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MEASUREMENT AND MODELLING OF LONG CHAIN BRANCHING IN CHAIN GROWTH POLYMERIZATION

By

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A Thesis

Submitted to the School of Graduate studies

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MEASUREMENT AND MODELLING OF LONG CHAIN BRANCHING IN CHAIN GROWTH POLYMERIZATION

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ABSTRACT

The measurement and modelling of long chain branching(LCB) in free-radical chain growth polymerization is examined. A new method, the "instantaneous" property method, is presented for the calculation of the full molecular weight distribution(MWD) of branched polymers when the branching is due to chain transfer to polymer. The method is shown to be accurate and consistent with the method of moments, the method that is generally used to calculate molecular weight averages. The method can give additional detail about the MWD of the various branched families in the polymeric mixture. Such information can be quite useful in correlating processing properties with molecular structure.

Two polymers that produce LCB when polymerized were examined. Bulk polymerization of vinyl acetate(VAc) and p-methyl styrene were carried out. Gel permeation chromatography , intrinsic viscosity and low angle laser light scattering measurements were used to measure molecular weight averages and LCB frequencies. Two methods were used to calculate LCB frequencies and they both gave results that were consistent with the method of moments.

The "instantaneous" method was applied to the data from the polymerization of PPMS since for this polymer LCB is due to chain transfer to polymer. The predictions from the "instantaneous" method, when compared to the method of moments and the experimental data, were shown to be of acceptable accuracy.

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TABLE OF CONTENTS

CHAPTER 4 DEVELOPMENT OF METHODOLOGY USED FOR LONG CHAIN BRANCHING MEASUREMENT IN THIS INVESTIGATION

CHAPTER 5 SOLUTION OF THE POPULATION BALANCE EQUATIONS

CHAPTER 6 EVALUATION OF LONG CHAIN BRANCHING MEASUREMENT METHODS-APPLICATION TO EXPERIMENTAL DATA

CHAPTER 7 CONTRIBUTIONS,LIMITATIONS AND PROPOSED FUTURE RESEARCH

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

a	Mark Houwink constant
A_2	second virial coefficient
B_n	number average number of branch points per molecule
C_p	ratio of rate constant for transfer to polymer to that for propagation
$F_D(r,0,\bar{t})$	frequency distribution for instantaneous linear dead polymer born at time $\bar{t}$
$F_L(r,0,t)$	frequency distribution for live linear polymer chains at time t
$F(v)$	GPC chromatogram at elution volume v
k_p	rate constant for propagation
k_{tc}	rate constant for termination by combination
k_{tCTA}	rate constant for transfer to chain transfer agent
k_{td}	rate constant for termination by disproportionation
k_{tm}	rate constant for transfer to monomer
k_{tp}	rate constant fortransfer to polymer
K	Mark Houwink constant
m	number of branch points per molecule
M_n	number average molecular weight
M_w	weight average molecular weight
$M(t)$	monomer concentration at reaction time t

$M(\bar{t})$	monomer concentration at birth time $\bar{t}$
$P(r,i,t)$	concentration of dead polymer of chain length r with i branch points at time t
$P(r,i,t,\bar{t})$	concentration of dead polymer of chain length r with i branch points at time t and born at some previous time $\bar{t}$
$R(r,i,t)$	concentration of live polymer of chain length r with i branch points at time t
$Q_n(i,t)$	nth moment of dead polymer with i branch points at time t
$Y_n(i,t)$	nth moment of live polymer with i branch points at time t

Greek Letters

β	dimensionless parameter related to termination by combination
ε	exponent in the relationship between the intrinsic viscosity ratio and the mean square radius of gyration ratio of branched and linear polymer
η_{sp}	specific viscosity
$[\eta]$	intrinsic viscosity
$[\eta]_b$	intrinsic viscosity of branched polymer
$[\eta]_l$	intrinsic viscosity of linear polymer
γ	dimensionless parameter related to transfer to polymer

μ,σ	parameters in the log normal distribution
τ	dimensionless parameter related to transfer to monomer, transfer to chain transfer agent and termination by disproportionation
ϕ	$=1/(1+\tau+\beta+\gamma)$

Abbreviations

CSTR	continuous stirred tank reactor
GPC	gel permeation chromatography used interchangeably with SEC
LALLS	low angle laser light scattering
LCA	long chain approximation
LCB	long chain branching
MALLS	multiple angle laser light scattering
MWBD	molecular weight and branching distribution
MWD	molecular weight distribution
PD	polydispersity
PMS	para-methyl styrene
PPMS	poly(para-methyl styrene)
PVAc	polyvinylacetate
SCB	short chain branching
SEC	size exclusion chromatography

SSH	stationary state hypothesis
VAc	vinyl acetate

CHAPTER 1

INTRODUCTION

1.1 General

Long chain branching and its control is becoming of increasing commercial importance as the demands grow for polymers having properties that are needed for more sophisticated applications. In certain cases the branching is intentionally introduced in the polymer chains in order to utilize the benefits it imparts to the properties of the polymer. For example, in the copolymerization of a vinyl monomer, a small amount of a difunctional monomer such as divinyl benzene is used in the synthesis to give controlled levels of long chain branching and improved processability. In other cases the process is such that branching occurs naturally. For example, when chain transfer to polymer and terminal double bond polymerization reactions are significant in the polymer synthesis mechanism, long chain branching occurs. More recently, there has been tremendous interest in the possibilities of using metallocene catalysts to produce polyolefins having sufficiently high degrees of branching to give good processability simultaneously with narrow molecular weight distributions to give good mechanical properties(Soares and Hamielec,1996)

The synthesis of polymer with long branches produces polymer chains having more than two chain ends and with branches sufficiently long to affect the rheological properties of a polymer melt. The concept of long chain branching has been known as early as the 1930's when the fundamental idea of high molecular weight compounds was developed. Stockmayer and Fixman(1953) indicated that long chain branching was used to explain deviations from those expected for linear polymeric chains.

1.2 Definition of Long Chain Branching

Branched polymers are described as having branched points which refer to the atom or groups of atoms from which more than two long chains emanate. In order for branching to occur in a step-growth polymerization, a monomer must have a functionality(i.e. the number of reactive groups per molecule) of at least three. In the case of chain-growth polymerization, transfer to polymer and terminal polymerization reactions are the typical mechanisms for producing branching. There are two types of branches : short chain branches and long chain branches. Short chain branches(SCB) contain a small number of monomer units of the order of 2-10. Long chain branches(LCB) would typically have a length comparable to the main chain and be sufficiently long to affect melt rheology. Crosslinking may be considered as an advanced stage of branching since it occurs when branched molecules become interconnected to form extremely large molecular weight compounds. Figure 1.1 illustrates these concepts.

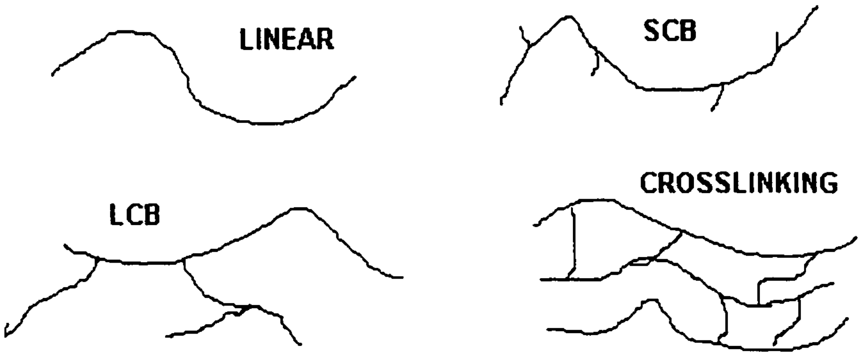


Figure 1.1

Another important characteristic of branching in polymers is the distribution of the branches along the main chain. Short chain branches may be introduced via ionic copolymerization(for example, ethylene with butene-1,hexene-1,....) or via backbiting or copolymerization in free-radical polymerization. Long chain branches may be isolated as typically produced by chain transfer to polymer or could be produced as comb-like molecules as a result of grafting of one polymer onto the backbone of another. It is also possible to produce star-like branched molecules where many long chain branches emanate from a single point. The properties of the branched polymer will depend on the number of branches, the type and the distribution. Since no absolute direct method exists for the measurement of the number and distribution of branch points, the measurement of branching by indirect methods continues to be a challenging area in polymer characterization methodology.

1.3 Effect of Long Chain Branching on Processability

In general branched polymers in solution or in a melt have a smaller size than their linear counterpart of the same molecular weight. It follows that solution and melt properties of polymers that are directly related to their overall dimensions are strongly affected by LCB. In practice LCB can have very beneficial effects on the processability of a given polymer.

Some of the melt rheological properties affected by LCB are summarized below:

Die Swell- This may be defined as the ratio of the diameter of a polymer melt extrudate to the die diameter. It reflects the stored elastic energy due to distortion of the fluid elements when flowing through a die. It is known that LCB can increase die swell (Hamielec and Vlachopoulos,1983).

Shear Thinning- This may be described as the reduction of the viscosity of a polymer melt with an increase in shear rate. Typically it is measured by the ratio of the melt flow indices using nominal weights of 10 and 2kg(I_{10}/I_2) .LCB is known to increase shear thinning.

Melt Fracture- This refers to the distortion of the polymer extrudate on exit from a die. LCB reduces melt fracture at higher throughput.

Melt Strength- Thin film can be produced if a polymer has sufficient melt strength. LCB imparts strain hardening to the polymer i.e. the polymer gets stronger on stretching. This property allows thinner films to be made.

From the above it is clear that LCB can substantially improve the processability of polymers. There is thus substantial incentive to develop methodology for the valid measurement of LCB and to develop strategies to control LCB levels in polymer manufacturing processes.

1.4 Status of Kinetic Modeling of Long Chain Branching(LCB)

The solution of the population balance equations for the synthesis of polymers with LCB is a formidable task. There may be as many as 20000 ordinary differential equations for the live and dead species that must be solved for a batch reactor using conventional ODE techniques.. Even with the fastest computers available today solution times are so large as to be prohibitive. To overcome this problem of excessive computation time, the method of moments has been used by others extensively but with a severe penalty. The leading moments of the full molecular weight distribution can be solved for readily. Previous researchers in this area have invariably used the method of moments (Bamford and Tompa,1954;Graessley et al,1965; Small,1972,.....) . However the full molecular weight distribution cannot be reconstructed from the leading moments since the distributions are complex with high molecular weight shoulders. Thus a great deal of most useful information contained in the full molecular weight distribution is lost when the method of moments is used. Recently, a novel solution method coined the "numerical fractionation" technique(Teymour and Campbell,1994) provides the full molecular weight distribution(MWD) using the method of moments for families of polymeric molecules with narrow MWD's. An analytical distribution function for the MWD is assumed and the moments are used to calculate the parameters. This most interesting and promising method is discussed more fully in the body of the text. There is thus a need for more rigorous and efficient methods of solving the population balance equations and this is one of the challenges faced in this thesis. The other challenge is experimental in nature and involves the measurement of LCB.

1.5 Objectives

The objectives of this study are as follows:

(a) To develop a valid method for the measurement of LCB in polymers using size exclusion chromatography.

(b) To apply the method to poly(vinyl acetate) and poly(p-methylstyrene).

(c) To develop a rigorous but practical method(i.e. one that makes few assumptions and requires reasonable computation times) of solving the population balance equations when long chain branching occurs during polymer synthesis via chain transfer to polymer.

CHAPTER 2

LITERATURE REVIEW

2.1 General

In this review, research on long chain branching during chain growth polymerization is covered exclusively. There is little or no coverage of short chain branching or long chain branching during step growth polymerization. This review examines the measurement of long chain branching frequency, kinetic modeling of reaction systems where long chain branching occurs, the reactor systems that are utilized and studies of long chain branching for some commercially important polymers.

A number of reviews on long chain branching in polymers has been published. Small(1975) gave a comprehensive review of the properties of branched polymers both in dilute solution as well as in a melt. An examination of the significant effect of long chain branching(LCB) on the space filling properties of polymers was given. Some of the solution properties that are affected by LCB are discussed, for example, the angular distribution of scattered light, intrinsic viscosity, and the sedimentation constant in centrifugation. The effect of LCB on melt viscosity, its shear rate dependence and melt elasticity are also treated. The dimensions and thermodynamics of branched polymeric molecules, their hydrodynamic properties and the kinetics of reactions that lead to LCB are some of the other key areas covered.

Nagasawa and Fujimoto(1972) dealt extensively with the methods of preparing specific types of branched polymers, for example, star-shaped and comb polymers. Their main emphasis ,however, was on branched comb polymers and their viscoelastic properties.

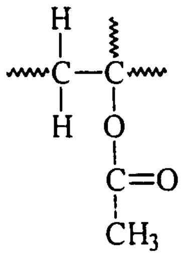
Roovers(1985) considered the characteristics of the various monomers that produce LCB and the various strategies and methods for the preparation of well-defined branched polymers. Detailed sections on the measurement of properties in dilute solution are also covered. A final section on bulk properties of branched polymers is presented.

The following section in this review examines the various approaches used to measure long chain branching frequency. Graessley(1968) presented the first review of this subject.

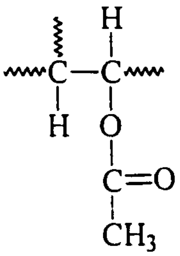
2.2 Measurement of Long Chain Branching Frequencies

2.2.1 Substance specific methods

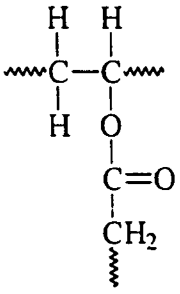
In the measurement of long chain branching frequency it is useful to distinguish between methods that depend on the specific chemical structure of the polymer and those that are universally applicable. Poly(vinyl acetate)(PVAc) is a good example of a polymer where long chain branching can be examined by making use of the chemical nature of the branches. Graessley and co-workers(1969) had shown that branch points exist in three chemically distinct structures, through the α-carbon(I), the β- carbon (II), and the acetate group (III):



I



II



III

Agarwal and co-workers(1982) started with a PVAc having an M_w of 750,000, a polydispersity of 3.85 and a B_n(average number of branch points per molecule) of 2.2. B_n was measured by size exclusion chromatography on-line with low angle laser light scattering photometry. The PVAc was subjected to chain scission by mechanical as well as chemical(saponification and reacetylation) methods to investigate the effect of shear on branching distribution. They concluded that the branches through the acetate group are ruptured preferentially on shearing, the branches through the α-and β-carbons are not broken on shearing and the extent of branching through the acetate group is about 67% of the total branching.

Nozakura et al(1972a,1972b) examined LCB in poly(vinyl acetate) and poly(vinyl alcohol). They formed a crosslinked network by reacting partially saponified poly(vinyl acetate) and toluene diisocyanate in benzene. They were able to show that the urethane linkage was quantitatively cleaved by acids. In their second paper they polymerized ^{14}C-labelled vinyl acetate in the presence of crosslinked poly(vinyl acetate) at 60°C and 0°C. They concluded that in the polymerization of vinyl acetate , chain transfer to the polymer main chain takes place about 2.4 times as frequently as that to the acetoxy group at 60°C and about 4.8 times as frequently at 0°C.

In the case of polybutadiene, ozonolysis followed by hydrolysis can be employed in the cleavage of branches or crosslinks(Koenig,1980).

Spectroscopic techniques have been employed to measure the concentration of end groups or branch points in which the specific nature of the polymer is exploited. Long chain branching in polyethylene is a classic example. The commercial importance of polyethylene has led to a number of publications where ^{13}C-NMR has been utilized to measure long chain branching. These papers would be reviewed in a later section.

In general, branching density is low and differences in properties between end groups or branch points and the normal repeat units are too small for effective and widespread use to be made of chemical or spectroscopic methods. As a result most of the focus has been on methods based on the relative molecular size of linear and branched polymers in solution.

2.2.2 Methods based on molecular size

Branched polymer molecules have a smaller size in solution or in a melt than linear polymer of the same molecular weight. Size is usually related to the mean square radius of gyration, $<s^2>$, which can in principle be measured from radiation scattering at zero or small angles and extrapolated to zero concentration(Zimm and Stockmayer, 1949). A distinction must be made between three different types of radii that have been used to measure molecular size:

$<s^2>$ refers to the mean square radius of gyration of polymer molecules in the solution under study

$<s^2>_0$ refers to the unperturbed mean square radius of gyration of the polymer. This quantity is based on the assumption that there's zero interaction between the various elements of the polymer chain which implies that the chains obey random flight statistics. All the theoretical models that have been developed to calculate the mean square radius of gyration are based on random flight statistics.

$<s^2>_\theta$ refers to the mean square radius of gyration at the theta temperature. The theta temperature is defined by Flory(1953) as the temperature of a polymer solution where the two opposing influences of intermolecular interaction and solvent effects are in balance.

It is usual to define a branching parameter g that compares the size of a branched polymer to that of the linear polymer of the same molecular weight:

$$g=\langle s^2\rangle_b/\langle s^2\rangle_l \tag{2-1}$$

where subscripts b and l refer to branched and linear polymer respectively.

It is possible to define g for the actual state, the unperturbed state and the theta state. The most direct method of measuring branching would be to use angular light scattering to determine $\langle s^2\rangle$ and compute the appropriate g's. For polydispersed polymers(the normal situation) the $\langle s^2\rangle$ determined by light scattering is a z-averaged value. This necessitates the calculation of the z-average molecular weight in order to calculate g. This is not easily achieved unless the full molecular weight distribution is available. Some workers have attempted to estimate the weight-average $\langle s^2\rangle$ from the z-average value by assuming a molecular weight distribution function(Moore and Millns,1969. Hama et al,1972).

The effect of branching is most easily measured from the intrinsic viscosity of the polymer. The intrinsic viscosity of a branched polymer is always less than that for the linear polymer of the same molecular weight. This relative effect is quantified as

$$g'=[\eta]_b/[\eta]_l \tag{2-2}$$

$[\eta]$ is the intrinsic viscosity

In order to relate g' to the relative molecular size g the following relationship is used:

$$g^{\varepsilon} = g' \tag{2-3}$$

Zimm and Stockmayer(1949) proposed a value of 1.5 for ε whereas Zimm and Kilb(1959) suggested a value of 0.5. More recently it has been shown that ε may vary from 0.5 to 1.5 for different polymers. Roovers(1985) summarized in a table the different values quoted for ε in the literature. For example, Berry et al (1964) established a value in the range 0.7-0.9 for randomly branched poly(vinyl acetate). Foster et al(1980a,1980b) showed that a value of 0.75 for ε fitted the data for polyethylene.

In order to express g in terms of the number of branch points, theoretical models are generally used. Zimm and Stockmayer(1949) developed expressions for g for different types of branch points (trifunctional vs tetrafunctional) and different types of branching(comb vs random). Roovers(1985) lists some of the expressions that have been used. The most widely used are those by Zimm and Stockmayer(1949) for randomly branched polymer:

For monodispersed, trifunctional and tetrafunctional randomly branched polymers

$$g_3=\left[(1+m/7)^{1/2}+4m/9\pi\right]^{-1/2} \qquad (2\text{-}4)$$

$$g_4=\left[(1+m/6)^{1/2}+4m/3\pi\right]^{-1/2} \qquad (2\text{-}5)$$

where m is the number of branch points per molecule

For polydispersed, trifunctional and tetrafunctional randomly branched polymer, the weight average $\langle g\rangle_w$ is

$$\langle g_3\rangle_w=\frac{6}{n_w}\left[1/2\left(\frac{2+n_w}{n_w}\right)^{1/2}\ln\left(\frac{(2+n_w)^{1/2}+n_w{}^{1/2}}{(2+n_w)^{1/2}-n_w{}^{1/2}}\right)-1\right] \qquad (2\text{-}6)$$

$$\langle g_4 \rangle_w = \left(\frac{1}{n_w}\right) \ln(1 + n_w) \qquad (2\text{-}7)$$

where n_w is the weight average number of branch points per molecule

Myers and Dagon(1964) performed computations for the intrinsic viscosity of trifunctional, randomly branched whole polymers. They employed the Beasley(1953) molecular weight distribution function and compared the Zimm-Stockmayer and the Zimm-Kilb relationships for the intrinsic viscosity ratio. They also compared Beasley's function with the one derived by Flory(1941) for trifunctionally branched condensation polymers at different degrees of branching. They found that the two functions are in good agreement for low extents of branching but at high degrees of branching the calculated intrinsic viscosities and weight average degree of polymerization differed significantly.

Benoit et al(1966) and Grubisic et al (1967) proposed that the hydrodynamic volume for all polymers in dilute solution is proportional to $[\eta]$ M and the proportionality constant is the same for all polymer types(homopolymers, copolymers, polymer chains with long branches). This universal parameter has made size exclusion chromatography one of the most important tools available for the determination of the molecular weight distribution of polymers. Most of the recent estimates of branching have used size exclusion chromatography with either single or multiple detectors.

2.2.3 Size Exclusion Chromatography

The development of size exclusion chromatography(SEC) as a key tool in characterizing polymeric material made it possible to develop methods to estimate the degree of long chain branching. In the methods to be described in this section the mass concentration detector that is normally used is a differential refractive index detector. The intrinsic viscosity of the whole polymer is usually needed and is measured off-line.

Applying the universal parameter to any given SEC system at any elution volume, it follows that

$$[\eta]_l M_l = [\eta]_b M_b \qquad (2\text{-}8)$$

For branched polymers the difficulty lies in how the product $[\eta]_b M_b$ is separated in order to produce an appropriate calibration curve.

Two approaches have been used when applying SEC to the estimation of long chain branching. In the first and older approach, the number of branch points is treated as proportional to the molecular weight of the polymer by defining a branching frequency λ as

$$\lambda = n/M \qquad (2\text{-}9)$$

where n is the number of branch points per molecule

and M is the molecular weight

λ is normally treated as a constant. The more recent approach is to relate the intrinsic viscosity of the branched polymer to its molecular weight and to estimate the number of branch points using a generalization of the Zimm-Stockmayer/Zimm-Kilb theories.

Drott and Mendelson(1968,1970) used the universal calibration curve together with a constant λ in equation (2-9) to estimate long chain branching. They generated a series of molecular weight calibration curves for different values of λ and for both the Zimm-Stockmayer and Zimm-Kilb models. This allowed them to produce a nomograph relating elution volume, intrinsic viscosity, molecular weight and λ. They applied their method to determine long chain branching in low density polyethylene. They concluded that the effect of branching on intrinsic viscosity is best described by

$$<g_3>_w^{1/2} = [\eta]_b / [\eta]_l \qquad (2\text{-}10)$$

where $<g_3>_w$ is given by equation (2-6).

Ram and Miltz(1971) also assumed a constant branching frequency but went on to propose a modified relationship to replace equation (2-9) :

$$n = \alpha(M - M_0) \qquad (2\text{-}11)$$

where M_0 represents a threshold molecular weight below which there is no branching. They took M_0 to be 5,000 - 12,000 for low density polyethylene. Cervenka and Bates(1970) also supported the idea of a constant branching frequency except at low molecular weights where they proposed the use of Schultz's branching distribution function

$$n = (1 + \gamma^2 z^2)^{1/2} - 1 \qquad (2\text{-}12)$$

where γ is a branching index that ranges from zero for linear polymer to unity for polymer at incipient gelation and z is the degree of polymerization.

Schultz(1970) used the defintion of g′ and the Mark Houwink equation for $[\eta]$ for linear polymers in applying SEC to branched polymers. His paper was a theoretical treatment for condensation polymers and used the Zimm- Kilb theory. He deduced two branching distribution functions , equation (2-12) and equation (2-13):

$$n = \gamma^{1/2} z \qquad (2\text{-}13)$$

It was concluded that equation (2-12) was a good approximation over the whole molecular weight range whereas equation (2-13) was adequate for high molecular weights.

Cote and Shida(1971) used probability functions to calculate the branching distribution and concluded that the branching frequency λ varies at low molecular weights but approaches a constant value at higher molecular weights. Saito et al(1969) obtained results that supported this view.

Coleman and Fuller(1975) also assumed a constant λ in calculating long chain branching in polychloroprene. They prepared polychloroprene at 40°C as a function of conversion. They used SEC together with the intrinsic viscosity of the whole polymer to estimate LCB. They concluded that the degree of branching increases with conversion in a manner consistent with the accepted mechanism of free radical diene polymerization.

The main weakness of the above method is the assumption of constant λ. Wild et al(1971) utilized polymer fractions to show that λ varies with molecular weight with higher values for higher molecular weights. Even though their results contradict the experimental results of Drott and Mendelson(1968) ,it nevertheless emphasized the weakness of the assumption of constant λ.

As stated previously, the more recent approach is to relate the intrinsic viscosity of the branched polymer to molecular weight. Ram and Miltz(1971) proposed a cubic equation for the intrinsic viscosity:

$$\ln[\eta]_b = \ln K + a \ln M + b(\ln M)^2 + c(\ln M)^3 \quad \text{for } M \geq M_0 \qquad (2\text{-}14)$$

$$\ln[\eta]_l = \ln K + a \ln M \quad \text{for } M < M_0 \qquad (2\text{-}15)$$

where K,a are the Mark Houwink constants.

Hamielec and Ouano(1978) clarified the application of the concept of the universal parameter when applied to chromatograms for branched polymers. They showed that the correct parameter within the detector cell containing branched polymeric species is $[\eta]\, M_N$ where M_N is the number average molecular weight of the mixture in the cell. Their analysis to prove the above assertion is as follows: Consider a mixture of polymer molecules that have eluted from the columns of a SEC into the detector cell at any specified elution volume. They would all have the same hydrodynamic volume. Therefore,

$$[\eta]_{ps} M_{ps} = [\eta]_1 M_1 = [\eta]_2 M_2 = \ldots \qquad (2\text{-}16)$$

where species 1, 2, ... may refer to linear, branched, copolymers or blends of homopolymers. The $[\eta]$ in the detector cell is given by

$$[\eta] = W_1 [\eta]_1 + W_2 [\eta]_2 + \dots \qquad (2\text{-}17)$$

where W_1, W_2, ... are the weight fractions of the species in the detector cell. Equation (2-17) can be rearranged as

$$[\eta] = \frac{W_1}{M_1} [\eta]_1 M_1 + \frac{W_2}{M_2} [\eta]_2 M_2 + \dots \qquad (2\text{-}18)$$

Using equation (2-16), equation (2-18) can be written as

$$[\eta] = [\eta]_{ps} M_{ps} \left(\frac{W_1}{M_1} + \frac{W_2}{M_2} + \dots \right) \qquad (2\text{-}19)$$

By definition, the number average molecular weight M_N is given by

$$M_N = \frac{1}{\frac{W_1}{M_1} + \frac{W_2}{M_2} + \dots} \qquad (2\text{-}20)$$

Thus the correct universal calibration parameter is given by

$$[\eta] M_N = [\eta]_{ps} M_{ps} = [\eta]_1 M_1 = \dots \qquad (2\text{-}21)$$

An implication of this analysis is that in using SEC for branched polymer, the M_w for the whole polymer will generally be underestimated and indicates the need for additional information as can be obtained from a second detector. Hamielec et al(1978) and Foster et al(1980a,1980b) applied equations (2-14) and (2-15) for the intrinsic viscosity and developed what was called the molecular weight and branching distribution method(MWBD).Assuming that there's no branching below M_0, the constant c in equation (2-14) is given by

$$c=-b/\ln M_0 \qquad (2\text{-}22)$$

The unknown constant b is determined by making [η] for the whole polymer agree with [η] calculated from SEC. The procedure reduces to a single parameter search for b. They applied the method to low density polyethylene and poly(vinyl acetate) and showed that their long chain branching results were consistent with the reaction kinetics. In addition they correlated their LCB results to the rheological and blown film properties for polyethylene.

2.2.4 Size Exclusion Chromatography with an additional Detector

The use of GPC or SEC was first introduced in the early 1960's (Moore,1964). Since its introduction it has become the single most important technique for determining molecular weight distribution(MWD) of polymers. Not surprisingly, significant research effort has been expended to improve the performance of SEC. Advances have been made in the following three areas:
(a) the development of high performance columns using micropacking for high speed and high resolution separations; (b) the inclusion of computers for control, data acquisition and analysis; (c)the development and use of additional detectors sensitive to molecular size.

Conventional SEC includes a mass concentration detector which would typically be a differential refractive index(DRI) detector. Ultra-violet(UV) and infra-red(IR) detectors may also be used(Hamielec,1982,Balke,1991). The two most important molecular size detectors that have been coupled with the mass concentration detector in a multidetector system are the light scattering and viscometric detectors.

Polymer characterization by SEC in general has been reviewed by Janca(1981), Hagnauer(1982), Styring and Hamielec(1989) and Balke(1991). Several texts have appeared. one of the most useful is that of Yau et al(1979).The text by Balke(1984) is very thorough in its treatment of the statistics associated with SEC measurement and error analysis. Quivoron(1984) reviewed some aspects of multidetector coupling and Hamielec(1982) considered their use in SEC for branched and random copolymers. In this section a review of the use of each of these two detectors . with emphasis on long chain branching, is given.

Use of a Light Scattering Detector with SEC

Light scattering as a technique has been used to characterize polymers since the early part of this century. Steubing(1908) and Mecklenburg(1914) introduced a photometer to measure the intensity of scattered light of a monochromatic, depolarized light beam. Putreys and Brosteaux(1935) proposed an empirical relation between the scattered light intensity and the molecular weight of polymer molecules in solution. It was in the early 1940's that Debye(1946) published the theoretical analysis for light scattering photometry as an absolute method for the determination of molecular weights and sizes of substances in solution. Doty and Zimm(1944,1945) applied some of these theoretical results to the analysis of polymers. The scattered light intensity is a function of the angle of measurement and the polymer solution concentration. In order to remove the effects of polymer-solvent interaction it was necessary to extrapolate the results to zero angle and zero concentration using the Zimm plot(Zimm,1948). A number of monographs and review articles have since been published detailing the theory of light scattering and its use in polymer characterization.(van de Hulst,1957;Kerker,1969;Casassa and Berry,1975: Huglin,1972; Burchard, 1983).

The introduction of lasers in light scattering photometers has allowed the use of a much smaller scattering volume which is ideal for on-line measurement. The most successful on-line molecular weight detector uses low-angle laser light scattering photometry(LALLSP) and was developed by Kaye(1973). This photometer was commercialized by Chromatix and sold as Chromatix KMX6. More recently the Chromatix CMX-100 and the LS-8000 (Tosoh Corporation,Japan) have been introduced. These are true LALLS photometers in that they measure light intensities at angles less than 7°. There are other photometers that allow measurements at angles less than 15°.

Many very useful publications on the use of LALLSP in characterizing macromolecules have appeared . Lindner and Huang (1991) give a comprehensive overview of the subject although the coverage of long chain branching is very brief.

Ouano and Kaye(1974) and Ouano(1976) were the first to publish the simultaneous and continuous monitoring of the DRI and LALLS detector responses. They applied the method to polystyrene standards and broad molecular weight samples of poly(methyl methacrylate). They showed that their determination of M_N and M_W was consistent with the literature values.

Hamielec and Meyer(1978) considered the on-line molecular weight and long chain branching measurement of polymers using SEC and LALLS. They dealt in detail with the use of the technique for both linear and branched polymers. The development of the equations to correct for peak broadening for these multidetector systems was presented .Some guidelines as to when peak broadening corrections are important are also given. For long chain branching they also developed the correct equations to be used for the molecular size ratio g when measured at constant elution volume and at constant molecular weight.

Hamielec et al(1978) used SEC with LALLSP to characterize a number of samples of poly(vinyl acetate) synthesized by bulk polymerization at different temperatures(50°C- 80°C). They introduced an electronic device and a new technique to optimize the sensitivity and the signal-to-noise ratio of the LALLS photometer. They also showed that the commonly used parameter with SEC, $[\eta]\ M_w$, is incorrect for polymers with long chain branching, copolymers with composition drift and polymer blends. The correct universal calibration parameter was shown to be $[\eta]\ M_N$.

Kato et al(1979) used SEC combined with a laser light scattering detector to measure the degree of branching of comb-shaped branched polystyrenes. They employed a scattering angle of 90° and concluded that the method was useful for determining the degree of branching if the type of branching is known and provided that the extent of branching is not too high.

MacRury and McConnell(1979) used LALLSP and SEC to determine the molecular weight distributions for three polyethylene standards(two high density and one low density) without resorting to column calibration procedures. In the case of the low density polyethylene the LALLSP detected a small quantity of microgel that was not detected by the SEC detector.

Axelson and Knapp(1980) used SEC and LALLS to study long chain branching in polyethylene. They assumed a constant branching frequency λ and together with the Zimm-Stockmayer relationship for g in terms of n_w they were able to calculate the number of long chain branches per 1000 carbon atoms as a function of elution volume.

Jordan(1980) presented a review of SEC with LALLS detection. A summary of light scattering theory, instrumentation configurations , principles of operation and selected applications are included. A short section discussed the suspected branching in some epoxy resin samples . No attempt was made to quantify the degree of branching.

Malihi et al(1984) used SEC/LALLS to determine the molecular weight of a styrene-butyl acrylate emulsion copolymer. They were able to determine the weight average molecular weight as well as the parameters which reflect the heterogeneity in composition of the copolymer. It was stated that the samples analysed were gel free which seems to imply that any existing gel was filtered out. The formation of long chain branches and gel was not addressed.

Use of a Viscometric Detector with SEC

While there are significant advantages of SEC over other methods for molecular size measurement (viz. speed, simplicity, reproducibility), a major drawback for the SEC system with a single detector is the need to calibrate the instrument with known standards indicating that SEC is an indirect method for molecular size measurement. The previous section on light scattering dealt with a method that can be used for molecular size measurement without the need for calibration standards. This section deals with the other molecular size measurement technique, the on-line viscometric detector(VISC). This method ,however, requires the use of calibration standards.

The earliest attempts at introducing an on-line viscometer involved the discontinuous discharge of SEC effluent in small batches into an Ubbelohde type capillary viscometer(Meyerhoff,1968; Goedhart and Opschoor,1970; Grubisic-Gallot et al,1972; Servotte and DeBruille,1975; Park and Graessley,1977; Constantin,1977). The efflux time together with the mass concentration detector response of each batch of effluent were used to calculate $[\eta]$ for each batch.

Goedhart and Opschoor(1970) connected a capillary viscometer to a Waters Associates GPC and employed an electronic timing device to obtain reproducible efflux times to within 0.005%. They developed the universal calibration curve in the usual way using polystyrene standards and Mark-Houwink constants for polystyrene in tetrahydrofuran(THF) :

$$[\eta] = 1.17\times10^{-4}\, M_w^{0.725} \qquad (2\text{-}23)$$

Equation (2-23) was developed from narrow fractions supplied by Waters and data from Schulz and Baumann(1969). Measurement of [η] vs. elution volume for broad samples of polystyrene(PS), poly(vinyl chloride)(PVC) and PVAc were made. The value of [η] for the whole polymer was calculated from the values of [η] for the different eluting batches and compared to the off-line measurement using an Ubbelodhe viscometer. Good agreement was achieved. Mark-Houwink constants for linear PVC and PVAc in THF were also deduced from the on-line viscometric data:

PVC $\quad [\eta] = 1.6\times10^{-4}\, M_w^{0.77} \quad$ (2-24)

PVAc $\quad [\eta] = 3.5\times10^{-4}\, M_w^{0.63} \quad$ (2-25)

They concluded that the equipment will be useful in the characterization of branched polymers and copolymers.

Servotte and De Bruille(1975) used a Waters Model 200 GPC coupled with an automatic viscometer(supplied by FICA) equipped with an Ubbelodhe tube. They examined linear and branched polyethylene(PE) at high temperature(135°C). The universal calibration curve was used together with the Mark-Houwink constants for linear PE in 1,2,4-trichlorobenzene at 135°C(Otocka et al,1971):

$$[\eta] = 5.1\times10^{-2}\, M^{0.706}\ \text{mL g}^{-1} \qquad (2\text{-}26)$$

and calculated g' for three branched PE samples and compared their results with values obtained by fractionation, viscometry and light scattering. They concluded that the GPC-VISC method allows a rapid detection of LCB in PE.

Park and Graessley(1977) used a Waters Model 200 GPC with the effluent going to a siphon that was attached directly to a viscometer of the Ubbelodhe type. This system was used to characterize linear polymers. The effect of siphon transfer line delay, zone spreading in the columns and calibration at high molecular weights were identified as important areas for correction in using this GPC-VISC system. The transfer line delay was the least important whereas it was essential to correct for zone spreading. It was felt that calibration at high molecular weights was aided by on-line viscometry. Mark-Houwink constants for PS, polybutadiene(PB) and PVAc in THF at 25°C were deduced from their data:

PS $[\eta] = 1.25\times10^{-4}\,M^{0.713}$ (2-27)

PB $[\eta] = 1.6\times10^{-4}\,M^{0.776}$ (2-28)

PVAc $[\eta] = 5.1\times10^{-5}\,M^{0.791}$ (2-29)

Constantin(1977) used a GPC coupled with an automatic capillary viscometer supplied by FICA to study LDPE. The Zimm-Stockmayer and Zimm-Kilb formulae were used to estimate λ from g '.It was found that λ increases with molecular weight in the region of high molecular weight. A useful table giving comparative values of λ obtained by different workers is included. Mark-Houwink constants for linear HDPE and polybutene-1 were extracted from the data:

HDPE $[\eta] = 5.65\times10^{-4}\,M^{0.696}$ (2-30)

Polybutene-1 $[\eta] = 1.18\times10^{-4}\,M^{0.729}$ (2-31)

With the introduction of high performance, high speed SEC the use of Ubbelodhe type on-line viscometer was no longer practical. Ouano(1972) was the first to introduce an on-line viscometer that measured the pressure drop across a section of the capillary tube continuously. The main problem with this original design was the noisy signal that resulted from the extreme sensitivity of the pressure transducer in the flow cell to the variations in solvent flow rate.

Lecacheux et al(1982) coupled a high temperature liquid chromatograph(Waters 150C) to a home-made continuous capillary viscometer to measure LCB in PE. $[\eta]$ was measured from the pressure drop across the capillary and the concentration measurement from the differential refractive index detector. They applied their method to linear and branched PE and compared their results to those obtained by conventional SEC and off-line viscometry. For commercial LDPE , a value of 0.5×10^{-4} was obtained for λ which was found to be independent of molecular weight. Lecacheux and co-workers applied the same technique to ethylene/VAc copolymers. These were commercial samples with vinyl acetate composition in the range 0-45 weight per cent. They found that the experimental viscosity law(log$[\eta]$ vs. log M) exhibited two parts, a linear part with a Mark-Houwink exponent of 0.7 in the lower molecular weight range and a marked curvature in the upper molecular weight range. It was concluded that LCB does not occur below a limiting molecular weight of 50, 000 and that $\lambda = 0.5\times10^{-4}$ similar to LDPE.

Styring et al(1987) carried out an experimental evaluation of the Viscotek Model 100 instrument which was a capillary-bridge viscometer and had a much improved signal to noise ratio. The universal calibration curve was constructed using well characterized narrow PS and poly(methyl methacrylate) (PMMA) standards from commercial sources. Branched PVAc was prepared in their laboratory using bulk polymerization at 100±1°C with 2,2'-azobis(2-methylpropionitrile)(AIBN) as initiator(1.02×10^{-4} mol dm^{-3}). The following Mark-Houwink constants were used for linear PS(Benoit,1967):

$$[\eta] = 1.50\times10^{-2}(\mathrm{cm}^{3}\ \mathrm{g}^{-1})\ M^{0.70} \qquad (2\text{-}32)$$

and for linear PVAc (Atkinson and Dietz,1979)

$$[\eta] = 1.56\times10^{-2}(\mathrm{cm}^{-3}\ \mathrm{g}^{-1})\ M^{0.708} \qquad (2\text{-}33)$$

No calculations for the degree of LCB were given but an outline of the procedure together with the various assumptions that are required in the calculation of LCB are clearly stated. The utility of the viscometer in detecting small amounts of high molecular weight impurity in a polymer sample was demonstrated.

Kuo et al(1987) presented a methodology for automated data analysis for an on-line viscometer coupled with a Waters Model 150C ALC/GPC. Using narrow PS standards they applied Yau and Malone's(1967) non linear equation to obtain the calibration curve. They were able to deduce Mark- Houwink constants from broad samples of linear PS, PMMA and PVC. Analysis of a narrow 12-arm star branched PS sample showed a value for ε of 0.71.Two broad samples of PVAc, shown to be branched by Foster et al(1980b), were analyzed and Mark-Houwink constants were determined from the linear portion of the log[η] vs. log M curve for the two samples:

$$[\eta] = 0.89\times10^{-4}\ M^{0.757} \qquad (2\text{-}34)$$

$$[\eta] = 0.86\times10^{-4}\ M^{0.761} \qquad (2\text{-}35)$$

These values compared favorably with other workers(Park and Graessley,1977; Atkinson and Dietz,1979; Coleman and Dawkins,1986). Plots of g' vs molecular weight for the branched PVAc were presented without any attempt to determine degree of branching.

Some researchers have attempted to develop the on-line viscometer as a tool for the direct characterization of macromolecules. This would mean that there would be no need for narrow standards for the generation of a calibration curve. Yau and Rementer(1990) defined various statistical averages and polydispersities based on $[\eta]_i$ for each chromatogram slice as a function of C_i, the corresponding polymer concentration for that slice:

$$[\eta]_{+1} = [\eta] = \Sigma\ C_i\ [\eta]_i\ /\ \Sigma\ C_i \qquad (2\text{-}36)$$

$$[\eta]_{\#} = \Sigma\ (C_i\ [\eta]_i\ /\ M_i)\ /\ \Sigma\ C_i\ /\ M_i \qquad (2\text{-}37)$$

$$[\eta]_0 = \Sigma\ C_i\ /\ \Sigma\ C_i\ /\ [\eta]_i \qquad (2\text{-}38)$$

$$[\eta]_{+2} = \Sigma\ C_i\ [\eta]_i^2\ /\ \Sigma\ C_i\ [\eta]_i \qquad (2\text{-}39)$$

Two polydispersities $[\eta]_{+1} / [\eta]_{\#}$ and $[\eta]_{+1} / [\eta]_0$ were defined. All these quantities can be calculated from the intrinsic viscosity distribution(IVD). Kirkland et al(1991) used the same concept of the IVD and the averages in equations (2-36 to2-39) to characterize polymer samples. In their work the viscometer was hooked to a system using SEC in one case and thermal field-flow fractionation in another. No specific applications to LCB were presented.

2.2.5 Size Exclusion Chromatography with Multiple Detectors

In order to capture the benefits of both methods of measuring molecular size, some researchers have combined viscometry , light scattering and SEC in one instrument. This combination however increased the need for more sophisticated instrumentation and data handling. Lesec and Volet(1990) carried out experiments with a custom made continuous viscometer using pressure transducers and a light scattering detector(LALLS- Chromatix-CMX 100). They worked with two systems, one for aqueous soluble polymer analysis and the other for organic soluble polymer analysis. Verification of the data reduction procedure was given for dextran, acrylamide and a commercial polyelectrolyte. They noted the increased difficulty of data analysis for polymers with LCB since such polymers follow a non-linear viscosity law.

Recently, multiangle laser light scattering(MALLS) has been employed in order to measure not only the molecular weights but also the radius of gyration for linear and branched polymers. Wintermantel et al(1993) combined SEC with MALLS and a viscosity detector in order to examine narrow PS standards, a broad linear PS sample and a highly branched PS/divinylbenzene microgel. The MALLS photometer was capable of measuring simultaneously 19 different scattering angles in the range

25°- 153°. They deduced for the broad PS samples in toluene the Mark-Houwink constants and the radius of gyration-molecular weight relationship:

$$\langle s^2\rangle_z^{1/2} = 1.35\times10^{-9}\, M^{0.59}\ \mathrm{cm} \qquad (2\text{-}40)$$

$$[\eta] = 1.05\times10^{-2}\, M^{0.73}\ \mathrm{cm^3\, g^{-1}} \qquad (2\text{-}41)$$

It was also shown that adsorption of the PS microgel on the columns can lead to significant deviations from the universal calibration curve.

Lesec et al(1995) used a Waters GPC 150CV which had a DRI detector and a single capillary viscometer. A LALLS detector(Chromatix CMX-100) was inserted between the column set and the GPC 150CV. THF at 40°C was used as the solvent to examine a star-branched copolymer of poly(methyl methacrylate) and poly(tert-butyl acrylate). It was possible to determine the number of branches from the ratio of M_n of the star polymer to the M_n of the uncoupled linear branches. The use of M_n from GPC-VISC gave approximately the same number of branches as that obtained using M_n from GPC-LALLS.

It should be noted that the use of MALLS with SEC to characterize polymer structure is receiving some attention. Johann and Kilz(1991) used this technique to examine copolymers and Podzinek(1994) used it to examine a range of organic and water soluble polymers. Mourey and Coll(1995) utilized SEC with a two angle laser light scattering detector (SEC-TALLS) to examine branched polyesters.

2.3 Kinetics and Reactor Type

2.3.1 Free Radical Polymerization Kinetics

Background

There is a growing interest in practical methods for calculating the full molecular weight distribution(MWD) and long chain branching distribution(LCBD) of commercial polymers. This type of information is fundamental for scientists and engineers who need to develop methods of tailoring the properties of polymers to meet the increasingly demanding specifications of the market. The calculation of MWD and LCBD in free radical polymerization usually involves the identification of the elementary reactions that describe the process, the construction of the population balance equations for the chosen set of reactions and finally the solution of these equations.

Hamielec and Tobita(1992) listed the basic reactions and assumptions that are used in free radical polymerization:

Initiation

$$I \xrightarrow{k_d} nR_{in}^{\bullet} \tag{2-42}$$

$$R_{in}^{\bullet} + M \xrightarrow{k_i} R_1^{\bullet} \tag{2-43}$$

Propagation

$$R_r^{\bullet} + M \xrightarrow{k_p} R_{r+1}^{\bullet} \tag{2-44}$$

Transfer to monomer

$$R_r^{\bullet} + M \xrightarrow{k_{fm}} P_r + R_1^{\bullet} \tag{2-45}$$

Transfer to a chain transfer agent(CTA)

$$R_r^{\bullet} + CTA \xrightarrow{k_{CTA}} P_r + CTA^{\bullet} \tag{2-46}$$

$$CTA^{\bullet} + M \xrightarrow{k_p'} R_1^{\bullet} \tag{2-47}$$

Termination by disproportionation $R_r^\bullet + R_s^\bullet \xrightarrow{k_{td}} P_r + P_s$ (2-48)

Termination by combination $R_r^\bullet + R_s^\bullet \xrightarrow{k_{tc}} P_{r+s}$ (2-49)

In order to derive tractable kinetic rate equations the following assumptions are usually made:

1. All rate constants are independent of chain length.

2. The total rate of monomer consumption can be equated to the rate of monomer consumption in the propagation reaction alone.[This is called the long chain approximation(LCA)].

3. Radicals generated by transfer reactions propagate with monomer rapidly and so do not affect the polymerization rate.

4. The stationary state hypothesis(SSH) is valid for radical reactions.

The set of equations (2-42) to (2-49) describe a system that will produce linear polymers. There are several reactions that lead to non-linear or branched polymers but in the case of free radical polymerization, the reactions that are relevant to this work are chain transfer to polymer and terminal double bond polymerization.

Chain transfer to polymer involves the attack of a growing radical $R_r^\bullet$ on a dead polymer chain with the extraction of an atom. The attack may occur on the backbone of the dead polymer or at sites on pendant groups. This reaction is represented as

Transfer to polymer $R_r + P_s \xrightarrow{k_{tp}} P_r + R_s^\bullet$ (2-50)

When transfer to monomer occurs or termination by disproportionation a dead polymer chain with a terminal double bond is formed. This terminal double bond may add to a growing radical leading to the formation of a trifunctional branch point and eventually a branched polymer chain. This is called terminal branching.

Proper formulation of the population balance equations for live and dead polymer chains leads to an infinite set of differential and algebraic equations. For linear polymer described by equations (2-42) to (2-49), Hamielec and Tobita(1992) developed the following set of equations:

Live Polymer

$$[R_1^\bullet] = \frac{\tau + \beta}{1 + \tau + \beta}\ [R^\bullet] \tag{2-51}$$

$$[R_r^\bullet] = (\tau + \beta)\phi^r\ [R^\bullet] \qquad \text{for } r \geq 2 \tag{2-52}$$

where

$$\tau = \frac{k_{td}[R^\bullet] + k_{fm}[M] + k_{fCTA}[CTA]}{k_p[M]}$$

$$\beta = \frac{k_{tc}[R^\bullet]}{k_p[M]}$$

$$\phi = \frac{1}{1 + \tau + \beta}$$

$[R^\bullet]$ is the total concentration of radicals

$[R_r^\bullet]$ is the concentration of radicals of chain length r

For the dead polymer, the population balance is given by

$$\frac{1}{V}\frac{d(V[\mathrm{P_r}])}{dt} = k_p[R^\bullet][M](\tau+\beta)\left\{\tau+\frac{\beta}{2}(\tau+\beta)(r-1)\right\}\phi^r \tag{2-53}$$

Solving (2-51) to (2-53) leads to an analytical solution for the instantaneous weight chain length distribution W(r) for the linear dead polymer:

$$W(r) = (\tau+\beta)\left\{\tau+\frac{\beta}{2}(\tau+\beta)(r-1)\right\}r\phi^{r+1} \tag{2-54}$$

When chain transfer to polymer is present resulting in dead polymer with long branches the solution of the population balance equations becomes more complex and most methods proposed to date have been based on calculating the dead polymer moments and the various molecular weight averages. Recent exceptions which calculate the full MWD are those of Teymour and Campbell(1994) and Tobita(1993) and these methods will be discussed subsequently. The live and dead polymer moments are defined respectively as

$$\mathrm{Y_n} = \sum_{r=1}^{\infty} \mathrm{r^n}\,[\mathrm{R_r^\bullet}] \qquad \mathrm{n}=0,1,2,\ldots \tag{2-55}$$

$$\mathrm{Q_n} = \sum_{r=1}^{\infty} \mathrm{r^n}\,[\mathrm{P_r}] \qquad \mathrm{n}=0,1,2,\ldots \tag{2-56}$$

By converting the population balance equations to moment equations it is always possible to solve readily for the moments of the accumulated polymer numerically. For the kinetic scheme described by the set of equations (2-42) to (2-49) and including chain transfer to polymer , equation (2-50), the moment equations for a batch polymerization are given by Hamielec and Tobita(1992):

$$\frac{1}{V}\frac{d(VQ_0)}{dx} = \tau + \frac{\beta}{2} \tag{2-57}$$

$$\frac{1}{V}\frac{d(VQ_1)}{dx} = 1 \tag{2-58}$$

$$\frac{1}{V}\frac{d(VQ_2)}{dx} = \frac{2(1+C_{p2})}{\tau+\beta+C_{p1}} + \frac{\beta(1+C_{p2})^2}{(\tau+\beta+C_{p1})^2} \tag{2-59}$$

with initial conditions: $Q_0 = Q_1 = Q_2 = 0$

at x=0, where

$C_{pi} = \dfrac{k_{ip}Q_i}{k_p[M]}$ and V is the volume of the reacting mixture

Attempts have been made to reconstruct the full MWD from the moments with limited success, particularly when the MWD is complex (having a shoulder or being bimodal)(Bamford and Tompa,1954).

Solution of the Population Balance Equations when LCB occurs

Bamford and Tompa(1954) used a number of kinetic schemes for vinyl polymerization and developed population balances for the live and dead polymeric species. The basic scheme consisted of initiation, propagation, transfer to monomer and polymer and termination by disproportionation. Termination by combination was not included and the analysis was done for constant monomer concentration. Analytical solutions were obtained by converting the population balance equations to moment equations and solving by means of Laplace Transforms. The solution was given in terms of the modified Bessel function of the first kind of order one. An analytical solution was also given for each branched family of the dead polymer. When the monomer concentration was allowed to vary, analytical solutions were no longer possible and numerical methods were used. The MWD was constructed from the moments (up to 10 moments were used) with the use of Laguerre polynomials. Gelation was treated in the last section of the paper. Since gelation only occurs when branching via transfer to polymer is present in a system together with termination by combination, they added termination by combination to their basic kinetic scheme and used constant monomer concentration. A criterion for gelation was given based on the conditions existing when the second moment of the dead polymer distribution goes to infinity, which is consistent with Flory's criterion that $M_w \rightarrow \infty$ at the gelation point.

Beasley(1953) in studying the molecular structure of polyethylene developed an analytical expression for the MWD of the polymer formed in a continuous stirred tank reactor assuming that termination is by disproportionation only and transfer to polymer occurs:

$$W(r) = \frac{(1-B)a^2 r}{[1+Bar]^{(1+\frac{1}{B})}} \tag{2-60}$$

where B is a branching parameter equal to the fraction of the polymer contained in the branches

1/a is the number average number of monomer units added by a radical before termination or transfer

W(r) is the weight fraction of polymer of chain length r

The weight average and number average chain lengths were derived as

$$P_w = \frac{2}{a(1-2B)} \qquad \text{for } B < ½ \qquad (2\text{-}61)$$

$$P_n = \frac{1}{a(1-B)} \qquad (2\text{-}62)$$

Note that $P_w \rightarrow \infty$ as $B \rightarrow ½$. Small(1975) points out that in Beasley's analysis no account is taken of the fact that some growing radicals will be removed from the reactor before the growth of a new branch is completed. Beasley did not present a kinetic scheme so it is difficult to deduce the elementary reactions that he considered. His expression for the LCBD is given by

$$W_b(r) = \frac{(1-B)a^2r[ar-(1/B)\ln(1+Bar)]^b \exp(-ar)}{b!(1+Bar)} \qquad (2\text{-}63)$$

where $W_b(r)$ is the weight fraction of polymer of chain length r having b branch points.

Amundson and Luss(1968) presented a limited and short review of the methods available at the time for the computation of the MWD in polymer systems. The use of generating functions, z-transforms and Laplace transforms was discussed. A generating function G(s) can be defined by

$$G(s) = \sum_{r=1}^{\infty} P_r s^r \qquad (2\text{-}64)$$

where P_r is the concentration of polymer with chain length r and s is an auxiliary variable of the generating function. It can be seen that if G(s) is determined and expanded as a power series in s^r then the coefficients will be P_r . Similarly the z-transform P(z) of P_r is defined as

$$P(z) = \sum_{r=1}^{\infty} P_r z^{-r} \qquad (2\text{-}65)$$

By converting the population balance equations to equations involving the generating function, the large set of equations is reduced to a finite set and in some cases may be solved analytically for G(s). The concentrations P_r may be recovered by series expansion as shown by Gupta and Gupta(1964).The use of the z-transform is similar with an advantage that there are well developed methods available for inverting the transform. Amundson and Luss also reviewed the use of the Laplace transform which is applied when the chain length r is treated as a continuous variable. Their review covered some applications to continuous reactors.

Saidel and Katz(1968) presented an analysis of the dynamics of branching in free radical polymerization. Initiation, propagation, termination by combination and transfer to polymer reactions were all considered in their kinetic scheme. The population balance equations were converted to moment equations and solved by Laplace transforms. Molecular weight averages and average number of branches as a function of conversion were calculated. It was shown that an increase in the value of the kinetic constant for chain transfer to polymer increases the polydispersity and the number of branch points per molecule. In their analysis it was necesary to deal with the moment closure problem. This problem relates to the special feature of the moment equations when they are written for individual branched families. In this case the moment equations are not closed in that the equation for the first moment depends on the second moment. In general if Q_{ni} represents the n^th^ moment of a polymer family containing i branch points per molecule , then

$$Q_{ni} = f(Q_{1i} , Q_{2i} , ..., Q_{ni} , Q_{n+1,i}) \qquad (2\text{-}66)$$

In order to solve for Q_{ni} it is necessary to relate $Q_{n+1,i}$ to $Q_1 , Q_2 , ...Q_n$. Saidel and Katz used an approximate moment closure method based on the work of Hulburt and Katz(1964).

Graessley et al(1965) converted the population balance equations to moment equations and solved them to determine the weight average chain length, P_w, and the number average chain length, P_n as a function of conversion. The kinetic scheme included propagation, transfer to monomer and polymer and terminal double bond polymerization. Initiation and termination reactions were not included since the analysis focused on systems where these reactions are relatively infrequent and so would have a negligible effect on the development of the MWD. Their solutions for P_w and P_n were compared to the data of Stein(1964a, 1964b) for the polymerization of vinyl acetate. Excellent agreement was obtained except that their estimation of the polymer transfer constant (C_p=1.2× 10^{-4}) was lower than that of Stein. A similar approach to the solution of the equations was used to predict the gel point in diene polymerization.

Jackson et al (1973) used a variation of the moment generating function approach and solved for the moments of the MWD of the product leaving a CSTR.

Generating functions for the live polymer, $Y_r(u)$, and the dead polymer, $Q_r(u)$, were defined in terms of a dummy variable u :

$$Y_r(u) = \sum_{i=1}^{\infty} i^r u^{i-1} R_i^{\bullet} \qquad (2\text{-}67)$$

$$Q_r(u) = \sum_{i=1}^{\infty} i^r u^{i-1} P_i \qquad (2\text{-}68)$$

Assuming that the series converge for u in the range 0 to 1 inclusive, then $Y_r(1)$ and $Q_r(1)$ give the r^th^ moments of the live and dead polymer distribution respectively. Jackson et al applied their method to a kinetic scheme involving initiation, propagation, transfer to small molecules and polymer and both modes of termination. It was concluded that Beasley's prediction of $P_w \rightarrow \infty$ for $\beta \rightarrow \frac{1}{2}$ occurred because the removal of radicals from the reactor was neglected. Both Beasley and Jackson et al assumed that any growing polymer chain will have only one active centre. Jackson et al in fact recognized that this assumption will not be valid as the molecular weight of the polymer increases due to branching and in particular as the gel point is approached.

Kuchanov and Pismen(1971) were probably the first to study a kinetic scheme that allowed for a growing polymer chain to have more than one active centre. Initiation ,propagation, both types of termination and transfer to monomer were included in the study of MWD development for linear polymer in a batch reactor. For the study of branching and gelation transfer to polymer was included. C_n (l,t) was defined as the concentration of dead polymer chains in a batch reactor at time t having n active centres and a chain length between l and l+dl. Implicit in this definition is the treatment of the chain length as a continuous variable and the number of active centres as discrete. A generating function was defined as

$$G(p,s,t) = \sum_{n=0}^{\infty} s^n \int_0^{\infty} e^{-pl}\, C_n(l,t)\, dl \qquad (2\text{-}69)$$

where p and s are parameters of the generating function. The introduction of the generating function into the population balance equations led to a partial differential equation. In the case of the linear polymer the equation was solved using the method of characteristics but for the case involving transfer to polymer, no analytical solution was possible for the characteristics and so numerical methods were applied. Gelation in diene polymerization was also studied by these workers who concluded that any gel formation kinetics must include polyradicals (chains with more than one active centre).

Tompa(1976) gave a review of the methods for calculating MWD from kinetic schemes up to that time. A very detailed chapter dealt essentially with the use of generating functions and Laplace transforms for the solution of the population balance equations. In effect this review represented an elaboration and updating of the paper by Bamford and Tompa(1954).

Instead of employing the deterministic solution of the population balance equations to calculate MWD and LCBD, some workers applied a probabilistic treatment to the problem. Mullikin and Mortimer(1970) considered a kinetic scheme similar to Beasley and employing a CSTR. Probabilities were defined in terms of the kinetic constants and relevant concentration variables as follows:

1. The probability that one monomer unit is attached to another as a result of straight chain addition polymerization.

2. The probability that there is one LCB point on a given monomer unit in a polymer chain.

The analysis was restricted to the existence of only one branch point on any chain. This restriction was later relaxed. First and second moments were constructed for the whole and branched polymeric species in terms of these probabilities. Molecular weight averages and polydispersities were calculated and compared to Beasley's results. It was shown that contrary to Beasley , no infinite polydispersity was predicted for that polymer system. Small(1972) applied moment generating functions to the method of Mullikin and Mortimer and was able to confirm their results. Small(1975) further included termination by combination in the reaction scheme and derived a condition for gelation.

In the 1980's the majority of researchers published on applications of the method of moments to specific reactors and monomers. A review of some of these papers will be given later. The most useful addition to the available techniques for calculating MWD and LCBD is the "numerical fractionation' method proposed by Teymour and Campbell(1994). Teymour and Campbell considered a kinetic scheme consisting of initiation, propagation, transfer to monomer and polymer and both modes of termination. Moment equations were derived for the whole polymer as well as individual branched families. An important step in the method is the choice of the families or generations so that they have reasonably narrow MWD and number of LCB. This was done by carefully specifying rules by which polymer would move from linear to first generation and from first to second generation etc. For example, first generation branched polymer can only become second generation by reacting with first generation polymer, not with linear polymer. By building these rules into the population balance analysis, equations were written for each generation and linear polymer. The population balance equations were converted to moment equations in order to effect a solution. There was a moment closure problem for the individual generations. The method of Saidel and Katz was used to resolve the moment closure. Teymour and Campbell were able to use the method to predict the gel point in a polymerization system by examining the locus of the maxima of the first or second moments of the individual generations. Prediction of the MWD was achieved by assuming a Schulz distribution for each generation and summing these distributions after assigning the proper weights.

Many workers have since used successfully the numerical fractionation method to calculate MWD in their polymer systems. Arzamendi and Asua(1995) examined gelation and the corresponding MWD of sol in emulsion polymerization using the numerical fractionation method. Topalis et al(1996) considered the behaviour of high pressure multizone LDPE autoclaves and used the same technique to predict gel formation and number chain length distribution. Mazzotti et al(1996) and Ghielmi et al(1997) studied LCB in emulsion polymerization and used the numerical fractionation technique to calculate the MWD.

Recently Tobita(1993) proposed a new theory for calculating MWD and LCB in free radical polymerization based on the branching density distribution of the primary polymer molecules. The primary polymer molecule is defined as that polymer molecule that would exist if all branch points connected to it were severed. This implies that the primary polymer molecule is linear. By using the branching density distribution it was possible to calculate the probability of connection between a primary molecule born at some chosen conversion to other molecules in the mixture. An expression can also be derived for the probability of connection via combination. The MWD is developed by applying a Monte Carlo simulation to the various probability equations. It was shown that the method is consistent with the results from the method of moments in a batch polymerization. Tobita(1994a) applied the method in developing a simulation model for LCB in the batch polymerization of vinyl acetate polymerization. It was found that the method of moments is a good approximation for calculation of not greater than the second moment. Tobita(1994b) also considered vinyl acetate polymerization in a CSTR and compared successfully his results with the data of Chatterjee et al(1977b). It was also concluded that the method of moments cannot be used for the CSTR without accounting for the outflow of radicals and the existence of polyradicals.

Since LCB is an intermediate stage of gelation, it is useful and relevant to consider very briefly some of the literature on gelation in free radical polymerization.

Tobita and Hamielec(1988,1989) gave a brief review of the previous methods used to predict gelation. They identified the classical method of Flory(1941) and Stockmayer(1943,1944) that was developed essentially for condensation polymers. The treatment by Gordon(1962) based on stochastic branching processes as well as that by Macosko and Miller(1976) were shown to be equivalent to the Stockmayer/Flory model. An alternative model based on percolation theory was suggested by Stauffer et al(1982) and Durand(1986). In any case these two approaches were not very satisfactory for gel formation in addition polymerization. Tobita and Hamielec proposed the use of pseudo-kinetic rate constants based on the terminal model of free radical co-polymerization. Using this approach kinetic models were developed for both the pre and post gelation periods. For the pre-gel period the model consisted of general moment equations. Charmot and Guillot(1992) proposed an alternative model for network formation in styrene butadiene emulsion copolymers. The model was based on an instantaneous primary chain distribution and was found to agree with the model proposed by Tobita and Hamielec. While the previous papers dealt with copolymerization, Zhu and Hamielec(1994) considered gel formation in free radical polymerization via chain transfer and terminal branching. The method of moments was used and it was possible to identify the required basic set of elementary reactions that can lead to gel formation. In particular it was shown that gel formation is possible if there is chain transfer to polymer and terminal branching due to disproportionation termination. The formation of multivinyl macromonomers during the course of the polymerization is the reason given for gelation in the absence of termination by combination. Zhu(1996) considered the effect of polyradicals on gel formation in free radical polymer modification. It was concluded that the reaction of polymeric radical combination is responsible for gel formation in free radical polymer modification. Criteria were given under which the monoradical assumption is valid.

2.3.2 Ionic Polymerization Kinetics

LCB has always been important in the production of low density polyethylene(LDPE) by means of free-radical polymerization. The new metallocene catalyst systems have introduced the possibility of tailoring the structure of polymers in a manner which has not been achieved before(Kaminsky,1996). The desire to control MWD and LCB in these systems has increased the need for reliable models to characterize them.

Soares and Hamielec(1996) considered the copolymerization of olefins and polyolefin chains containing terminal double bonds. The kinetic scheme included propagation, long chain branch formation via reaction with dead polymer chains containing terminal vinyl double bonds, transfer to chain transfer agent and β-hydride elimination(generating dead polymer chains with terminal vinyl unsaturation). An analytical solution for the frequency distribution of dead polymer chains of chain length r and having n LCB was developed:

$$f(r,n) = \frac{1}{(2n)!} r^{2n} \tau^{2n+1} \exp(-r\,\tau) \qquad (2\text{-}70)$$

where $$\tau = \frac{R_\beta}{R_p} + \frac{R_{CTA}}{R_p} + \frac{R_{LCB}}{R_p}$$

and

R_β	rate of β-hydride elimination
R_p	rate of monomer propagation
R_{CTA}	rate of transfer to chain transfer agent
R_{LCB}	rate of macromonomer propagation

The analytical solution agreed with the direct solution of the population balance equations obtained with a Monte Carlo simulation model for a CSTR at steady state.

Zhu and Li(1997) considered the development of MWD and LCB in a metallocecne catalyst system using binary catalysts. It was shown that using a single catalyst dendritic polymer structures are favoured. With the binary catalyst system the content of comb polymers formed is high. The comb polymers gave a much narrower MWD than the dendritic polymer with the same branch density. In these analyses the kinetic scheme consisted of activation/deactivation of active centres, propagation, addition of an active centre to dead polymer with a terminal double bond, chain transfer to chain transfer agent, β-hydride elimination and deactivation. Analytical expressions were derived for the frequency distribution of polymer of chain length r and m branch points for both the single and binary catalyst systems. The expression for the single catalyst system was compared to that of Soares and Hamielec(1996) as well as an expression derived by Tobita(1996).

2.3.3 The Effect of Reactor Type on Long Chain Branching

While most polymerization kinetic studies in the laboratory are carried out in the batch mode, many industrial processes are carried out continuously. The MWD and LCBD obtained in these two modes of operation are quite different. Momentum, heat and mass transfer can play a significant role in these large scale continuous systems and their effects may have to be taken into account in the analysis of these reactors.

Denbigh(1944,1947) was the first to point out that a change from a batch to a continuous system may lead to a broader or narrower MWD. Denbigh(1944) presented a pioneering analysis of kinetic behaviour of ideal continuous reactors, the CSTR and the plug flow reactor(PFR). The analysis was applied to polymerization systems(Denbigh,1947) and molecular weight distribution functions for various conditions were derived. The design of these continuous and batch systems(calculation of required reactor volume) in polymerization systems was presented(Denbigh,1951).

After Danckwerts(1953) had introduced the concept of residence time distribution(RTD) to describe mixing in continuous vessels and methods of measuring it, many studies on the performance of batch and continuous polymerization reactors have been published. Tadmor and Beisenberger(1966) investigated the role of segregation on MWD in continuous isothermal linear polymerization. Kilkson(1964) compared MWD from batch and CSTR's. Zeman and

Amundson(1965) carried out a theoretical study of polymerization in a CSTR. The chain length was treated as a continuous variable so that the infinite set of algebraic equations for the polymeric species in the reactor was converted to a set of differential equations. Solutions were presented for a variety of linear and non-linear mechanisms. In a series of papers Hamielec and co-workers presented theoretical and experimental analyses of MWD in batch and continuous stirred tank reactors (Duerksen et al,1967; Hamielec et al,1967; Hui and Hamielec,1968; Duerksen and Hamielec,1968).

The analysis of MWD and LCB in a CSTR was presented by Nagasubramanian and Graessley(1970a,1970b). The first paper gave a theoretical analysis of branching in free radical polymerization in continuous reactors. The kinetic scheme chosen was the one established for vinyl acetate polymerization. Four elementary reactions were considered: propagation, transfer to monomer and polymer and terminal double bond polymerization. Moment equations were derived from the population balance equations and these equations were applied to a CSTR assuming either a segregated flow reactor or a micromixed reactor. The micromixed reactor showed a significant increase in the polydispersity as the number average number of branch points per molecule increased. For the batch and segregated reactors the increase in polydispersity was much smaller. In the experimental work(Nagasubramanian and Graessley,1970b) vinyl acetate was polymerized in a CSTR with t-butanol as solvent and azobis-isobutyronitrile(AIBN) as initiator at

60°C. Residence times ranged from 1.5 to 8.3 hours and monomer conversion from 13 to 63%. The data confirmed that the CSTR produced a polymer with a broader MWD and one that was more highly branched than that produced in the batch reactor.

Friis et al(1974) and Friis and Hamielec(1975) considered MWD and LCB in batch emulsion polymerization. The method of moments was used(Friis et al,1974) to compare predicted and experimental values for M_n and M_w in vinyl acetate emulsion polymerization. The average number of branch points per molecule was also calculated for various values of the kinetic parameters. Friis and Hamielec(1975) re-examined the kinetics of vinyl chloride and vinyl acetate emulsion polymerization and showed that the MWD for poly(vinyl chloride) is the most probable distribution and the number of LCB per repetition unit is less than 2×10^{-4} at high conversion. In the case of poly(vinyl acetate) the MWD broadened markedly with the number of LCB per molecule increasing rapidly with conversion. The increase in M_n was attributed to terminal double bond polymerization and the increase in M_w to transfer to polymer.

Chatterjee et al(1977a) re-examined the batch polymerization of vinyl acetate at 60°C in t-butanol. Values of M_n and M_w were measured and used to establish the individual transfer constants. It was found that all the constants were independent of solvent concentration except C_p, the polymer transfer constant, which decreased systematically with increasing solvent concentration. Chatterjee et al(1977b) polymerized the same monomer at 60°C in t-butanol in a CSTR. Mean residence times ranged from 1.35 to 7.2 hours and steady state conversion from 15 to 61%.

Tracer studies were used to establish that good macroscopic mixing existed in the reactor. The molecular weights obtained at high conversion agreed more closely with predictions based on a segregated flow system, but the segregated flow model was not supported by independent mixing studies. It was concluded that the prediction of molecular structure for that system remained unresolved. As was stated in an earlier section Tobita(1994a,1994b) used a probabilistic model to simulate the data of Chatterjee et al.

2.4 Long Chain Branching in commercially important polymers

The most important commercial polymer where LCB is important is polyethylene and this is reflected in the large number of papers that examine LCB in this polymer. Reference to some of these publications have been made in earlier sections of this literature survey. In this final section of the survey a small sample of the other publications on polyethylene is reviewed. The emphasis on research work involving industrial scale reactors.

Chen et al(1976) developed a computer model for tubular high pressure polyethylene reactors. Plug flow was assumed and variations of viscosity and density of the fluid along the reaction coordinate were taken into account. The population balances were converted to moment equations using a similar approach to Saidel and Katz(1968). The stiff set of differential equations was solved using the Gear algorithm. The large polydispersity was partially ascribed to LCB and partially to the high temperature dependence assumed for the β-scission termination step.

Feucht et al(1985) used a detailed kinetic scheme in the study of the high pressure polymerization of ethylene in an autoclave reactor. The model consisted of an initiation step, propagation, termination by disproportionation and combination, transfer to monomer, polymer and modifier and intramolecular chain transfer in the polymer radical. Generation functions were used to solve for the molecular weight averages. Short and long chain branching as well as polydispersity predicted by the model showed good agreement with experimental data.

Shirodkar and Tsien(1986) also developed a computer model to simulate the production of LDPE by free radical polymerization in a one or two zone tubular reactor. A known heat transfer profile was combined with the theoretical polymerization kinetics in order to develop a set of non-linear differential equations. The calculated molecular weight averages were similar to measured data and it was shown that the model was capable of handling short and long chain branching.

Lorenzini et al(1992) proposed a new method for calculating MWD in the homopolymerization of ethylene. The kinetic scheme was similar to that of Feucht except that termination by combination was excluded whereas β-scission termination was included. The population balance equations were divided into three families based on the mechanisms in the kinetic scheme leading to linear or branched polymer. These equations were converted to moment equations and a mathematical analysis was presented to show that the usual moment closure problem was avoided. A limited comparison of the predicted MWD with experimental data was given.

Zabisky et al(1992) presented a review and an update of the kinetic models available for olefin polymerization in high pressure tubular reactors. A very useful appendix listing the recent attempts to model LDPE tubular reactors is included. The model was developed for free radical high pressure copolymerization in a commercial tubular type reactor with multiple feed points. The set of reactions considered were peroxide initiation, oxygen initiation, retardation and re-initiation, thermal self-initiation, termination by disproportionation and combination, transfer to monomer, polymer and transfer agent, β-scission of terminal and backbone radicals and backbiting. Pseudokinetic rate constants were employed, and population balance and moment equations were written. There was a moment closure problem that was resolved by two methods: the method of Hulburt and Katz(1964) and a relationship based on the assumption of a log-normal distribution. Plant data was used to estimate the kinetic constants and reasonable agreement between the polymer properties measured on the plant and those predicted by the model were obtained.

Nordhus et al(1997) developed a model to predict the MWD and LCBD of LDPE using a kinetic scheme similar to Zabisky except that β-scission reactions were excluded. Three cases were examined in the simulation: an ideal CSTR. A system consisting of three CSTR's in series and a reactor consisting of 31 control volumes that was used to model an existing industrial autoclave. The population balance equations were converted to recursion formulas to describe the steady state behaviour of the mixed reactors. In the algorithm used to solve the equations, the chain length is transformed into a continuous variable resulting in a set of differential-algebraic equations. Adequate comparisons between LCB predicted by the model and those measured in the industrial autoclave were achieved.

CHAPTER 3

EXPERIMENTAL WORK

3.1 Bulk Polymerization of Vinyl Acetate and p-Methyl Styrene

Materials Used

For the bulk polymerizations of vinyl acetate(VAc) and p-methyl styrene(PMS) that were done, VAc was obtained from Glidden Company and PMS from Aldrich Chemical Co. Inc. Thermal initiation was used in the case of p-methyl styrene(PMS) whereas the initiator 2,2 azobisisobutyronitrile(AIBN) obtained from Polysciences,Inc. was used, as received, in the polymerization of VAc. In the isolation and purification of the polymer, reagent grade toluene from Caledon Laboratory Ltd. was used to dissolve both polymers. Reagent grade methanol from Caledon Laboratory Ltd. was used to precipitate PPMS and n-hexane was used to precipitate PVAc.

Monomer Purification

VAc was distilled at 50°C under vacuum in order to remove the inhibitor, hydroquinone. In the case of PMS, a 10 weight % solution of sodium hydroxide in distilled water was used to wash the monomer to remove the inhibitor, t-butyl catechol. The monomer was washed at least three times with the sodium hydroxide solution followed by multiple washings with water until it became neutral.

Bulk Polymerization

AIBN was weighed and added to the distilled VAc in order to produce solutions having initiator concentrations in the range 5×10^{-5} to 4×10^{-3} mol L^{-1}. The VAc mixture or the purified PMS was put into glass ampoules having OD of 5-8 mm. Oxygen, which is a free radical scavenger, was then removed using the freeze-thaw method. In this procedure the ampoule containing the monomer is connected to a high vacuum line and carried through the following stages:

1. With the ampoule isolated by a valve on the vacuum system, the liquid in the ampoule is frozen by immersion in liquid nitrogen.

2. The isolating valve is then opened and the ampoule evacuated down to a pressure of 10^{-5} mm Hg.

3. The ampoule is again isolated and the contents allowed to thaw.

4. Steps 1-3 are repeated three to four times at least but until there is no evidence of gas leaving the liquid.

5. At the end of the last cycle, the frozen ampoule is sealed using a methane-oxygen flame.

6. The sealed ampoule after thawing is kept in an ice bath prior to polymerization.

In the VAc polymerization the sealed ampoules containing the reactant mixture were placed in a water bath with temperature controlled at 50°C ± 0.5°C. At different time intervals ampoules were removed and placed in an ice bath to quench the polymerization. Each ampoule was then broken and the polymer-monomer mixture dissolved in toluene. The polymer was then recovered by precipitation with n-hexane and filtration. The dissolution-precipitation process was repeated and the polymer then dried under vacuum at 40°C. Conversion of monomer was determined gravimetrically. These polymerizations were done at 50°C, 60°C, 70°C and 80°C.

In the PMS polymerization the sealed ampoule was placed in an oil bath maintained at 120°C ± 0.5°C. Ampoules were removed at different time intervals and cooled in an ice bath. Polymer was recovered in a manner similar to that used for PVAc except that precipitation of polymer(PPMS) was effected with methanol.

3.2 MWD and LCB using GPC with single and multiple detector systems

GPC can be used to measure LCB by the molecular weight-branching distribution(MWBD) method(Foster et al,1980). For conventional GPC/DRI this method requires the off-line measurement of the intrinsic viscosity of the whole polymer. If a GPC/DRI/VISC system is used then the intrinsic viscosity is obtained directly as a function of number-average molecular weight using the principle of universal calibration. The use of the GPC/DRI/ LALLS system presents additional information that may be used in the characterization of the polymer. In this work, the intrinsic viscosity of the PVAc samples was measured off-line and a GPC/DRI/LALLS system was used for measurement of polymer concentration versus weight-average molecular weight. For the PPMS a GPC/DRI/VISC system was used for measurement of polymer concentration versus intrinsic viscosity and number-average molecular weight using the principle of universal calibration.

Off-line Intrinsic Viscosity Measurement

A Cannon Ubbelodhe viscometer was used to measure the intrinsic viscosity of PVAc samples in tetrahydrofuran(THF) at 25°C. The viscometer containing pure solvent was placed in the constant temperature water bath and allowed 30 minutes to equilibrate. The efflux time of the solvent was measured until the readings agreed to within 0.1% of the mean value of three readings. A stock solution of polymer (0.5 g dL^{-1}) was prepared and the efflux time of the solution determined. By adding measured quantities of solvent to the viscometer, efflux times for solutions of different concentrations were determined. The intrinsic viscosity was determined by extrapolating η_{sp}/c to zero concentration:

$$\eta_{sp} = (t-t_0) / t_0 \qquad (3\text{-}1)$$

where t -efflux time for the polymer solution

t_0-efflux time of the solvent

and

$$[\eta] = (\eta_{sp} /c)_{c\to 0} \qquad (3\text{-}2)$$

c -concentration of polymer solution(g dL^{-1})

GPC/DRI/LALLS system

The system used was not a commercial one but was built from components at McMaster Institute for Polymer Production Technology(MIPPT). It consisted of 5 high speed Microstyragel columns having permeability limits between 10^3 Å to 5×10^6 Å. The outlet of the columns was connected to the LALLS sample cell and the outlet from the cell was connected to a Waters Associate R401 differential refractometer. The LALLS filter and sample cell had a total volume of 10 μL.

The concentration of polymer in the GPC effluent must be determined in order to calculate the weight average molecular weight on-line. The following illustrates the method:

Let M_p be the mass of polymer injected into the columns in grams.

υ be the volumetric flow rate through the columns in mL min^{-1}

v be the elution volume in counts with the volume per dump(counts)

=4.80 mL

t be the time measured from the time of sample injection in minutes

$$\text{Then } v = \upsilon\, t / 4.80 \text{ counts} \qquad (3\text{-}3)$$

A mass balance on polymer flowing through the detector cell over a short time interval dt is given by

$$\upsilon\, c(t)\, dt = 4.80\, c(v)\, dv$$

where c(t) or c(v) is the concentration of polymer in the fluid.

Therefore M_p is given by

$$M_p = \upsilon \int_0^\infty c(t)\, dt = 4.80 \int_0^\infty c(v)\, dv \qquad (3\text{-}4)$$

Let H(v) be the DRI detector response

Then
$$H(v) = k\, c(v) \qquad (3\text{-}5)$$

$$\therefore \qquad M_p = \frac{4.80}{k} \int_0^\infty H(v)\, dv \qquad (3\text{-}6)$$

$$\therefore \qquad k = \frac{4.80}{M_p} \int_0^\infty H(v)\, dv \qquad (3\text{-}7)$$

where the integral is the area under the chromatogram.

Equations (3-5) and (3-7) allow the concentration of polymer at any count interval to be calculated.

The equation relating M_w to the intensity of scattered light is

$$\frac{1}{M_w(v)} = \frac{K\,c(v)}{\overline{R_\theta}(v)} - A_2\,c(v) \qquad (3\text{-}8)$$

where $M_w(v)$ - weight average molecular weight at elution volume v

$c(v)$ - polymer concentration at elution volume v

$\overline{R_\theta}(v)$ - excess Rayleigh factor = $R_\theta(v)^{\text{solution}} - R_\theta(v)^{\text{solvent}}$

$$R_\theta(v) = \left(\frac{G_\theta(v)}{G_0}\right)\frac{D}{\sigma l}$$

$G_\theta(v)$ - measured intensity of light at angle θ from the incident light. ($\theta = 6.5°$)

G_0 - measured intensity at $\theta = 0°$

D - optical attenuation

σ - solid angle

l - effective optical path length

$(\sigma\, l)^{-1}$ - is an instrumental constant supplied by the manufacturer

K - is a polymer constant = $\dfrac{2\pi^2 n_0^{\,2}\left(\dfrac{dn}{dc}\right)^2\left(1+\cos^2\theta\right)}{\lambda_0^{\,4} N_{Av}}$

n_0 - is the refractive index of the solvent

n - is the refractive index of the solution

λ_0 - is the wave length of the incident light in vacuo

N_{Av} - Avogadro's number

A_2 - is the second virial coefficient

A_2 which was determined off-line by LALLS is obtained by plotting $\frac{K\,c}{R_\theta}$ vs c. The slope of the resulting straight line is A_2. ($\frac{dn}{dc}$) was measured in THF at 24°C using a Brice Phoenix differential refractometer. The light source was a mercury lamp with a filter at 6100 Å wavelength. The concentration of polymer was varied from 2 g L^{-1} to 10 g L^{-1}. For PVAc in THF, it was found that $\frac{dn}{dc} = 4.80 \times 10^{-2}$ mL g^{-1}.

GPC/DRI/VISC system

For PPMS, the Waters 150 CV-plus GPC system was used. It was operated at 140°C with three Waters Styragel HT6E linear columns with trichlorobenzene(TCB) as the solvent. The flow rate of TCB was 0.946 mL min^{-1} and the injection volume was 300 μL.

CHAPTER 4

DEVELOPMENT OF METHODOLOGY USED FOR LONG CHAIN BRANCHING MEASUREMENT IN THIS INVESTIGATION

4.1 Introduction

The most useful method for determining LCB from a conventional GPC is the MWBD method described earlier in Chapter 2. This method will be presented briefly in section 4.2. When a second detector is available, as was used in this research, the challenge is to use the measured data to determine LCB taking into account the polydispersity(M_w/M_n) of the polymer in the detector cell. In section 4.3 a method is proposed for such an analysis.

4.2 The Molecular Weight and Branching Distribution(MWBD) Method based on the molecular weight average in the detector cell

The MWBD method, as developed by Foster et al,1980a, assumes that a GPC having a mass detector is used to generate a universal calibration curve as well as a chromatogram of the polymer being analysed. The intrinsic viscosity of the whole polymer is also measured. It should be pointed out that before the MWBD method is used, corrections for axial dispersion should either be taken into account or be negligible. For the high performance GPC columns used in this investigation, corrections for axial dispersion were negligible.

For a branched polymer let

$$\ln[\eta]_b = \ln K + a \ln M + b\,(\ln M)^2 + c\,(\ln M)^3 \qquad (4\text{-}1)$$

where	$[\eta]_b$	- intrinsic viscosity of branched polymer
	K,a	- Mark-Houwink constants for linear polymer
	M	- molecular weight of the branched polymer
	b,c	- constants to be fitted

Assume that M_0 is a minimum molecular weight below which no LCB occurs. Then equation (4-1) can be written as

$$\ln[\eta]_b = \ln K + a \ln M + b(\ln M)^2\,(1 - \ln M / \ln M_0) \quad (4\text{-}2)$$

Let F(v) be the normalized chromatogram of the polymer sample. Then

$$[\eta]_{whole} = \int_0^{\infty} [\eta]_b\, F(v)\, dv \qquad (4\text{-}3)$$

where	$[\eta]_{whole}$	- intrinsic viscosity of the whole polymer
	F(v)	- normalized chromatogram values at elution volume v

Hamielec and Ouano(1978) showed that the appropriate molecular weight average to be used for the detector cell contents when applying the universal calibration curve is the number average molecular weight, $M_{n\,cell}$. It follows that

$$[\eta]_{cell}\, M_{n\,cell} = [\eta]_{PS}\, M_{PS} \qquad (4\text{-}4)$$

where	$[\eta]_{cell}$	- intrinsic viscosity of polymer in the detector cell

PS - a subscript to indicate that polystyrene is used to construct the universal calibration curve

In order to utilize the universal calibration curve to produce a calibration curve for branched polymer, equation (4-2) must be rewritten as

$$\ln[\eta]_b = \ln K + a \ln M_{n\ cell} + b\,(\ln M_{n\ cell})^2\,(1 - \ln M_{n\ cell} / \ln M_0) \qquad (4\text{-}5)$$

The only unknown constant in equation (4-5) is b. The method uses a single variable search for b in order to construct a calibration curve that is consistent with equations (4-3), (4-4), and (4-5). The calculated b is used to determine $[\eta]_b$, g' and g at each elution volume :

$$g' = [\eta]_b / [\eta]_l \qquad (4\text{-}6)$$

$$g^{\varepsilon} = g' \qquad (4\text{-}7)$$

where $[\eta]_l$ - intrinsic viscosity of linear polymer at the particular elution volume

ε - a constant having a value between 0.5 and 1.5

The number of LCB per molecule can then be calculated for a trifunctional branch point from

$$g = \left[(1 + m/7)^{1/2} + 4m/9\pi\right]^{-1/2} \qquad (4\text{-}8)$$

where m - number of branch points per molecule

The number average number of branch points per molecule for the whole polymer, $\overline{m}$, is calculated from

$$\bar{m} = \int_0^\infty m\, F(v)/ M_{n\,cell}\, dv \qquad (4\text{-}9)$$

The full procedure may be summarized as follows:

(1) Guess b in equation (4-5) and calculate $[\eta]_b$ at each elution volume v using equation (4-4).

(2) Calculate $[\eta]_{whole}$ from equation (4-3).

(3) Compare the calculated and measured values of $[\eta]_{whole}$ .If the difference is not within a preset tolerance, go back to step (1).

(4) For a chosen ε calculate $\bar{m}$ from equations (4-8) and (4-9).

4.3 The determination of LCB based on the Polydispersity (PD Method) in the detector cell

Consider the contents of the detector cell at any given elution volume v when a polymer sample is injected into the GPC system. The mixture will contain polymer molecules all having the same hydrodynamic volume. It is expected that this mixture will consist of linear and branched polymer molecules. In order to characterize the detector cell contents, it is necessary to specify the fraction of the detector cell contents that is linear as well as the distribution of the branched molecules. The modelling of the detector cell contents can be simplified by assuming a MWD for the branched polymer. For example, the three parameter log-normal distribution may be used:

$$W(M) = \frac{1}{\sqrt{2\pi}\sigma(M - M_{min})}\exp\left\{-\frac{1}{2}\left[\frac{\ln(M - M_{min}) - \mu}{\sigma}\right]^2\right\}$$

(4-10)

where M_{min} = minimum molecular weight in the cell

μ , σ are distribution parameters

The choice of such a distribution takes into account the fact that the branched polymer cannot have a molecular weight less than the molecular weight of the linear molecule eluting at the elution volume v. Hence,

$$M_{min} = M_l$$

where M_l can be calculated from the universal calibration parameter

$$[\eta]_l M_l = [\eta]_{PS} M_{PS}$$

The present method for analysis was developed using a simpler one parameter distribution, the exponential distribution. This distribution was chosen in order to test the applicability of the analysis before attempting to apply the two parameter distribution. Let the normalized weight molecular weight distribution of the branched polymer in the detector cell at elution volume v be w(v,M) so that

$$\int_{M_l}^{\infty} w(v,M)\, dM = 1 \tag{4-11}$$

Let $$w(v,M) = d_1 \exp(-d_2 M) \tag{4-12}$$

where d_1, d_2 are functions of v

Using equation (4-11) the distribution can be written as

$$w(v,M) = d \exp\{-d(M - M_l)\} \tag{4-13}$$

where d is the single parameter of the distribution

Let f be the weight fraction of the linear polymer in the detector cell at elution volume v. Then,

$$M_{w,cell} = f\, M_l + (1-f) \int_{M_l}^{\infty} M\, w(v,M)\, dM \qquad (4\text{-}14)$$

Equations (4-13) and (4-14) give

$$M_{w,cell} = fM_l + (1-f)\,(M_l + \frac{1}{d}) \qquad (4\text{-}15)$$

Similarly,

$$(M_{n,cell})^{-1} = \frac{f}{M_l} + \int_{M_l}^{\infty} (1-f)\, \frac{w(v,M)}{M}\, dM \qquad (4\text{-}16)$$

Equations (4-13) and (4-16) give

$$(M_{n,cell})^{-1} = \frac{f}{M_l} + (1-f)\, d\, \exp(\, d\, M_l) \int_{M_l}^{\infty} \frac{\exp(-d\, M)}{M}\, dM$$

$$(4\text{-}17)$$

The integral in equation (4-17) is the exponential integral and has no analytical solution so that a numerical solution is used in this analysis.

The universal parameter when applied to the detector cell will give

$$[\eta]_{cell}\, M_{n,cell} = [\eta]_{PS}\, M_{PS} \qquad (4\text{-}18)$$

For the whole polymer, the intrinsic viscosity is given by

$$[\eta]_{whole} = \int_0^{\infty} [\eta]_{cell}\, F(v)\, dv \qquad (4\text{-}19)$$

In the application of the method it is assumed that an average f can be used across the chromatogram. It should be noted also that $M_{w,cell}$ is equivalent to the $M_w(v)$ measured by LALLS. The input data are the GPC chromatogram, $M_w(v)$ from LALLS and the intrinsic viscosity of the whole polymer.

The full procedure is summarized as follows:

(1) Guess a value for f and use $M_w(v)$ and equation (4-15) to determine the distribution parameter d at each elution volume.

(2) Use equation (4-17) to determine $M_{n,cell}$ at each elution volume.

(3) From (4-18) calculate $[\eta]_{cell}$ at each elution volume. $[\eta]_{whole}$ is calculated from (4-19) and compared to the experimental value.If the comparison is not satisfactory, go back to step (1).

(4) For a chosen ε, calculate g for each elution volume using

$$g = \left(\frac{M_1}{M_{n,cell}} \right)^{\frac{1+a}{\varepsilon}} \tag{4-20}$$

(5) Use (4-8) to determine m, the number of branch points per molecule at each elution volume.

(6) Calculate $\overline{m}$ using (4-9).

CHAPTER 5

SOLUTION OF THE POPULATION BALANCE EQUATIONS

5.1 General Introduction and Background

The present investigation was motivated by the lack of rigorous and efficient methods that can solve the population balance equations for chain growth polymerization with long chain branching(LCB) and calculate the full molecular weight distribution(MWD) of the various branched species(chains with 0,1,2,--- LCB/chain). The development of advanced polymer manufacturing processes requires valid relationships between polymer molecular properties(MWD, copolymer composition distribution(CCD),LCB frequencies) and rheological and mechanical properties and as a consequence there is a growing demand for polymerization models which can calculate full MWD and CCD to meet these objectives(Hamielec and Soares,1996 and Soares and Hamielec,1996). The standard method of solving the population balance equations for chain growth polymerization with long chain branching is to employ the method of moments. Moment equations can be readily derived and easily solved for most dynamic simulations. Moment closure problems do, however, arise for certain problems such as with visbreaking of polypropylene(random scission) and as will be later illustrated, with moment equations for different branched species(Teymour and Campbell,1994).The major weakness with the method of moments, however, is the problem of construction of the full MWD for a complex distribution(such as a bimodal distribution) from the moments. This approach can give multi-solutions for these complex distributions.

The recent semi-empirical approach by Teymour and Campbell defines a number of polymer families, uses an empirical distribution function for each family and calculates the parameters of the distribution functions using the method of moments for each family. There is, however, a moment closure problem associated with this method although as the branching frequency of polymer species increases, the distributions for these species narrow and the moment closure problem becomes less significant. This approach, after Teymour and Campbell, appears to be the only practical method available when the full population balance equations cannot be solved efficiently.

The use of "instantaneous" property methods to calculate full molecular weight and composition distributions started many years ago with the derivation of Stockmayer's bivariate distribution(Stockmayer,1945) for binary chain growth copolymerization of linear polymer chains. Flory's most probable molecular weight distribution is a special case of the bivariate distribution. The first application of "instantaneous" property methods for polymerization reactor modelling was for the bulk free radical polymerization of vinyl chloride where different "instantaneous" molecular weight distribution functions were used in the monomer-rich and polymer-rich phases(Abdel-Alim and Hamielec,1972). PVC chains were considered linear in this modelling study. When exclusively linear chains are being synthesized(no long chain branching reactions occur), the MWD, CCD and mass of polymer chains produced "instantaneously" at some birthtime, $\bar{t}$, do not change later in the polymerization in the time interval $\bar{t}$ to t where t is the present time. With long chain branching reactions the situation is more complex. In this case mass, MWD and CCD of polymer chains produced instantaneously at the birthtime $\bar{t}$ may change in the time interval $\bar{t}$ to t. For polymerizations where long chain branching is exclusively due to terminal branching (terminal double bonds on polymer chains add to active centers as with a copolymerization involving a macromonomer), the MWD and CCD do not change with time. Only the mass of polymer produced instantaneously decreases with time due to the terminal branching reaction(Hamielec and Soares,1996 and Soares and Hamielec,1996). The implicit assumption is that the rate of terminal branching is independent of the size of the macromonomer. In a series of recent publications, Tobita(1996a-c,1997a,1997b) has applied sophisticated procedures based on probability theory along with Monte Carlo methods to calculate the full MWD for a number of chain growth polymerization processes.

5.2 Introduction to the Instantaneous Property Method for linear polymer chains

These methods apply for chain growth polymerization where dead or temporarily dead polymer molecules are being formed continuously via reactions such as termination by combination and disproportionation (during free radical polymerization),chain transfer (to monomer, chain transfer agent,β- hydride elimination),site deactivation and others(for both free radical and polymerization with a coordination catalyst system). These methods do not apply for a pure living polymerization where chain lifetimes are very long and dead polymer chains are not being formed during polymer chain growth. When polymer chain lifetimes are small compared to the total polymerization time, one can argue that the dead polymer chains born at time $\bar{t}$ over a small time period Δt will have certain molecular properties, for example, chain length and composition distributions. These "instantaneous" properties (MWD,CCD,...) can be solved for algebraically, and often analytically, directly from the population balance equations without the need to solve the associated large set of ordinary differential equations. Consider the following example of such an "instantaneous" distribution function that is available in the literature:

Stockmayer's Bivariate Distribution(Stockmayer,1945)

$$w(r,y)=(1+\delta y)(\tau+\beta)(\tau+\beta/2(\tau+\beta)(r-1))r\exp(-(\tau+\beta)r).\ \exp(-y^2/2\sigma^2)/\sqrt{(2\pi\sigma^2)}$$

where $w(r,y)drdy$ is the weight fraction of binary copolymer with chain length r, and composition deviation y with $y= F_1-y_1$.

F_1 is the mean mole fraction of monomer 1 in copolymer chains formed "instantaneously" at some time $\bar{t}$ ($\bar{t}$ is the birthtime of these chains).

δ is a correction for differing molecular weights of the two monomer types and is given by $\delta = \dfrac{(1-MW_2/MW_1)}{MW_2/MW_1+F_1(1-MW_2/MW_1)}$

where MW_1 and MW_2 are monomer molecular weights.

The dimensionless parameters, τ and β are given by

$$\tau = \frac{R_{tm}}{R_p} + \frac{R_{tCTA}}{R_p} + \frac{R_{td}}{R_p} + \ldots$$

$$\beta = \frac{R_{tc}}{R_p}$$

for free radical polymerization where

R_{tm} is the rate of chain transfer to monomer

R_{tCTA} is the rate of chain transfer to chain transfer agent(CTA)

R_{td} is the rate of radical termination by disproportionation

R_{tc} is the rate of radical termination by combination

R_p is the rate of propagation

For coordination polymerization(anionic,cationic,Ziegler-Natta,metallocene catalyst systems), $\beta = 0$ and τ is given by

$$\tau = \frac{R_\beta}{R_p} + \frac{R_{tH_2}}{R_p} + \frac{R_{de}}{R_p} \quad \text{where}$$

R_β is the rate of β-hydride elimination

R_{tH_2} is the rate of chain transfer to hydrogen

R_{de} is the rate of site deactivation

The variance of the normal distribution σ^2 is given by

$$\sigma^2 = F_1(1 - F_1)K / r \quad \text{where}$$

$$K = \sqrt{[1 + 4F_1(1 - F_1)(r_1 r_2 - 1)]}$$

r_1, r_2 are reactivity ratios

In the derivation of Stockmayer's bivariate distribution it is assumed that the terminal model for copolymerization is valid. It is worth mentioning a few points about the validity of this equation. These are summarized below.

(1) Stockmayer's composition distribution is a good approximation for chain lengths larger than 50. In fact, for a chain length as small as 20,the errors may be acceptable for most practical calculations(Tobita and Hamielec,1991).

(2) Chain-length dependence of the termination rate constants was not accounted for in Stockmayer's original derivation but this effect can be easily incorporated into the "instantaneous" bivariate distribution(Tobita and Hamielec,1991).

(3) When deviations from the terminal copolymerization model are significant, Stockmayer's composition distribution will not be valid.

(4) To account for shorter chain lengths, Stockmayer's molecular weight distribution should be modified by replacing $\exp(-(\tau+\beta)r)$ with $(1/(1+\tau+\beta))^r$.

(5) Stockmayer's bivariate distribution does not account for long chain branching and an appropriate distribution function which accounts for terminal branching(Soares and Hamielec,1996) may find use as an "instantaneous" molecular weight distribution function for polyolefin synthesis.

5.3 Generalization of the Instantaneous Property Method for polymer chains with long branches

Free Radical Polymerization with Long Chain Branching via Chain Transfer to Polymer

Population Balance Equations and Terminology

$P(r,i,t)$ is the concentration of dead polymer chains of chain length r and having i trifunctional branch points(a dead polymer chain is bereft of an active radical center)

$R(r,i,t)$ is the concentration of live polymer chains with chain length r and having i trifunctional branch points (live polymer chains have one active radical per chain, either on the chain end or the polymer backbone).When long chain branching is extensive larger polymer chains may have two or more radical centers, but this possibility is not addressed in this analysis..

The population balance equations account for the usual free-radical reactions(initiation, propagation, chain transfer and termination by combination and disproportionation).

Population Balance Equations(i=0)

Live Polymer Balances(r =1)

$$\frac{dR(1,0,t)}{dt}=R_I+k_{tm}MY_0+k_{tCTA}CTA\ Y_0$$

$$-(k_pM+k_{tm}M+k_{tCTA}CTA+k_{tc}Y_0+k_{td}Y_0+k_{tp}Q_1\ )R(1,0,t) \qquad (5\text{-}1a)$$

Live Polymer Balances(r ≥ 2)

$$\frac{dR(r,0,t)}{dt}=k_pMR(r-1,0,t)-(k_pM+k_{tm}M+k_{tCTA}CTA+k_{tc}Y_0+k_{td}Y_0$$

$$+k_{tp}Q_1)R(r,0,t) \qquad (5\text{-}1b)$$

R_I is the initiation rate and

$$Y_0=\sum_{r=1}^{\infty}\sum_{i=0}^{\infty}\ R(r,i,t)$$

$$Q_1=\sum_{r=1}^{\infty}\sum_{i=0}^{\infty}\ r\ P(r,i,t)$$

Application of the stationary state hypothesis(SSH) and some algebraic manipulation gives:

$$R(r,0,t)=R(1,0,t)\,\phi^{r} \qquad (5\text{-}1c)$$

where $\phi=1/(1+\tau+\beta+\gamma)$

and $\tau=\frac{k_{tm}}{k_p}+\frac{k_{tCTA}CTA}{k_pM}+\frac{k_{td}Y_0}{k_pM}$

$$\beta=\frac{k_{tc}Y_0}{k_pM}$$

$$\gamma=\frac{k_{tp}Q_1}{k_pM}=\frac{C_pQ_1}{M}$$

Also $R(1,0,t)=(\tau+\beta)Y_0$ (5-1d)

The frequency distribution of these live linear polymer chains is given by

$$F_L(r,0,t)=R(r,0,t)/Y_0=(\tau+\beta)\,\phi^{r} \qquad (5\text{-}1e)$$

and the chain length averages by

$$\overline{r_{NL}}(0,t)=\frac{1}{1-\phi} \qquad (5\text{-}1f)$$

$$\overline{r_{WL}}(0,t)=\frac{2}{1-\phi} \qquad (5\text{-}1g)$$

where $\overline{r_{NL}}(0,t)$ and $\overline{r_{WL}}(0,t)$ are number and weight average chain lengths of live linear polymer.

Dead Polymer Balances($r\geq 1$)

$$\frac{dP(r,0,t)}{dt}=k_pMY_0\{(\tau+\gamma)\frac{R(r,0,t)}{Y_0}+(\beta/2)\left[\sum_{s=1}^{r-1}\frac{R(s,0,t)}{Y_0}\frac{R(r-s,0,t)}{Y_0}\right]-\gamma\, r\frac{P(r,0,t)}{Q_1}\}$$

(5-2)

Moment Equations for Dead Polymer(i=0)

The definition of linear dead and live polymer moments is as follows:

$$Q_n(0,t)=\sum_{r=1}^{\infty} r^n P(r,0,t)$$

$$Y_n(0,t)=\sum_{r=1}^{\infty} r^n R(r,0,t)$$

Using equation (2) the moment equations for linear dead polymer are

$$\frac{dQ_0(0,t)}{dt}=k_p M Y_0\{(\tau+\gamma)\frac{Y_0(0,t)}{Y_0}+(\beta/2)\left(\frac{Y_0(0,t)}{Y_0}\right)^2-\gamma\frac{Q_1(0,t)}{Q_1}\} \qquad (5\text{-}2a)$$

$$\frac{dQ_1(0,t)}{dt}=k_p M Y_0\{(\tau+\gamma)\frac{Y_1(0,t)}{Y_0}+\beta\frac{Y_0(0,t)}{Y_0}\frac{Y_1(0,t)}{Y_0}-\gamma\frac{Q_2(0,t)}{Q_1}\} \qquad (5\text{-}2b)$$

$$\frac{dQ_2(0,t)}{dt}=k_p M Y_0\{(\tau+\gamma)\frac{Y_2(0,t)}{Y_0}+\beta\left[\left(\frac{Y_1(0,t)}{Y_0}\right)^2+\frac{Y_0(0,t)}{Y_0}\frac{Y_2(0,t)}{Y_0}\right]-\gamma\frac{Q_3(0,t)}{Q_1} \qquad (5\text{-}2c)$$

It is clear that chain transfer to polymer introduces a moment closure problem for the linear dead polymer moment equation set. For branched families(i=1,2,...) the moment closure problem also exists. This solution limitation does not exist when solving the moment equations for the full MWD.

Moment Equations for Live Polymer(i=0)

$$\frac{Y_0(0,t)}{Y_0}=\frac{(\tau+\beta)}{(1-\phi)} \qquad (5\text{-}3a)$$

$$\frac{Y_1(0,t)}{Y_0}=\frac{(\tau+\beta)}{(1-\phi)^2} \qquad (5\text{-}3b)$$

$$\frac{Y_2(0,t)}{Y_0} = \frac{2(\tau+\beta)}{(1-\phi)^3} \tag{5-3c}$$

Instantaneous Properties

P(r,0,t,$\bar{t}$) is the concentration of dead polymer of chain length r having zero long chain branches and formed at t = $\bar{t}$ over a small time interval Δt (the birthtime of this newly formed dead polymer is $\bar{t}$). The concentration of this dead polymer at birthtime is given by

$$P(r,0,\bar{t},\bar{t}) = k_pMY_0\{(\tau+\gamma)\,\frac{R(r,0,\bar{t})}{Y_0} + (\beta/2)\sum_{s=1}^{r-1}\frac{R(s,0,\bar{t})}{Y_0}\,\frac{R(r-s,0,\bar{t})}{Y_0}\}\,\Delta t \tag{5-4}$$

The consequences of chain transfer to polymer are that some of the chains of P(r,0,$\bar{t}$,$\bar{t}$) will be consumed and the chain length distribution will be distorted in the time interval , t > $\bar{t}$. These changes can be readily tracked in a batch polymerization as follows:

$$\frac{dP(r,0,t,\bar{t})}{dt} = -\,k_pMY_0\,\{\gamma\, r\,\frac{P(r,0,t,\bar{t})}{Q_1}\} \qquad \text{for } t \geq \bar{t} \tag{5-5}$$

The concentration of a family born at $\bar{t}$ at any time t > $\bar{t}$ is obtained by integrating equation (5) after including the monomer balance:

$$P(r,0,t,\bar{t}) = P(r,0,\bar{t},\bar{t})\left\{\frac{M(t)}{M(\bar{t})}\right\}^{C_p r} \tag{5-5a}$$

The total concentration of dead polymer at time t is given by

$$\mathrm{P(r,0,t)} = \int_0^t P(r,0,\bar{t},t)\left\{\frac{M(t)}{M(\bar{t})}\right\}^{C_p r} d\bar{t} \qquad (5\text{-}5b)$$

It should be noted that it is possible to develop an analytical expression for the frequency distribution of instantaneous linear dead polymer for the system being considered. This distribution, $F_D(r,0,\bar{t}\,)$ is given by

$$F_D(r,0,\bar{t}\,) = (A/B)\,\eta^2 \exp(-\,\eta\, r\,) \qquad (5\text{-}6)$$

where

$A = (\tau + \gamma\,) + (\beta/2)\,(r-1)(\tau + \beta)$

$B = \eta(\,\tau + \gamma\,) + (\beta/2)(\,\tau + \beta)$

$\eta = \tau + \beta + \gamma$

Note that τ ,β and γ depend on $\bar{t}$. Equation (6) reduces to Flory's most probable distribution when β and γ are zero.

The instantaneous method can be applied to branched species($i \geq 1$) by writing equations similar to (4),(5),(5a) and (5b) after developing the population balance equations.

Population Balance Equations ($i \geq 1$)

Live Polymer Balances ($r > i$)

$$\frac{dR(r,i,t)}{dt} = k_p M Y_0 \left\{ \frac{R(r-1,i,t)}{Y_0} + \gamma\, r\, \frac{P(r,i-1,t)}{Q_1} - (1+\tau+\beta+\gamma)\frac{R(r,i,t)}{Y_0} \right\}$$

(5-7)

Note that R(r,i,t) = 0 when i ≥ r

Dead Polymer Balances

$$\frac{dP(r,i,t)}{dt} = k_p M Y_0 \{\ (\tau+\gamma)\frac{R(r,i,t)}{Y_0} + (\beta/2)\sum_{y=0}^{i}\sum_{s=1}^{r-1}\frac{R(s,y,t)}{Y_0}\frac{R(r-s,i-y,t)}{Y_0}$$

$$-\gamma\, r\,\frac{P(r,i,t)}{Q_1}\ \} \tag{5-8}$$

Live Polymer Moments (i ≥ 1)

$$\frac{Y_0(i,t)}{Y_0} = \frac{\gamma}{(1-\phi)}\frac{Q_1(i-1,t)}{Q_1} \tag{5-9}$$

$$\frac{Y_1(i,t)}{Y_0} = \frac{\gamma}{(1-\phi)}\left[\frac{1}{(1-\phi)}\frac{Q_1(i-1,t)}{Q_1} + \frac{Q_2(i-1,t)}{Q_1}\right] \tag{5-10}$$

$$\frac{Y_2(i,t)}{Y_0} = \frac{\gamma}{(1-\phi)}\left[\frac{2}{(1-\phi)^2}\frac{Q_1(i-1,t)}{Q_1} + \frac{2}{(1-\phi)}\frac{Q_2(i-1,t)}{Q_1} + \frac{Q_3(i-1,t)}{Q_1}\right] \tag{5-11}$$

Dead Polymer Moments (i ≥ 1)

$$\frac{dQ_0(i,t)}{dt} = k_p M Y_0\left\{(\tau+\gamma)\frac{Y_0(i,t)}{Y_0} + \beta\left[\sum_{y=0}^{\langle i\rangle}\delta_y\frac{Y_0(i-y,t)}{Y_0}\frac{Y_0(y,t)}{Y_0}\right] - \gamma\frac{Q_2(i,t)}{Q_1}\right\} \tag{5-12}$$

where $\langle i\rangle = i/2$ for i even and $(i-1)/2$ for i odd

$\delta_y = 1$ for $2y \neq i$ and ½ for $2y = i$

$$\frac{dQ_1(i,t)}{dt} = k_pMY_0\left\{(\tau+\gamma)\frac{Y_1(i,t)}{Y_0}+\beta\left[\sum_{y=0}^{i}\frac{Y_1(i-y,t)}{Y_0}\frac{Y_0(y,t)}{Y_0}\right]-\gamma\frac{Q_2(i,t)}{Q_1}\right\} \qquad (5\text{-}13)$$

$$\frac{dQ_2(i,t)}{dt} = k_pMY_0\left\{(\tau+\gamma)\frac{Y_2(i,t)}{Y_0}+\beta\left[\sum_{y=0}^{\langle i\rangle}\sum_{j=0}^{2}\frac{2!}{j!(2-j)!}\delta_y\frac{Y_{2-j}(i-y,t)}{Y_0}\frac{Y_j(y,t)}{Y_0}\right]-\gamma\frac{Q_3(i,t)}{Q_1}\right\}$$

(5-14)

Instantaneous Properties ($i \geq 1$)

As was shown for i=0, the corresponding equations for dead polymer with i branch points are as follows:

$$P(r,i,\bar{t},\bar{t}) = k_pMY_0\{(\tau+\gamma)\frac{R(r,i,\bar{t})}{Y_0} + (\beta/2)\sum_{y=0}^{i}\sum_{s=1}^{r-1}\frac{R(s,y,\bar{t})}{Y_0}\frac{R(r-s,i-y,\bar{t})}{Y_0}\}\Delta t$$

(5-15)

$$\frac{dP(r,i,t,\bar{t})}{dt} = -\,k_pMY_0\,\{\gamma\, r\,\frac{P(r,i,t,\bar{t})}{Q_1}\} \qquad \text{for } t \geq \bar{t} \qquad (5\text{-}16)$$

$$P(r,i,t,\bar{t}) = P(r,i,\bar{t},\bar{t})\left\{\frac{M(t)}{M(\bar{t})}\right\}^{C_pr} \qquad (5\text{-}17)$$

$$P(r,i,t) = \int_0^t P(r,i,\bar{t},\bar{t})\left\{\frac{M(t)}{M(\bar{t})}\right\}^{C_pr} d\bar{t} \qquad (5\text{-}18)$$

5.4 Solutions of the population balance equations with transfer to polymer using the generalized Instantaneous Property Method

Sample Calculations and Discussion

To illustrate the use of the method and the effect of long chain branching reactions(in this case ,chain transfer to polymer) the dimensionless parameters τ and γ will be varied for the different example calculations. Initially the model is tested for $\gamma = 0$.

$\gamma = 0$ (linear chains are produced exclusively)

Case 1 : Chain transfer to monomer is dominant in producing dead polymer chains. For an isothermal polymerization ,since $\beta = 0$ and $\tau = k_{fm}/k_p$,the "instantaneous" MWD is time -independent and should be the same as the MWD for the accumulated dead polymer. Numerical calculations have confirmed this as well as the fact that the polydispersity index is 2.

Case 2 : Termination by disproportionation is dominant in producing dead polymer chains. For these calculations which have been done to confirm that the numerical methods used are valid , we assume that termination is diffusion-controlled and we use typical gel effect equations (Hui and Hamielec,1972).For an isothermal polymerization one would expect that τ would change significantly with monomer conversion and hence the "instantaneous" MWD would also shift with time or conversion. The polydispersity index would remain at 2 even though the polydispersity index for the accumulated dead polymer would increase from 2 at zero conversion to some value greater than 2. Figure 5-1 shows the changing "instantaneous" MWD's and Figure 5-2 the changing MWD of the accumulated dead polymer. These are plots of $W_{DI}(r,0,t)$ and $W_{DA}(r,0,t)$, the weight chain length distributions of instantaneous and accumulated linear dead polymer. It should be noted that the weight chain length distribution of live polymer chains is the same as that for instantaneous dead polymer.

In Figure 5-1 the polydispersity index is 2 for all the distributions but the weight average chain length varies from 3100 at zero conversion to 8100 at 75% conversion. In figure 5-2 the polydispersity index moves from 2.0 at 25% conversion to 2.15 at 75% conversion.

Figure 5-1: Plot of weight chain length distribution of instantaneous dead polymer

Termination by disproportionation dominates

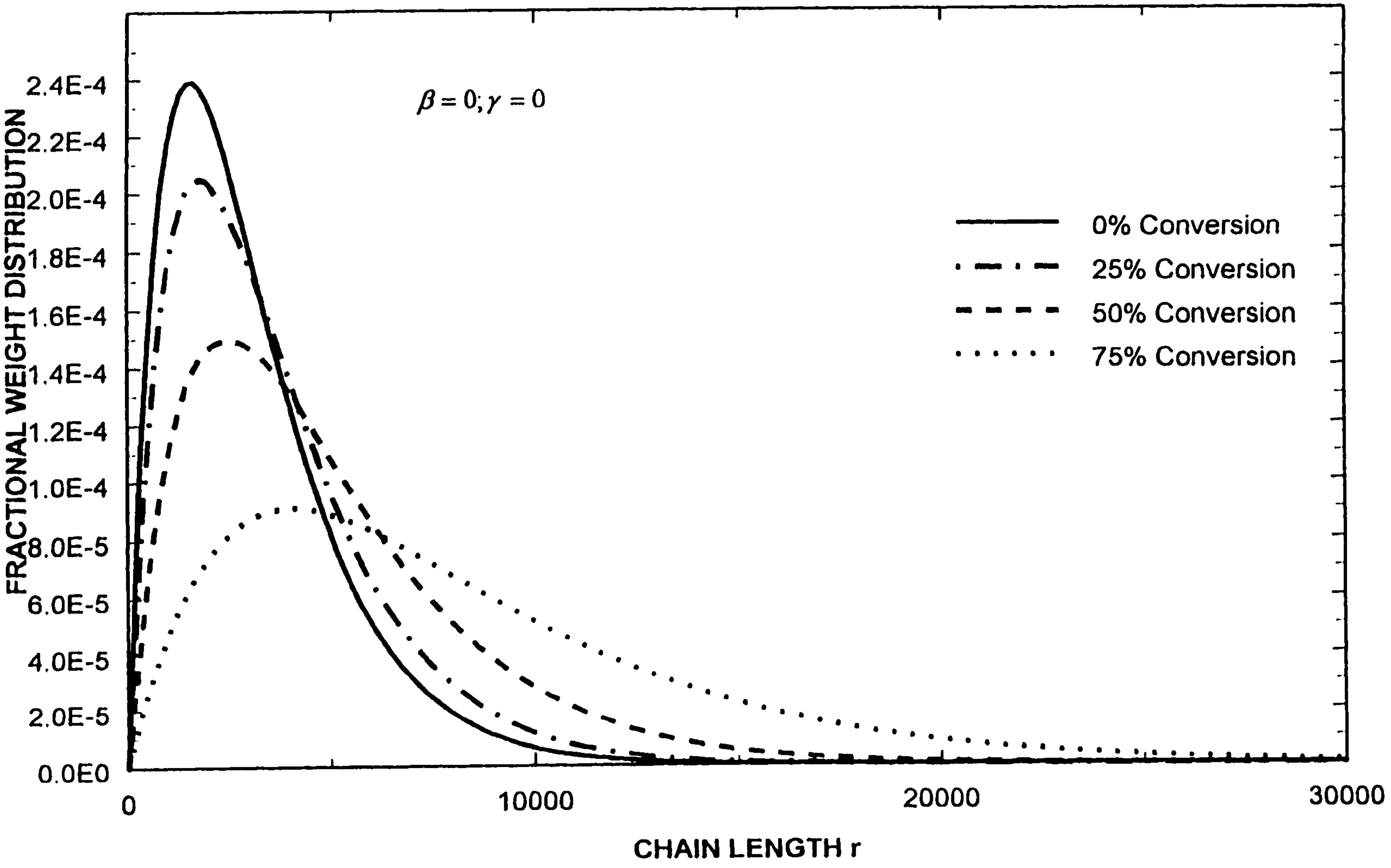


Figure 5-2: Plot of weight chain length distribution of accumulated dead polymer
Termination by disproportionation dominates

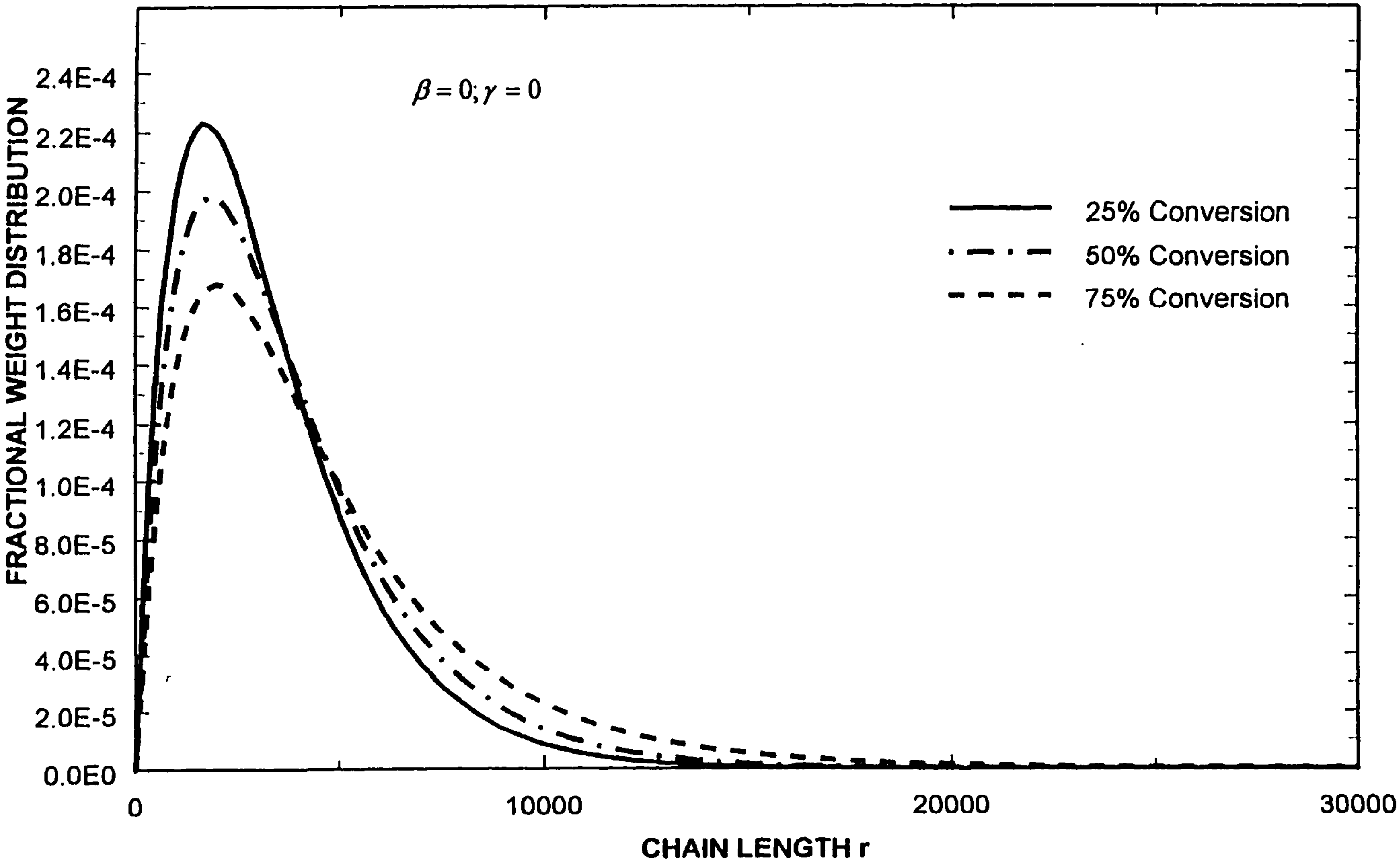


Figure 5-3: Plot of weight chain length distribution of instantaneous dead polymer

Termination by combination dominates

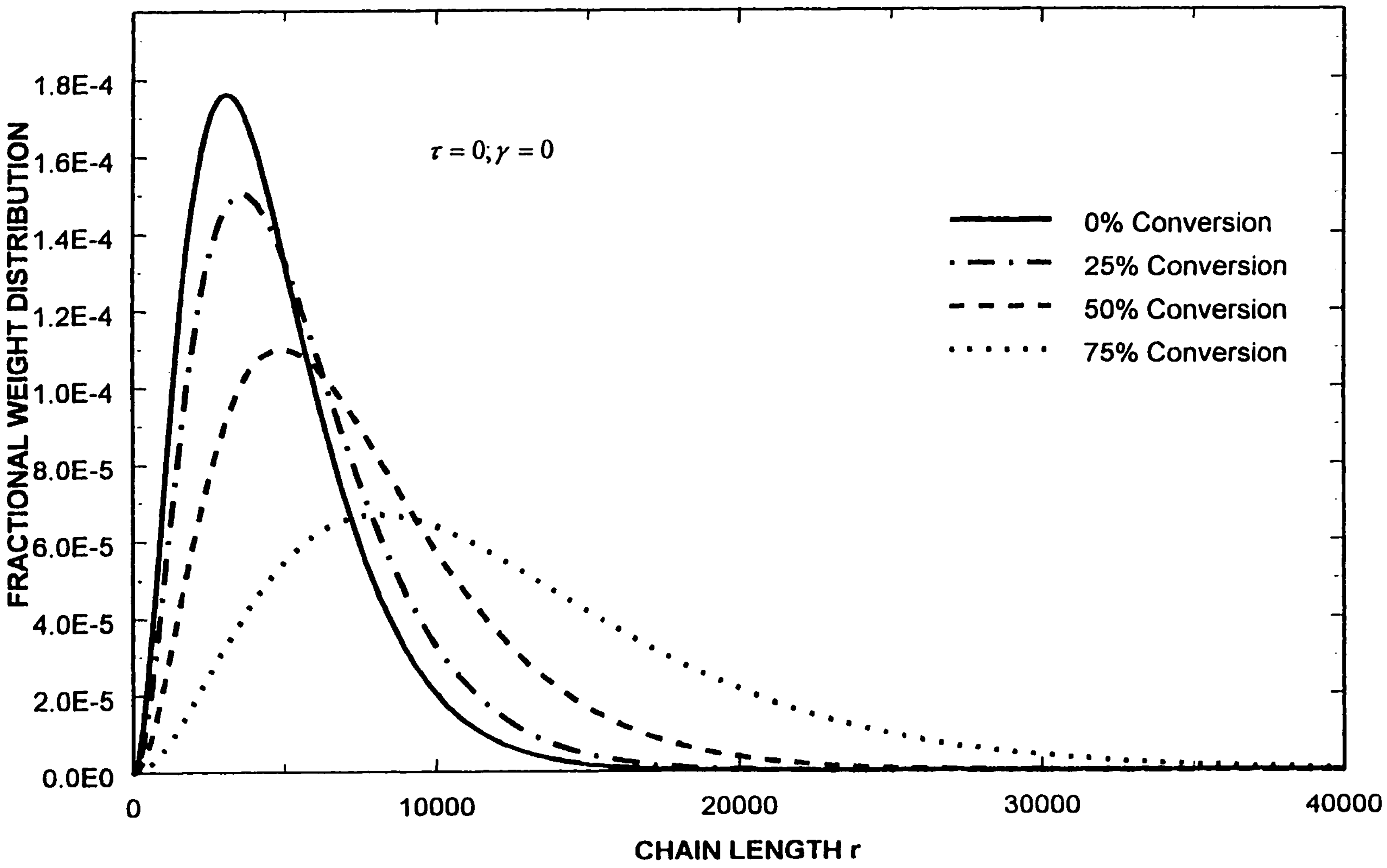
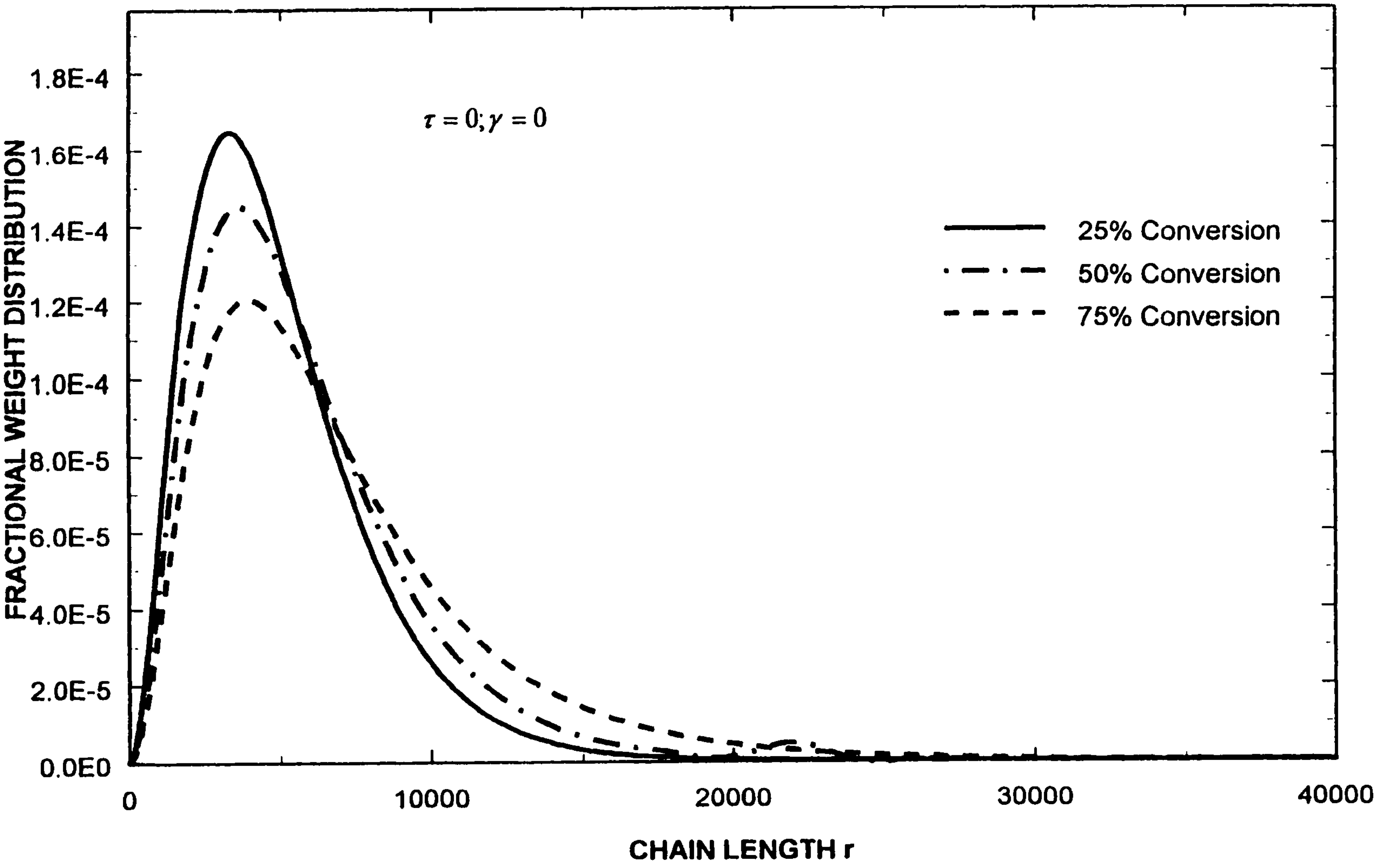


Figure 5-4: Plot of weight chain length distribution of accumulated dead polymer
Termination by combination dominates



Case 3 : Termination by combination is now dominant in producing dead polymer chains. The same gel effect equations are used. The polydispersity index is 1.5 for the

$W_{DI}(r,0,t)$ while the index starts at 1.5 and grows in value with monomer conversion for the accumulated dead polymer. $W_{DI}(r,0,t)$ and $W_{DA}(r,0,t)$ are plotted in figures 5-3 and 5-4. In figure 5-4 the polydispersity index varies from 1.5 at 25% conversion to 1.62 at 75% conversion.

$\gamma > 0$ (Branched Chains Produced by Chain Transfer to Polymer)

Case 4 : Transfer to monomer is dominant so that $\beta = 0$ and $\tau = k_{tm}/k_p$ for an isothermal polymerization. $W_{DI}(r,i,t)$ and $W_{DA}(r,i,t)$ can now be calculated for $i=1,2,...$ These distributions, $W_{DI}(r,i,\bar{t},\bar{t})$ for a family born at $t=\bar{t}$, would now change with time because of transfer to polymer in the time interval $t > \bar{t}$ with the mass of this family decreasing. $W_{DI}(r,i,t,\bar{t})$ becomes distorted because longer chains having more extractable hydrogen atoms are preferentially consumed by transfer to polymer. These distributions are plotted in Figures 5-5 and 5-6. Figure 5-5 is plotted for 75% conversion and the polydispersity index shows the general narrowing as i increases. Figure 5-7 is a plot of this variation for the families in Figure 5-5.

Case 5: Termination by disproportionation is dominant. The same gel effect equations are used and Figures 5-8 and 5-9 illustrate the effects that both transfer to polymer and the gel effect have on the instantaneous and accumulated distributions.

The polydispersity index decreases as the number of long chain branches per molecule increases, in a manner similar to what is shown in Figure 5-7.The weight average chain length for the instantaneous distributions in Figure 5-8 increases from 3900 for i = 0 to 13600 for i=3.

Case 6: Termination by combination is dominant and the same gel effect equations are used. Figures 5-10 and 5-11 show the behaviour of the distributions of instantaneous and accumulated dead polymer at 50% conversion. There is a similar narrowing of the distributions as the number of branch points per molecule, i, increases. These trends in the polydispersity would be further discussed in a later section where it is suggested that it could form the basis for the extension of the Instantaneous Method.

Comparison with the Overall Polymer Moments

The moment equations for the overall polymer population ,shown below, were used to check the results from the numerical procedure. In all the checks, the differences between the molecular weight averages were less than 2%. Table 5-1 gives some typical values.

Figure 5-5: Plot of weight chain length distribution of instantaneous dead polymer

Transfer to monomer dominates

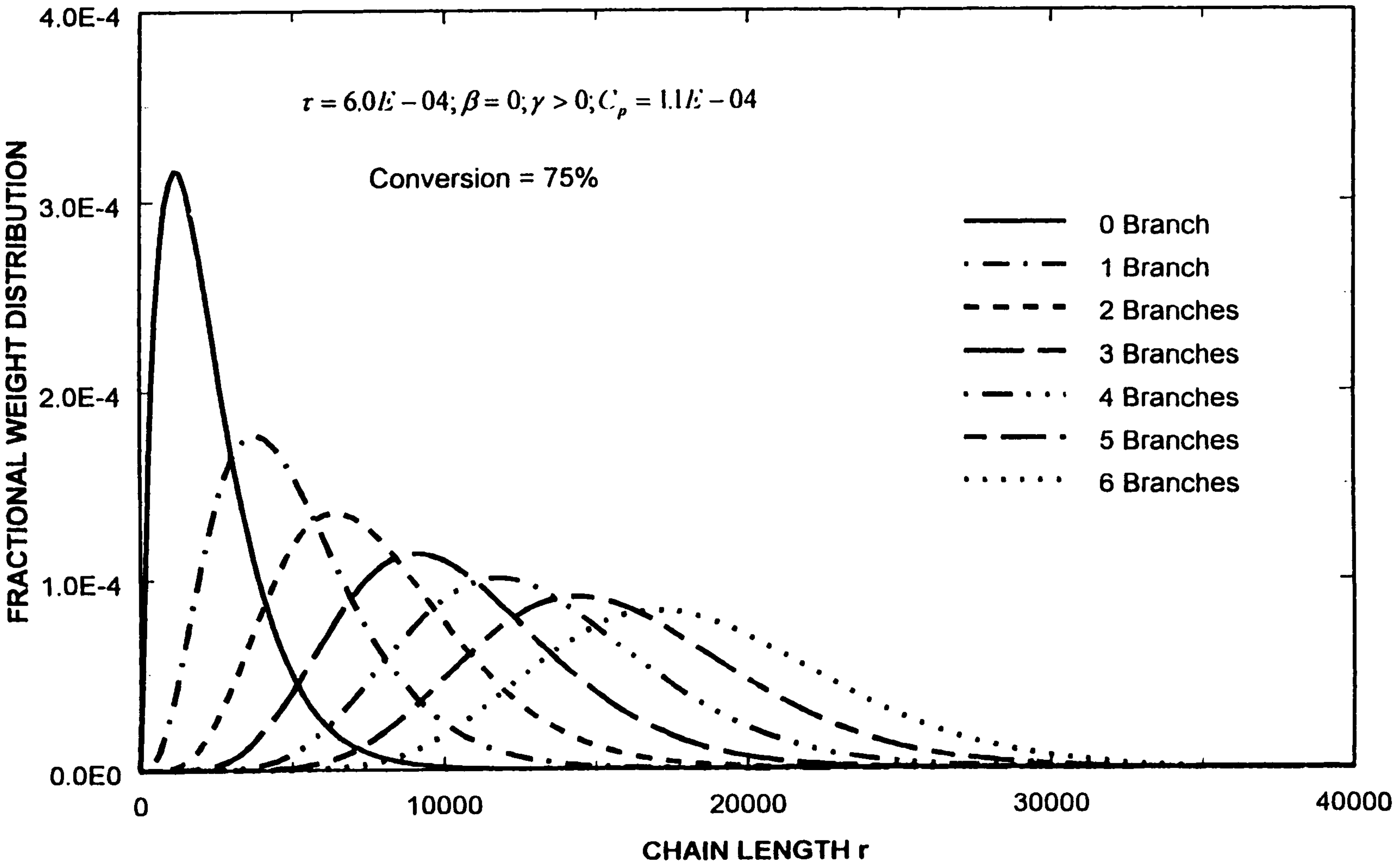


Figure 5-6: Plot of weight chain length distribution of accumulated dead polymer
Transfer to monomer dominates

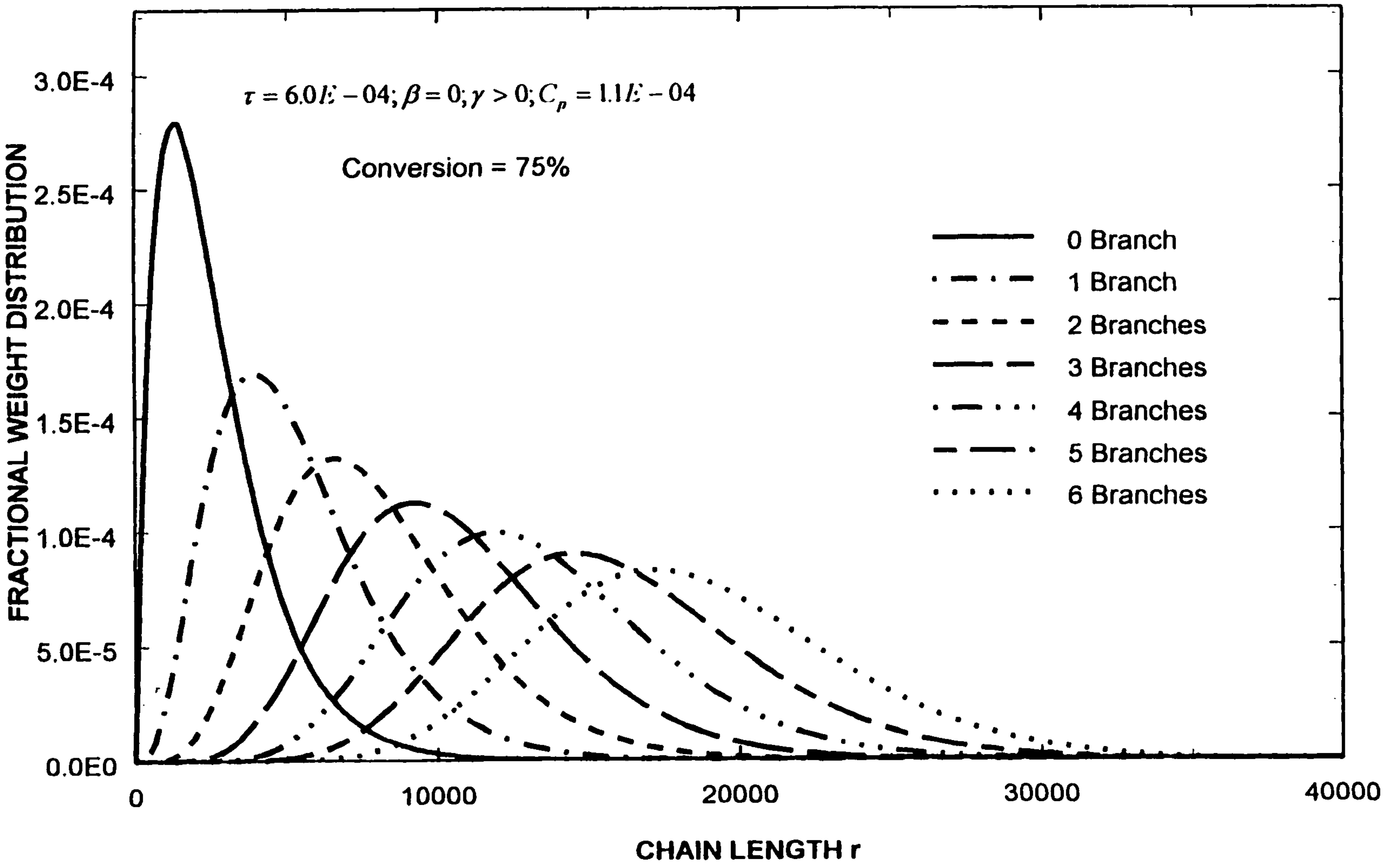


Figure 5-7: Plot of polydispersity vs. number of branch points /molecule

Transfer to monomer dominates

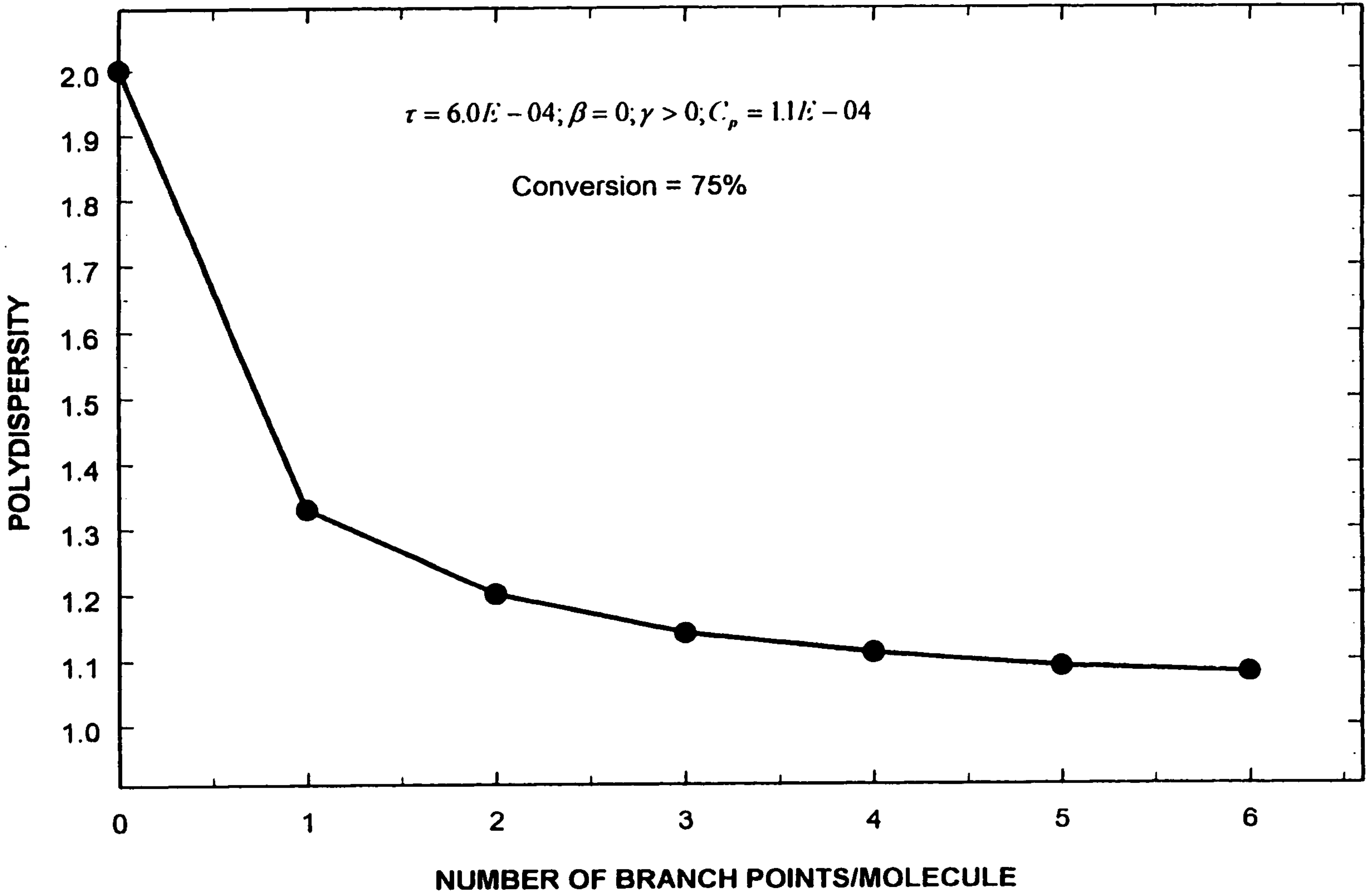


Figure 5-8: Plot of weight chain length distribution of instantaneous dead polymer

Termination by disproportionation dominates

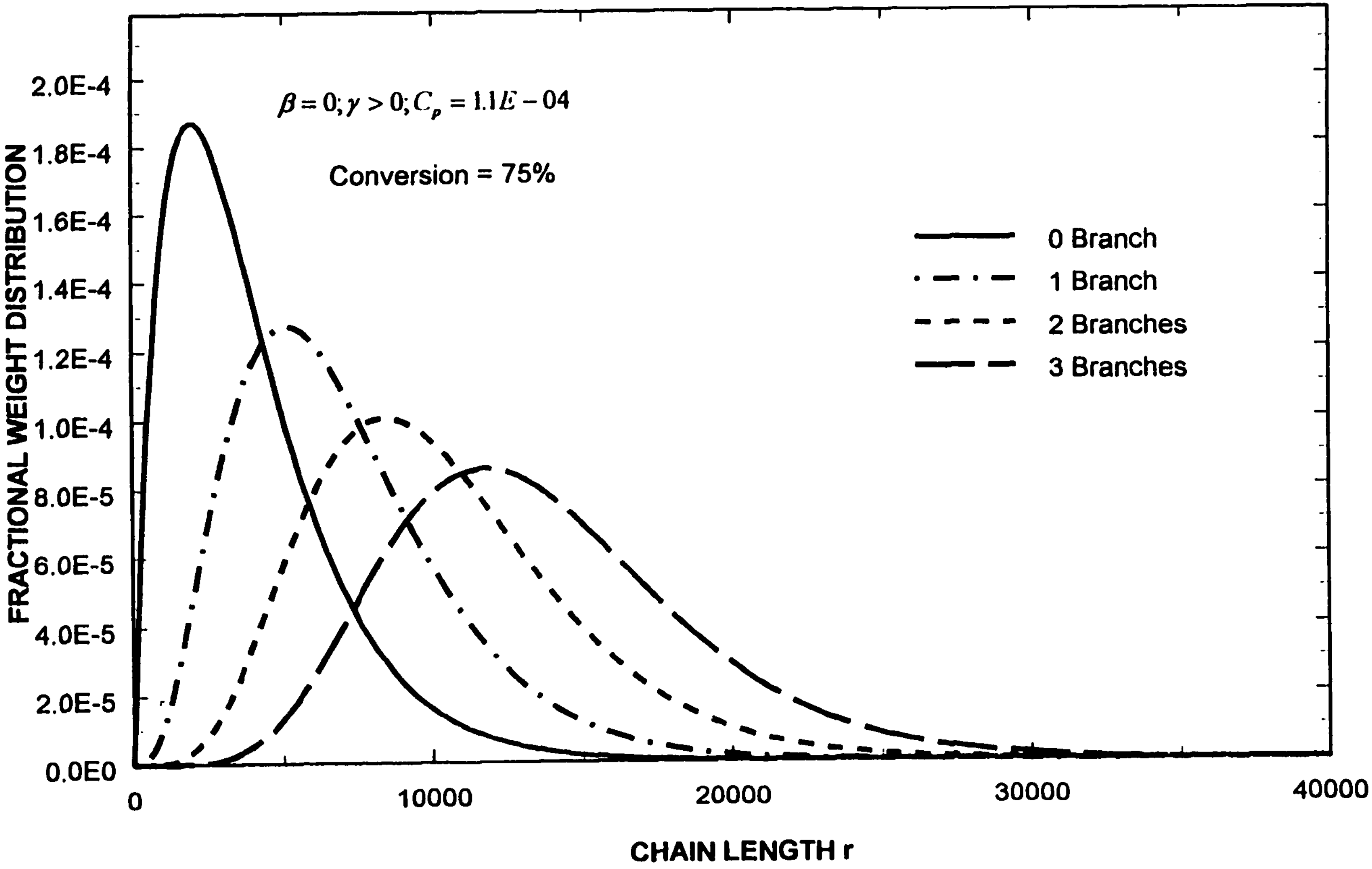
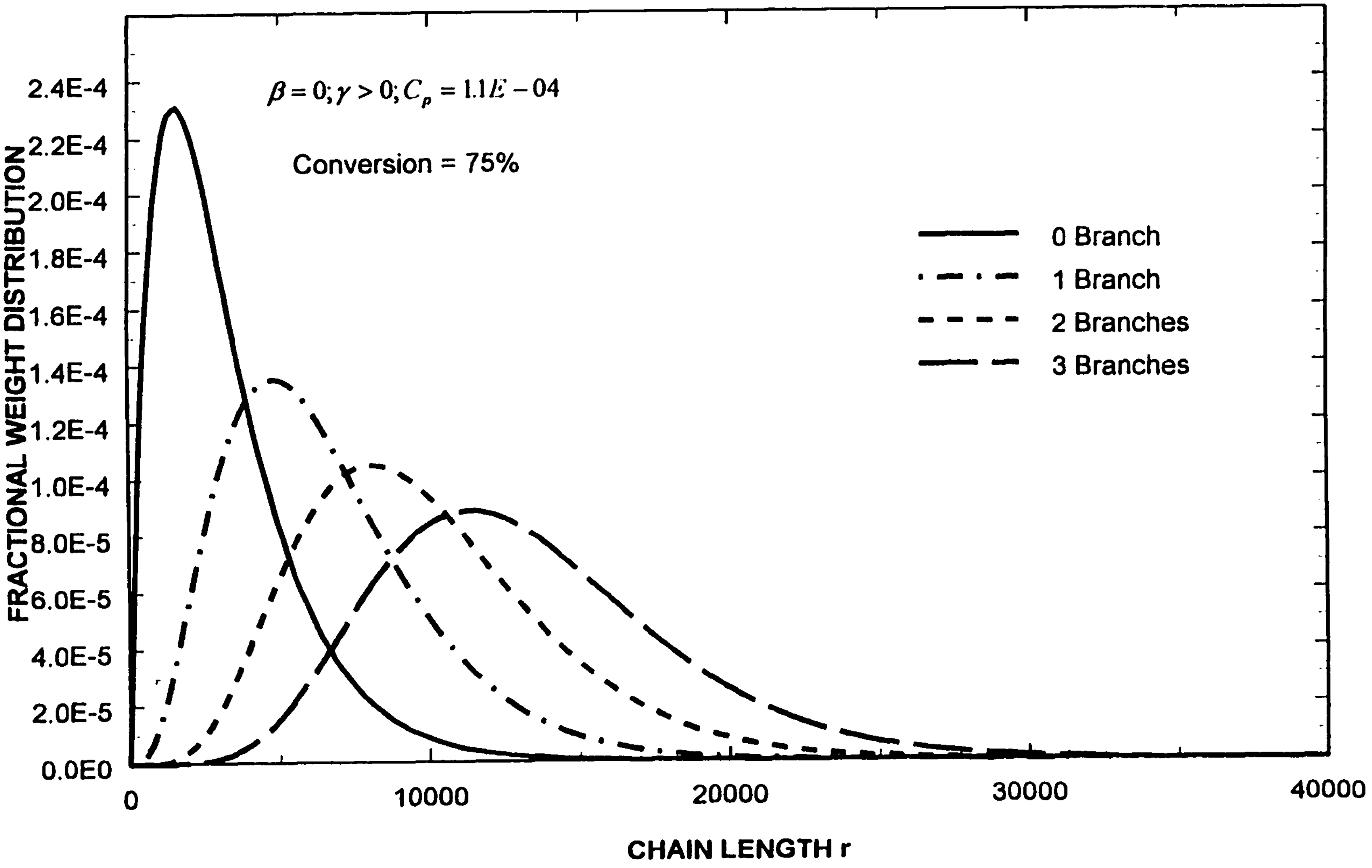


Figure 5-9: Plot of weight chain length distribution of accumulated dead polymer

Termination by disproportionation dominates



Moment Equations For The Overall Polymer Population

$$\frac{dQ_0(t)}{dt} = k_p M Y_0 \left[\tau + \beta / 2 \right] \tag{5-19}$$

$$\frac{dQ_1(t)}{dt} = k_p M Y_0 \tag{5-20}$$

$$\frac{dQ_2(t)}{dt} = k_p M Y_0 \left[2\left(\frac{1 + \gamma Q_2 / Q_1}{\tau + \beta + \gamma} \right) + \beta \left(\frac{1 + \gamma Q_2 / Q_1}{\tau + \beta + \gamma} \right)^2 \right] \tag{5-21}$$

TABLE 5- 1 Molecular Weight Averages(M_n,M_w) And Polydispersity(PD) Calculated By The Instantaneous Method(Inst.) And The Method Of Moments(Mom.)

Case	Con.	M_n	M_n	Error	M_w	M_w	Error	PD	PD
	(%)	Inst.	Mom	(%)	Inst	Mom	(%)	Inst	Mom
2	25	195110	194910	+0.1	390210	390660	-0.1	2.00	2.00
	50	218370	216400	+0.9	443900	440320	+0.8	2.03	2.03
	75	252120	249320	+1.1	542860	537810	+0.9	2.15	2.16
4	25	198280	196970	+0.7	406220	402700	+0.9	2.05	2.04
	50	198330	196970	+0.7	422130	416130	+1.4	2.13	2.11
	75	193740	196970	-1.6	431930	440290	+1.9	2.23	2.24

In order to apply the moment equations for the branched species(Equations 9-14) it was necessary to choose a method for dealing with the moment closure problem. The relationship between the zero, first ,second and third moments developed by Saidel and Katz(1968) and used by Teymour and Campbell(1994) was employed. In the cases checked the errors did not exceed 5%(Table 5-2). The higher deviations at 50% conversion are quite likely due to the use of an approximate moment closure technique. As mentioned earlier, a procedure will be proposed for dealing with the moment closure problem in the application of the Instantaneous Method.

A Useful Instantaneous Property

Equations (5-5a) and (5-17) can be used to track the distribution of a family of dead polymer born at $\bar{t}$ as it becomes distorted due to transfer to polymer. This was done for the linear species(i=0) and the branched species(i=2) for polymer born at 75% conversion for Case 4. Figures 5-12 and 5-13 show the changes that occur for i=0 and i=2 in going from 75% conversion to 95% conversion. What is most interesting is that the polydispersity remains constant at 2.0 for i=0 and 1.2 for i=2.This was confirmed analytically for i=0 by use of Equation 6.If this property proves to be true for all possible cases, it can be used to develop more efficient numerical procedures.

Figure 5-10: Plot of weight chain length distribution of instantaneous dead polymer

Termination by combination dominates

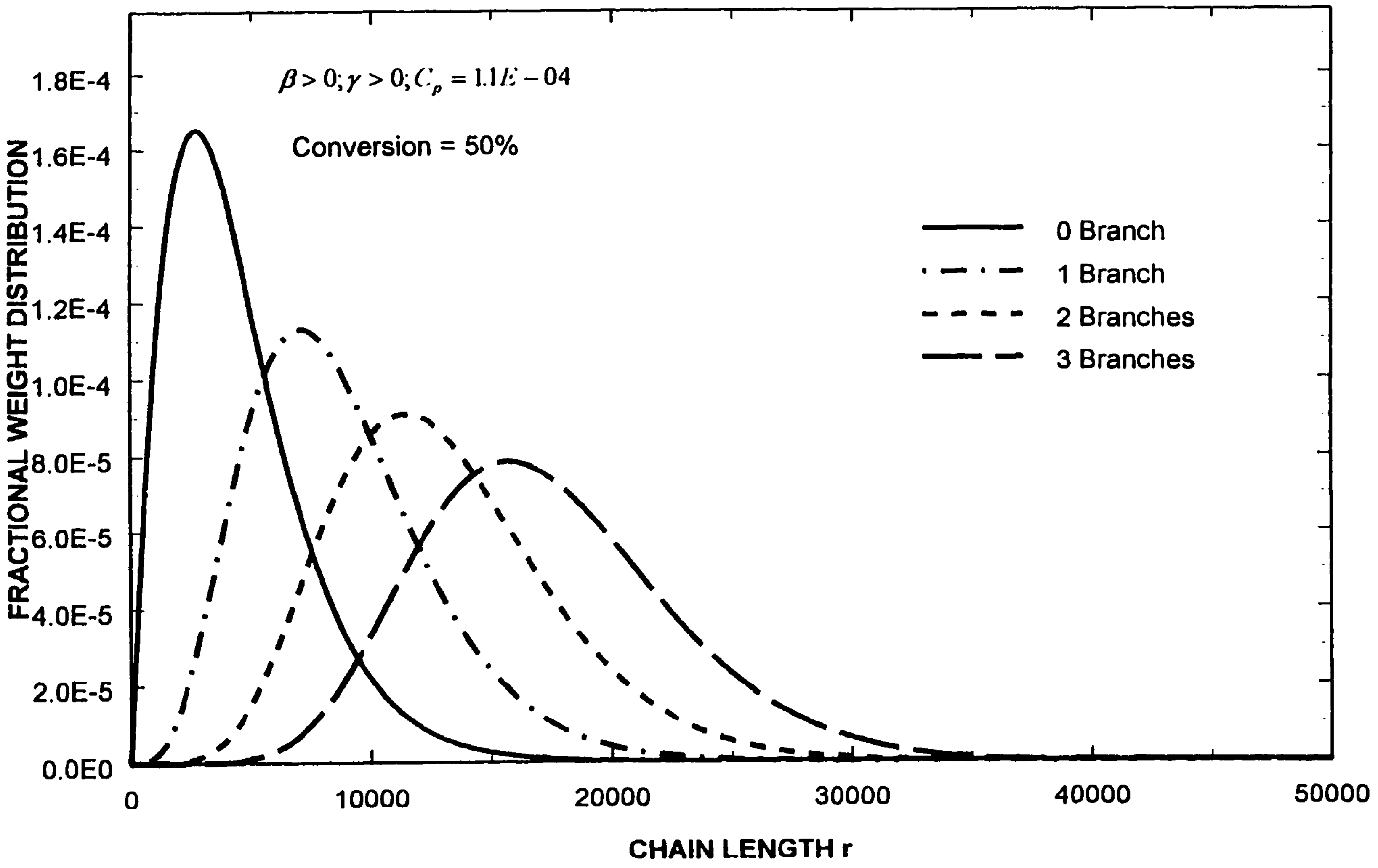


Figure 5-11: Plot of weight chain length distribution of accumulated dead polymer
Termination by combination dominates

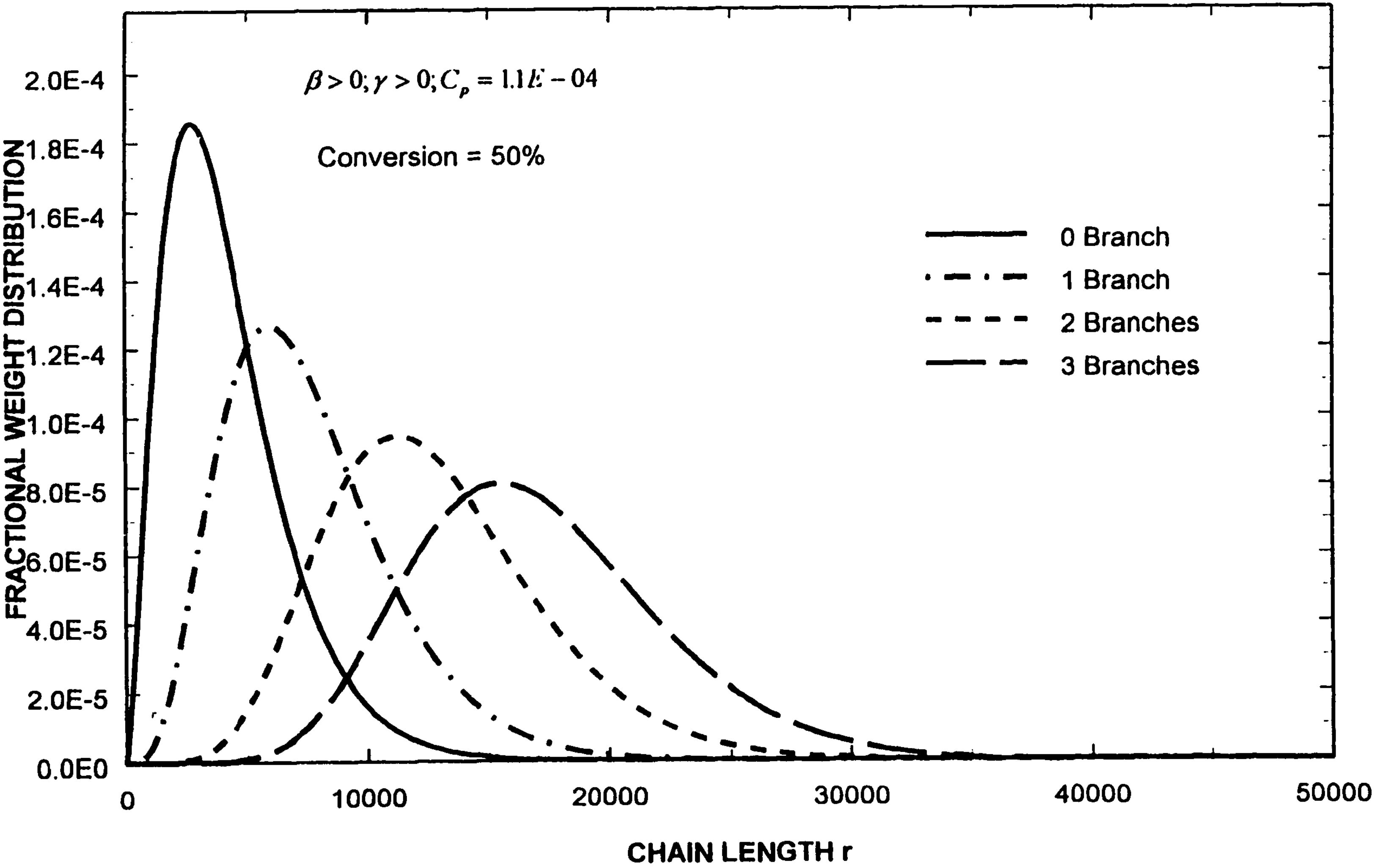


TABLE 5- 2 Molecular Weight Averages(M_n,M_w) And Polydispersity(PD) Of Branched Species Calculated By The Instantaneous Method(Inst.) And The Method Of Moments(Mom.)-CASE 5 (i - Number Of Branches per chain)

i	Con. (%)	M_n Inst.	M_n Mom	Error (%)	M_w Inst.	M_w Mom	Error (%)	PD Inst.	PD Mom
0	25	187080	190040	1.5	373910	380500	1.7	2.00	2.00
	50	192570	201000	4.2	388710	404800	4.0	2.02	2.02
1	25	557030	567810	1.9	743610	757470	1.8	1.33	1.33
	50	576890	602840	4.3	774790	806350	3.9	1.34	1.34
2	25	926090	944230	1.9	1112200	1133500	1.9	1.20	1.20
	50	960250	1002600	4.2	1158400	1205700	3.9	1.21	1.20

Numerical Procedure

The key equations to be solved in calculating the MWD by the instantaneous method are Equations 4 and15 as well as Equations 5(b) and 18. Calculation of Equations 4 and 15 is straightforward. Δt must be chosen to minimize the error introduced in the approximation used in the integration of Equations 2 and 8 to obtain equations 4 and 15. In these calculations a Δt of 1 minute was used for a reaction system where a conversion of 75% was achieved in 1500 minutes. The integration of Equations 5(b) and 18 was done using a modified Simpson's rule with a step size of 5 minutes. For highly branched systems the chain lengths can be quite large leading to a significant demand on computer time and memory. For such systems it will be necessary to modify the technique possibly using some of the results of the instantaneous method which show that more highly branched species have narrower MWD's and thus the solution accuracy is less sensitive to the moment closure method used. This information would benefit the numerical fractionation method used by Teymour and Campbell(1994).

A Hybrid Method

Figure 5-7 illustrated the general narrowing of the polydispersity of the MWD of a branched family as the number of branches increases. This trend was observed for all kinetic schemes and it can be used as a basis for a method of dealing with the moment closure problem.

If the MWD of a branched family is sufficiently narrow, then a suitable distribution may be assumed as a good approximation. If the polydispersity can be predicted as a function of i, it would only be necessary to solve for two of the moments of the particular branched family in order to determine the MWD. This would eliminate the need for a moment closure formula or more correctly the polydispersity relationship would be the moment closure equation.

For the examples analysed earlier(Cases 4,5,6) it was found that

$$PD_i = 1 + \frac{1}{a + bi} \tag{5-22}$$

where PD_i = the polydispersity of a branched family having i branch points per molecule

a,b = constants to be determined

Figures 5-14 and 5-15 indicate the typical fit of equation (5-22) to the actual polydispersity calculated by the Instantaneous Method.

The procedure that is proposed for dealing with systems where the chain lengths can become extremely large and when a large number of branched families must be considered is as follows:

(1) Apply the Instantaneous Method up to i=4 or 5 at any particular conversion level and so determine the constants in equation (5-22).

(2) Equation (5-22) is combined with the equations for the moments of the branched families to solve for the zero and first moments.

(3) Assume a distribution function(for example, Zimm-Schulz) for the MWD of the branched families for i>5. The moment closure is effected by using

$$PD_i = \frac{Q_{2,i}Q_{0,i}}{Q_{1,i}^{\;2}}$$

or $$Q_{2,i} = PD_i \frac{Q_{1,i}^{\;2}}{Q_{0,i}} \qquad (5\text{-}23)$$

(4) The parameters of the MWD function can then be determined.

It should be clear that the above procedure would simply be a combination or hybrid of the Instantaneous Method and the Numerical Fractionation Method of Teymour and Campbell(1994).

Figure 5-12: Plot showing the distortion of linear dead polymer
Polymer born at 75% conversion

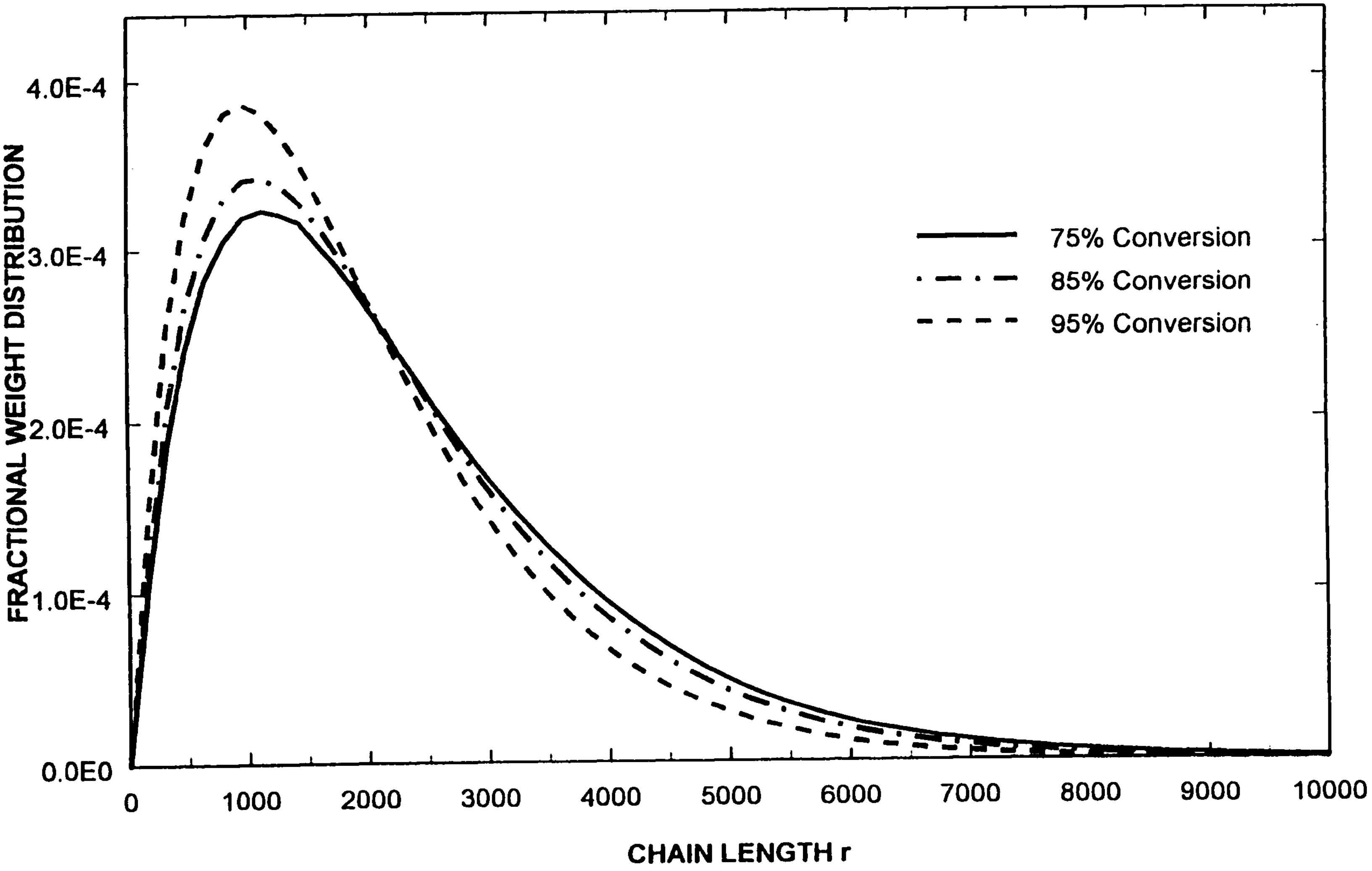


Figure 5-13: Plot showing the distortion of branched(i=2) dead polymer
Polymer born at 75% conversion

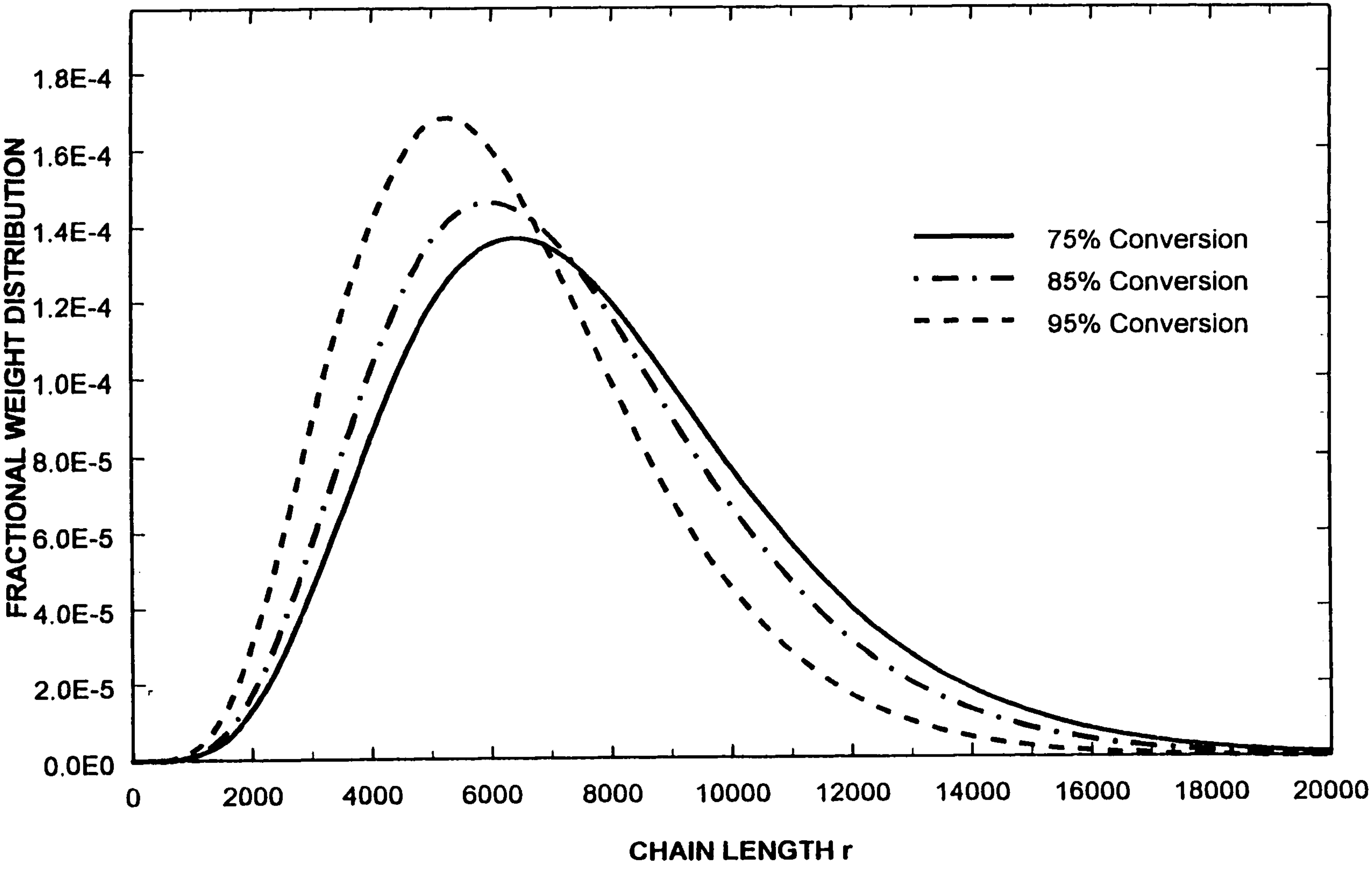


Figure 5-14: Plot of polydispersity vs no. of branches per molecule
Case 5 - 50% conversion

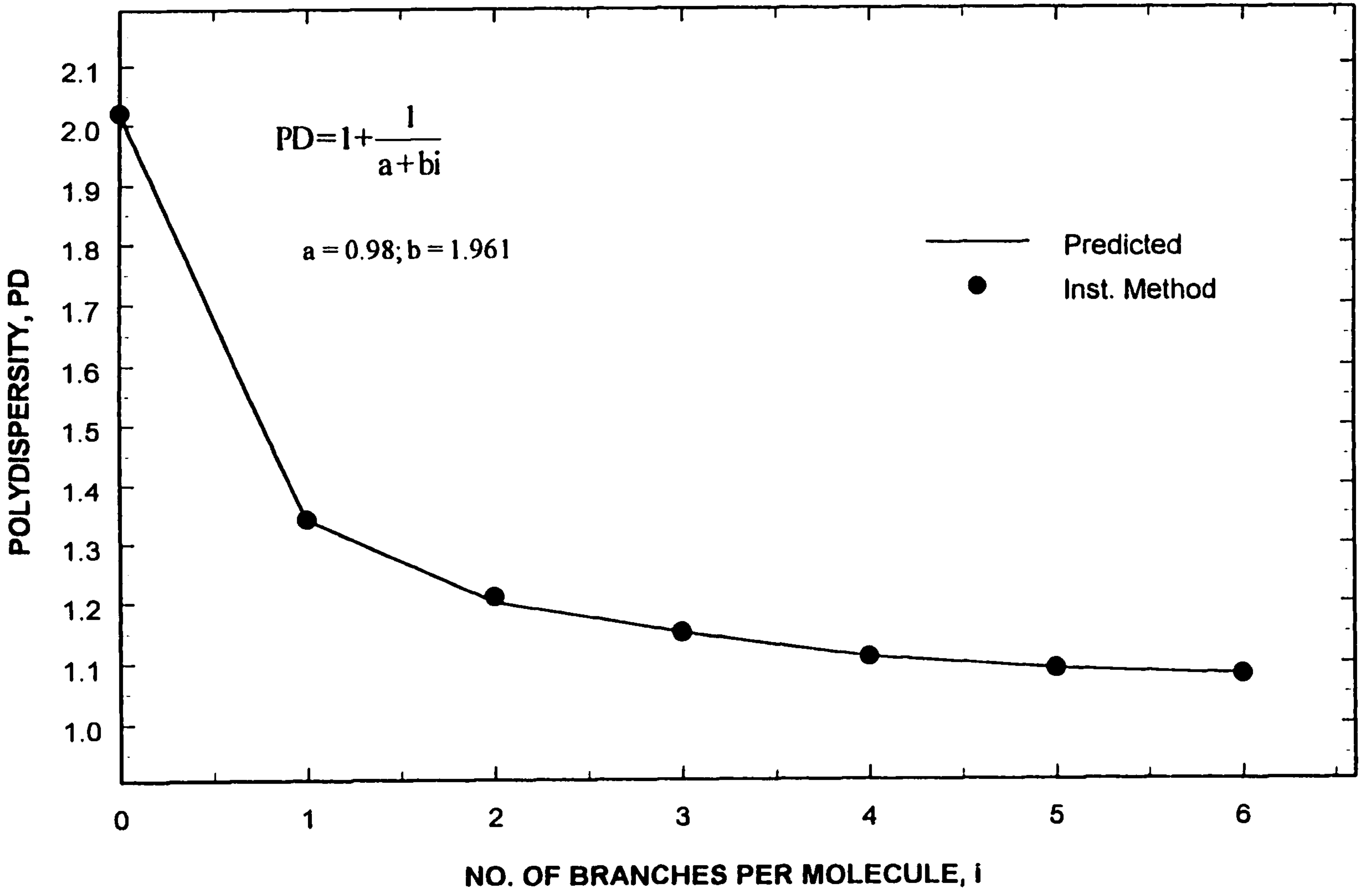
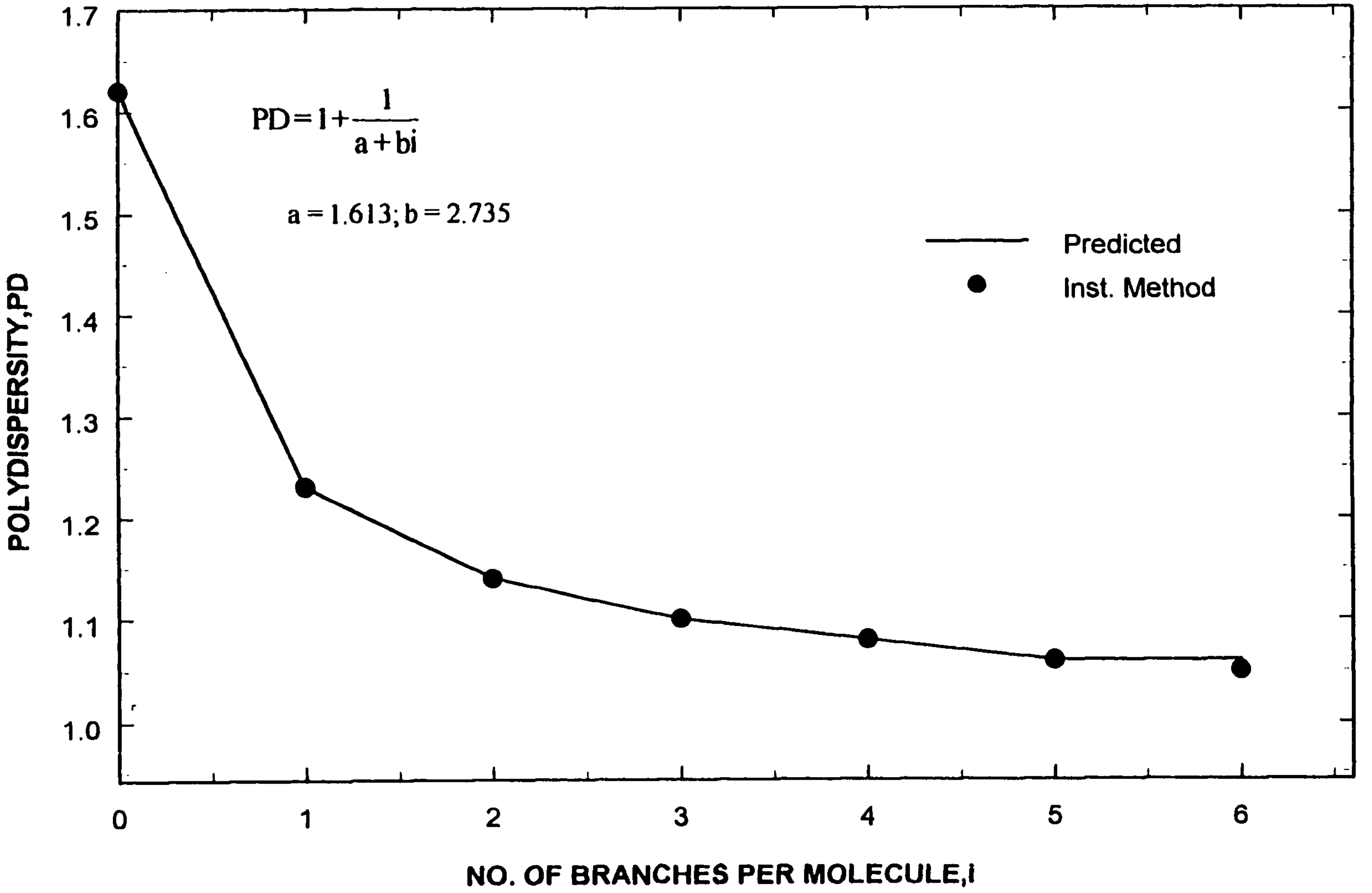


Figure 5-15: Plot of polydispersity vs no. of branches per molecule
Case 6 - 50% conversion



CHAPTER 6

EVALUATION OF LONG CHAIN BRANCHING MEASUREMENT METHODS - APPLICATION TO EXPERIMENTAL DATA

6.1 Introduction

The free-radical synthesis of PVAc and PPMS provides model branched polymers where the long chain branches are formed by one or both mechanisms of chain transfer to polymer and terminal branching. With PVAc long chain branches are formed by both chain transfer to polymer and by addition of polymeric radicals to terminal carbon-carbon double bonds on dead polymer chains. The source of these terminal double bonds is chain transfer to vinyl acetate monomer and the subsequent growth by propagation and death by some termination reaction (Graessley et al,1969). There are two backbone sites for chain transfer to PVAc, secondary and tertiary backbone hydrogens and chain transfer to the methyl hydrogens on the acetate group. Hydrolysis of PVAc chains followed by measurement of number average molecular weight change has shown that about 70% of the long chain branches are on the acetate groups and 30% are on the backbone. The PVAc must be synthesized using a chain transfer agent to reduce the concentration of terminal carbon-carbon bonds to a negligible level so that transfer to polymer is the sole long chain branching mechanism(Graessley et al,1969).

The free-radical synthesis of PPMS provides dead polymer chains with saturated chain ends and chain transfer to polymer is the sole long chain branching mechanism(Chiantore and Hamielec,1985). The site for chain transfer to PPMS is the methyl group on the benzene ring.

The development of "instantaneous" property methods to account for long chain branching should logically begin with a chain growth polymerization that involves one mechanism for long chain branch formation, either terminal branching or chain transfer to polymer. Both of these mechanisms produce long branches with trifunctional branch points. The more complex mechanism of addition of polymeric radicals to pendant carbon-carbon double bonds on the backbone of dead polymer chains produces tetrafunctional long chain branching. This more complex mechanism of long chain branching can rapidly lead to gelation and is beyond the scope of the present investigation. The development of the "instantaneous" property method to account for terminal branching has already been done(Soares and Hamielec,1996). This is the easiest case to consider as the molecular weight distribution of dead polymer chains formed instantaneously is not distorted in the reactor thereafter. This can be explained as follows:

Every dead polymer in the distribution has a terminal carbon-carbon double bond which can later add to active centres as a macromonomer. However, since the rate of addition of these macromonomer chains to active centres is proportional to the concentration of macromonomer(when the reaction of addition is not chain-length dependent), the molecular weight distribution is not changed or distorted in any way even though the mass of the instantaneously produced polymer is consumed later in the polymerization. Chain transfer to polymer is a more difficult case because of molecular weight distribution distortion. This distortion results from the fact that dead polymer chains with higher molecular weights have a larger number of extractable atoms and therefore have a higher probability of being attacked by a polymeric radical. This distortion which can occur later in the polymerization must be accounted for quantitatively. The present investigation considered the extension of the "instantaneous" property method to account for chain transfer to polymer. Taking account of simultaneous transfer to polymer and terminal branching in the context of the "instantaneous" property method is beyond the scope of the present investigation. However, kinetics and molecular weight and long chain branching data were measured for the bulk free-radical polymerization of vinyl acetate to provide the relevant information for future investigators who may attempt to extend this study to account for simultaneous transfer to polymer and terminal branching. In this study, the kinetics, molecular weight and long chain branching data were modelled using the method of moments.

6.2 Polymerization of Vinyl Acetate

There are limited amounts of kinetic and molecular weight data in the literature(Graessley et al,1969; Friis and Hamielec,1974). Unfortunately, the use of a solvent which acts as a chain transfer agent adds an additional reaction type generating dead polymer chains with and without terminal double bonds and thus making it necessary to keep track of additional polymer families(Chatterjee et al,1977). Emulsion polymerization of vinyl acetate, although widely studied, is not sufficiently understood for use in an investigation of this kind(Friis and Hamielec,1974). It was therefore felt necessary to provide new kinetic and molecular weight data as well as long chain branching data for the bulk polymerization of vinyl acetate. Two levels of temperature (60°C and 80°C) and different levels of initiator(AIBN) were used to provide suitable PVAc samples for molecular weight and long chain branching characterization. A suitably low AIBN level was used at 80°C to give adequately long polymerization times for good temperature control and small sampling time/quenching time errors. Intrinsic viscosity versus conversion data for the bulk polymerization of VAc are shown in Appendix A. Table A-1(E-series) and Table A-2(5-series) show the samples that were used in the GPC analysis.

The measured $\overline{M}_n, \overline{M}_w$ and $\overline{B}_n$ are shown graphically in Figures 6-1 to 6-6. The molecular weight averages and average number of branch points per molecule are modelled using the method of moments. The moments for the molecular weight and branching development in an isothermal bulk polymerization of VAc are described by the following differential equations(Graessley et al.,1969):

$$\frac{dQ_0}{dx} = C_m - \frac{KQ_0}{1-x} \tag{6-1}$$

$$\frac{dQ_1}{dx} = 1 \tag{6-2}$$

$$\frac{dQ_2}{dx} = \frac{2\left[1+\frac{Kx}{1-x}\right]\left[1+\frac{Kx}{1-x}+\frac{C_pQ_2}{1-x}\right]}{\left[C_m+\frac{C_px}{1-x}\right]} \qquad (6\text{-}3)$$

$$\frac{d(Q_0\bar{B}_n)}{dx} = \frac{C_px+KQ_0}{1-x} \qquad (6\text{-}4)$$

where Q_i = ith moment of the polymer frequency distribution

and the parameters are ratios of rate transfer constants:

$$C_m = \frac{k_{tm}}{k_p};\ C_p = \frac{k_{tp}}{k_p};\ K = \frac{k_p^{\bullet}}{k_p}$$

$k_p^{\bullet}$ = transfer constant for terminal double bond polymerization

Solution of equations (6-1) to (6-4) depends on the parameters C_m, C_p and K and can easily be obtained using a differential equation solver provided that the parameters are known as a function of conversion. The estimation of the parameters was done as follows: At low monomer conversions, where polymer concentrations are small, the parameters C_p and K do not significantly influence $\overline{M}_n$ and $\overline{M}_w$ and as a consequence low conversion $\overline{M}_n$ and $\overline{M}_w$ values may be used to estimate C_m. Chain transfer to polymer with the associated parameter C_p causes $\overline{M}_w$ to increase with conversion of monomer but has no effect on $\overline{M}_n$. Therefore K is estimated by fitting $\overline{M}_n$ at high conversions and once K is known, C_p can be estimated by fitting $\overline{M}_w$ at high conversions. K and C_p both cause $\overline{M}_w$ to increase with monomer conversion. It should be mentioned that the reaction which involves the addition of a polymeric radical to a terminal double bond appears to be diffusion-controlled(Friis and Hamielec,1974). In this investigation as well as that of Friis and Hamielec, it was necessary to let $k_p^{\bullet}$ fall with monomer conversion to give an adequate fit of $\overline{M}_n$ versus conversion at higher conversion levels. The equation used by Friis and Hamielec for the emulsion polymerization of vinyl acetate to account for the decrease in $k_p^{\bullet}$ was slightly modified for the bulk polymerization study done in this investigation. The following values for the parameters were used to calculate the moments:

At 60°C, $C_m = 0.208E\text{-}03$ and $C_p = 0.487E\text{-}04$

At 80°C, $C_m = 0.347E\text{-}03$ and $C_p = 2.09E\text{-}04$

$$k_p^{\bullet} = A_0 + A_1x + A_2x^2 + A_3x^3$$

where $A_0 = 1.25\times10^7 \exp(-5650/RT)\ \mathrm{L\ mol^{-1}s^{-1}}$

$A_1 = -169.59$; $A_1 = -479.92$; $A_3 = -1014.3$

x = fractional conversion and T is the temperature(K)

$k_p = 1.89\times10^7 \exp(-5650/RT)\ \mathrm{L\ mol^{-1}s^{-1}}$

Measured $\overline{B}_n$ values were not used for estimation of C_p and K, but rather using the method of moments and the C_p and K values found with $\overline{M}_n$ and $\overline{M}_w$ data, B_n values were predicted for various monomer conversion levels and the agreement seems quite satisfactory. The determination of $\overline{B}_n$ from the GPC data was done by the two methods outlined in Chapter 4 and a short discussion of the results follow.

In the MWBD method the input information required is the universal calibration curve, the DRI response of the sample and the intrinsic viscosity of the whole polymer. The Zimm-Stockmayer model, equation (4-8), is used to convert g', the intrinsic viscosity ratio in equation (4-6), calculated at each elution volume to a number of branch points per molecule assuming a particular value for ε in equation (4-7). It was found that for PVAc a value of $\varepsilon = 0.8$ was needed to produce an adequate fit of $\bar{B}_n$ versus conversion shown in Figure 6-3 and Figure 6-6. The results of the application of the PD method are shown in figure 6-7 for the 60°C data. Agreement is also quite good for $\bar{B}_n$ but a value of $\varepsilon = 1.2$ is used. The value of $\varepsilon = 0.8$ is comparable to those that Berry et al(1964) obtained. They determined values of ε in the range 0.7-0.9 for PVAc in their study. It is worth pointing out that in the PD method, while no attempt was made to smooth the weight average molecular weight versus elution volume data, it was necessary in the calculations to ensure that no weight average molecular weight was less than the corresponding molecular weight of the linear polymer. The value of $\varepsilon = 1.20$ may have been high because of the type of distribution assumed in the cell. However, the initial objective in the use of the PD method was to show that the method can work with a relatively simple distribution. Note that it was not necessary to show plots of the molecular weight averages from the PD method since it is almost identical to the MWBD method.

A typical printout of the GPC data and branching results is presented in Appendix B but the full set of data for the PVAc samples are stored on diskette and will be available for future investigators.

Figure 6-1: Bulk Polymerization of Vinyl Acetate
Plot of Mn vs conversion

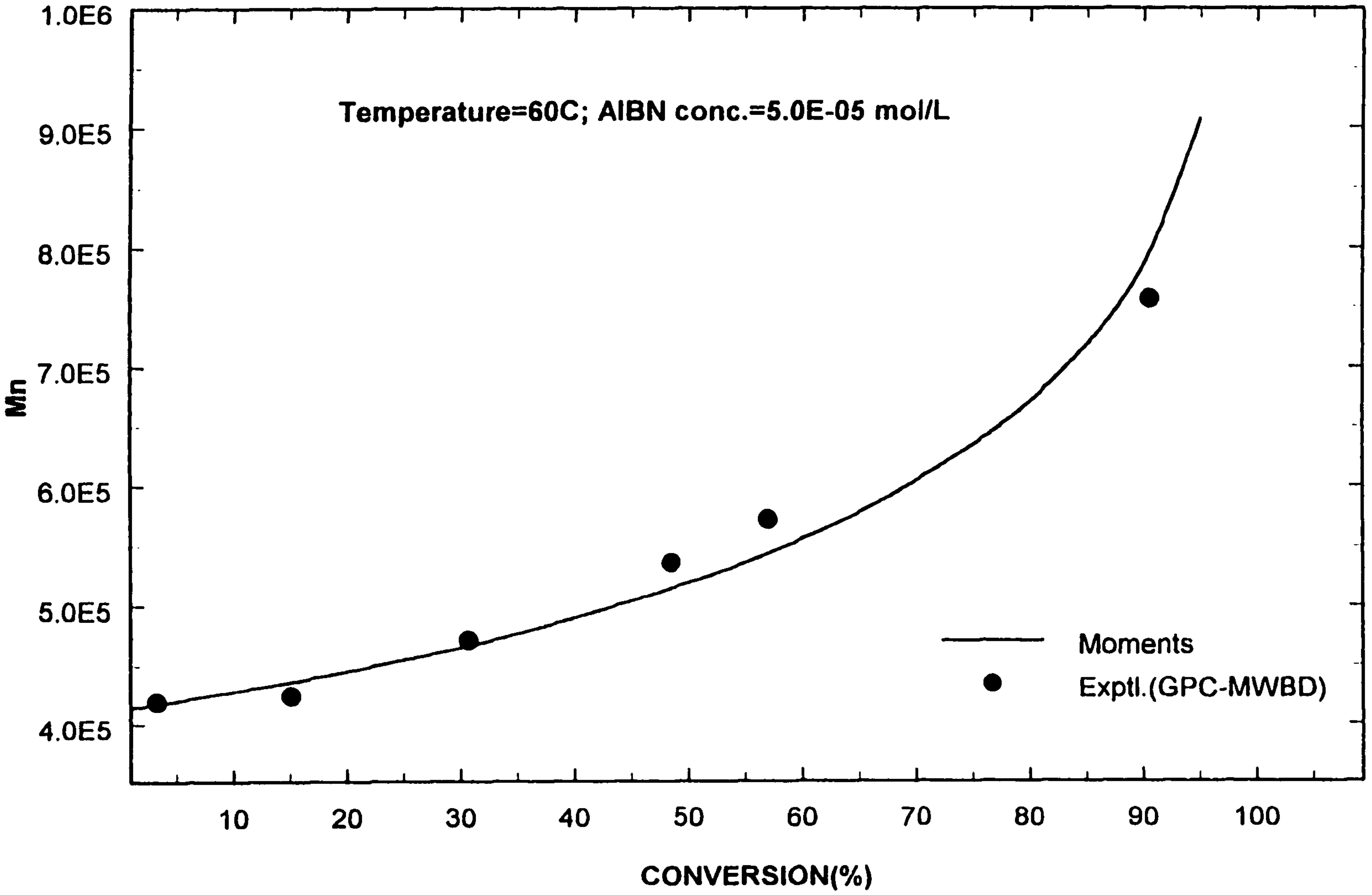


Figure 6-2: Bulk Polymerization of Vinyl Acetate
Plot of Mw vs conversion

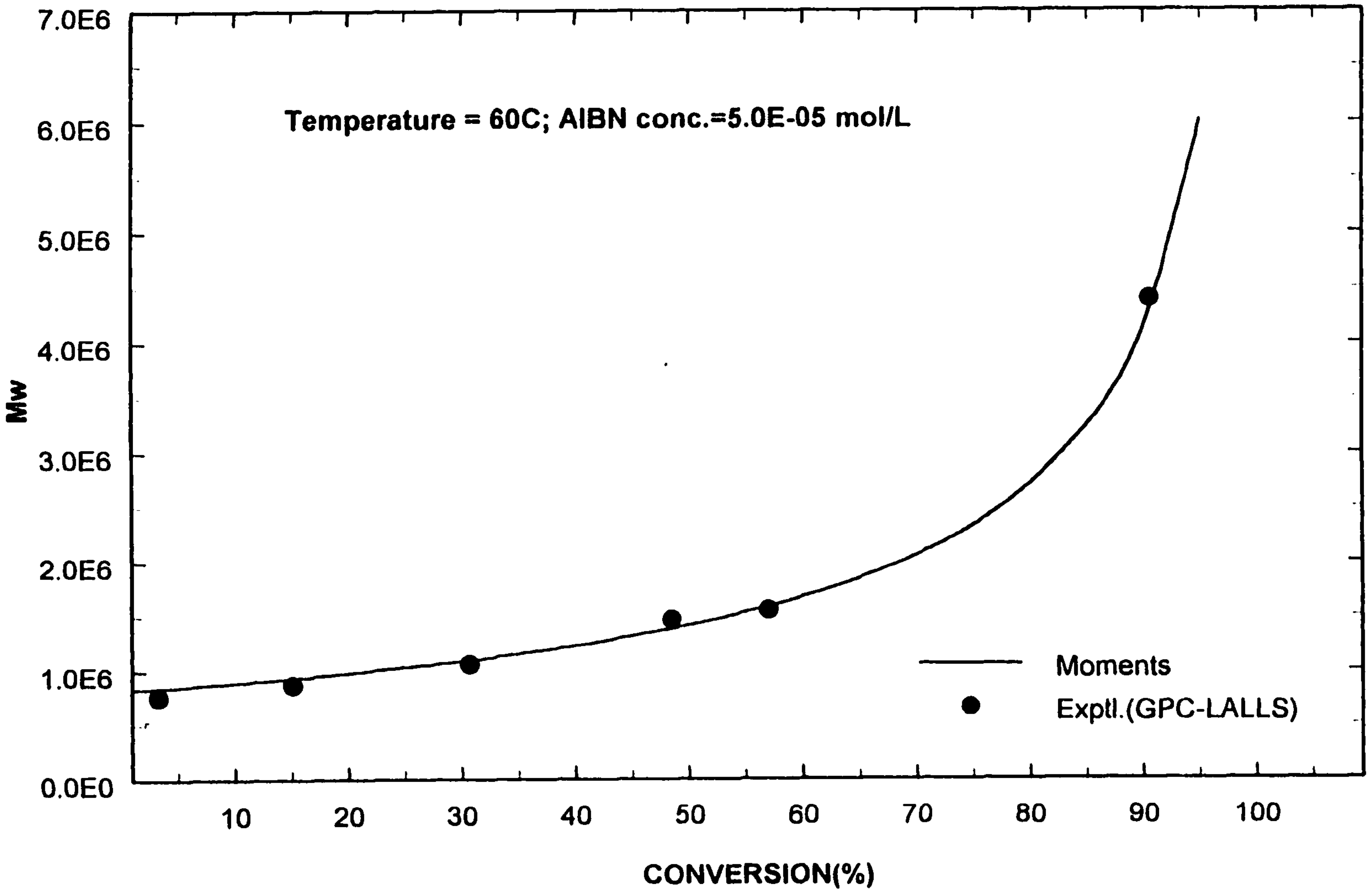
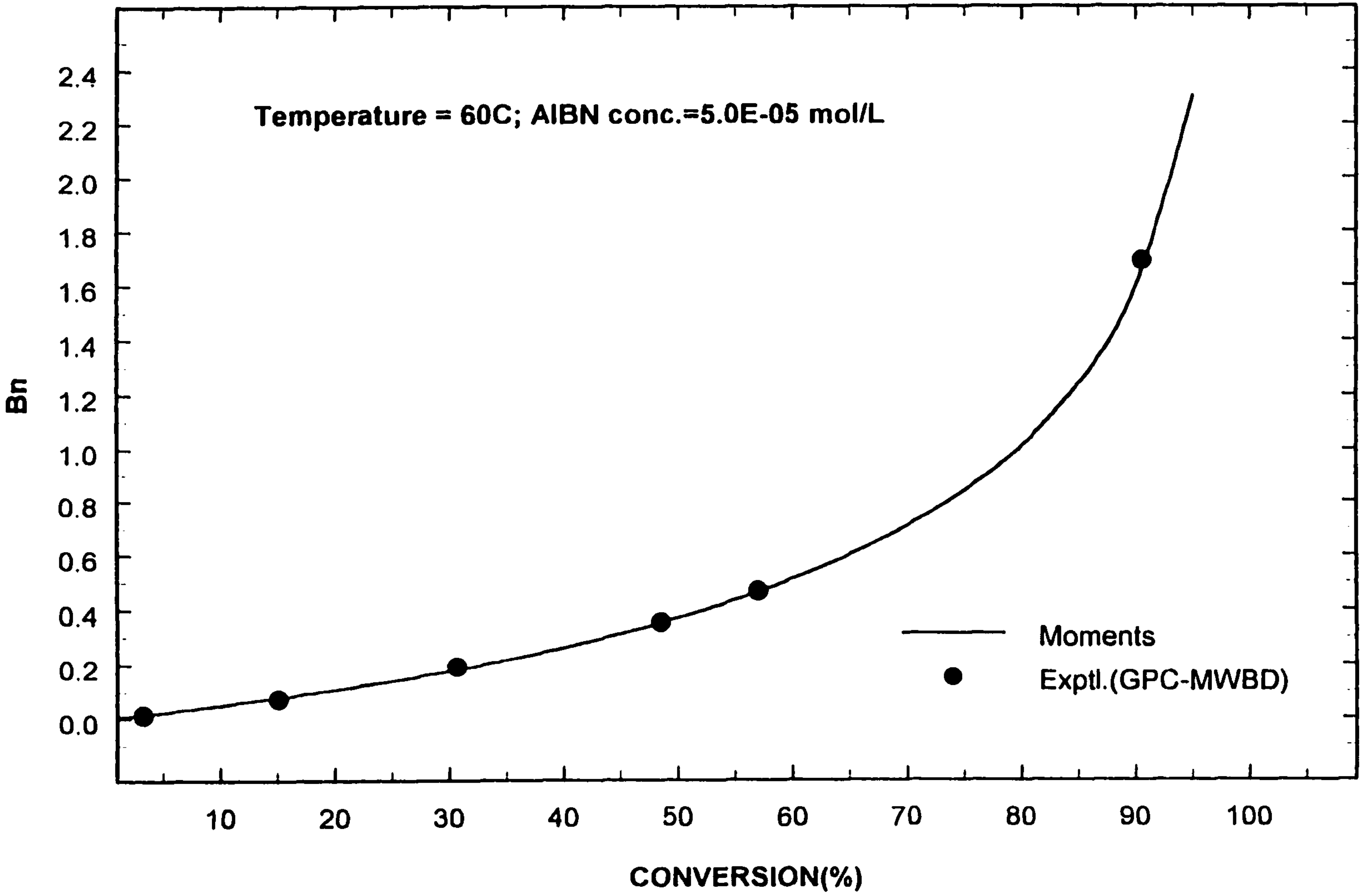


Figure 6-3: Bulk Polymerization of Vinyl Acetate
Plot of Bn vs conversion



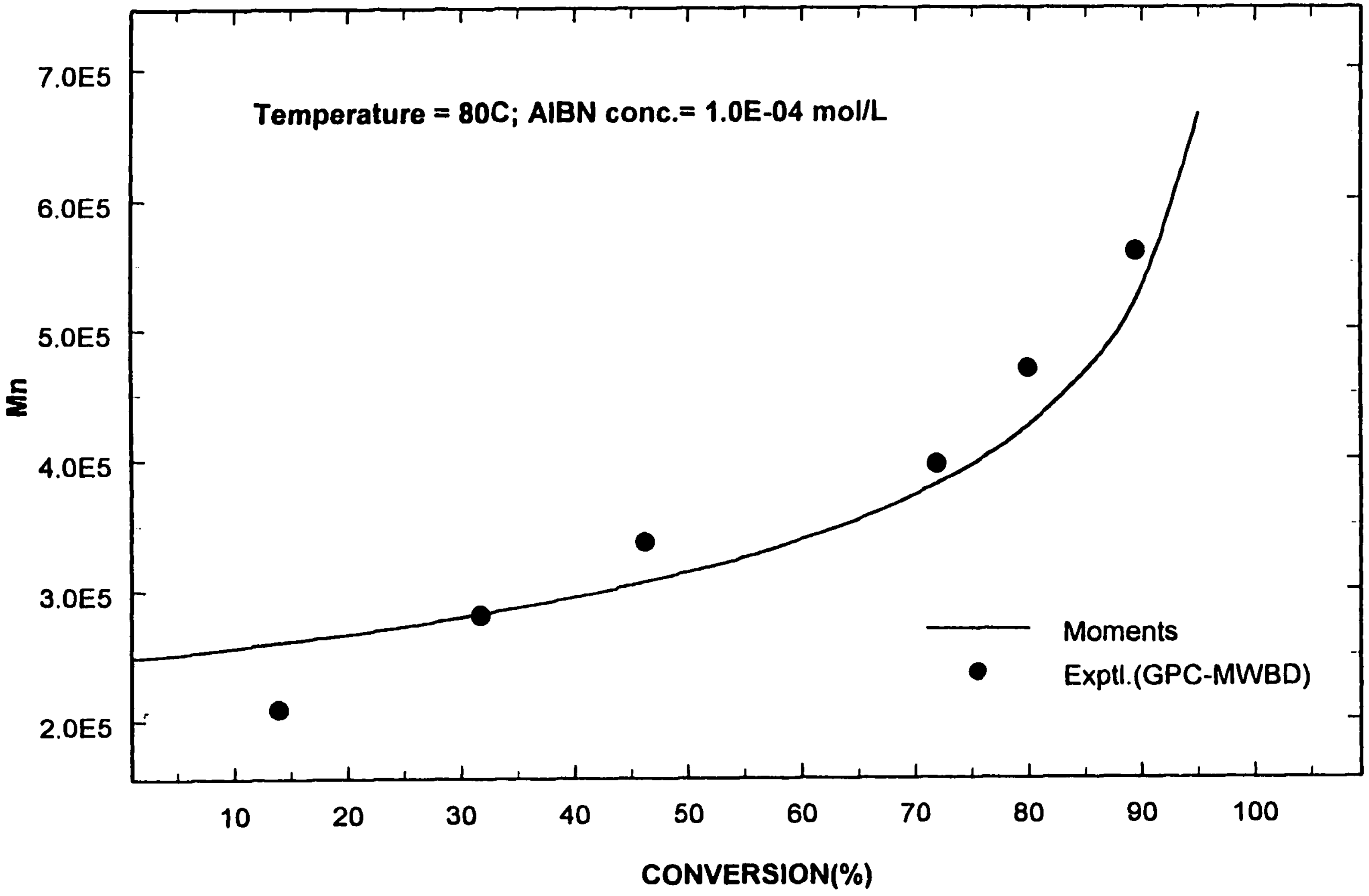


Figure 6-4: Bulk Polymerization of Vinyl Acetate
Plot of Mn vs conversion

Figure 6-5: Bulk Polymerization of Vinyl Acetate
Plot of Mw vs conversion

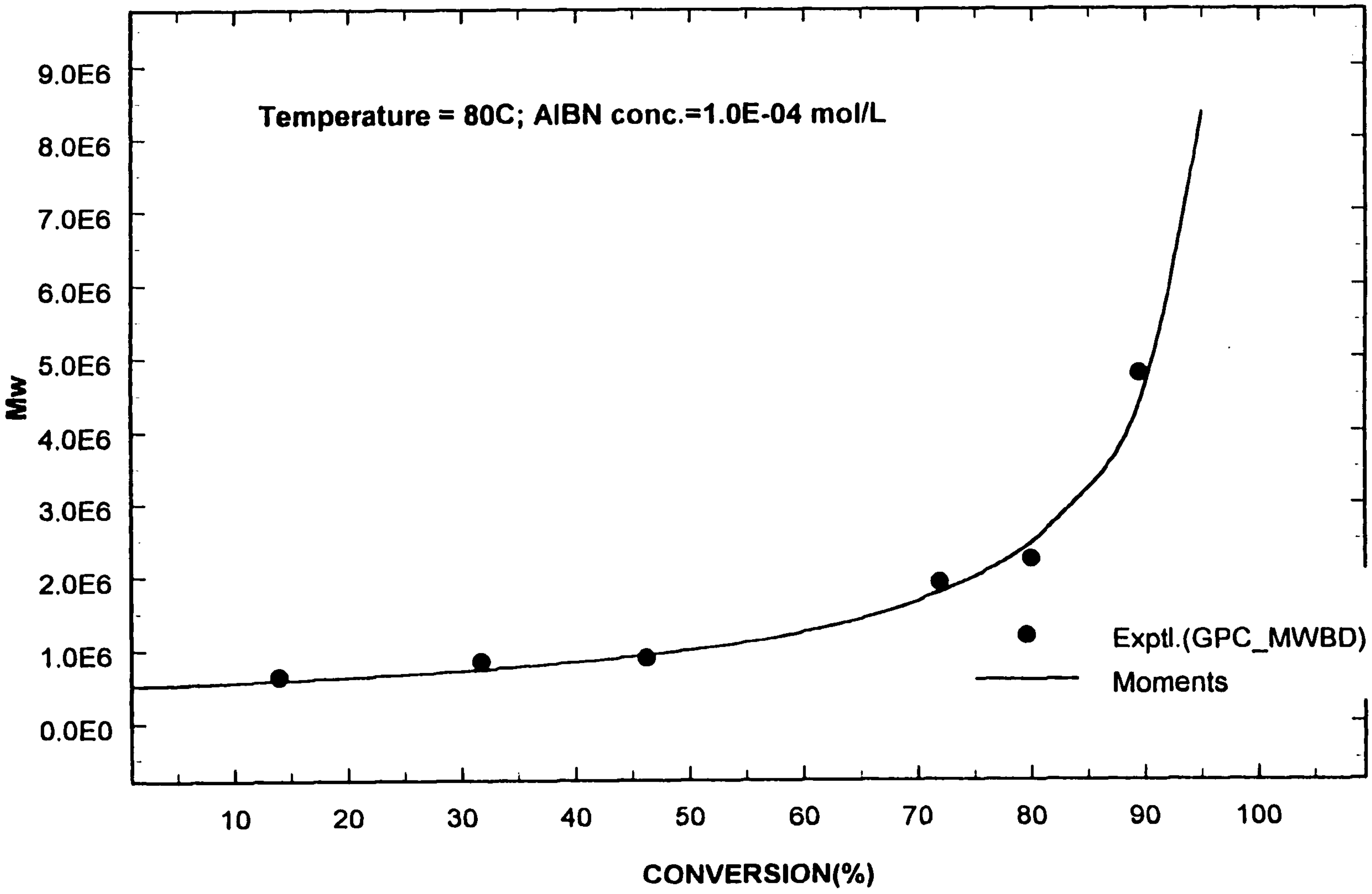


Figure 6-6: Bulk Polymerization of Vinyl Acetate
Plot of Bn vs conversion

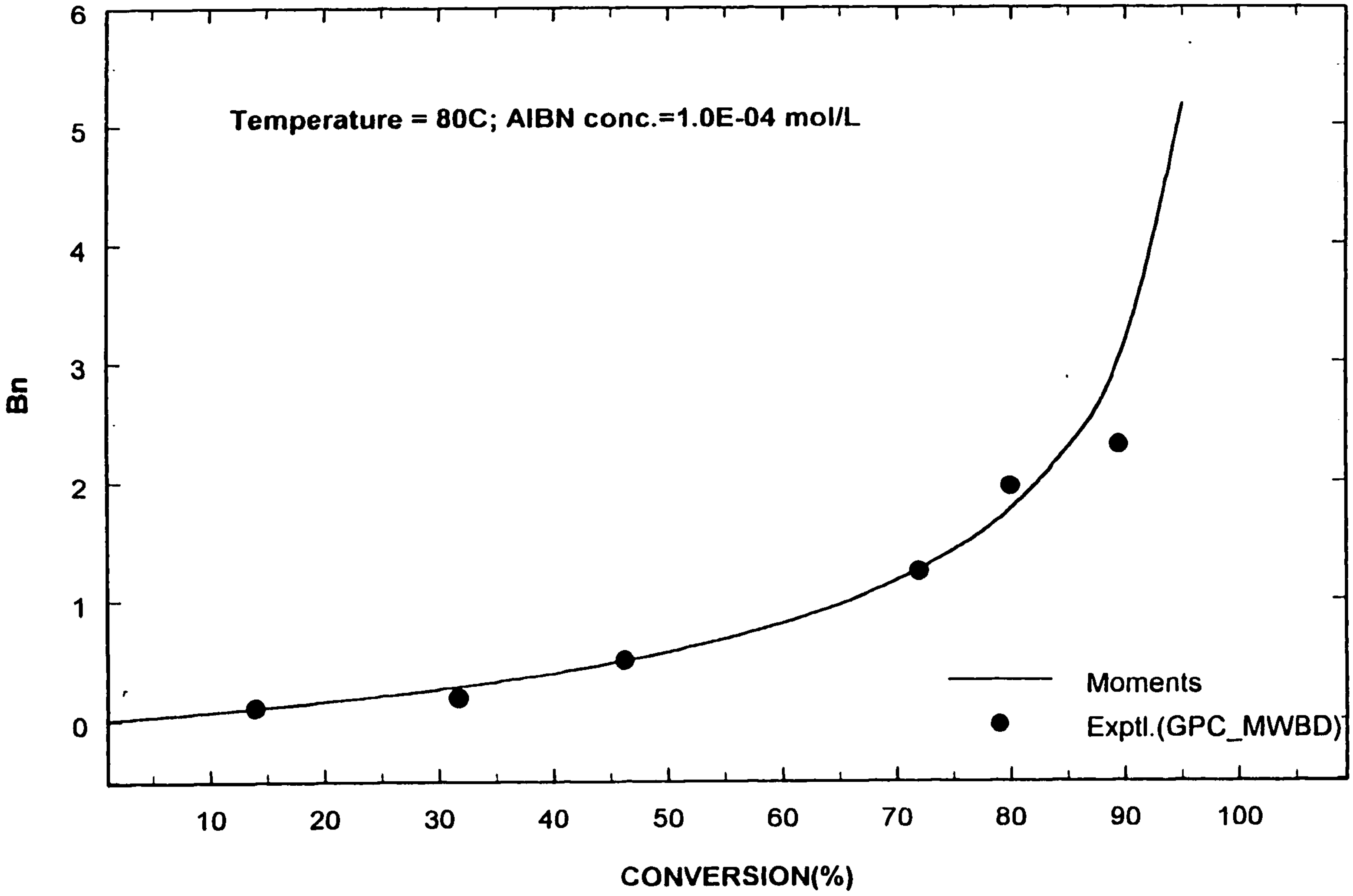
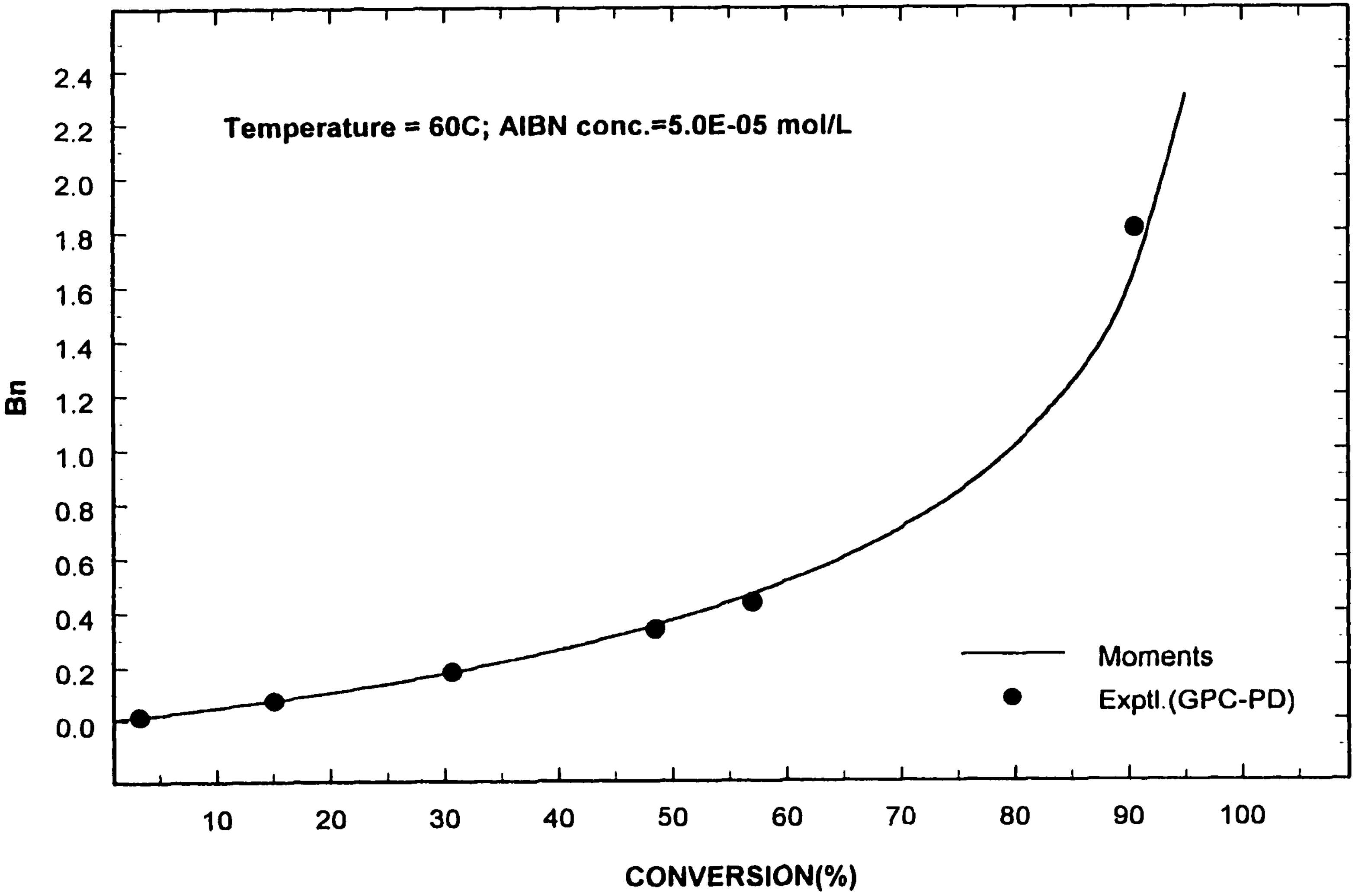


Figure 6-7: Bulk Polymerization of Vinyl Acetate
Plot of Bn vs conversion



6.3 Polymerization of p-Methyl Styrene

Although kinetics and molecular weight data($\overline{M}_n$ and $\overline{M}_w$) for the bulk thermal polymerization of p-methyl styrene are available, molecular weight distributions measured by GPC are no longer available as they were not properly stored for future retrieval(Chiantore and Hamielec,1985). It was therefore necessary to repeat and extend these earlier measurements. Chiantore and Hamielec used the method of moments to model these polymerizations. In addition they did not use GPC with viscometry to measure the branching frequencies of the PPMS samples that they synthesized. In the present investigation, B_n values were measured using GPC/viscometry and with application of the Zimm-Stockmayer branching model(MWBD). GPC cannot provide an accurate molecular weight distribution for a polymer with significant levels of long chain branching for the following reasons. GPC separates polymer chains in solution according to their hydrodynamic volume(or mean square radius of gyration). When separating polymer chains in a mixture which contains some linear chains and chains with variable branch length and frequency, the contents of the GPC detector cell comprise chains with the same hydrodynamic volume but with possibly very different molecular weight. In fact there is a distribution of molecular weights in the detector cell, even when axial dispersion(instrumental spreading) is negligible. The detector(DRI ,UV or IR) gives the mass of polymer in the detector cell, however, one cannot assign a single molecular weight to the polymer in the detector cell and as a consequence GPC alone cannot provide a full MWD for a polymer with significant levels of long chain branching. Therefore to test the validity of the "instantaneous" property method which accounts for long chain branching as developed in this investigation, two approaches were used: The first was to compare $\overline{M}_n$, $\overline{M}_w$ and $\overline{B}_n$ calculated with the method of moments for the whole polymer(not accounting individually for polymeric species with 0,1,2,3,... long chain branches per polymer molecule) and to compare experimentally measured $\overline{M}_n$, $\overline{M}_w$ and $\overline{B}_n$ with these same quantities predicted using the "instantaneous" property method. This has been done and the comparisons are shown in Figures 6-8 and 6-9 and Table 6-1. In Table 6-1 the values determined by the method of moments are assumed to be the correct averages. It is clear that the agreement for $\overline{M}_n$, $\overline{M}_w$ and $\overline{B}_n$ are satisfactory and it can be concluded that the "instantaneous" property method which accounts for chain transfer to polymer is valid. It should be pointed out that the "instantaneous" property method provides a great deal of additional detailed information about the various branched species having 0,1,2,.... long chain branches per polymer molecule. This kind of information should greatly assist one in the development of quantitative relationships between long chain branching frequencies and rheological responses such as zero shear viscosity, shear thinning, elongational viscosity and delayed melt fracture for polymer flows in the melt.

Finally, it should be stated that the kinetic parameters used to predict the molecular weight averages and branching frequencies by the method of moments were established from the conversion versus time data in a manner similar to Chiantore and Hamielec(1985).

Table 6-1 Molecular weight averages calculated by the method of moments(Mom) and the Instantaneous method(Inst)

Conv. (%)	M_n (Mom)	M_n (Inst)	Error (%)	M_w (Mom)	M_w (Inst)	Error (%)
11.0	2.31E+05	2.35E+05	+1.7	4.01E+05	4.09E+05	+2.0
27.9	2.28E+05	2.32E+05	+1.8	4.2E+05	4.29E+05	+1.9
57.8	2.38E+05	2.36E+05	-0.8	5.15E+05	5.10E+05	-1.0
69.7	2.39E+05	2.35E+05	-1.7	5.56E+05	5.50E+05	-1.1
82.9	2.38E+05	2.34E+05	-1.7	5.99E+05	5.97E+05	-0.3

Figure 6-8: Bulk Thermal Polymerization of p-Methyl Styrene
Plot of Molecular weight vs. Conversion

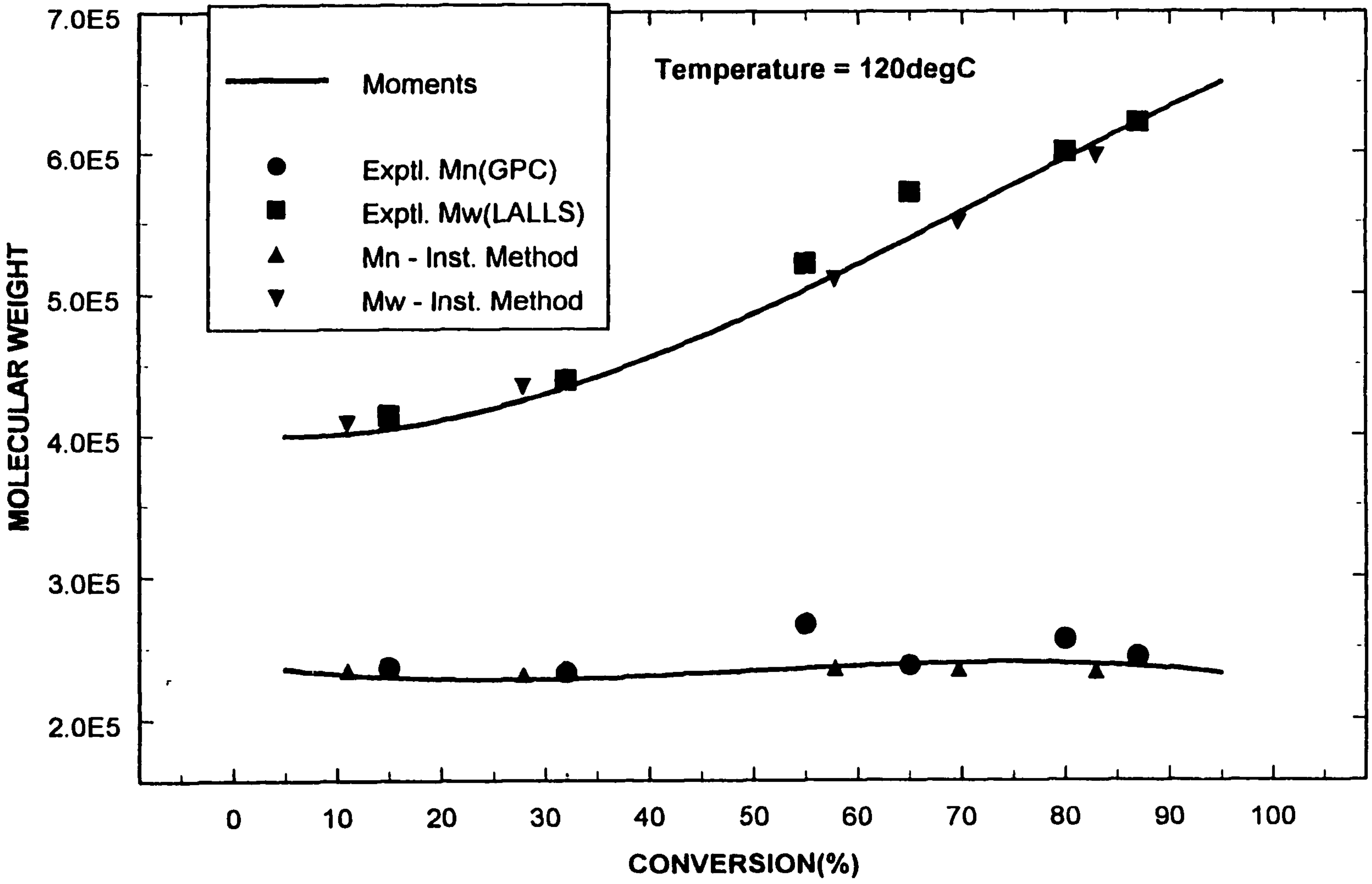
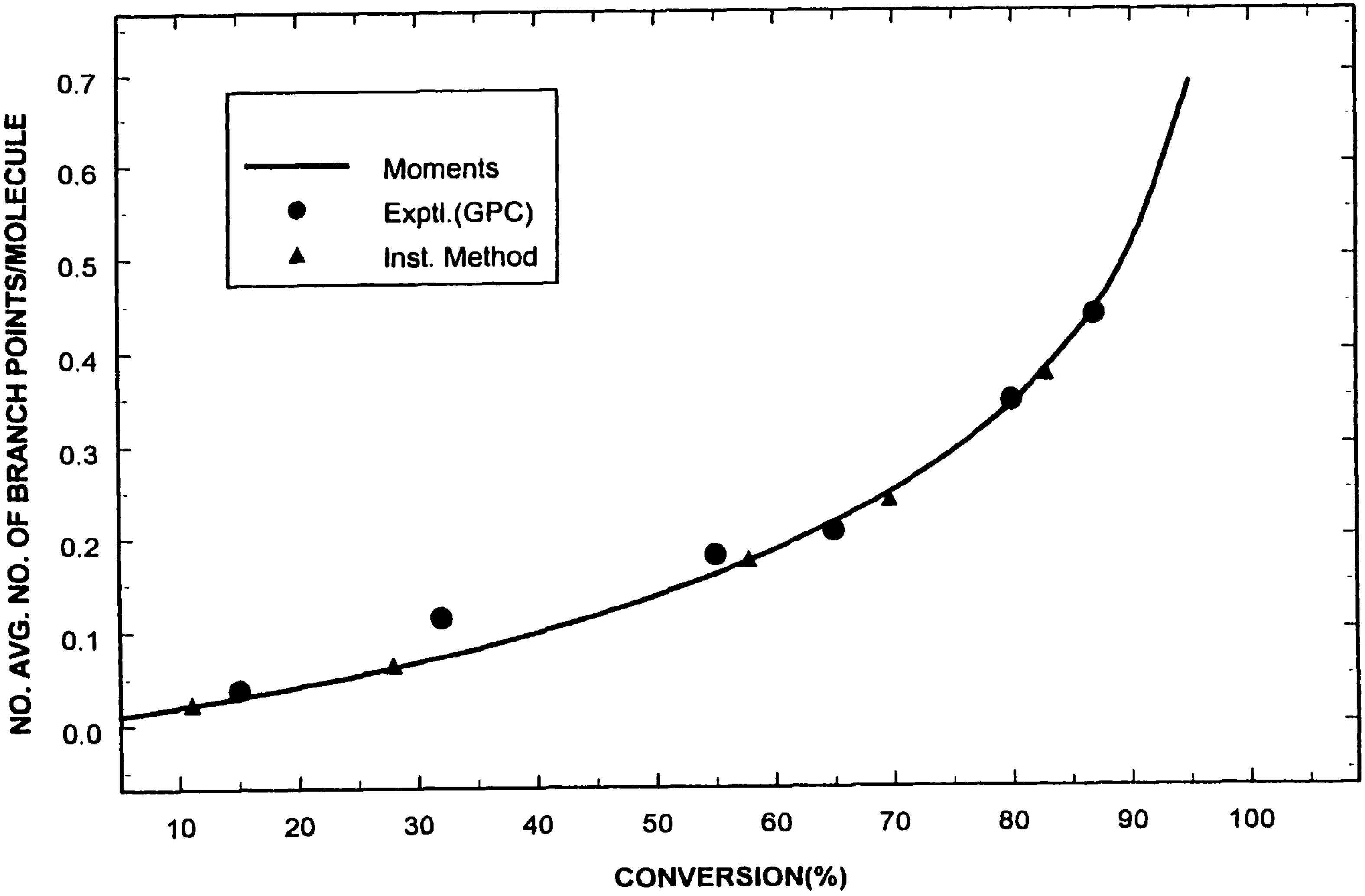


Figure 6-9: Bulk Thermal Polymerization of p-Methyl Styrene
Plot of No. Avg. No. of Branch Points/molecule vs. Conversion



CHAPTER 7

CONTRIBUTIONS , LIMITATIONS AND PROPOSED FUTURE RESEARCH

7.1 Contributions

(1) A new, rigorous and practical method, the "instantaneous" property method, has been developed to calculate the full molecular weight distribution of linear and branched species for polymers with long chain branching produced by free-radical chain growth polymerization where the long chain branching is due to chain transfer to polymer. All methods are based on the solution of the population balance equations for the polymeric species in the reactive system and these equations can consist of thousands of differential equations. The majority of previous methods utilized a transformation process(method of moments or Laplace Transform) with the consequent need for some type of inversion process to recover the molecular weight distribution. This inversion process is always less than adequate especially when the molecular weight distribution is complex. Our experience with the method of moments for the two monomer systems has shown that the calculation of weight average molecular weight and branching frequency is quite reliable. However this is not so for number average molecular weight. It is recommended that users of the method of moments should consider this. The numerical fractionation technique

proposed by Teymour and Campbell(1994) is the only recent practical method for the calculation of the molecular weight distribution for high branching frequency as gelation approaches. It however requires the use of an approximate moment closure technique and a distribution function for the chosen branched families.. The "instantaneous" property method does not require a moment closure technique. It was also shown that a method could be developed that combines the "instantaneous" property method with the numerical fractionation method to produce a powerful method for calculating molecular weight distributions from the population balance equations for kinetic schemes where long chain branching is due to chain transfer to polymer.

(2) Experimental data for long chain branching frequencies for two model polymers: PVAc where the long chain branching is due to two mechanisms, chain transfer to polymer and terminal double bond polymerization and PPMS where the long chain branching is due to a single mechanism, chain transfer to polymer, is presented. It was established that the Zimm-Stockmayer branching model can be used to determine long chain branching frequencies from GPC and intrinsic viscosity data using the MWBD method. It was shown that a branching exponent of $\varepsilon = 0.8$ for PVAc gave long chain branching frequencies consistent with those predicted by the method of moments.

(3) A method for calculating long chain branching frequency where GPC/DRI/LALLS data are available that takes into account the polydispersity in the detector cell(PD method) was developed. It was shown that when this method is applied to PVAc data, the long chain branching frequencies measured are consistent with the method of moments for $\varepsilon = 1.2$.

(4) The predictions of the "instantaneous" property method were successfully compared to the measured molecular weight averages and long chain branching frequencies for PPMS as well those determined by the method of moments.

(5) For PPMS, in the application of the MWBD method to calculate long chain branching frequency, a value of $\varepsilon = 0.5$ gave values consistent with the method of moments.

7.2 Limitations

(1) For polymers that have very large molecular weight species and a very high degree of branching, the "instantaneous" property method would be limited by the need to consider very large chain lengths and a large number of branched families. Such systems would require very large computer memory as well as significant computer time. It follows that the method as developed would have difficulty in computing molecular weight distributions for systems approaching gelation.

(2) The "instantaneous" method has herein been developed for polymeric species with long chain branching produced by transfer to polymer where polymer

radicals have only one radical centre per chain. This would limit its use to long chain branching frequency far below where gelation is approached. Also, it cannot be applied to polymer systems where additional or different mechanisms are responsible for producing long chain branching.

7.3 Proposed Future Research

(1) Priority should be given to developing solution techniques for the population balance equations that combine the "instantaneous" property method and the numerical fractionation method and account for multiple active centres as gelation is approached. This would produce a method that could possibly predict gelation.

(2) The development of the "instantaneous" method for a polymer such as PVAc where long chain branch formation is due to two mechanisms would be a useful extension of this work. The resulting method should be tested with the PVAc data provided in this thesis.

(3) A further development of the PD method for calculating LCB frequency from GPC/DRI/LALLS data can involve the use of other and possibly more appropriate distributions to describe the polydispersity in the detector cell.

APPENDIX A

BULK POLYMERIZATION OF VINYL ACETATE

Table A-1

Temperature = 60°C; AIBN conc. = 5.0×10^{-5}

Sample Number	Conversion (%)	Intrinsic Viscosity (dL g^{-1})
E1(a)	3.3	1.980
E2(e)	15.1	2.113
E3(c)	30.7	2.330
E4(f)	48.5	2.540
E5(b)	57.0	2.750
E6(c)	90.6	3.300

Table A - 2

Temperature = 80°C; AIBN conc. = 1.0×10^{-4}

Sample No.	Conversion (%)	Intrinsic Viscosity (dL g^{-1})
5-40(b)	13.9	1.245
5-80(b)	31.7	1.610
5-120(c)	46.2	1.780
5-160(e)	62.7	2.010
5-240(e)	80.0	2.300
5-360(b)	89.5	2.550

APPENDIX B

TYPICAL GPC DATA AND BRANCHING RESULTS

```
SAMPLE     PVAC  E1SMALLA
EXPERIMENTAL INTRINSIC VISCOSITY=  1.980
B= .15272E-04
CALCULATED INTRINSIC VISCOSITY=  1.980
CALC. MN= .41962E+06    CALC. MW(GPC)= .65793E+06
EL. VOL(V)      HT(V)        ETA-LIN(V)   ETA-BR(V)    BN(V)      FV(V)
       5.625   .10000E+00      5.668          5.657     .037    .42911E-02
       5.750   .19000E+01      4.775          4.766     .034    .81530E-01
       5.875   .74000E+01      4.022          4.015     .032    .31754E+00
       6.000   .14100E+02      3.388          3.382     .030    .60504E+00
       6.125   .21400E+02      2.853          2.849     .028    .91829E+00
       6.250   .25500E+02      2.403          2.400     .025    .10942E+01
       6.375   .25300E+02      2.025          2.022     .023    .10856E+01
       6.500   .21900E+02      1.705          1.703     .021    .93975E+00
       6.625   .18500E+02      1.436          1.435     .020    .79385E+00
       6.750   .14400E+02      1.210          1.209     .018    .61792E+00
       6.875   .11500E+02      1.019          1.018     .016    .49347E+00
       7.000   .87000E+01       .858           .858     .015    .37332E+00
       7.125   .61000E+01       .723           .723     .013    .26176E+00
       7.250   .44000E+01       .609           .609     .012    .18881E+00
       7.375   .26000E+01       .513           .513     .010    .11157E+00
       7.500   .16000E+01       .432           .432     .009    .68657E-01
       7.625   .80000E+00       .364           .364     .008    .34329E-01
       7.750   .50000E+00       .307           .307     .007    .21455E-01
       7.875   .00000E+00       .258           .258     .006    .00000E+00
NO. AVG. NO. OF BRANCH POINTS=   .018
AVG. NO. OF BRANCH POINTS PER 1000 CARBON ATOMS=   .002
MARK HOUWINK CONSTANTS:K= .51000E-04    A= .791
UNIVERSAL CAL.:LN(ETA.M)=D1+D2*V;  D1= .3390E+02  D2=-.3107E+01
MINIMUM MOLECULAR WT. FOR BRANCHING=  10000.0
MODEL EXPONENT= .50
```

```
SAMPLE     PVAC  E1SMALLA
EXPERIMENTAL INTRINSIC VISCOSITY=  1.980
B=  .15272E-04
CALCULATED INTRINSIC VISCOSITY=  1.980
CALC. MN=  .41962E+06     CALC. MW(GPC)=  .65793E+06
EL. VOL(V)      HT(V)       ETA-LIN(V)   ETA-BR(V)    BN(V)       FV(V)
        5.625   .10000E+00     5.668            5.657    .023    .42911E-02
        5.750   .19000E+01     4.775            4.766    .022    .81530E-01
        5.875   .74000E+01     4.022            4.015    .020    .31754E+00
        6.000   .14100E+02     3.388            3.382    .019    .60504E+00
        6.125   .21400E+02     2.853            2.849    .017    .91829E+00
        6.250   .25500E+02     2.403            2.400    .016    .10942E+01
        6.375   .25300E+02     2.025            2.022    .015    .10856E+01
        6.500   .21900E+02     1.705            1.703    .013    .93975E+00
        6.625   .18500E+02     1.436            1.435    .012    .79385E+00
        6.750   .14400E+02     1.210            1.209    .011    .61792E+00
        6.875   .11500E+02     1.019            1.018    .010    .49347E+00
        7.000   .87000E+01      .858             .858    .009    .37332E+00
        7.125   .61000E+01      .723             .723    .008    .26176E+00
        7.250   .44000E+01      .609             .609    .007    .18881E+00
        7.375   .26000E+01      .513             .513    .006    .11157E+00
        7.500   .16000E+01      .432             .432    .006    .68657E-01
        7.625   .80000E+00      .364             .364    .005    .34329E-01
        7.750   .50000E+00      .307             .307    .004    .21455E-01
        7.875   .00000E+00      .258             .258    .004    .00000E+00
NO. AVG. NO. OF BRANCH POINTS=   .011
AVG. NO. OF BRANCH POINTS PER 1000 CARBON ATOMS=   .001
MARK HOUWINK CONSTANTS:K= .51000E-04    A= .791
UNIVERSAL CAL.:LN(ETA.M)=D1+D2*V;  D1= .3390E+02  D2=-.3107E+01
MINIMUM MOLECULAR WT. FOR BRANCHING=   10000.0
MODEL EXPONENT= .80
```

```
EL. VOLUME     ...MN(V)...      ...MW(V)...
   5.625       .23914E+07      .82510E+07
   5.750       .19252E+07      .22530E+07
   5.875       .15498E+07      .15550E+07
   6.000       .12477E+07      .13570E+07
   6.125       .10044E+07      .11120E+07
   6.250       .80859E+06      .91500E+06
   6.375       .65094E+06      .76930E+06
   6.500       .52403E+06      .65750E+06
   6.625       .42187E+06      .56830E+06
   6.750       .33962E+06      .43580E+06
   6.875       .27340E+06      .36710E+06
   7.000       .22010E+06      .29260E+06
   7.125       .17719E+06      .21280E+06
   7.250       .14264E+06      .17410E+06
   7.375       .11483E+06      .18120E+06
   7.500       .92444E+05      .11030E+06
   7.625       .74421E+05      .73520E+05
   7.750       .59911E+05      .73000E+05
   7.875       .48231E+05      .72000E+05
 WT. AVERAGE MOL. WT.(LALLS)=  .76394E+06
```

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