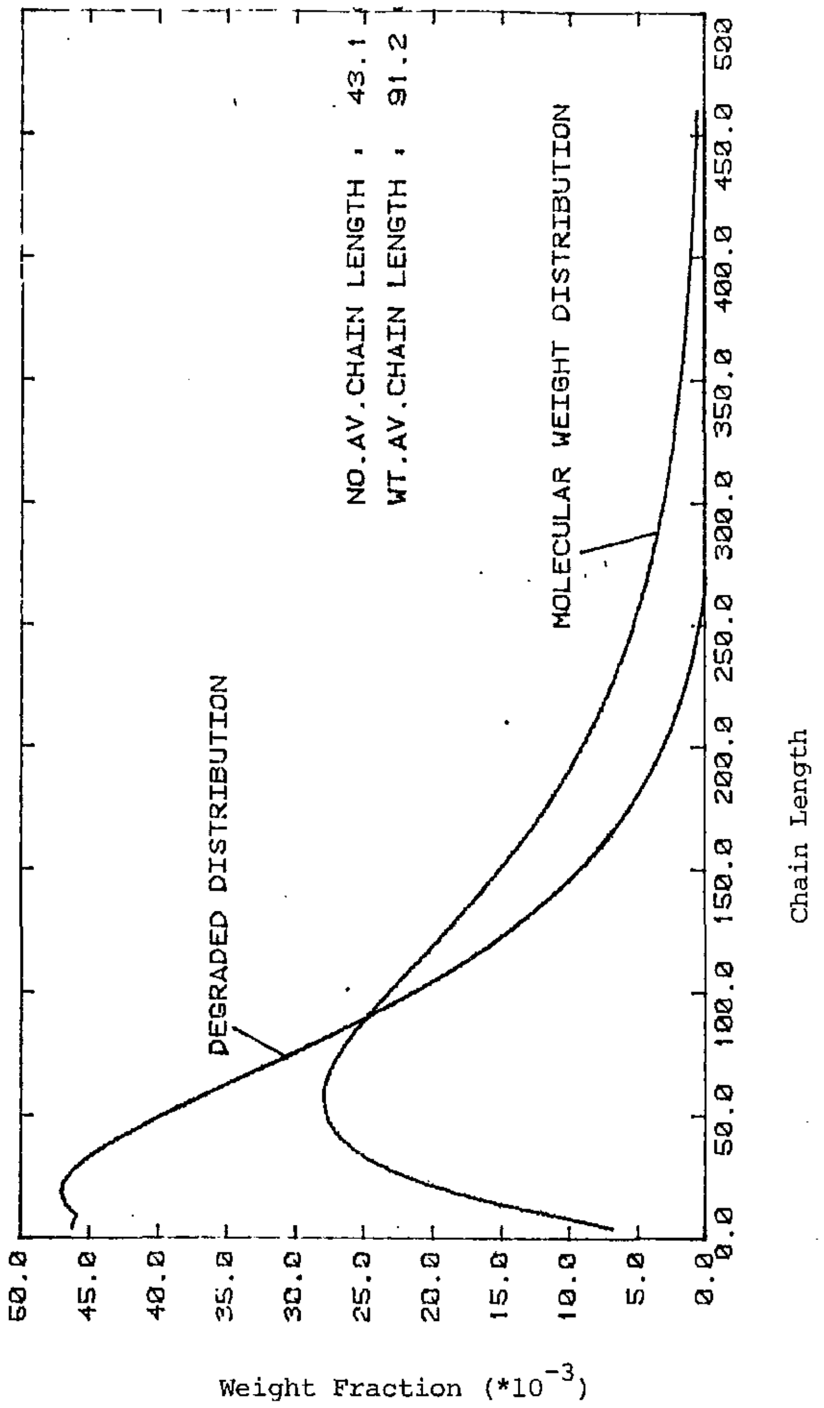


Figure 2.5
Example Model Output Demonstrating Degraded Molecular Weight Distribution;temperature=230C; degradation effect exxagerated for clarity

The time constants of interest and related phenomena for the kinetic system being modelled are given below.

tau(f) == volume/flow == flow time constant
tau(i) == [I]/Ri == initiator time constant
tau(m) == [M]/Rp == monomer time constant
tau(d) == [dimer]/Rdim == dimer time constant
tau(t) == [trimer]/Rtrim == trimer time constant
tau(r) == 1/sqrt(Ri*kt) == radical time constant

The dynamics of interest are those involving the polymer properties and monomer. These are directly related to the time constants of monomer and radicals. Separation of other kinetic phenomena from those of interest allow for simplifications of the kinetic treatment. Common assumptions in polymer modelling can be reduced simply to this principle of separation of time constants. These assumptions are given below.

KINETIC ASSUMPTIONS IN POLYMER REACTION MODELLING

Reactor Steady State Hypothesis (RSSA)

tau(f) >> tau(i) radicals are not washed out of the reactor

Steady State Hypothesis (SSH)

tau(m) >> tau(r) radicals at steady state relative to monomer rate; no dead-ending

Long Chain Approximation (LCA)

tau(i) >> tau(m) slow initiation to provide for long chains

These and other assumptions involved in deriving the bulk, thermal copolymerization model are discussed at length below.

2.7.1 Kinetic Constants Independent Of Chain Length -

This assumption greatly simplifies the model development in that one constant is required for one reaction type. Essentially "reactivity is concerned with the ultimate group only"; the effects of all preceeding or penultimate groups in the polymer chain are taken as negligible.

Chemical reactivity of monomers is considered to be due to electron density, described by the phenomena of resonance, polarity, and geometry, or steric effects. However, in most polymer systems, mass transfer plays an important role in limiting reaction rates. This is diffusion control. Generally, either mechanism operates simultaneously but at extremes of conversion one can safely assume one mechanism dominates.

Chemical control is typical of low conversion with resistance to reactivity primarily due to chemical activation energies. In this region, it is postulated...

1. except for highly conjugated monomers (dienes) resonance stabilization due to chain length will be negligible.
2. geometric effects from preceeding groups will not affect reactivity since they are far away from the reaction site.
3. polarity may be slightly influenced by preceeding groups if they possess a strong inductive side group.

Diffusion control will predominate during high conversion when mass transfer of macroradicals through viscous media becomes the dominant resistance to reaction. In this region, the kinetics will certainly depend on chain length. Higher chain length will reduce the rate of segmental and translational diffusion and slow the termination rate.

This effect will be most noticeable on the large molecule reaction of termination but may, in extreme cases, include propagation and transfer reactions as well, when polymerization temperatures are close to the glass-transition temperature of the reacting solution.

2.7.2 Steady State Hypothesis -

This assumption really restates those presented earlier with respect to separation of time constants describing monomer and radical kinetics. The SSH assumption involves two parts; the first dealing with the overall reactor steady state (RSSA), with volume/flow rate time constant and second, the radical steady state hypothesis. It is this assumption that causes great concern in polymer reaction modelling. It is, however, very common since it allows ready solutions of the species balances.

The radical steady state assumption states that the rate of change of radical concentrations is very much smaller than the rate of generation of radicals or the rate of termination of radicals. This leads to the assumption that radical lifetimes are very much shorter than reaction time constants for modelling interval being studied. Practically, it means that the time derivatives of the radical differential equations can be set to zero and the resulting algebraic solutions solved in each interval. The need to solve a set of stiff differential equations is thus eliminated.

One can write a radical balance for a time interval and region of reaction as the following.

d [R]/dt = Ri - kt *[R]**2 + [R]/theta - [R]/theta (24)

.. where the last two terms represent inflow and outflow from the unit volume and theta is the mean residence time of the CSTR.

For all real systems the process time constant ,theta, is a very large number and we can say that [R]/theta is very small relative to the other two terms. This is the reactor steady state assumption.

If the now simplified differential equation is solved we find from Bamford et.al. (8),

[R]/ [R]o = tanh { sqrt(Ri)*kt) } * time

The steady state criteria is that [R]/[R]o =1.0000. Therefore..

time > 1/ sqrt{ Ri*kt } (25)

Substituting common values for Ri and kt, we find that the time constant governing radical concentration is approximately 0.2 seconds. The monomer time constant for thermal polymerization of styrene is roughly 1000-2000 seconds. There is no doubt that these kinetic phenomena are separated in time horizon and can be assumed to operate without interaction.

Marano (9) poses a number of concerns with the SSH assumption.

1. initiator mechanism may change during the course of the reaction.
2. if the rate of initiation drops to zero, the [R] will, by this assumption, be zero; no dynamic in radical concentration is allowed

These concerns are all valid, but are covered in the time expression presented above. If the rate of initiation falls to zero the required interval time for modelling is infinity, or the steady state assumption becomes invalid.

Also, Biesenberger (25) points out that modelling gel effect may put a strain on the model steady state assumptions. If we allow that gel effect does involve rapid termination rate constant reduction than it is believed that the above criterion is sufficient to determine when the fixed interval basis in simulation is warranted. Biesenberger and Capinpin (35) looked at the effect of the SSH assumption against dead-ending polymerizations (those in which Ri goes to zero before the monomer is depleted). They found no significant effect in the cumulative properties. Minor deviations were noticed at low conversions.

The alternative to not using the SSH is the solution of a set of very stiff differential equations. In this method, a numerical integration technique involving variable interval lengths is required. This method allows for the changing time constant of the system and integrates over periods of steady state only. This method was not used in this study and provided care is taken in the choice of interval, no difficulties were expected.

2.7.3 Long Chain Assumption (LCA) -

This assumption has been studied in this work by modelling with two different rate subroutines. Monomer is consumed terminating chains through transfer, propagating chains, or forming oligomers.

$$Rp = R(transfer)+R(propagation)+R(oligomerization) \qquad (26)$$

The propagation term usually is dominant. The LCA assumption states that all monomer is consumed by propagation on polymer chains, therefore creating long chains. This simplifies the rate expressions for homopolymerization rate, but for computer simulations, does not provide any particular benefit. The difficulty that is overcome by the LCA assumption in copolymer modelling is that it provides a way of solving for the radical concentrations, with the SSH assumption, without having to solve their differential equations.

In copolymer modelling, the LCA assumption allows one to conclude that the number of 1-2 links in a polymer chain equal the number of 2-1 linkages. This implies that the rates of cross-propagation are equal. This will always be true with deviation of 1/N, where N is the number of linkages in the chain. Obviously for long chains the deviation approaches zero. For short chains however, those produced by high temperature thermal polymerization, the error may become significant.

The expression derived from the LCA assumption is given below.

$$kp12 * [M2] * [R1] = kp21 * [M1] *[R2] \qquad (27)$$

This gives a relationship between the two radical concentrations which allows for a simple copolymer rate expression.

At higher temperatures, transfer and oligomerization reactions are more frequent and will not be equal for each monomer. It is likely that the rates of cross-propagation will deviate.

Therefore, in copolymer modelling, another relation for radical concentrations must be found. This relation is taken directly from the radical balances, equations (6,7,8). By using the SSH assumption, the radical concentrations can be solved as two non-linear simultaneous equations in each interval by an appropriate solving routine.

It is easily shown that the radical differential equations, from equations (6,7,8), reduce to the equal cross-propagation expression given above when the rates of initiation, transfer and termination are small compared to propagation. This is also the requirement for long chains.

For the particular monomers under study in this work, simple calculation can be used to test the validity of the LCA assumption.This has been done below, for styrene/acrylic acid (50:50 weight) thermal polymerization at 260 C using literature values of kinetic constants. As is readily seen, propagation dominates all other rates.

Propagation...
Rhomostyrene = 6.2 10**-4 mol/l/s
Rhomoacrylic = 3.4 "
Rcrossprop.12 = 0.6
Rcrossprop.21 = 29.1

Other.........
Ri = 0.0141
Rtransfer = 0.0233
Rtermination = 0.0303
Rdimerization = 0.459
Rtrimerization = 0.162 "

2.7.4 Ideal Reactor Performance -

In the derivation of the polymer properties it was assumed that ideal reactor performance for both the stirred tank and tube reactors could be assumed. These will be specifically dealt with here.

For the tube reactor it is assumed that there exists a constant velocity profile along the tube (ideal plug flow) and radial gradients are negligible.

These assumptions allow for great simplification of the describing equations. A more comprehensive model of a tube reactor was done by Husain (31). He checked for the effect of radial diffusion and non-plug flow velocity profiles. He found that the fluid power law index had little effect on the predicted polymer product and therefore concluded that flow radial velocity profile had no significant effect on the model. He also found that setting a radial diffusion coefficient equal to zero had only a 1-2 % lowering of predicted conversion and no effect on molecular weights. For this reason, it is believed that the plug flow model is an adequate structure for kinetic modelling, at low conversions.

For the CSTR modelling, non-ideality is reflected in the reactor steady state assumption and mixing effects which are included in the model and documented in Appendix 7.4.

2.7.5 Choice Of Modelling Interval -

This quantity is generally the time interval chosen in batch reaction modelling or, the axial increment in ideal PFR cases. Its selection must allow the user to view the kinetics of interest, without involving the extra complexity of other kinetics. In well resolved systems, where the kinetic phenomena are completely separated in time frame, the choice becomes narrowed to some fraction of the monomer kinetic time constant.

In not so well defined cases such as those involving non-ideal mixing, severe gel effect , extremely fast rates , multi-phase reactions, and more commonly, dead-end polymerization ,the kinetic time constants will surely interact and the simplifying modelling assumptions will become invalid. The result will be a much more complicated model involving numerical integration of a set of stiff differential equations.

In this model, the sampling interval is defaulted as 1/25th of the monomer time constant, to a maximum of 500 intervals. This implicitly assumes that the time constants of radical and monomer kinetics are distinctly separate and that no other kinetic phenomena overlap with the monomer time frame. To police this assumption, the time constants of monomer and radical are outputted. Should these approach each other, error in the model results will be unavoidable.

2.8 Summary Of Model Equations

Mass Balances	Equation#
monomer 1 == d[M1]/dt	1
monomer 2 == d[M2]/dt	2
rate of poly. == Rate1,Rate2,Rp	2,3,14
termination constant == kt(conversion)	23,3a
rate of initiation == R(initiation)	12
Instantaneous Polymer Properties	
molecular weight distribution == w(r,t)	15,22
no.av.mol.wt == Mn(t)	15a
wt.av.mol.wt == Mw(t)	15a
copolymer composition == F1(t)	14
dimer fraction(t) ==	21
trimer fraction(t) ==	21a
Cumulative Polymer Properties	
molecular weight distribution == w(r,T)	15b
no.av.mol.wt == Mn(T)	15b
wt.av.mol.wt.== Mw(T)	15b
copolymer composition == F1(T)	14
dimer fraction(T) ==	21b
trimer fraction(T) ==	21b

CHAPTER 3.0

3 EXPERIMENTAL PLAN AND EQUIPMENT

3.1 Equipment And Materials Description

The reactor schematic (Figure 3.1) shows the set-up used to perform the high temperature experimentation. It consists of a high pressure, continuous stirred tank reactor in series with a tube reactor and product/waste receivers. For the majority of the characterization and kinetic study work, only the CSTR was utilized.

3.1.1 Reactor Description -

The continuous flow stirred tank reactor is diagrammed on Figure 3.2 . It is a 1.4 liter ,agitated ,aluminum core, stainless steel lined vessel. It is electrically heated by a single 200 Watt coil. The voltage to the coil is controlled by an analog PID controller. Agitation is provided by a variable speed motor through a magnetic coupling to allow for leak proof operation at high pressure. Both motor and drive RPM are monitored to check for slippage. In addition, a high-temperature limit switch is provided.

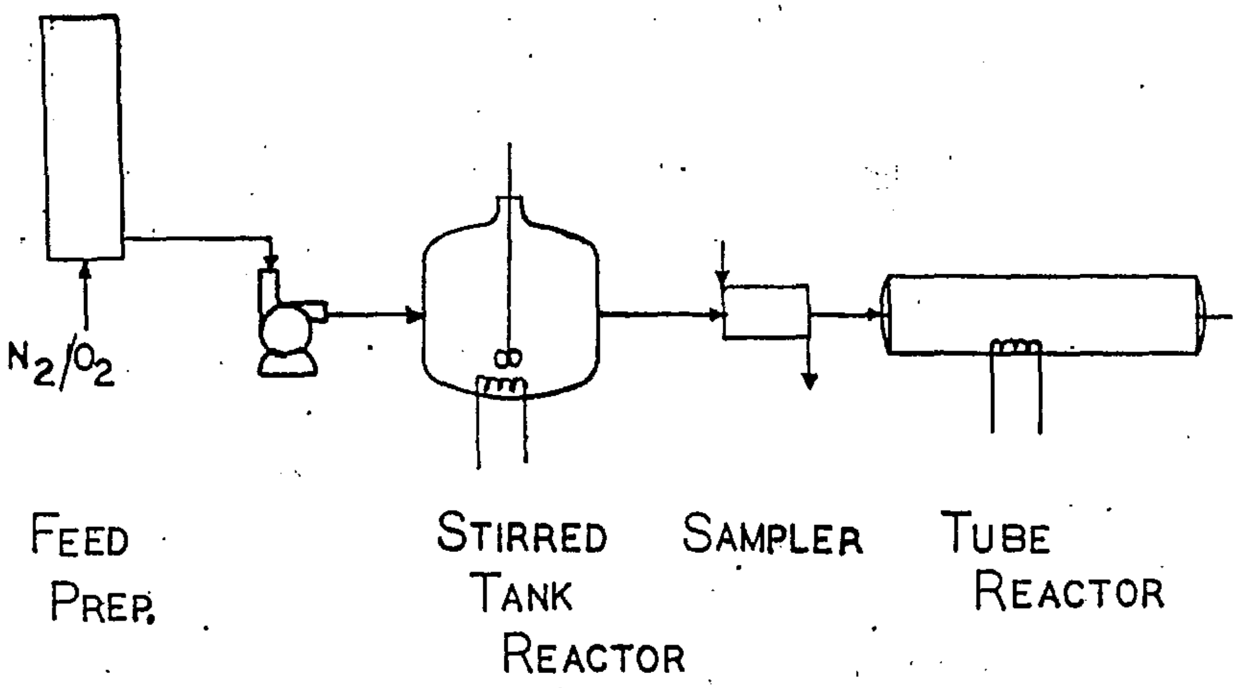


Figure 3.1
Experimental Pilot Plant Set-up for Continuous Polymerizations

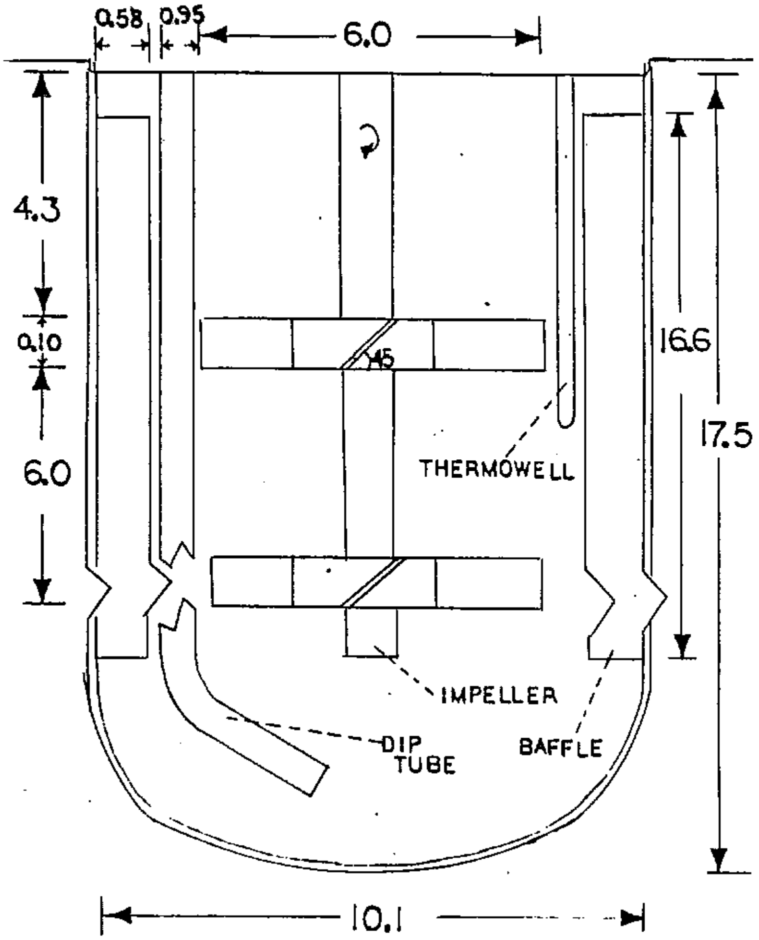


Figure 3.2
Pilot Scale Reactor and Agitator Dimensions.
All Dimensions are in centimetres

Agitation is controlled by the drive RPM controller. The dimensions of the agitator are provided in Figure 3.2 . In order to determine the mixing efficacy of the agitation system, a residence time distibution (RTD) study was undertaken. Such a study was necessary because the stirred tank operating points will be used to do kinetic parameter estimation. It is therefore important that the state of mixing of the tank not influence the kinetics. This requires that the characteristic mixing times be much less than the kinetics of the reaction.

Feed monomers are introduced cold into the bottom of the reactor through a dip tube. Product is removed at the top of the reactor through a discharge line. This will ensure that the reactor will fill itself completely before flow is established.

3.1.2 Tube Reactor Description -

The tube reactor is a 10.5 feet long, 3/8 inches inside diameter stainless steel tube wound in an approximately 7 inch diameter coil. It has a volume of 0.242 liters. Thermocouples are attached at the inlet, outlet and through the loops. The reactor is immersed in silicone oil maintained at a constant temperature.

3.1.3 Monomers And Solvents -

The considerable amount of styrene that was required for continuous pilot plant experimentation was obtained from Aldrich Chemical and also provided by S.C. Johnson and Son, Brantford, Ontario. No monomer preparation was done in the experimental work. Therefore, inhibitor and possibly other contaminants will be present. Purification of the large amounts of feeds was impractical with a continuous pilot plant. It is understood that the model is meant for commercial application. The acrylic acid was obtained from the Johnson Company in Brantford as well.

3.1.4 Sampling Procedure -

Samples were taken from the product stream from a continuous purge line. Due to the highly viscous condition of the resin, a continuous sampling system was required. Cooling or stoppage of flow could not be tolerated since plugging can be very common. Samples were taken by capturing the flowing stream in a known amount of solvent. The solvent was cooled to condense any residual monomer that may flash at the discharge. The amount of monomer lost in this procedure is unknown, but it is not considered to be significant. The sample collected is re-weighed and analyzed for conversion. The amount of sample collected was approximately 1-2.0 grams in 10-20 grams of solvent.

The conversion range possible with the sampling method used was limited to greater than 50-60 %, depending on temperature. At lower conversions excessive flashing made sampling futile and dangerous. Attempts to extend the range by cooling the sample line failed since the polymer merely froze to the cool surface and plugged. Capturing the hot resin in solvent has to date been the only successful method of sampling in this study.

3.2 Analytical Methods - Homopolymerization Study

The product polymer, captured in a solvent sample, is analyzed to determine the following..

- conversion
- molecular weight distribution and averages
- dimer and trimer weight fraction

The methods are outlined below. The solvent used for polystyrene sampling was toluene.

3.2.1 Conversion -

Weight percent conversion is calculated from the following relation, utilizing area responses from GC analysis and solvent as an internal standard.

$$1\text{-conversion} = \frac{\text{grams residual monomer}}{\text{grams of polymer} + \text{grams of residual monomer}} \qquad (28)$$

$$\text{grams styrene} = \frac{\text{area styrene} * \text{Kf} * \text{grams toluene}}{\text{area toluene}}$$

The GC used was a Varian Model 5880A. The column packing chosen was a Carbowax 1540 on Chromosorb T.

3.2.2 Molecular Weight Distribution And Averages -

The molecular weight information was taken from gel permeation chromatography (GPC) analysis. With this method, a full distribution, averages and oligomer fraction was obtained.

The GPC instrument was a Waters 150-C with autoinjection and a Waters DRI detector. Columns used were TSK H series, 2500, 3000, 4000, and 5000. Pore sizes were 500, 1500, 10**4 and 10**5 Angstroms. Solvent was toluene, at a flow rate of 1 ml/min and temperature of 40C. An injection volume of 100 microliters with polymer concentrations of 0.1-0.4 grams/ 100 ml was found to give reasonable response given the very low molecular weights encountered.

Calibration was done by a series of narrow molecular weight distribution polystyrene standards. These were TSK standards A-500, A-1000, A-2500, A-5000, F-1 (10 000), F-2 (16 000), F-4 (43 000), F-10 (100 000), and styrene monomer. The peak elution volumes were regressed against the logarithm of molecular weight. The curve equation is given below.

$$\log_{10}(Mw) = C1 + C2*EV + C3*EV^{2} + C4*EV^{3} \qquad (29)$$

The values of C1-C4 were taken by fitting the peak counts corresponding to the sample known molecular weight to the above expression. Although highly correlated, all four C parameters were used in the scheme. The relative errors in molecular weight estimation become more significant at lower molecular weights. No correction for column non-ideality was employed.

3.2.3 Oligomer Fractions -

The computation of weight fraction dimers and trimers was done by taking area fraction of oligomer to polymer. Since no standards for dimer and trimers were available, response factors were assumed to be equal to 1.0 for both oligomers.

The GPC estimates of oligomer fractions were verified by high temperature gas chromatography. This method was capable of resolving the oil fraction much better than the GPC. The method was taken from Schroder et.al. (40). The GC used was an HP-5880A. The column packing was 5% SE-54 GAW-DMCS 60/80. The column was 6 feet long and 1/8 inch diameter. Gas (nitrogen) flow rate was roughly 20 ml/min. A simple temperature program was found to be adequate. A rate of 2 C/min was used to bring an initial temperature of 75 C to 250 C.

Quantification of the HTGC response was done similar to Schroder(40). Peak areas were referenced to styrene with a correction factor of 1.00, after the results of Schroder (40) who found little deviation with such calibration.

3.3 Analytical Methods - Copolymerization Study

For the copolymer system, a new set of instrumental methods and solvent (tetrahydrofuran) was required.

3.3.1 Copolymer Total Conversion -

Total conversion is defined below.

$$1\text{-conversion} = \frac{\text{grams residual styrene} + \text{grams resid. acid}}{\text{sample weight}} \qquad (30)$$

Gravimetry was attempted to try to get total conversion of monomers. This was unsuccessful due to the problem of drying a glassy polymer. The films tended to crust over and harden before complete drying was attained.

Titration for residual acid was selected as the simplest and most reliable method of determining acid weight from a polymer sample. A polymer sample of known mass, collected in THF, was washed with excess water (50:50 sample:water volume). The polymer and styrene are not soluble in de-ionized water. The acrylic acid monomer is infinitely soluble in water. The mixture was then filtered and rewashed with water up to a volume of 4 dilutions. The resulting solution was then titrated with strong base to give the amount of free acrylic acid in the original sample. Sharp end points were obtained and repeatability of 5-10 milligrams of acid was measured. (The pKA of acrylic acid is 4-5.0).

Combining the GC for residual styrene with the titration for residual AA, all conversions are readily calculated.

3.3.2 Copolymer Composition And Distribution -

Average composition was inferred by the combination of GC , titration and mass balance. Composition distribution was not measured but was assumed to approach monodisperse, from the operation of the steady state CSTR. The calculation is shown below. The LCA assumption is implicitly assumed in the development.

wt. styrene in polymer= f1*sample - resid styrene
wt. AA in polymer= (1-f1)*sample - resid AA

$$F1 = \frac{\text{wt.styrene in polymer / Mol.Wt. styrene}}{\text{wt.styrene in polymer /Mol.Wt.styrene + wt.AA in polymer/Mol.Wt.AA}} \qquad (31)$$

The potential of using an in-line UV detector in series with the GPC was investigated (Garcia-Rubio (39)). This extremely elegant method of getting combined molecular weight and composition distribution information is ,however, not without its complications. This instrument system utilized was an HP-1040A high speed scanning UV spectrophotometer. The scan was in the range of 200-600 nm. The absorbance at 254 +/ 10 nm was used to indicate styrene. The GPC column was Dupont bimodal EV1027 and EV 1028. Solvent (UV grade THF) flow rate was 1 ml/min. A Waters 401 differential refractometer was used to infer polymer concentration.

Composition estimation was verified by proton NMR analysis.

3.3.3 Molecular Weight Averages And Distribution -

GPC was again used to measure the molecular size distribution and averages. The calibration was done using the previous polystyrene curve and with estimated Mark-Houwink-Sakurada (MHS) constants. The procedure for estimation of MHS constants and subsequent recalibration of narrow molecular weight curves is described in Rudin (13) and Chiantore et.al. (36). Calibration for copolymers by the universal calibration technique rely on the estimates of the Mark-Houwink constants. These can then by readily applied to the C parameters in the narrow molecular weight calibration curve by the following transformation.

$$C1'' = C1^{*}\,\frac{(1+As)}{(1+Ax)} + \frac{\log 10(Ks/Kx)}{(1+Ax)} \qquad (32)$$

$$\begin{array}{l}
C2'' = C2^{*}\,(1+As)/(1+Ax) \\
C3'' = C3^{*} \quad \text{"} \qquad \text{"} \\
C4'' = C4^{*} \quad \text{"} \qquad \text{"}
\end{array}$$

Estimation of the Mark-Houwink parameters was done by comparing measurements of weight average molecular weight by low angle laser light scattering (LALLSP) with GPC predictions, based on the polystyrene calibration curve. Software to do the estimation was taken from Chiantore (43).

The light scattering instrument used was a Chromatix KMX-6. The solvent used was tetrahydrofuran, at a flow rate of 0.3 ml/min. Polymer concentrations required to get reasonable response were high, in the range of 0.5 to 5.0 grams/100ml.

Implicit in the use of LALLSP for weight average molecular weight determination for copolymers is the assumption of mono-disperse composition. Each polymer molecule is the same with respect to composition and sequence length. They differ in chain length only. The governing equation is taken from Huglin (38).

$$Mw(LALLSP) = Mw(actual) + \frac{P^{*}(va-vb)}{v} + \frac{Q^{*}(va-vb)^{**}2}{v} \qquad (33)$$

As is seen above, for composition heterogeneity, the actual Mw must be obtained by plotting the LALLSP response for a variety of refractive index increments, therefore, a variety of solvent systems. The use of light scattering for Mw estimation of heterogeneous copolymers is not trivial.

One of the problems with the use of off-line LALLSP for this system is that the measured Mw will include all oligomers. The Mw's taken from the GPC trace do not. It is not practical to physically separate out the oligomers at low temperatures. This will cause some deviation in the calibration procedure, since the oligomer fraction of thermal polymers is not insignificant. It is known ,however, the the LALLS response is most sensitive to the larger molecules of the sample. Therefore, in this study it was assumed that oligomers will not contribute significantly to the LALLSP estimate of Mw when measured off-line.

3.3.4 Oligomer Fraction -

Oligomer fraction was obtained by the same method as described above and was also checked by high temperature gas chromatography, as in the homostyrene procedure.

3.4 Experimental Design And Parameter Estimation

The power of the derived computer simulation of the kinetics of the process is greatly extended by using the model in a parameter estimation mode. In this way, actual process information may be injected into the model equations.

Assuming that the model expressions , correlations and equation structures are applicable, the major problem is to estimate good kinetic parameters for the particular system being investigated. Certainly homopolymer studies provide propagation and termination constants which can be readily and safely extended to copolymer modelling.

There remains , however, an excessive number of parameters in the model which must be estimated from new data. These include cross-termination, cross-initiation, reactivity ratios, cross-transfer, gel effect and other transfer constants. The statistical problems in trying to estimate such a large number of interacting parameters prevents this from being practical. It is therefore necessary to rely on literature values and past experience in reducing the number of unknown parameters. This, unfortunately, makes the estimates of the new parameters contingent on the literature values. The alternative is an entirely empirical modelling approach which provides little comparison of results and poor insight into the kinetics.

The parameters taken from the literature in this study are discussed below.

The cross-termination factor is the geometric mean of the two homo-termination constants. Statistically phi should be equal to 1.0 since it is rationalized that encounters between dissimilar radicals is twice as likely as similar radicals in an equal radical distribution environment. It has been found to deviate considerably from 1.0, due to non-equal radical concentrations, and differences in radical reactivities. The temperature dependence of phi depends on the nature of the cross versus homo-termination reactions. It is likely to be mildly temperature independent.

Recent work by Rudin et.al. (1) has found an empirical expression for rate involving phi which they claim is composition independent. Barb (10) claims the composition dependancy arises from the penultimate effects, which may justify the empirical expression of Rudin (1).

Similar monomers will generally have phi close to 1.0, as with the styrene/alpha-methyl styrene system. Rudin et.al. (1) gives a plot of phi versus r1*r2 for a variety of systems. The shape of this curve is supported by a theoretical derivation of Bamford et.al. (8), using the Q-e scheme, who finds that phi should be related to 1/ sqrt(r1*r2).

This parameter has been assumed to be 1.0 in this study. No literature value was found.

Reactivity ratios have been well documented in the literature since they are the simplest copolymer parameters to measure. However, only recently have the experimental errors associated with r measurements been resolved by the use of correct statistical methods . Most early methods of r determination suffer grave errors due to curve fitting problems.

The sensitivities of reactivity ratios have been documented. Temperature effects seem to be minimal due to the cross versus homo-propagation reactions having similar activation energies. Problems could be developed , however, with systems involving pH or multiple phases, which could have an influence on the relative rates of cross or homo-propagation.

Ratios are generally obtained by differential composition measurements. For this system, styrene-acrylic acid, a number of references for reactivity ratios can be found. The most frequent values were selected for use in the model. These are (1 == styrene, 2 == acrylic acid) $r1 = 0.25$ and $r2 = 0.06$.

Past experience with acrylic acid monomer shows that it does not homo-polymerize thermally to a great extent (Hamielec (41)). For this reason, cross-initiation and homoacrylic acid initiation rate parameters are set to zero.

Ideal mixing was verified by reactor impulse response testing.

The conventional rate expression was used since it was found that the LCA assumption is not severely tested at these conditions and also permitted much faster computation time.

3.4.1 Parameter Estimation -

It is desirable that the number of experiments required to estimate these parameters is small, especially for continuous pilot plant experimentation. For this reason some pre-experimental planning was done to determine a number of things:

- what parameters can be estimated ?
- how confident can we be in these estimates ?

These properties of the parameter estimation are constrained by

- the number of independent experiments available
- the range of the dependent variables possible
- the confidence available from the measurement of the response variables and independent variables

The amount of data limitations are, of course, time limits only. More experimentation leads to a cumulative effect on the information content of the model. In this study, steady state operating points were used to generate data for kinetic parameter estimation. This will limit the amount of data since long waits for steady state are required.

The range of the experiments is limited by the physical method of sampling. Although conversion data over the entire range of 0-100% is desirable, the practicalities of designing a sampling system to handle both extremely viscous and highly volatile materials are limited.

The sensitivities and accuracies of the measured variables are taken from replicate measurements from independant instruments and replicate samples.

These three factors in the experimental program will have a significant impact on the quality of the fit. Each was studied with respect to the limitations imposed by the system. This was done by fitting the model to a test data set, designed to represent actual data. The results of this preliminary study demonstrate that only certain parameters may be estimated, and that these estimates will be highly uncertain. In fact, even with the minimum number of parameters chosen, no statistically verifiable fits are possible, and the converged estimates merely represent those values which reduce the deviation between model prediction and measured response. This is a direct consequence of insufficient number of experiments and low variance of the responses. This problem will be discussed at length in Chapter 4.0 .

For the homopolymerization model, the parameters to be estimated were chosen as:

- B1 : from equations (18) and (19), fitted separately
- A0 : from the elimination of equation (12) in eq. (2)
  (A0 = kp * sqrt(ki/kt))
- kdim : from equation (21)
- ktrim: from equation (21)

These parameters were chosen because they are the quantities which describe the properties of most interest, namely rate of polymerization , molecular weight and oil fraction.

It was discovered in initial fitting of the experimental data, that the significance of the transfer to monomer effect at high temperatures and conversions was not great. This is mainly due to the low monomer concentrations. This parameter cannot be estimated with the data available from this work.

It was also determined that there is not sufficient gel effect nor sufficient data to allow estimation of the terms in the termination polynomial from equation(24).

For the copolymerization model, the following parameters were estimated:

kt22 === from equation (3a)

B1,B2 === from equation (20)
or
B3 === from equation (18)

kdim === from equation (21)

ktrim === from equation (21)

It was found in early fitting of the data that the acrylic acid homopropagation constant (kp22) was very much larger than that of styrene. For this reason, it can be dropped from equation (2,3) and estimation of the acrylic homotermination constant was allowed.

3.4.2 Parameter Estimation Routine -

The parameter estimation program utilized is the "UWHAUS" program of weight least squares. This method uses the combined Marquardt and Gaussian search methods. The objective function chosen was to minimize the weighted trace of the residual covariance matrix. The form of the objective function is given below. It is assumed that the variance of the responses is independent of experiment number. The value of response variance was determined by replicate measurements, as described in Appendix 7.2 .

$$Z = \frac{\sum \{ Y(J,I) - F(J,I) \} ^{**}2}{VAR(I)} \qquad (34)$$

J : experiment number
I : responses..
  1 == conversion (total)
  2 == no.av.mol.wt. (Mn)
  3 == composition (F1)
  4 == dimer fraction
  5 == trimer fraction
VAR(I) : variance of ith measurement determined by repeatability analysis

3.4.3 Design Of Experimental Runs -

The pilot plant experiments were designed around a factorial type design, in the variables of temperature, residence time and feed composition. The variable ranges were chosen to accomodate the sampling procedure and to extend the study of the polymerization kinetics to higher temperatures than have previously been studied.

The first set of runs were designed with the goal of verifying the kinetics for thermal styrene to 300 C. The experimental range was 260-300 C with residence times of 15-60 minutes.

For the copolymer experiments, a similar scheme was set up with the extra variable of monomer feed ratio. The range was 200-260 C, residence times of 15-60 minutes and two feed compositions, 60 and 32 wt% styrene.

A final set of points were taken with the series tube reactor in place. These runs were used to test the utility of the tube reactor as a means of boosting per pass conversion without causing excessive product degradation or dispersity.

CHAPTER 4.0

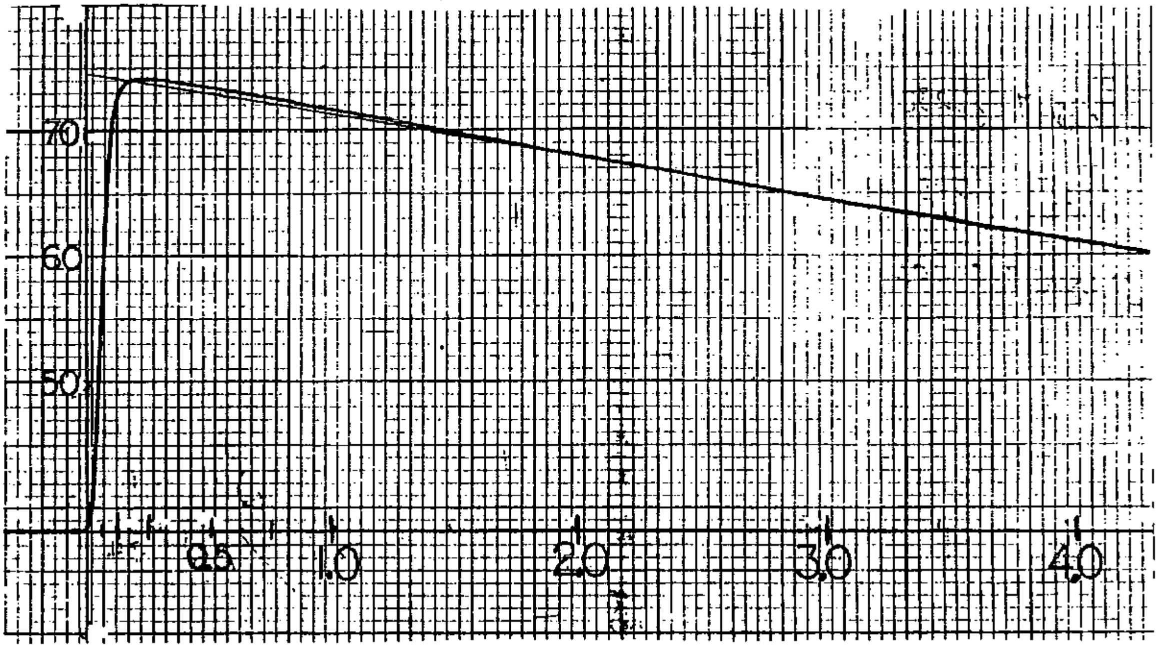
4 EXPERIMENTAL RESULTS

4.1 RTD Study And Conclusions

To test the mixing efficacy of the system an RTD (residence time distribution) study was undertaken.

The RTD analysis was done by injecting potassium permanganate into the feed line just prior to the entrance of the dip tube and reactor vessel. The flowing output was passed through a light transmission probe and the response plotted. The response is, from Beer's Law, logarithmic with concentration. Ideal flow will result in a linear response.

Initial testing was done with water at 25C. As shown in Figure 4.1, the RTD curve for water was ideal. The initial transient is due to the effect of input dispersion, or inability to provide a perfect impulse input. The input dispersion is easily estimated given the input velocity, and input quantity. For these tests, the dispersion will account for roughly 10 seconds of dynamic. Given the linear response and the insignificance of the initial transient, it is established that ideal mixing was attained.



TIME (minutes)

Figure 4.1
Impulse Response of Stirred Tank Reactor
with Water (viscosity 1cp) as Continuous
Phase

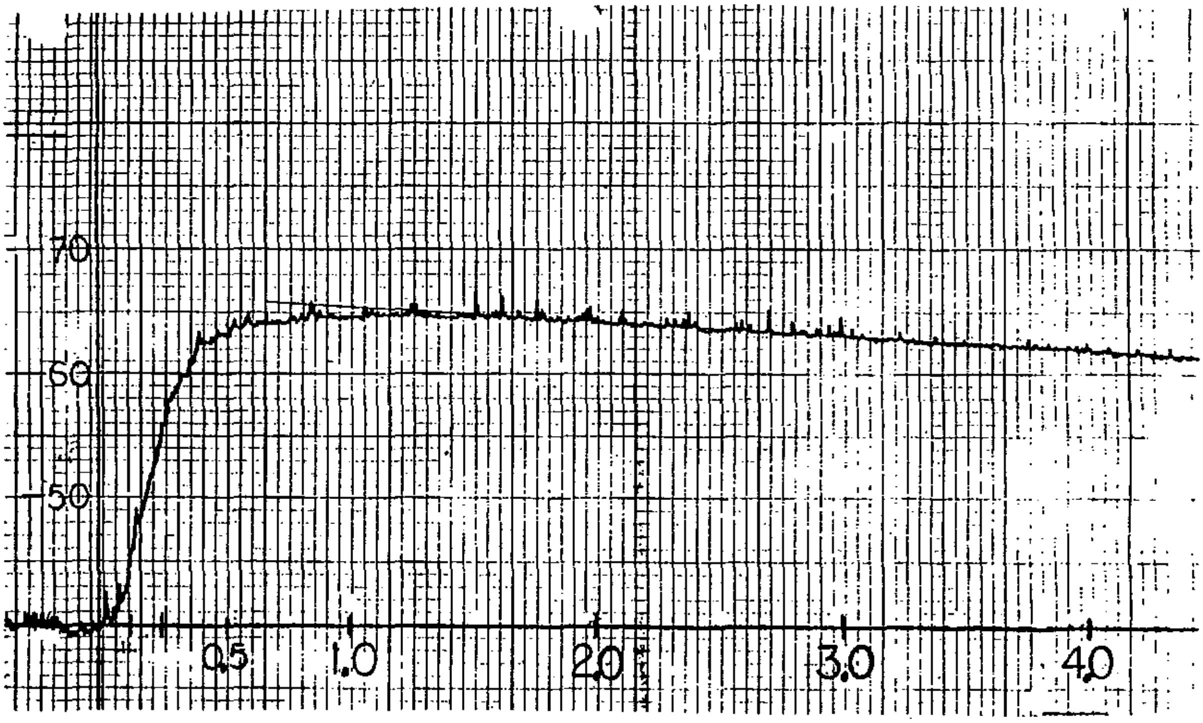


Figure 4.2
Impulse Response of Stirred Tank Reactor with Oil (viscosity 300cp) as Continuous Phase

To duplicate the process viscosity of the polymer system, (Lukow (30)), glycerine was used as the flowing medium. The RTD response obtained for high viscosity is shown in Figure 4.2. The response shows ideal linearity expected for CSTR's. The initial dispersion time at 1000 RPM was 60 seconds; at 1500 RPM it was 30 seconds. Given that input dispersion could account for only 10-15 seconds it is concluded that the degree of turbulence required to ensure effective macro-mixing demands the highest RPM possible. However, since the monomer time constant, tau(m), is roughly 1000-2000 seconds, it is concluded that mixing will play no important role in modelling and estimating the kinetics of interest for the reactor size used in this study.

4.2 First Series - Homostyrene Polymerization

The first series of experiments involved polymerizing bulk styrene at temperatures of 260, 280 and 300 C over a conversion range of 79-90 %. This corresponds to flow rates of 1.5- 5.5 liter/hour and residence times of 60 to 15 minutes. The results are given in Table 4.1 . The results of the high temperature GC analysis of the oil fraction produced at these temperatures in provided in Table 4.2 .

TABLE 4.1

HOMOSTYRENE THERMAL POLYMERIZATION AT HIGH TEMPERATURE

Flow Rate (lit /hr)	Temp. (C)	Conversion (w/w)	Dimer (wt%)	Trimer (wt%)	Mn (g/mol)	Mw (g/mol)	Mw/Mn (dim.)
1.5	260	0.8910	0.50	2.05	2994	5160	1.72
1.5	280	0.9032	3.98	9.28	1180	1960	1.66
2.8	260	0.8851	0.79	2.38	3552	6238	1.75
3.2	240	0.7948	0.34	0.41	7384	13056	1.77
3.2	260	0.8550	0.95	2.59	4218	7173	1.70
3.2	280	0.8850	3.30	4.50	1727	3355	1.94
3.2	300	0.9192	4.43	8.22	1066	2458	2.30
5.5	260	0.8165	1.10	2.03	5184	9252	1.78
5.5	280	0.8548	3.81	3.76	2370	4208	1.77
5.5	280	------	8.37	15.16	2740	4348	1.60

Note: last entry is sample contaminated with chloroform
: oligomer fraction as grams oligomer per gram of polymer

The analytical techniques used proved very easy and reproducible. The GPC calibrated by narrow molecular weight standards was a very convenient way of obtaining the molecular weight distribution and oligomer fractions. Gas chromatography for residual monomer also proved to be a very good method of determining conversion. Error analysis of the measurements is found in Appendix 7.2 and collated in Table 4.3 .

Data obtained at 240C was from a partial run only. The results of this particular run demonstrate clearly a problem of high temperature bulk polymerization. A plug developed in the outlet line at a process condition of 240C and roughly 90% conversion. It is believed this is due to premature cooling and freezing of the product. The melting point of polystyrene is roughly 240C .

The run at 300 C proved very difficult to operate at steady state due to the oily nature of the resin. It is believed that the excessive oil fraction separated from the polymer in the purge line and caused large pressure fluctuations. Figure 4.3 shows the GPC chromatogram of the polystyrene made at 300 C.

The data are all consistent with respect to temperature and residence time. The data do, however, lack variation. This is due to the very high operating rate of polymerization and conversion. As Figure 2.2 to 2.5 illustrate, invariance of

TABLE 4.2

OLIGOMER FRACTION BY HTGC AND GPC

	SPECIES				DIMERS		TRIMERS	
Temp.	DCB	DCB-	TPH-	PT	GPC	HTGC	GPC	HTGC
(C)	(all in wt % of polymer)							
240	1.23	0.22	1.10	1.20	0.34	1.45	0.43	2.30
260	1.52	----	1.53	2.48	1.10	1.52	2.83	4.01
280	1.00	0.80	3.55	3.63	3.30	1.99	3.63	7.18
300	2.61	----	5.54	5.84	4.43	2.61	8.20	11.40

Note: conversion to monomer greater than 80 % in all samples;
: abbreviations are

GPC : gel permeation chromatography
HTGC : high temperature gas chromatography
DCB- :diphenylcyclobutene
DCB :diphenylcyclobutane
PT :phenyltetralin
TPH- :triphenylhexene
--- :undetectable amount

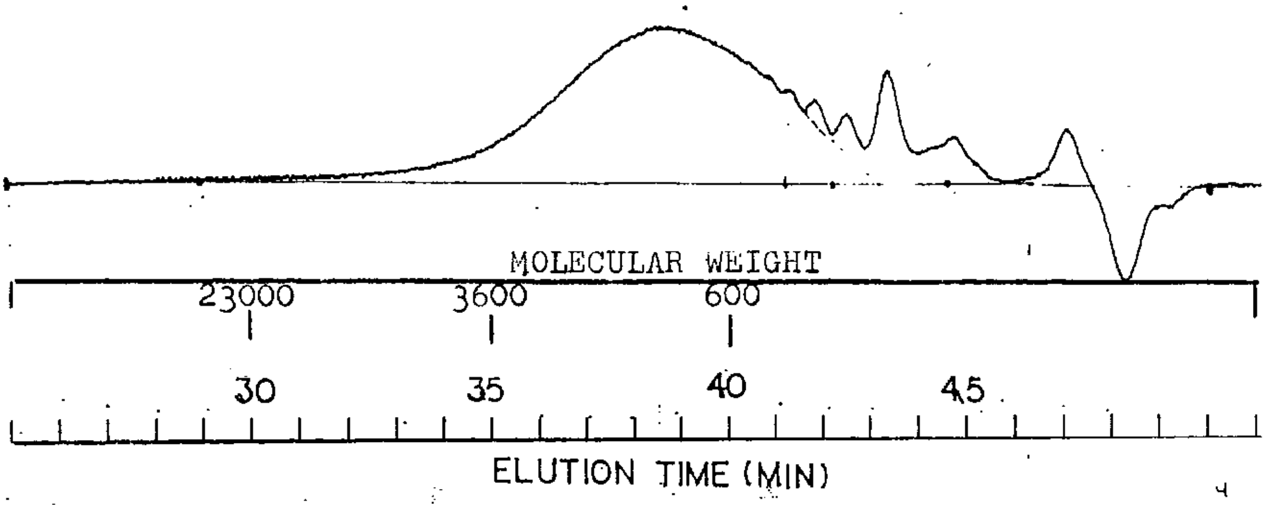


Figure 4.3
Molecular Weight Distribution of Polystyrene
Sample (300C) ; Mw = 2400 Mn = 1000

TABLE 4.3

ERROR ANALYSIS RESULTS

Deviation in conversion estimation (wt % total)
instrument : 0.70
sampling : 0.93
total : 0.97

Deviation in composition estimation (mol.fr.styrene)
method : 0.40 %
accuracy : 3-5 %

Deviation in molecular weight estimation (g/mol)
instrument : 500
sampling : 1000
calibration(homopoly.) : 200
calibration(copoly.) : 2000

Deviation in oligomer fraction estimation (wt % of polymer)
dimer....
repeatability : 0.73 %
accuracy : 1.33

trimer....
repeatability : 0.36 %
accuracy : 2.63

Note: deviation is assumed to be two standard deviations
: deviation obtained from replicate samples and analysis
: accuracy obtained from independant measurement

all responses is a characteristic of this system. To generate sufficient variation, large residence time changes would be required. Such feed rate variation was not possible with this system. Also, the sampling procedure placed a lower limit of 50-60 % conversion.

4.2.1 Model Verification- Homostyrene -

The data from the experimentation at each temperature were run through a parameter estimation routine which was set up to provide estimates of kinetic parameters involved in the styrene thermal polymerization model. The resulting parameters were then compared to the previous work of Hui (26).

The results of the model verification study are presented in Table 4.4 . A word of caution in the interpretation of the estimation results and new parameters is in order. There is simply not enough information in the data to allow statistically verifiable estimates of the kinetic parameters. The estimates are those which simply minimize the differences between the model and the experimental results. The estimates should be considered to be first approximations only, and are to be used as guides for further kinetic investigation.

It would appear from Table 4.4 that the rate parameter estimated for the polystyrene data up to 300 C compares favourably with those predicted by Hui(26). Note that the

TABLE 4.4

APPROXIMATE PARAMETERS FOR THERMAL POLYSTYRENE

Temp.	B1		A0		kdim		ktrim	
(C)	fitted	model	fitted	model	fitted	model	fitted	model
	(10**-2)		(10**-3)		(10**-5)		(10**-5)	
240	1.773	0.460	0.475	0.621	0.685	1.327	0.551	0.624
260	3.355	0.486	1.277	1.285	1.188	3.678	2.620	1.281
280	4.284	0.494	2.425	2.560	8.380	9.440	8.540	2.500
300	10.600	0.497	14.420	4.825	40.300	22.800	50.460	4.630

RE-FITTED B3 PARAMETER

Temperature (C)	B3
240	0.485
260	1.070
280	0.5485
300	0.068

Note: B1 molecular weight parameter from equation (19) (mol/g)
: A0 rate of poly. parameter from equations (2,12) (1/mol/s)
: kdim rate of dimer formation parameter from equation (21) (1/mol/s)
: ktrim rate of trimer formation parameter from equation (21) (1/mol/s)
: B3 revised molecular weight parameter from equation (18) (mol/gram)

estimated rate parameter has been corrected for gel effect by equation (24).

Minor deviation is noticed at 300 C, or at the limit of styrene thermal polymerization. At this temperature, the apparent rate is much higher than predicted. This may be due to the greatly increased consumption of monomer to dimers, which is not included in the model. It would seem that this effect greatly overrides the depolymerization effect which is believed to occur near this temperature.

The molecular weight prediction is not consistent with past results. The re-estimated B1 parameter is about 10 times larger than predicted. The new fitting technique whereby transfer phenomena is correlated directly with oligomer concentration is included in Table 4.4 . There is, naturally, no comparison possible, since oligomers were not measured by Hui(26).

Attempts to fit molecular weight to conversion through the empirical form chosen in the previous work will not succeed, mainly because at high rates of polymerization, conversion becomes invariant, but molecular weight does not. The resulting parameters will have to be highly correlated to temperature to effect a fit. This is consistent with the estimated B1 parameter being very much higher than expected (Figure 4.15). By correlating molecular weight directly to the small molecule concentration, as is the classical approach, a better and more meaningful fit is possible.

The polydispersities of most of the samples were 1.7, and not 2.0 as is expected for transfer dependant polymer formation. Attempts to incorporate the beta parameter in the model were unsuccessful, as this parameter was driven to zero by the low monomer concentrations. Husain (31) also measured dispersities close to 1.7 at temperatures of 220 and 230 C. He found that the polydispersities were a function of conversion and rose to 2.00 at conversions higher than 90 %. Also, Ebert et.al. (12) reported that the calculated lowest polydispersity of thermally degraded polystyrene is 1.7 . This presents the possibility that thermal degradation may be significant in determining chain lengths at these temperatures.

4.2.2 Oligomer Fraction Characterization -

Oligomers were quite evident in all of the thermal polystyrene samples at temperatures greater than 260 C. At excessively high temperatures (greater than 300 C), the yellow discolouration, characteristic of oligomers, became dark brown.

A comparison of the HTGC and GPC results on oligomer quantification show (Table 4.2) that they are in general agreement, but certainly not exact. Both chromatographic methods suffer because the oil peaks occur at the extremes of either instruments resolution limits. For the HTGC, column bleed at the temperature extremes reduced the certainty in peak quantification. The GPC also suffers resolution problems at these very low molecular weights. To date, only approximate estimates of dimer and trimer fractions are possible.

An accidental result from one early run was the contamination of the reactor solvent with chloroform. At high temperature, the chloroform was very reactive and produced an oily, extremely noxious material. The molecular weight and oil fraction analysis of this contaminated sample is included in Table 4.1. Steady operation could not be maintained in this run, due to the excessive oil fraction, and conversion could not be measured.

Figure 4.4 displays the chromatogram of the contaminated polymer. Figure 4.5 displays a typical chromatogram of thermally produced polystyrene. It is readily apparent that there is, in this contaminated sample, a huge amount of oligomers. From Table 4.1, the molecular weights of the contaminated sample and the same temperature polystyrene sample are very close. From this observation, it is assumed that the oligomeric production mechanism is independent of the chain growth and termination process. This would support the initiation model proposed on Figure 2.1.

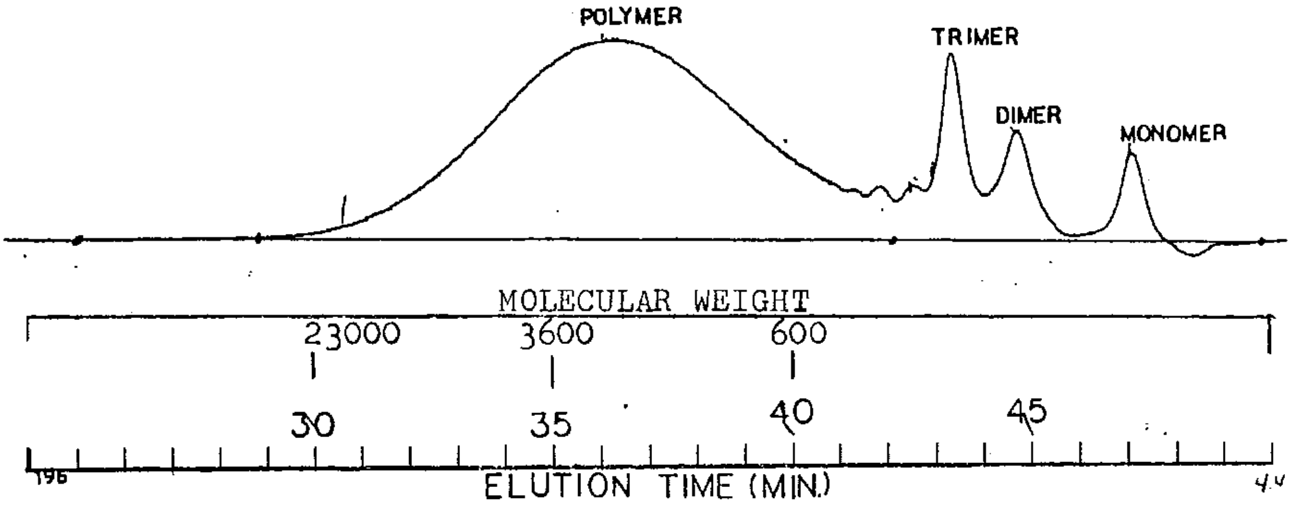


Figure 4.4
Molecular Weight Distribution of Polystyrene Sample (280C) Contaminated with Chloroform; Mw = 4400 Mn = 2700

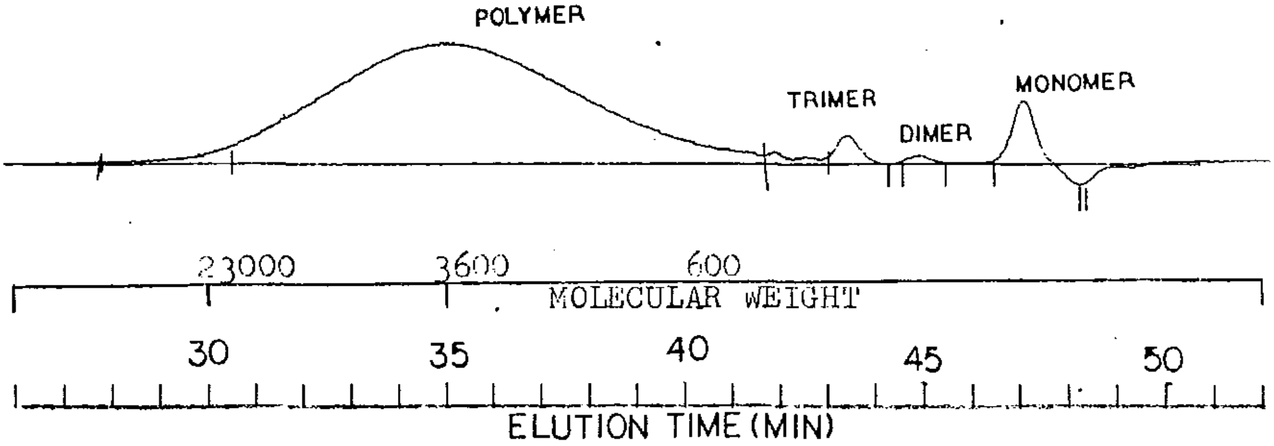


Figure 4.5
Molecular Weight Distribution of
Polystyrene Sample (240C);
Mw = 13000 Mn = 7000

At low temperatures, chloroform is noted for its chain transfer ability. At high temperature, it acts as an inhibitor to the rate of production of polymer, but not in chain transfer and molecular weight development. Being more reactive than styrene, it is believed the chlorine reacted with the initiation intermediate forming trimer, and prevented the production of growing macroradicals. This would lead to a decrease in styrene monomer consumption and an increase in styrene concentration, which can explain the higher dimer fraction. This is speculative since conversion could not be measured.

Since the polymer chain lengths were not affected, it is assumed that the excess fraction of chlorinated oligomers must also contribute in transfer reactions similar to the conventional dimers and trimers of styrene. The chlorinated oligomers, however, seem to be considerably less active. This would imply that there exist many abstractable protons from oligomers, some less active than others.

From Table 4.4 and Figure 4.16, the parameters and model of Kirchner et.al.(37) for the prediction of dimer fractions are supported by this data set, except for the 300 C level. The much higher value at 300 C, is likely compensation for dimers produced by thermal degradation. The parameters of Kirchner et.al.(37) for trimer prediction show similar deviation with the experimental results.

To attempt to uncover whether degradation is influencing the kinetics and also as an independent means of verifying oligomer fraction quantification, an analysis of the oligomeric fraction from the reactor was performed. The method was taken from Schroder et.al.(40), who was able to separate and identify some 15 molecules from the oligomer fraction of degraded polystyrene. He employed combined GC/mass spectrometry to identify and quantify peaks.

Figure 4.6 displays an example chromatogram of the low molecular weight end of a high temperature polystyrene sample. It contains similar peaks to that of Schroder et.al.(40) for a 6% degraded polystyrene sample. From this comparison,it is concluded that extensive degradation is not occurring. The deviation of molecular weight parameter estimates must be due to more significant kinetics than previously predicted. It is verified that mildly degraded polystyrene, and thermal polystyrene are identical in oil fraction components.

The expected effect of such degradation on the kinetics can be analyzed. Both degradative unzipping and depropagation have the effect of reducing the rate of monomer consumption or conversion at any given set of conditions. In a production sense, it is impossible to discriminate between these effect. The data do not suggest that either is significant since the estimates of rate parameter compare favourably with the parameters from the lower temperature correlation of Hui(26).

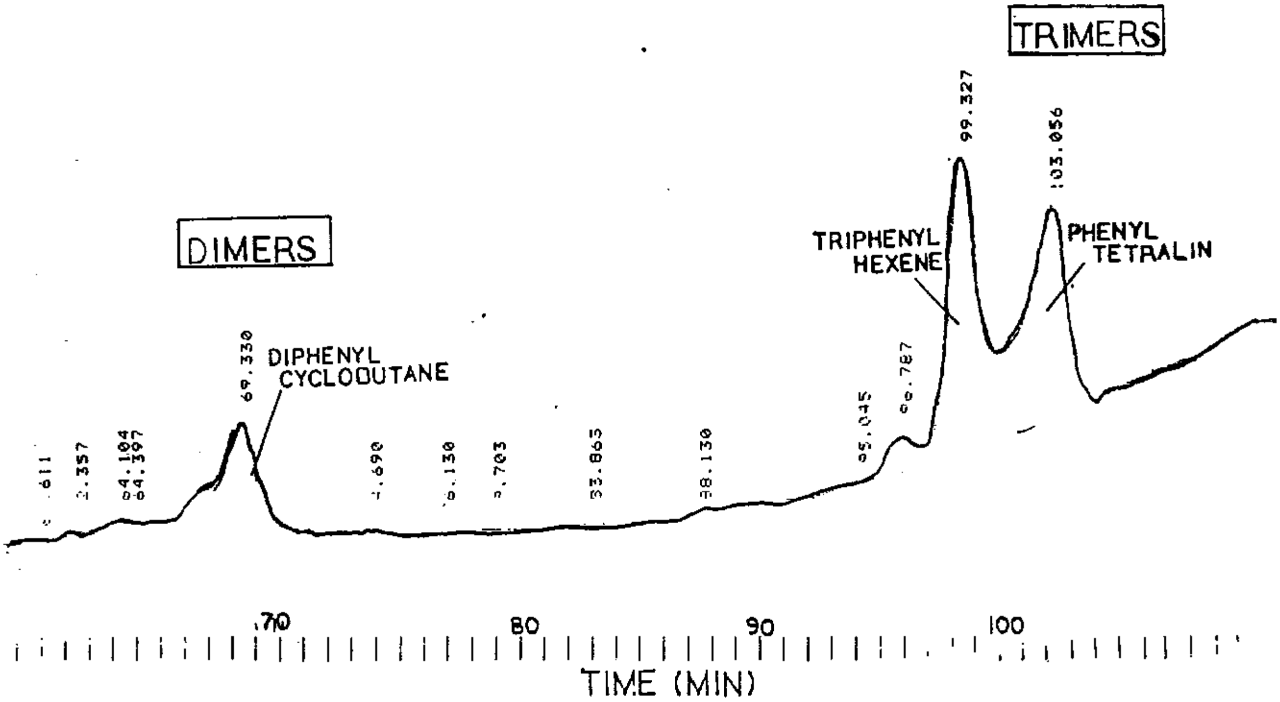


Figure 4.6
Gas Chromatogram of Polystyrene
Sample (300 C) Displaying Oligomer
Fractions

The significance of random chain scission is likely, as this process is instrumental in reducing chain length and dispersity. Model predictions using the parameters and equation structure of Ebert et.al (12) for degraded molecular weight demonstrate that the limiting cases for this structure of equations can give polydispersities of 1.7, but cannot explain the very low molecular weights obtained. At most , the degradative equations can account for only 50% of the molecular weight deviation. It would appear that transfer to small molecules plays a more vital role in chain termination than originally predicted.

As regards the composition of these oils, the high temperature gas chromatography is able to consistently detect two dimers and two trimers. This is also in agreement with Schroder (40) and his peak identification has been used in this work.

Table 4.2 displays the results for four polystyrene samples which show that trimers are far more predominant than dimers. Of the dimers, diphenylcyclobutane is most predominant. This is in agreement with Kirchner et.al. (37), who found that DCB comprised 90% of the dimers produced at 180C.

Trimers are formed by a kinetic rearrangement of the initiation intermediate. It would appear from the limited data that neither phenyltetralin (PT) nor triphenylhexene (TPH-) molecules are particularly favoured. At lower temperatures, it has been found by Kirchner et.al.(37) that PT is predominant and accounts for 90% of the trimers. Schroder (40) also found that PT is the major component of the trimer fraction of degraded polystyrene.

4.3 Second Series - Styrene/Acrylic Acid

The purpose of these runs was to verify and estimate kinetic parameters for the copolymerization form of the model. Possibly the largest challenge in doing copolymerization kinetic study is the development of methods to measure the molecular properties of interest.

The analytical procedures followed for the copolymer analysis proved considerably more difficult than those of the homopolymer study. Conversions and compositions were estimated from residual analysis. The residual styrene was easily obtained by gas chromatography, as was done with the homostyrene work. Residual acrylic acid could not be obtained by GC because of pre-polymerization of the acid in the injection port. A titration method was developed to measure residual acrylic acid.

The molecular weight measurements were very difficult and quite uncertain. Most of the error involved in estimation lies with the inability to do accurate calibration. There are currently no molecular weight standards available for this copolymer. Calibration must proceed based on another independent technique. Low Angle Laser Light Scattering (LALLSP) was chosen as the method of estimating weight averages of the copolymers to enable calibration. A program to do the calibration suffers robustness problems and its results depend on both the resolution of the GPC and the accuracy of the LALLSP instrument. Further comment on this method will be made in the discussion part of this section.

The estimation of oligomer fraction by GPC areas failed completely. Grossly overestimated peak responses and poor resolution made oligomer fraction estimation impossible. The HTGC method had to be relied upon for these measurements.

Estimation of molecular weights of copolymers always is a challenge. In this case, the measurement by off-line LALLSP and subsequent re-calibration of the GPC response proved difficult. This is unfortunate since errors in molecular weight estimation for such low molecular weight polymers are relatively high. This fact contributes to the rather large uncertainty in the experimental values of molecular weight.

The specific refractive indices of two copolymer samples of differing composition were measured to allow for dn/dc determination for other, perhaps differing composition samples that are obtained.

Copolymer Composition	DN/DC
0.35	0.1378
0.58	0.1489

Note: composition as obtained by residual analysis and mass balance inference; units are mole fraction styrene

: refractive index increment measured by laser differential refractometer model Chromatix KMX-16 by regressing measured refractive index of sample minus solvent versus concentration; concentrations were nominal 0.1,0.2,0.3,0.4 and 0.5 grams/100ml; temperature 25C; units are ml/gram; solvent was tetrahydrofuran

Since the dn/dc of a copolymer is a linear function of copolymer weight fraction , one can estimate the dn/dc of polystyrene and polyacrylic acid in this solvent at 25C from the above measurements. These are found to be 0.1689 and 0.1210 for PS and PAA, respectively. A literature value for PS in THF at 25 C (Brandup (42)) is 0.19; a literature value of PAA in dioxane at 25 C is 0.088 .

The values of weight average molecular weight and second virial coefficient are included in Table 4.5 . As is readily apparent, there is a large dependance of 2nd virial coefficient on molecular weight. The concentration dependence of light

TABLE 4.5

COPOLYMERIZATION OF STYRENE-ACRYLIC ACID AT HIGH TEMPERATURE

NOMINAL FEED COMPOSITION = 55 wt% styrene

Nominal Flow Rate (l/hr)	Feed Comp. (w/w)	Total Conv. (w/w)	Polymer Comp. (mol.fr. styrene)	Conv. Styrene (w/w)	Conv. Acrylic (w/w)	Temp. (C)
1.5	0.528	0.5928	0.406	0.6626	0.9302	200
1.5	0.549	0.7982	0.583	0.8431	0.9552	230
1.5	0.519	0.7991	0.537	0.8373	0.9618	260
1.5	0.492	0.8473	0.551	0.8973	0.9499	270
3.2	0.599	0.5390	0.452	0.5970	0.9425	200
3.2	0.575	0.7508	0.596	0.8049	0.9458	230
3.2	0.565	0.7578	0.607	0.8235	0.9279	260
5.5	0.558	0.4799	0.350	0.5736	0.9062	200
5.5	0.611	0.7538	0.620	0.7884	0.9654	230
5.5	0.643	0.8080	0.678	0.8387	0.9691	260

TABLE 4.5 cont'd

POLYMER MOLECULAR PROPERTIES BY RECALIBRATED GPC

NOMINAL FEED COMPOSITION = 55 wt% styrene

Nominal Flow Rate (liter/hr)	Mw (g/mol)	Mn	Mw/Mn	dimer (wt %)	trimer	Temp. (C)
1.5	29490	11240	2.62	2.20	0.44	200
1.5	24760	8410	2.95	1.15	0.70	230
1.5	7699	2867	2.68	5.2	1.71	260
1.5	1890	850	2.24	0.84	0.09	270
3.2	43570	14330	3.03	1.02	0.30	200
3.2	22470	8580	2.62	0.68	0.40	230
3.2	(12900)	5160	(2.50)	1.62	0.43	260
5.5	88050	32527	2.70	0.59	0.67	200
5.5	24710	8890	2.77	1.26	0.70	230
5.5	12680	5840	2.17	0.94	0.59	260
Commercial Resin	15400	3700	4.16	0.0		?

POLYMER LALLSP RESULTS

Flow Rate (liter/hr)	Temp. (C)	DN/DC (ml/gram)	LALLS Mw (gram/mol)	A2 (ml*mol/gram**2) 10**4
5.5	200	0.1425	91 000	8.45
1.5	260	0.1473	5993	11.9

Note: refractive index increment by interpolation
: sample concentrations in the range 0.7-3.5 g/100 ml;
: commercial resin sample obtained from S.C.Johnson and Son Company, Racine, WI
: values in brackets denote averaged estimate

scattering intensity decreases with increasing molecular weight. This will have a negative effect on the accuracy of LALLSP estimates for low molecular weight polymers.

The recalibration of the GPC chromatograms was done by software written for estimation of the Mark-Houwink constants (Chiantore et.al. (43)) and the subsequent re-generation of the calibration curve from that of polystyrene. This software uses the chromatograms of two broad polymer samples with known weight average molecular weight, and from these, solves for K and a. Although in principle this should give estimates of these parameters, poor estimates were encountered in this case. It is believed that the robustness of this method is poor. The selection of calibration function coefficients was done manually, to approach the molecular weight predictions of LALLSP.

Early in the work, it was discovered that pre-mixed monomer feed will polymerize by itself if left for a period of 1-2 days. Although both monomers were inhibited (styrene from Aldrich at 10 ppm TBC and acrylic acid, with HDQ from Johnsons, Brantford), when mixed together they are not stopped from polymerizing. It is believed that acrylic acid is a very fast polymerizer which requires only a trace of radicals to become initiated.

Steady operation at 280C was attempted but failed, due to wild pressure fluctuations characteristic of excessive oil fraction.

The 60/40 weight fraction styrene feed copolymer was not soluble in toluene or water. It is soluble in dimethyl formamide, any basic aqueous solution, dioxane or tetrahydrofuran.

Referring to Table 4.5 ,conversions of acrylic acid were very high at all temperatures and flows, certainly 90% or greater. This fact,combined with the apparent high reactivity of AA in contact with styrene even at low temperatures in a feed tank, suggest that AA is a very fast polymerizer once initiated. It would seem that even the low radical concentrations produced by inhibited styrene at room temperature are enough to set off the reaction.

All data points are consistent except for the highest temperature, flow rate combination. This was a very difficult point to collect, since there was a great deal of hot residual monomer which could not be caught by the sampling procedure utilized. This would account for the higher than expected conversion. The molecular weight estimates also compare favourably with the original patent results (47).

The overall conversions and styrene conversions are all significantly lower than those of homo-styrene. This is believed due to the presence of AA in the feed, diluting the styrene monomer concentration. Styrene monomer concentration plays a controlling role in initiation mechanism of the copolymerization.

The sensitivity of temperature on rate for each monomer is very different. Acrylic acid consumption rate is not temperature sensitive at the temperatures studied in this work while styrene rate is. This implies that copolymer composition will be strongly influenced by temperature. At lower temperatures, the styrene rate diminishes and the chain composition drifts to the acrylic end.

Flow rate or residence time sensitivity to conversion is quite small. This was also found for the homostyrene polymerization and is a characteristic of this system.

4.3.1 Oligomer Fraction Characterization -

The analysis of the copolymerization oil fraction was surprising. The HTGC found greatly reduced trimer fractions. Referring to Figure 4.6 and Figure 4.7 , which are HTGC chromatograms of copolymer and homostyrene, we see only a few recognizable peaks. The dimer peak appears very similar to the dimer peak for polystyrene, and can be identified as

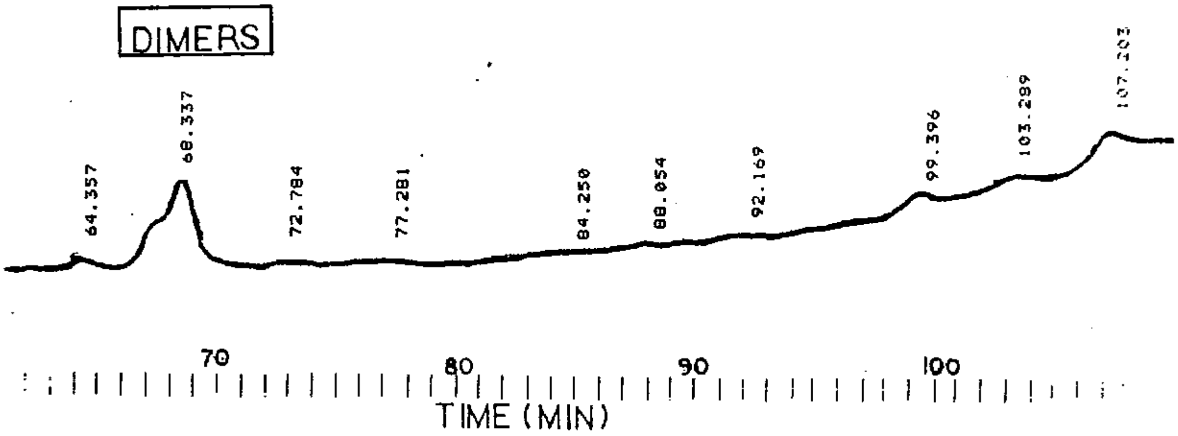


Figure 4.7
Gas Chromatogram of Styrene-Acrylic
Acid Copolymer Sample (260 C) Displaying
Oligomer Fractions

diphenylcyclobutane. Referring to Tables 4.1 and 4.5, the dimer fractions appear higher for the copolymerization over the homopolymerization. The trimer fraction is virtually eliminated in the copolymerization.

The higher dimer fraction is reasonable since copolymer conversions are generally much lower than homostyrene conversions. The absence of trimer is assumed to be a result of the high activity of the acrylic radical, which prevents the intermediate rearrangement (Figure 2.1).

Estimates of the dimer fraction by HTGC and GPC did not agree. The GPC area fraction grossly overestimates the oil fraction for this copolymer. The major factor in this error is the composition difference between polymer ,oligomer and monomer molecules. Composition changes in eluting molecules affect detector response and separation mechanism. At low molecular weights the problem is further aggravated by chain end effects.

Detector response (DRI) is linear in composition and concentration for high molecular weight polymer. The copolymer is most likely to be homogeneous in composition for reasons stated earlier. Oligomers and residual monomers will have vastly different compositions from the polymer. For this reason, response comparisons between polymer and oil fractions are impossible, unless compensation for composition non-homogeneity is accorded.

Composition effects on polymer-column interaction are mainly due to differences in polarity , chemical absorption or other intermolecular force between the eluting molecules and packing material. Such forces become important for very small molecules and this becomes the separation mechanism that makes liquid chromatography possible. The TSK columns used were cross-linked polystyrene/divinylbenzene particles of 8-10 microns diameter, packed in tetrahydrofuran solvent. These columns are essentially inert and non-polar so that strong intermolecular forces are not expected.

The effect of polymer-solvent interaction is also very important in understanding the separation mechanism of GPC. If we assume that there are no significant polymer-column interaction, then the conventional GPC separation mechanism of hydrodynamic volume will apply. The size of the polymer chain in solution is strongly affected by the solvent type, polymer molecular weight and composition. Chain hydrodynamic volume (size in solution) in dilute solution may be given by the following relation taken from Rudin (13).

Vh= 4*pi * K * (molecular weight**(a+1)) / 9.2E24 (35)

For polystyrene in THF, the MHS constants are 11.7e-03 and 0.725. For polyacrylic acid, they are 76.e-03 and 0.50 . Therefore, for the same molecular weight, the hydrodynamic

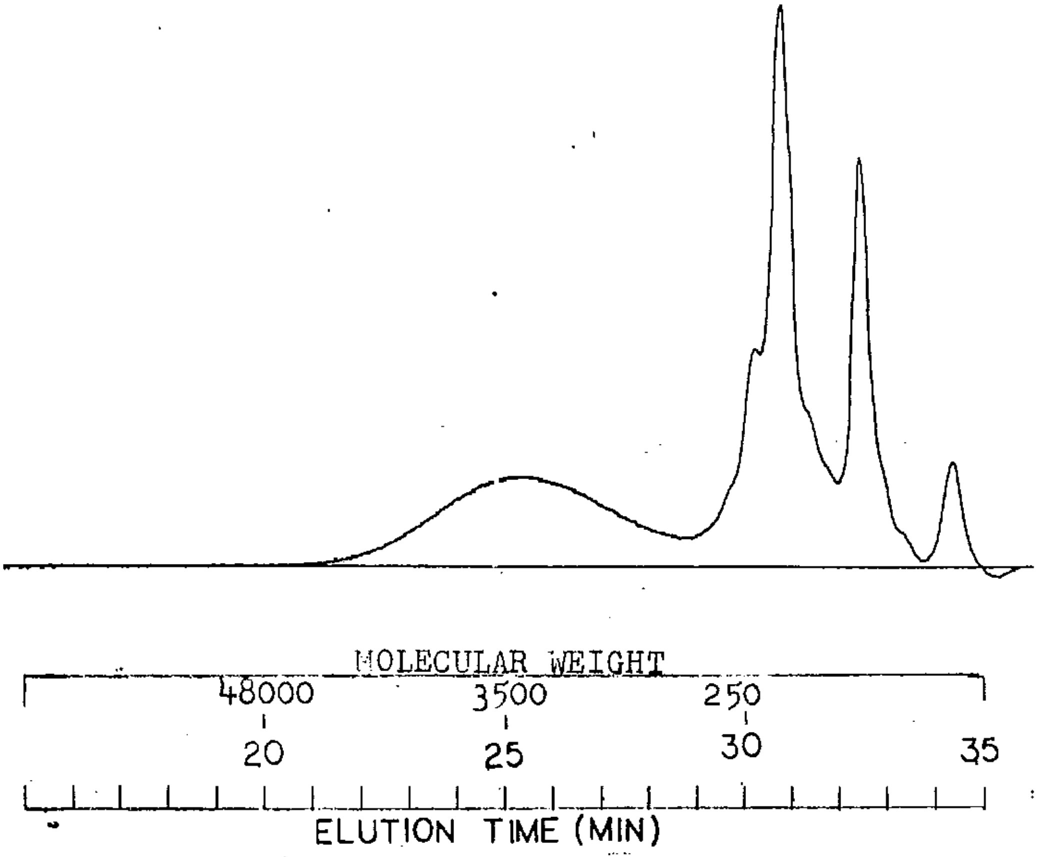


Figure 4.8
Molecular Weight Distribution of Styrene-Acrylic Acid Copolymer Sample (260 C);
Mw = 4100 Mn = 1850

volume of acrylic polymers will be roughly 7 times larger than that corresponding to styrenic chains. This implies that high acrylic content copolymers will elute much earlier in the chromatogram, relative to high styrenic chains. This would help in the resolution of acrylic polymer from the styrenic oligomers. But,this would also mean that residual acrylic acid monomer will elute on top of the oligomer or polymer peaks.

The addition of an extra column (TSK 1000H) to the three column set and pre-washing the polymer to remove residual acrylic acid was attempted to improve separation of oligomers and residual monomers. As Figure 4.9 shows, resolution is improved only slightly.

In a further attempt to discover how composition is changing with molecular weight, dual UV and DRI detectors with size separation was attempted. The results of such analysis are given on Figures 4.10 and 4.11 . Figure 4.10 is the dual trace of a copolymer sample, as well as a commercial resin containing no oil or residual fraction. Figure 4.11 is a spectra scan of a sample copolymer. The ratio of the DRI to UV response for the sample copolymer is found on Figure 4.12 . Garcia et.al.(39) used this ratio as an indication of polymer composition drift. Figure 4.12 demonstrates clearly the composition dispersity of the lower molecular weight fractions of the copolymer sample. The ratio response is constant down to 1000 molecular weight, after which the ratio is upset.

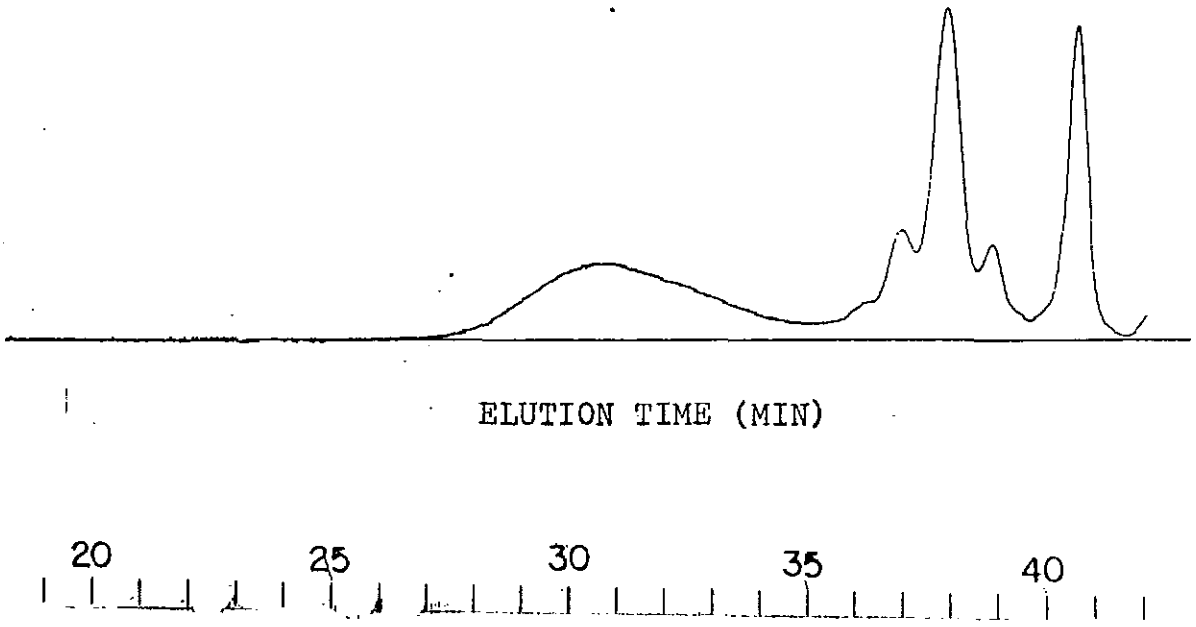


Figure 4.9
Molecular Weight Distribution of Styrene-Acrylic Acid Copolymer (260 C) With Extra GPC Column (TSK1000H)

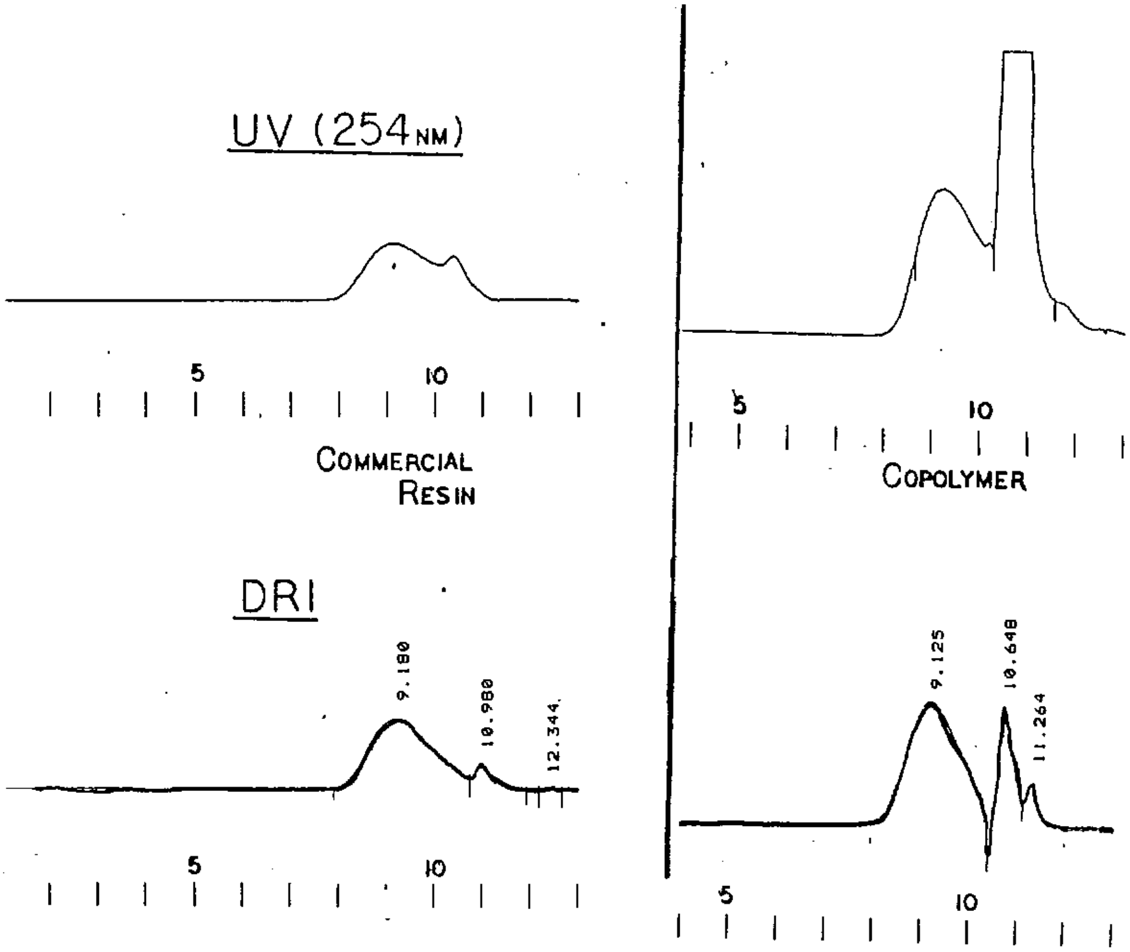


Figure 4.10
Dual Detector Responses for a Commercial and Pilot Scale Styrene-Acrylic Acid Copolymer Demonstrating Detector Non-linearity at Low Molecular Weight; detectors are UV@254nm and Differential Refractometer

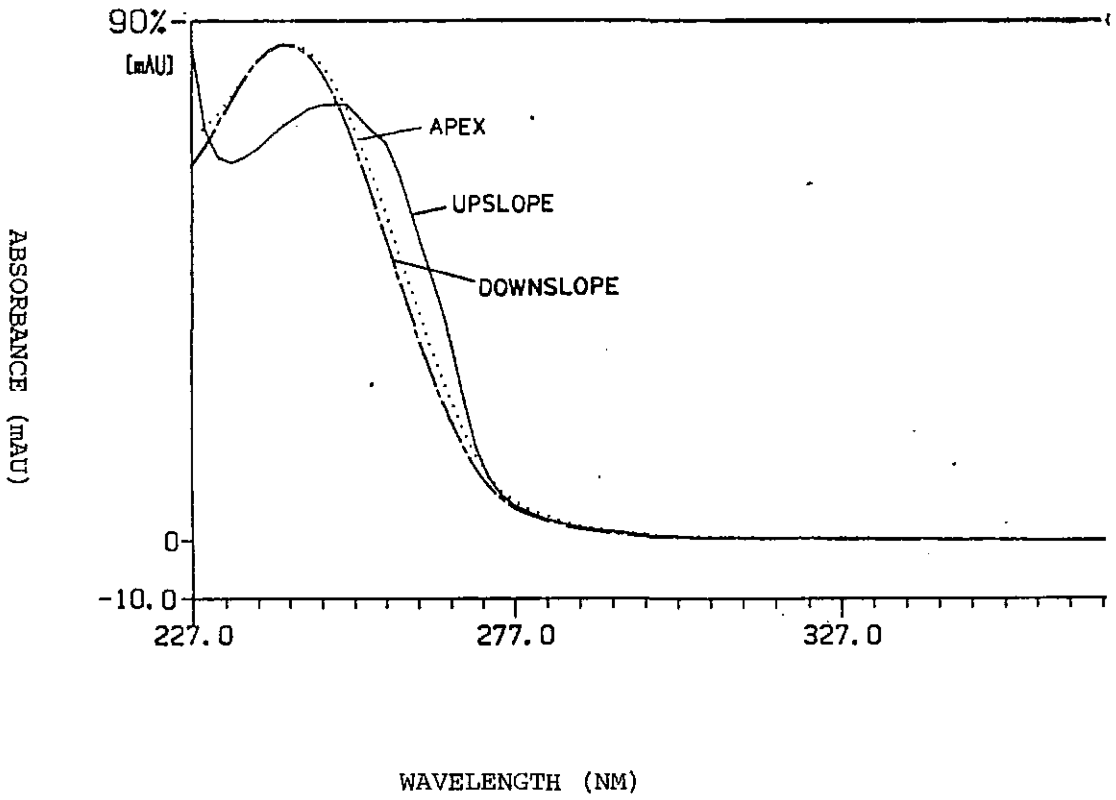


Figure 4.11
UV Spectra of Styrene-Acrylic Acid Copolymer Sample Across Eluting Peak Displaying Composition Heterogeneity

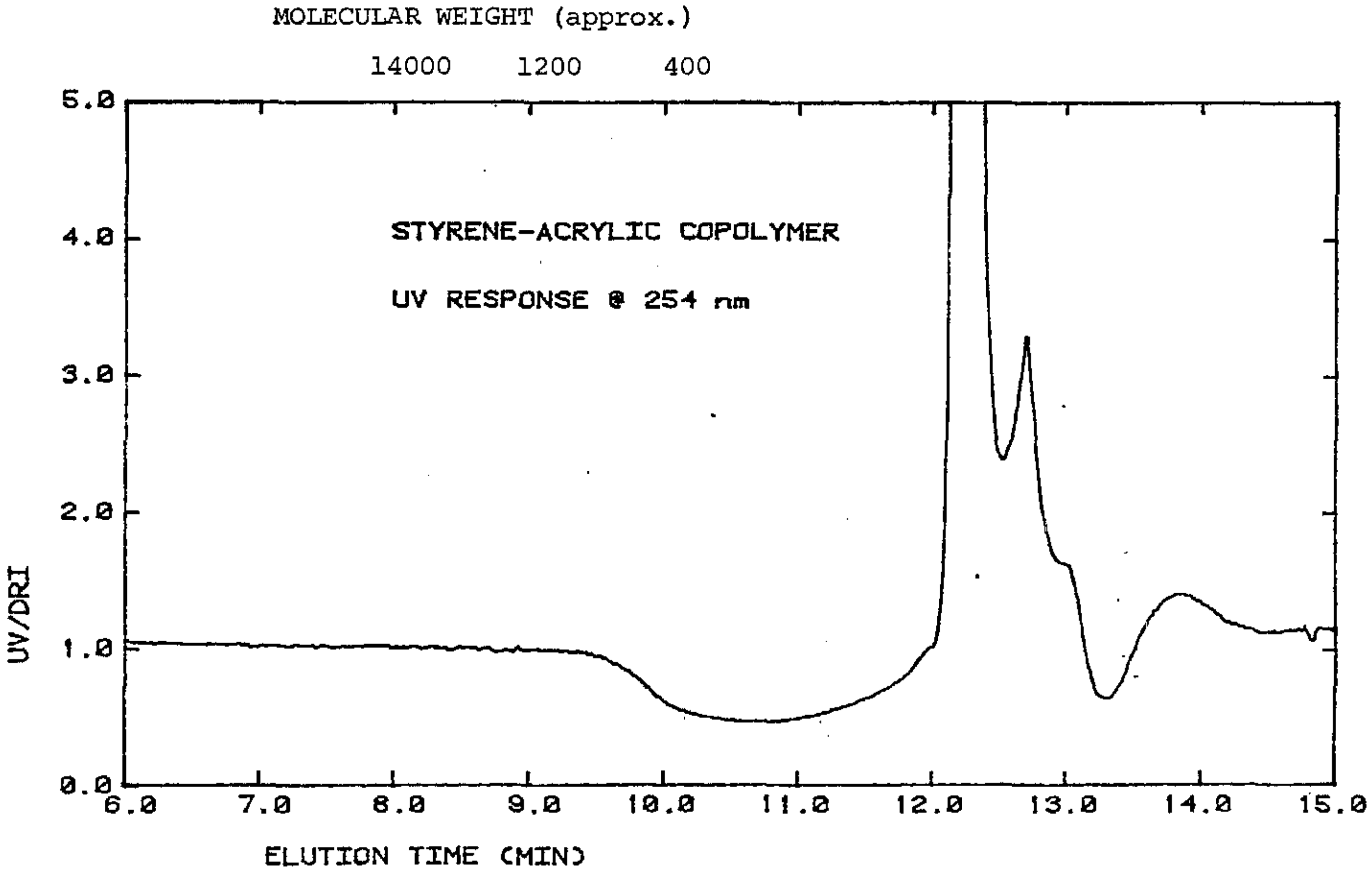


FIGURE 4.12
Ratio of UV and Differential Refractometer Responses Across Eluting Fractions Demonstrating Detector Non-linearities With Molecular Weight

These fractions correspond to the appearance of oligomers.

The instantaneous spectra (Figure 4.11) also demonstrate the composition changes at lower molecular weight. Strong absorption at 243 nm, characteristic of styrene with this polymer, is found on the downslope. The upslope has absorption far beyond 243 nm. Solvent (THF) absorbs at 230 nm and below. The low molecular weight fraction shows higher styrenic absorption compared to the high molecular weight fractions.

Garcia et.al.(39) found that the UV extinction coefficient was highly positively correlated to styrene sequence length. This might infer that as styrene fraction increases, UV detector sensitivity will increase. This is certainly apparent in Figure 4.10 . Although in no way does this provide any quantification of composition, the increasing response can be said to be due to increasing styrene content in the eluting fractions. It is this rapid composition change that denies area comparison between fractions.

The overestimation of oligomer fraction is then partly due to exaggerated detector response effects, but mostly due to non-ideal separation mechanism resulting from composition changes and chain end effects becoming significant in the eluting oil fractions of low molecular weight copolymers.

The use of GPC to characterize non-homogeneous fractions can be very successful, as with the work of Garcia (39). What is required, however, is extensive study of the copolymer-detector-column sensitivities at low molecular weight. This type of study is well beyond the scope of this work.

Referring to Table 4.5, the measured molecular weights show the normal trends with temperature and flow rate as found with polystyrene and predicted by the model. The copolymer molecular weights are generally much higher than polystyrene. Molecular weight sensitivity with temperature is also quite high.

Figure 4.13 displays the chromatogram of a commercial styrene-acrylic acid resin. The commercial resin has a comparatively broad polydispersity and lack of residual or oil fraction. The lack of oil fraction is due to devolatilizing the resin after the reactor.

4.4 Third Series - Styrene/Acrylic Acid

The third series of experimental runs was at 35 % styrene feed. The identical experimental procedure was followed for this set, as described above. Also, the same established variances, analytical techniques were used. Parameter estimation was done with both series of copolymerizations.

The operation of the third set of copolymerization runs proved similar to the second except for one operating detail. In all the previous runs, both homostyrene and 60% styrene runs, no heat input or removal was required. Heat of polymerization was evenly balanced with the in- and outflow heat removal. In the operation of the 35% styrene copolymerization, net heating was required to maintain temperature. A 30-40 C difference was maintained between the jacket and the reactor contents. This gradient does not imply a large heat input since heat transfer coefficients in high viscosity systems are very small.

Referring to Table 4.6, the total conversions are generally higher than the previous set at 60 % styrene feed. Acrylic acid conversion is lower; styrene conversion is higher. This is due to the higher acrylic acid input rate, which reduces acrylic conversion and lower styrene flow rate which increases styrene conversion.

Residence time sensitivity is slightly higher for this series. Temperature sensitivity is much lower. The same composition trend is noticed for this series as in the previous. Styrene consumption rate is more temperature and flow sensitive than acrylic, therefore, polymer composition drops as residence time and temperature decrease.

TABLE 4.6

COPOLYMERIZATION OF STYRENE-ACRYLIC ACID AT HIGH TEMPERATURE

NOMINAL FEED COMPOSITION = 35 wt% styrene

Flow Rate (l/hr)	Feed Comp. (w/w)	Total Conv. (w/w)	Polymer Comp. (mol.fr.sty.)	Conv. Styrene (w/w)	Conv. Acrylic (w/w)	Temp. (C)
1.5	0.353	0.7220	0.3624	0.8508	0.8712	200
1.5	0.344	0.8307	0.4079	0.9240	0.9067	230
1.5	0.374	0.8282	0.4656	0.9393	0.8910	260
3.2	0.336	0.6838	0.2931	0.8160	0.8670	200
3.2	0.344	0.7505	0.3965	0.8903	0.8602	230
3.2	0.350	0.8352	0.4070	0.9272	0.9080	260
5.5	0.353	0.6483	0.2892	0.7894	0.8589	200
5.5	0.357	0.7391	0.3610	0.8503	0.8888	230

POLYMER MOLECULAR PROPERTIES BY RECALIBRATED GPC

Flow Rate (lit/hr)	Mw (g/mol)	Mn	dp	dimer (wt %)	trimer	Temp. (C)
1.5	30400	11700	2.59	0.52	0.12	200
1.5	11300	3440	3.2	0.23	0.10	230
1.5	2800	1430	1.98	1.52	0.76	260
3.2	41650	14000	2.97	0.09	0.09	200
3.2	2870	1740	1.65	0.35	0.33	230
3.2	4100	1850	2.23	0.83	0.30	260
5.5	44650	18300	2.44	0.13	1.88	200
5.5	9110	3800	2.39	0.39	0.24	230

The molecular weights show the expected trends with temperature and flow rate as found in all other runs. Generally, the molecular weights of this set of high acrylic copolymers are lower than the high styrene polymers made in the second series, and lower than polystyrene at similar temperatures. Higher acrylic content lowers copolymer molecular weight.

Oligomer development for the higher acrylic content is consistently lower than the previous comonomer composition. The dimer fractions are lower due to the lower styrene monomer concentration. The trimer fractions are reduced even further with the higher acrylic monomer content.

4.4.1 Model Verification- Styrene/Acrylic Acid -

Again, the limitations of the parameter estimation procedure used for the copolymer case are the same as those mentionned above for the homostyrene study. The estimates of the parameters will be even less confident however, due to the extra complexity of monomer composition and even less certainty in response measurement. The results of the estimations are given in Table 4.7 . These estimates are from the results of all the copolymerization experiments.

TABLE 4.7

APPROXIMATE PARAMETERS FOR COPOLYMERIZATION KINETICS

Temp.	B1	B2	B3	kt22	Kdim
(C)	(10**3)			(10**-7)	(10**5)
200	6.3	13.6	1.44	7.34	0.695
230	23.7	84.3	1.23	11.7	1.48
240	17.7				0.68
260	-	100.0	0.521	11.8	5.79
260	33.5				1.18
280	42.8				8.38
300	106.				40.3

Note: B1,B2 molecular weight parameters
from equation (20); radical fraction replaced by
copolymer composition (mol/gram)
: B3 molecular weight parameter from equation (18) (mol/g)
: kt22 acrylic acid termination constant
from equation (2) (l/mol/s)
: kdim rate of dimer formation parameter
from equation (21) (l/mol/s)

A comparison between the parameters estimated in this study with those of Hui(26) on Figures 4.14, 4.15 and 4.16.

Literature values for termination of acrylic acid are not widely available. Those taken from Hruska (44) are given below.

kt (acrylic acid (literature) 200 C) = 4.01 10**7
kt (styrene (literature) 200 C) = 19.3 10**7
kt (acrylic acid (estimated) 200 C) = 7.34 10**7

kp (acrylic acid (literature) 200 C) = 1.0 10**5
kp (styrene (literature) 200 C) = 0.07 10**5

These parameter values demonstrate that acrylic acid polymerizes at least 150 times faster than styrene.

Molecular weight control by transfer to oligomers was first regressed against conversion, to allow comparison of these estimates to those already found for homostyrene. The results, from Table 4.7, verify that the estimated B1 kinetic constant is comparable to that obtained for polystyrene. The B2 constant, which reflects the contribution of acrylic macroradicals to chain transfer velocity, is higher than B1 for all temperatures. This would imply that chain ends are predominantly acrylic.

The molecular weight parameter, B3, fit to oligomer fraction was similar in magnitude to the fit for homostyrene. The B3 parameter decreases with temperature in both polymerization types, implying that chain transfer is kinetically not favoured at higher temperature. Molecular weights decrease mainly due to the accumulation of active oligomers. The absolute value of the estimates is quite uncertain due to the low variance and poor confidence in the measured response.

Attempts to discover the most influential oligomer in molecular weight development were unsuccessful, due to the low amount and range of data available. It was found that the molecular weight range over temperature was much greater for the copolymerizations and that the trimer concentration in the copolymerization runs was very small. Since the dimer fractions were comparable, between the homostyrene and copolymerization runs, it is suggested that trimers play an important role in chain transfer and their absence allows for quite high chain lengths.

Dimer generation rate parameter estimates appear to be consistent with the homostyrene polymerization results. This further supports the mechanism on Figure 2.1, which proposes that dimer formation rate is dependent on styrene monomer concentration and temperature only.

Trimer generation is greatly reduced in the presence of acrylic acid monomer. The estimates of trimer generation parameter will have to include the effect of acrylic concentration. The structure of this dependancy is unknown,

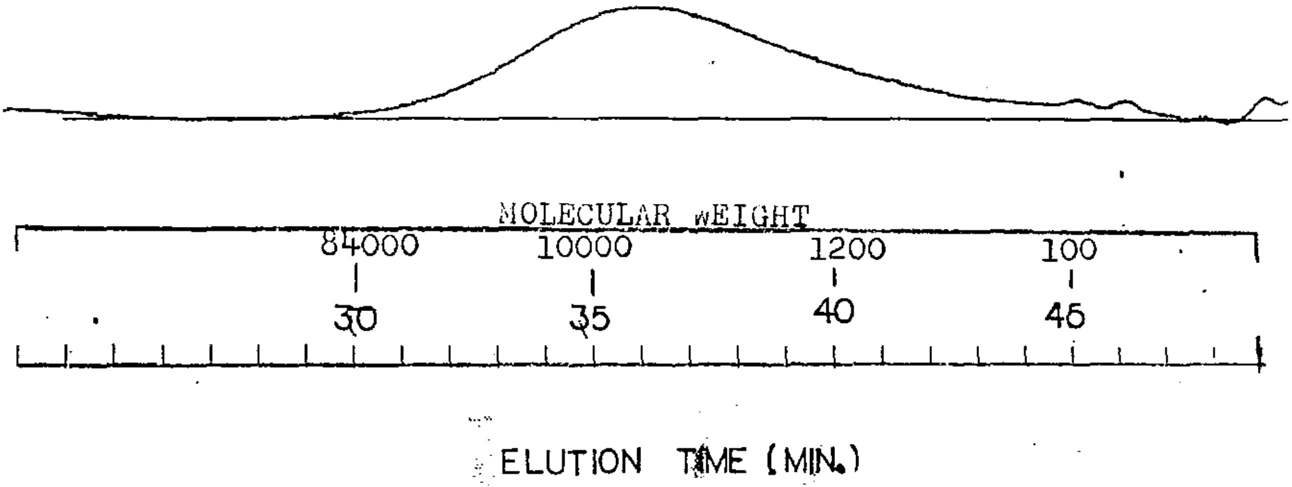


Figure 4.13
Molecular Weight Distribution of a Commercial Styrene-Acrylic Acid Resin Sample; Mw = 15000 Mn = 4000

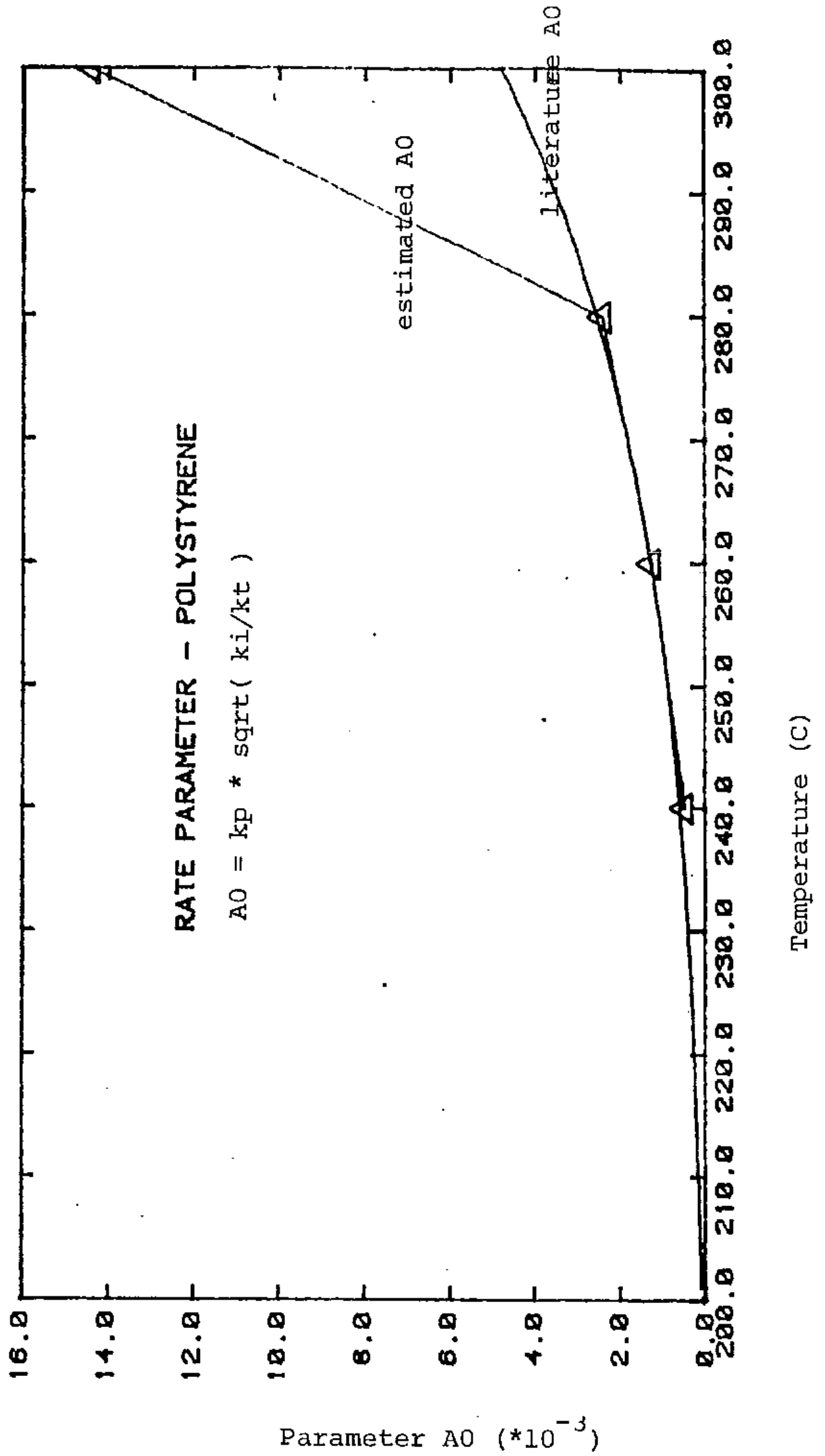


Figure 4.14
Estimates of Styrene Rate Parameter A0 Compared to Literature Predictions;literature correlation taken from Hui(26);

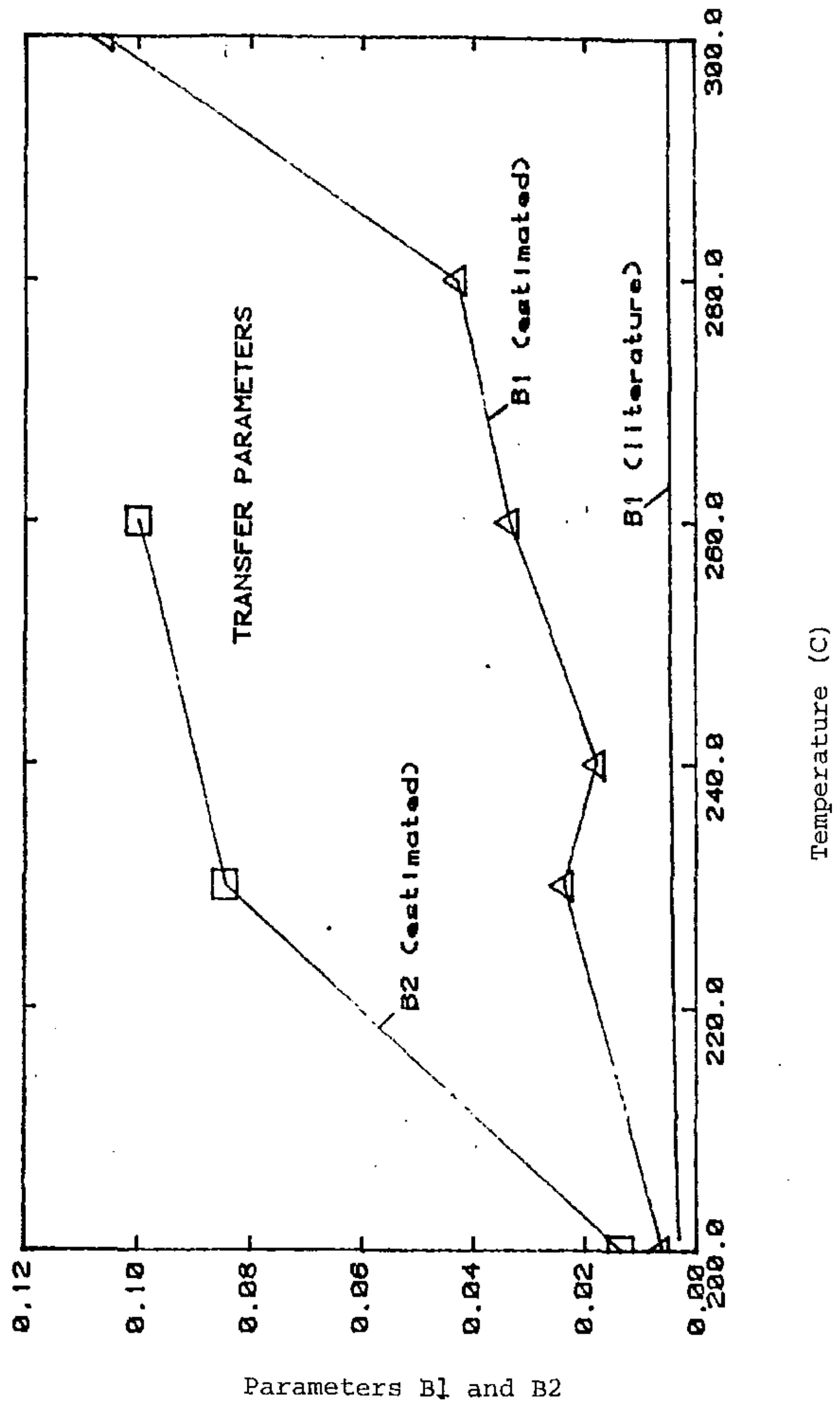


Figure 4.15
Molecular Weight Parameter Estimates Compared With Literature Prediction;B1 refers to styrene-ending copolymer chain transfer;B2 refers to acrylic acid ending copolymer chain transfer; literature correlation taken from Hui(26)

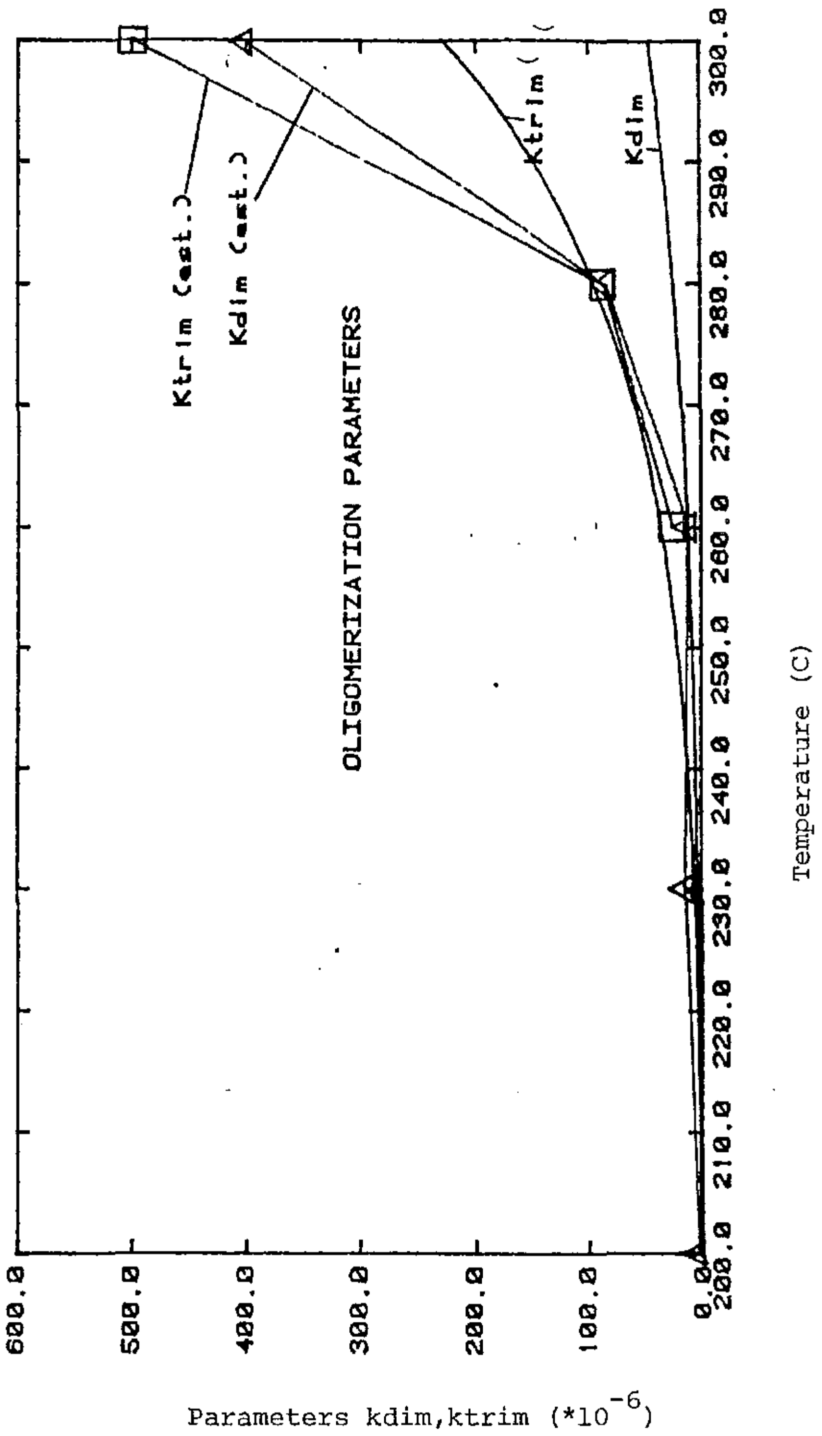


Figure 4.16
Oligomerization Rate Parameter Estimates Compared to Literature Predictions;kdim refers to dimer production rate;ktrim refers to trimer production rate;literature correlation taken from Kirchner(37)

and trimer generation parameters were not fitted in the copolymerization study.

4.5 Addition Of Tube Reactor

The results of the addition of a 250 ml. tubular reactor on the outlet of the 1.5 liter stirred tank are documented in Table 4.8 .

The operation of the two reactor system proved no difficulty. Pressures were kept well below 400 psi, compared to 200 psi for the stirred tank alone. The analytical techniques used and uncertainties were identical to past series.

The temperature gradient across the tube was monitored. The result for each run are given in Table 4.8 . It is seen that some exothermic polymerization was occurring, since the tube temperature hot spot is roughly 7 C above the bath temperature.

From Table 4.8, the extra residence time derived from the tube reactor resulted in a 2-5 % increase in total conversion. If allowance is made for the unintentional higher feed fraction, no significant composition drift was measured.

TABLE 4.8

RESULTS OF TUBE REACTOR EXTENSION

COPOLYMERIZATION OF STYRENE-ACRYLIC ACID AT HIGH TEMPERATURE

NOMINAL FEED COMPOSITION = 35 wt% styrene

Flow Rate (l/hr)	Feed Comp. (w/w)	Total Conv. (w/w)	Polymer Comp. (mol.fr.sty.)	Conv. Styrene (w/w)	Conv. Acrylic (w/w)	Temp. (C)
Base Case == stirred tank only						
1.5	0.344	0.8307	0.4079	0.9240	0.9067	230
Addition of Tube Reactor						
1.5	0.396	0.8534	0.4695	0.9285	0.9249	230
1.5	0.382	0.8740	0.4654	0.9514	0.9226	260

Flow Rate (lit/hr)	Mw (g/mol)	Mn	dp	dimer (wt %)	trimer	Temp. (C)
Base Case == stirred tank only						
1.5	11300	3440	3.2	0.23	0.10	230
Addition of Tube Reactor						
1.5	4840	2140	2.26	0.91	0.27	230
1.5	6000	2130	2.85	1.40	0.93	260

TUBE REACTOR TEMPERATURE GRADIENTS (C)

			Axial Position						
CSTR	Block	enter	1	2	3	4	5	exit	bath
230	265	208	227	230	232	232	232	223	225.1
230	265	208	253	258	260	260	260	250	253.5

Table 4.8 shows that along with boosting reactor conversion ,the tube also caused a decrease in both molecular weight and polydispersity. This is expected, since longer reaction times always lead to lower chain lengths, due to the buildup of active oligomers and the concurrent reduction in monomer concentration. Addition of monomer on radicals becomes very slow, while transfer to active oligomers increases.

The increase in oligomer fraction, particularly dimer fraction, is significant. It seems that the predominant reaction in the tube is oligomerization. Presumably, the lack of monomer allows the initiation intermediate concentration to build and result in faster trimerization. Similarly, dimer formation increases since dimerization is second order in monomer, while radical formation is third. These processes are enhanced by the lack of mixing in the tube.

The severe drop is molecular weight across the tube reactor suggests stongly that thermal degradation is important. It is unlikely that the increase in oligomer fraction alone could account for the 50% drop is chain length.

CHAPTER 5.0

5 CONCLUSIONS

5.1 Analytical Methods

Gel permeation chromatography is an excellent method for determining homopolymer molecular weight averages and distribution, even down to weights of 1000-2000 .The method is entirely reliable, easy to perform, and consistent.

Calibration by broad molecular weight standard or a series of narrow standards of known weight or number average should provide for reasonable accuracy.

The major drawback of GPC for copolymers is detector response and column non-ideality from non-homogeneous copolymers. If the polymer chains are not all the same composition, or, the standard(s) used for calibration do not have the same composition as the eluting sample, quantification of GPC response and identification of peaks will be uncertain.

Determining oligomer fractions of homopolymers is possible with high resolution columns and long run times. Accuracy may suffer due to broadening caused by the influence of column permeation limits, chain end effects, non-linear detector response and separation mechanism.

Using GPC to estimate oligomer fractions of copolymers is a very uncertain technique, mainly due to poor separation at low molecular weight and composition variations which make quantification doubtful.

Gas Chromatography for residual styrene is a useful, and accurate method for determining conversion. Errors associated with this procedure are entirely due to sampling.

Titration for residual acrylic acid is also deemed to be a fast, easy and consistent method for acrylic conversion estimation. Errors lie mainly in sampling and separation of polymer-oligomers from the filtrate. Accuracy of this method is in question for these reasons.

Composition estimation by inferred mass balance and residual monomer determination proved to be a very good, consistent method. Accuracy of this method, compared to NMR estimates was biased 4-6 % w/w . This was due to the problem of residual acid separation step in the method.

Oligomer fraction estimation by High Temperature Gas Chromatography can be successful. Prior calibration is required, both for peak area quantification and peak identification. Unfortunately, the method is limited to only a few oligomers and resolution requires quite long run-times.

The use of UV to estimate oligomer fraction may be useful. It has been used with success in the literature as an indirect estimate of polymer discolouration due to oligomers (U.S. Patent (47)) .

Light Scattering to determine molecular weight of low molecular weight copolymers may be the only truly accurate method. Unfortunately, estimation errors become more significant due to increasing concentration sensitivity of instrument response.

Proton NMR appears to be a very promising method for performing accurate analysis of copolymer composition, and sequence length.

Composition determination by dual UV-DRI detectors is a difficult method due to the problem of detector non- linearity with chain microstructure. This is especially true at low molecular weights. For high molecular weight polymers success with dual detectors is possible.

The characterization of low molecular weight polymers and copolymers poses the most difficult challenges in polymer reaction study. All previous methods of polymer characterization have relied on the special properties of macromolecules which are derived from their large size . Low molecular weight polymers can have significantly differing responses with molecular weight and hydrodynamic volume, and as such , are difficult to calibrate for.

The reproducibility of all the methods used in this work proved to be quite good. Accuracy was compromised in some, particularly the copolymer molecular weight and composition estimation.

5.2 Kinetic Modelling And Estimation

The various assumptions of polymer and copolymer modelling, including LCA and SSH, are of sufficient validity for parameter estimation purposes. The major problem with modelling such systems is not the model equation structures but lack of data and narrow experimental range, lack of variation and poor confidence in the measured variables. Without better and more numerous data, discrimination between model structures will not be possible.

Steady state stirred tank reactors will prove to be very difficult to use in a kinetic parameter estimation application. This is mainly due to the time and material required to get a single operating point. The difficulties and expense in its operation will limit the amount of data that can be collected. In this work, parameter estimation for even a simple homopolymer case was made doubtful due to lack of data. In more complex cases, such as copolymerizations or heterogeneous reactions, parameter estimation will become that much more uncertain.

However, for high temperature, bulk systems, it is doubtful whether kinetic study in any small scale batch system can succeed due to the problem of heat-up and mixing times interacting with the very fast kinetics. As such, continuous stirred tank reactors may prove to be the only way of studying high temperature polymerization kinetics.

The effect of thermal degradation is important at the conditions studied. It is necessary to incorporate the degradative equations in the molecular weight development of the model.

5.3 Rate Of Polymerization

The rate parameter and correlation after Husain et.al.(2) was supported in this work. The gel effect correlation could not be verified by direct estimation but is also believed to be adequate. Deviation in the rate expression was found at 300 C, mainly due to the effects of severe oligomerization and thermal degradation.

The estimated termination rate constant for acrylic acid was found to be in reasonable agreement with the results in the literature. It further demonstrates that, relative to styrene , acrylic acid is a very fast propagating monomer.

The thermal initiation of styrene controls the overall rate of monomer consumption. Acrylic acid seems to provide little radical generation of its own. However, once initiated acrylic acid polymerizes and cross-polymerizes rapidly in comparison to styrene.

Copolymer composition is effected largely by styrene consumption rate. Lower temperatures and higher styrene input rate will produce higher acrylic content copolymers.

5.4 Oligomer Formation Rates

The dimer model after Kirchner et.al.(37) was supported in this work. The kinetics proved adequate up to 300C for the homopolymerization and the copolymerization. Dimer production is entirely dependent on temperature and styrene monomer concentration only. The trimer model from Kirchner et.al.(37) was also supported, except at 300C.

The composition of the dimer fraction was found to agree with the literature. These include mostly diphenylcyclobutane with trace diphenylcyclobutene.

The composition of the trimers was found to be roughly split between phenyltetralin and triphenylhexene. This does not agree with the literature values (Kirchner(37)) which indicate that triphenylhexene is dominant.

The production of trimers in the copolymerization is almost completely suppressed. This is likely due to the activity of the acrylic acid monomer which does not permit the buildup of the initiation intermediate and subsequent reaction with styrene to form trimer. As such, trimer generation rate is dependent on comonomer composition and temperature.

The accidental addition of chlorine radicals to the reaction (as chloroform solvent) provided a further confirmation of the thermal initiation mechanism and its role in oligomer formation. The oligomer fraction was increased dramatically by the very active chlorine radical. The polymer formed ,however, was not influenced. This suggests that chlorine radicals did not contribute to chain transfer. This confirms that an active intermediate must lie between oligomerization and chain growth. Also, these chlorinated oligomers must be less active than ordinary oligomers of styrene in participating in transfer reactions. This would imply the existence of many abstractable protons on these oligomers, of varying reactivity.

5.5 Molecular Weight Development

It was concluded that at higher temperatures chain termination is by transfer to oligomers and thermal degradation. This is due to the relatively high concentration of oligomers and the very high reactivity of the macroradicals at elevated temperatures.

Attempts in the literature to correlate conversion to molecular weight will be unsuccessful due to the invariance of conversion at high temperature. This procedure leads to very high parameter correlation with temperature.

Molecular weight regressed to small molecule concentration is preferred and is the classical approach to chain transfer modelling. Parameter estimates are provided by this correlation for both the polystyrene and copolymerization reactions.

Higher acrylic content in the reactor leads to lower molecular weight. Acrylic macroradicals are more reactive that styrenic macroradicals. Also, it was found that acrylic monomer is more active that styrene monomer, and acts to prevent trimerization and accelerate growing macroradical production.

Both oligomers are believed to be active in chain termination. This is witnessed by the increased sensitivity of molecular weight with temperature found in the copolymerization results, in which the trimer concentration was very small. Unfortunately, there was not enough variance in the data to permit quantification.

5.6 Copolymerization Mechanism

The mechanism proposed on Figure 2.1 is consistent with the results of this work. The evidence for the existence of an initiation intermediate is further corroborated by the experience with acrylic acid comonomer and chlorine radical.

CHAPTER 6.0

6 RECOMMENDATIONS

It is the authors opinion that no great gains can be made in model development without concurrent increase in response measurement ability. Without better estimates of polymer properties, discrimination between model structures and confident parameter estimates will not be possible.

Certainly, the most frustrating problem with parameter estimation in this study was the lack of quality and quantity of data. Only wide generalizations are possible with the number of experiments used in this work. Unfortunately, the limitations of pilot plant experiments make the generation of the quantities of data necessary for adequate parameter estimation costly and time-consuming.

A necessary improvement in the modelling of high temperature polymerizations will be the incorporation of dynamic degradation equations into the molecular weight development. This will lead to more adjustable parameters, but may help to explain some of the molecular weight data.

Rate of monomer consumption due to oligomerization should be included in the model. Most of the extreme deviation in parameter estimates from the past correlations was at the very extreme temperature of 300C, where significant oligomerization occurs.

CHAPTER 7.0

7 APPENDIX

7.1 Safety, Health And Hygiene

This section will detail some of the potential hazards of the monomers studied in this work. Great care and consideration of the possibilities of spills, and personal contact with these chemicals is required to realize safe and controlled research work. It is important to recognize that all chemicals, especially monomeric species are hazardous when used at their limits of reactivity. Certainly in high temperature, high pressure polymerization systems such as this hazards are readily apparent.

As with most aromatic hydrocarbons styrene is an irritant and a potential carcinogen. Contact with the skin will result in defatting, drying and possible allergic reactions. It should be washed off immediately and all but incidental contact is to be avoided. It does not cause any immediate discomfort or pain, but may ultimately create blisters and skin sores. Clayton (48) and Leonard (49) describe most of the toxicology of such monomers at length.

Styrene vapor is particularly noxious and has a very characteristic and disturbing odor. Although not immediately dangerous to health, prolonged exposure at concentrations above 100 ppm, or detectable limits, is not advised. Incidental vapor contact is not hazardous. Use of a cannister breathing mask for prolonged exposure is advisable. Prolonged incidental exposure, as occurs during long runs, will result in eye irritation. Periodic breaks with lots of fresh air should be planned.

Spills of styrene monomer should either be cleaned up by an appropriate absorbent or left to evaporate. It should not be flushed down the sewer with water.

Styrene monomer has an autoignition temperature of 400 C. Furnace temperatures are not to exceed this value. Its flammability is high and naturally, all hot sources or flames are dangerous.

The reactivity of styrene is well understood. In this system the startup procedures provide for a safe and controlled reaction. Since both cooling and quenching capacity are virtually non-existent with this system, careful startup is essential.

Acrylic acid is a weak acid, similar to acetic acid and smells like sour vinegar. It is water-soluble but should not be taken lightly with respect to spills, or even incidental contact. It is an extreme skin irritant and will blister almost immediately given contact with exposed skin. The use of gloves is essential. Where splashing is remotely possible, gloves, face shield and protective clothing should be worn. Should acid be splashed on the skin washing immediately with baking soda and water will reduce the chance of blistering.

Acrylic acid vapors are also extremely irritating and potentially dangerous to health. Incidental contact is allowable with cannister type masks; prolonged exposures during upsets require self-contained breathing apparatus. The TLV of acrylic acid is 10ppm, or 10 times less than styrene.

Spills are to be either absorbed or left to evaporate. Small amounts of acid may be washed to drain; large spills must be absorbed or allowed to evaporate.

Certainly the operation of the equipment at high temperature , high pressure equipment will require special care to ensure safe operation.

7.2 Analysis Of Experimental Error

To determine the reproducibility and accuracy of the measured responses a program of replicate samples and measurements was done.

The analysis of repeatability was made by doing replicate GC injections, titrations, GPC injections and by re-analyzing samples of the same steady state. The number of available replicates is necessarily low, coinciding with the number of experiments performed. However, it is believed that the estimated variances will provide an idea of how significant the numbers are. The averaged deviations were assumed to approximate two standard deviations.

7.2.1 Styrene Residual Estimation -

Each sample was injected into the GC at least twice. Each steady state was sampled at least three times in time intervals of roughly 20-30 minutes. The quoted conversion errors are therefore the result of averaging deviations over some 60 measurements (comprising the homo-styrene runs).

average injection error === 0.52
average sample error === 0.83
total significance limit === 0.97 %

7.2.2 Acrylic Conversion -

By replicate titrations of a set of 6 samples from the same steady state point, the average deviation of acid conversion was found to be 0.70 % . Accuracy of the residual acid concentration was inferred from the composition estimation accuracy from NMR analysis (discussed later in this section). Residual acid estimation accuracy was found to be 2-3 %, biased high.

7.2.3 Total Conversion -

Combining the estimation errors for residual analysis, the total conversion estimation error is calculated to be 1.25 %.

The accuracy of the measured conversions is unknown since no comparative method was used to estimate conversion. Certainly, accuracy is affected by sampling technique, instrument or method bias and operator technique. It is believed that these values are sufficiently accurate for this work, and that regardless,the inaccuracy will certainly lie within the range of reproducibility.

7.2.4 Molecular Weight Average Estimation -

Replicate sampling and injections were used to establish repeatability of weight and number average molecular weights estimates. The number of samples for such analysis was limited to 12 due to instrument time constraints.

average injection error === 236 g/mol
average sample error === 500
total reproducibility === 550

calibration error === 200
average significance limit === 590

The accuracy quoted above was taken from the statistical analysis of the homopolymer narrow standard calibration fit. It is apparent that the major effect on molecular weight average estimation accuracy is the variation due to sampling and injection, not due to calibration. Efforts to perfect the calibration will not help reduce the uncertainty in the measured averages.

For the copolymer molecular weight measurement, the reproducibility is expected to be the same. The accuracy however will be much poorer. This is entirely due to the lack of well-characterized standards at these low molecular weights. Calibration by fitting GPC results to LALLSP estimates was not very accurate, in that the best fits still have deviations of 1500-3000 g/mol. Certainly with more light scattering results a more accurate calibration is possible. On top of the problem of calibration, is the uncertainty of copolymer composition heterogeneity and its effect on the separation mechanism and detector response of the instrument. This effect may become very significant at the lower molecular weights measured.

At best, it is felt that the copolymer molecular weights presented are internally consistent and useful in sensitivity study only.

7.2.5 Polydispersity -

The polydispersity measurement involves the division of two inexact numbers, namely Mn and Mw. In this case the percentage errors will add. These errors are roughly 25% for Mn and Mw. Therefore, error in the polydispersity will be greater than 50% .

7.2.6 Oligomer Fractions -

The estimation of polystyrene dimer and trimer weight fraction was done with the GPC area integration. Because the peaks associated with oligomers are small, some manipulation of the calculation parameters of the GPC method was required, such as forced base lines and start-stop integration limits. Naturally this variation in data treatment causes uncertainty in the final results.

The accuracy of the GPC area integration technique was compared to high temperature GC. The deviations are presented below.

dimer....
repeatability : 0.73 %
accuracy : 1.33

trimer....
repeatability : 0.36 %
accuracy : 2.63

Estimates of dimer and trimer fraction for copolymer samples could not be made with GPC area comparison. This is due to incomplete resolution and severe peak overlapping in the monomer/oligomer elution volumes. This is a direct result of composition variation among the eluting fractions, which make resolution and peak quantification dubious. High temperature gas chromatography and the method of Schroder et.al.(40) had to be relied upon alone to provide estimates.

7.2.7 Copolymer Composition -

The copolymer composition error measurements are derived from the residual analysis errors above. Repeatability was found to be 0.40 %.

Bias is expected in the estimation of composition by residual analysis. The titration method relies on complete separation of the free acid monomer from the precipitated polymer phase. Acrylic acid lost in this step will be counted as acid in the polymer phase, resulting in higher estimates of acrylic content.

The accuracy of the technique for composition determination was tested by using Proton NMR. The author would like to acknowledge the assistance of N. Storer-Folt (45) in the NMR analysis. The results of 3 samples tested are given on Table 7.1. The average deviation between the NMR and residual analysis estimates of composition is 6.5 %. All the NMR estimates were lower than the residual estimates, demonstrating that the loss of acid in the residual analysis technique was

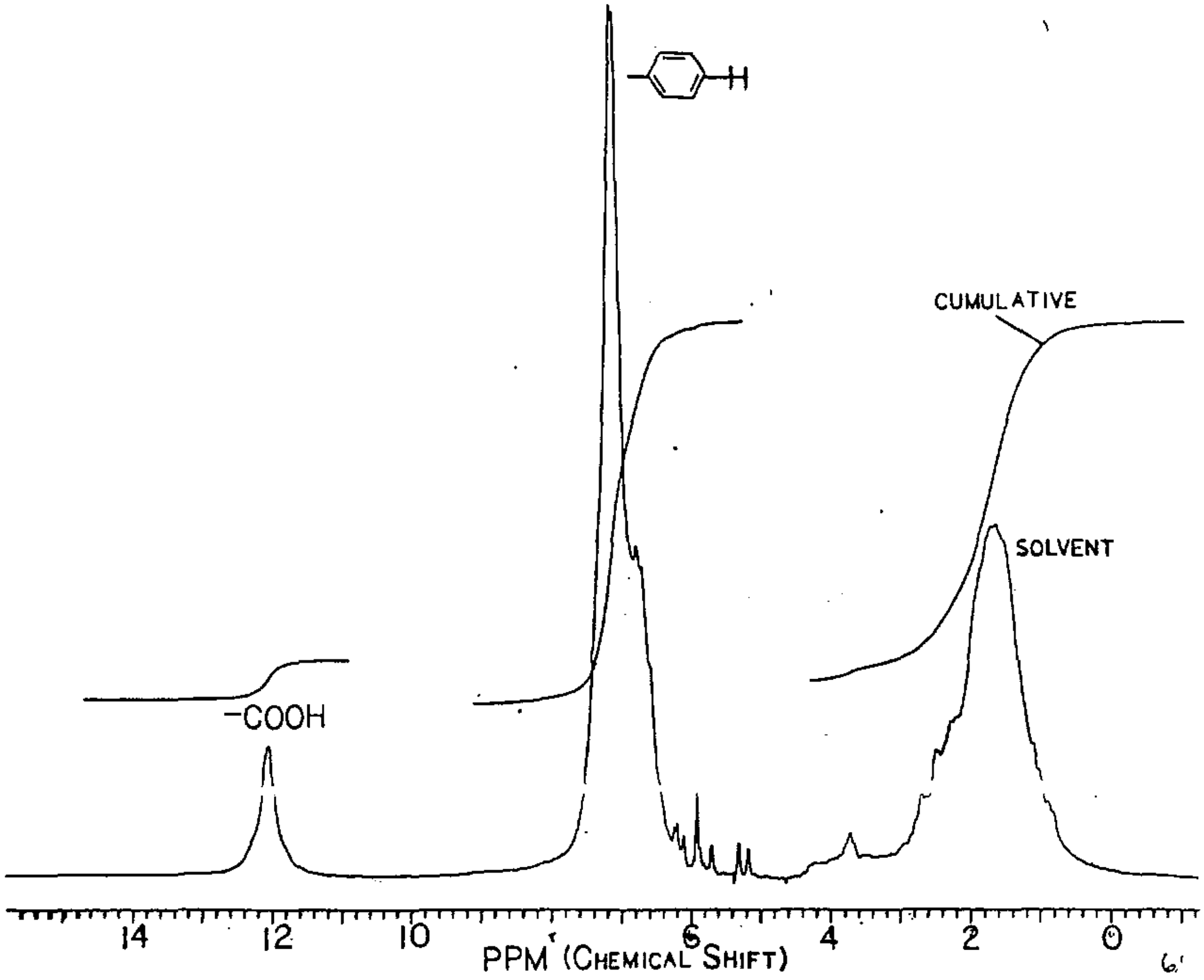


Figure 7.1
Proton NMR Response from a Styrene-Acrylic Acid Copolymer Sample

TABLE 7.1

NMR COMPOSITION ESTIMATION

SAMPLE		NMR	RESIDUAL ANALYSIS
Temperature (C)	Flow Rate (lit/hr)	(mol.fr.acrylic acid)	
230	5.5	30.0	38.8
230	1.5	33.9	42.0
260	3.2	35.6	39.3
Commercial Resin	-	38.2	-

Note: NMR method as outlined...
dried polymer prepared in 5mm OD NMR tubes; sample concentration approx. 15-20 % (g/ml); solvent was D6-DMSO ; instrument was proton NMR Bruker WP-80 FT at 30 C ; 16 scans with a 45 deg. pulse width and delay of 3.0 sec.;

TABLE 7.1 cont'd

TENTATIVE CHEMICAL SHIFT ASSIGNMENTS

PEAK TYPE	CHEMICAL SHIFT (ppm +/- 0.1)	COMMENT
1. carboxylic	12.1	acrylic group; exchange with trace water present in solvent
2. aromatic	6.5-7.8	styrenic protons
3. end groups	5.2-6.4	protons derived from hydroge abstraction at chain ends
4. water	3.85	trace solvent impurity
5. solvent	2.5 +/-0.2	D-6 DMSO
5. aliphatic	1.0-2.5	polymer backbone

Note : all chemical shifts referenced to TSP external standard of the first kind significant. Given that the NMR accuracy is roughly 2-4 %, and the residual repeatability was measured as 0.4 % , it may be concluded that the residual method is a very consistent ,but biased estimate of composition. Over a limited composition range this bias is approximately 2-3 % .

Figure 7.1 displays the NMR spectra for a copolymer sample from a 260C run. Absorbing protons from the carboxylic, aromatic, end groups and solvent are resolved. NMR should prove to be extremely useful in characterizing copolymer microstructure and composition. Sample preparation, particularly elimination of water and oligomers appears to be the major limitation in improving the accuracy.

7.3 Effect Of Oxygen

The possibility of using oxygen as an initiator at high temperature was explored in the literature. Unfortunately, due to time constraints, experimental work in this area could not be performed.

At low temperatures, oxygen plays a well-known role as an inhibitor to radical propagation. Early study by Mayo (18), Henrici et.al. (17) and Miller and Mayo (16), attempted to clarify the kinetics of oxygen-styrene copolymerization at low temperature. Mayo (18) concluded that a 1:1 copolymer of oxygen and styrene is formed, but is unstable and decomposes back to aldehydes, ketones and other stable oxygenated molecules. He also concluded that cross-termination factor and reactivity ratios are concentration dependent.

It is believed that at higher temperatures the decomposition of peroxidic radicals will occur and very high rates of polymerization may be possible.

7.4 Modelling Non-Ideal Mixing

7.4.1 Macro-Mixing -

Macro-mixing refers to the bulk dispersion of fluid elements. It is generally characterized by the mean length of macro-discontinuity of the fluid. Its treatment, from a kinetic modelling sense, is taken from Levenspiel (23). It involves characterizing the degree of macro-mixing by an appropriate RTD (residence time distribution) experiment.

A simple, one parameter model was chosen to describe the bulk macro-mixing efficacy. For CSTR modelling, this parameter is 'N', denoting number of equivalent equal- volume ideal CSTR's in series that approach the non-ideal mixing behaviour of the reactor system under study. For PFR modelling, the parameter is D/uL, or bulk axial dispersion coefficient. Descriptions of both of these parameters and models may be found in detail in Levenspiel (23) and Biesenberger (25).

The value of these parameters are taken from fitting appropriate mixing model equations to actual RTD data (Section 4.1).

The kinetic correction to account for non-ideal mixing for the PFR solution, was to incorporate the following revised kinetic expression for rate of monomer consumption.

D/uL * tau(f) *d**2[M]/dt**2 -d[M]/dt + Rp = 0.0

This system is mathematically solved by creating two first order expressions for rate of polymerization and solving the system simultaneously by a Runge- Kutta technique. These expressions are the rate of monomer consumption and the acceleration of rate by axial circulation. Note that poor axial dispersion plays a second order role in monomer (conversion) kinetics that generally reduces overall monomer consumption rate. The applicable value of D/uL can be obtained by appropriate RTD experiments.

The correction for the CSTR solution is to model the system as N ideal equal volume stages. This is done by solving the CSTR steady states consecutively.

7.4.2 Micro-Mixing -

RTD analysis gives no indication of the state of micro-mixing in a vessel. Micro-mixing is defined as the short path diffusional process by which inter-molecular mixing takes place. In fact, there is currently no practical method of quantifying the state of micro-mixing in the literature. It remains therefore to study the possible effects of micro-mixing on the performance of a reactor system.

Micro-mixing is a purely diffusion controlled kinetic phenomena whose time constant is represented by...

tau(mic) == l(seg)**2/D

L(seg) refers to the mean length of the segregated fluid in the vessel. D refers to the diffusion coefficient of monomer molecules in the reactor. If l(seg) is either very small (ideal CSTR) or very large (ideal PFR), than the time constant describing micro-mixing will undoubtedly be removed from the kinetics of interest. Certainly, effective macro-mixing is essential in placing l(seg) down to the molecular level so that diffusion and micro- mixing will occur.

Since the degree of non-ideal micro-mixing cannot be measured, its effect on polymer properties can only be dealt with theoretically. This was done by Biesenberger (25) quite extensively and some of his conclusions are described below.

EFFECT OF NON-IDEAL MICRO-MIXING ON POLYMER PROPERTIES

conversion	no effect
no.av.mol.wt.	no effect
wt.av.mol.wt.	increased by (1+conversion) for CSTR
composition	significant drift in CSTR's

The effect of inhibited micro-mixing will be witnessed by composition distributions in CSTR's, or a general increase in property dispersity. The effect of micro-mixing has not been included in the model.

CHAPTER 8.0

8 REFERENCES

1. Rudin,A. and Chiang,S.S.M, J.Macro.Sci.Chem. Vol. A9, 237,(1975)

2. Husain,A. and Hamielec,A.E., J.Poly.Sci. Vol. 22, 1207,(1978)

3. Melville,N.W.M and Noble, K. and Watson,W.F., J.Poly.Sci.,Vol.2,229,(1947)

4. Alfrey,T. and Bohrer,R. and Mark,H., "COPOLYMERIZATION", Interscience Publications, (1952)

5. Wall,C., J.Am.Chem.Soc. Vol. 63,1862,(1941)

6. Stockmayer,W.H., J.Chem.Phys. Vol. 13,199,(1945)

7. Walling,J., J.Am.Chem.Soc. Vol. 71,1930,(1949)

8. Bamford,C.H. and Barb,W.G., "THE KINETICS OF VINYL POLYMERIZATIONS BY RADICAL MECHANISMS", Butterworth,London,(1958)

9. Marano,J.P., Process Technology Notes-Polyethylene, MIPPT,McMaster University,156,(1976)

10. Barb,W.G., J.Poly.Sci. Vol. 11,117,(1953)

11. Hamielec,A.E., McMaster University CHE771 Course Notes, (1983)

12. Ebert,K.H.,Ederer,H.J.,Schroder,U.K. and Hamielec,A.E. J.Makro.Chem, Vol.183,1207,(1982)

13. Rudin,A., "THE ELEMENTS OF POLYMER SCIENCE AND ENGINEERING",Academic Press, (1976)

14. Bovey and Kolthoff, J.Am.Chem.Soc., Vol. 69,2143, (1947)

15. Barnes, C.E., J.Am.Chem.Soc. Vol. 72, 211, (1950)

16. Miller A.A. and Mayo, F.R., J.Am.Chem.Soc., Vol. 78, 1023, (1958)

17. Henrici, G. and Schulz G.C., Makro.Chemie. Vol.18-19, 437, (1955)

18. Mayo, F.R., J.Am.Chem.Soc. Vol. 80, 2465, (1958)

19. Wallis, J.P.A.,Ritter, R.A.,Andre,H. , AIChE, Vol. 21,687, (1975)

20. Ehrlich, P. and Pittillo, R.N., J.Poly.Sci Vol.43,389, (1960)

21. Gierth, V., Die Ang.Makro.Chemie , Vol. 9-23, (1970)

22. Webb, S.W., McMaster University Che771 Report (1984)

23. Levenspiel, O, "CHEMICAL REACTION ENGINEERING", Addison-Wesley, New York, pg.270-290, (1978)

24. Khac-Tien,N; Ph.D Thesis, Institute of Chemical Engineering, Swiss Federal Institute of Technology, Lausanne,Switzerland,(1984)

25. Biesenberger, J.A. and Sebastian D.H., "PRINCIPLES OF POLYMERIZATION ENGINEERING", Addison-Wesley, New York, (1983)

26. Hui, A., M.Eng. Thesis, McMaster University, (1967)

27. Lord, G., M.Eng. Thesis, McMaster University, (1983)

28. O'Driscoll, K.F. and Cardenas. J,,J. Poly. Sci. Vol.A-1,14, 883, (1976)

29. Sacks,M et al., Chem. Eng. Sci., Vol. 28, 24, (1973)

30. Lukow,K.F.; S.C. Johnson and Son Company, private conversation, Racine, Wisconsin, (1984)

31. Husain, A., M.Eng. Thesis, McMaster University (1970)

32. DeSomer, P. M.Eng. Thesis, McMaster University (1972)

33. Beuche, F.," PHYSICAL PROPERTIES OF POLYMERS", Wiley Interscience,New York, (1962)

34. Atherton, J.H. and North, A.M., Trans.Far.Soc., Vol.58, 2049,(1962)

35. Biesenberger, J.A. and Capinpin,K., J.Appl.Poly.Sci., Vol. 16,695,(1972)

36. Chiantore,O. and Hamielec, A.E., J.Liquid.Chromatography,,to be published

37. Kirchner,K and Riederle,K; Die Ang.Makro.Chemie, Vol.1-16,111,(1983)

38. Huglin M., "LIGHT SCATTERING FROM POLYMER SOLUTIONS", Academic Press,New York,New York, (1972)

39. Garcia Rubio, L.H., MacGregor, J.F. and Hamielec, A.E.; "Polymer Characterization", Series no.17, 181st ACS Symposium, American Chemical Society, pg.311, (1983)

40. Schroder, U.K.O., Ebert, K.H. and Hamielec, A.E.; Die Ang.Makro.Chemie, Vol.185,991,(1984)

41. Hamielec, A.E, private conversation, (1984)

42. Brandup, V et al., "POLYMER HANDBOOK", 2nd edit., Wiley Interscience, II-205, (1975)

43. Chiantore, O and Hamielec, A.E., MIPPT report (1983)

44. Hruska, V, M.Eng Thesis, Master University, (1985)

45. Storer-Folt,N., McMaster University, Dept.of Chemistry, unpublished data

46. Wingler, F., Pedain,J., Appel,H., and Bartl,H.; Bayer Aktiengesellschaft,"Pulverisable Acrylate Resins", U.S. Patent 3753958, (1973)

47. Hamielec, A.E., Lawless, G.P. and Schultz, H.H.; S.C. Johnson and Company, "Process for the Continuous Bulk Copolymerization of Vinyl Monomers", U.S. Patent 4414370, (1983)

48. Clayton, G.D. et al., "PATTY'S INDUSTRIAL HYGIENE AND TOXICOLOGY",3rd edit.,Vol. 2B, Wiley Interscience, (1981)

49. Leonard, C.C., "VINYL AND DIENE MONOMERS',Wiley-Interscience,(1970)