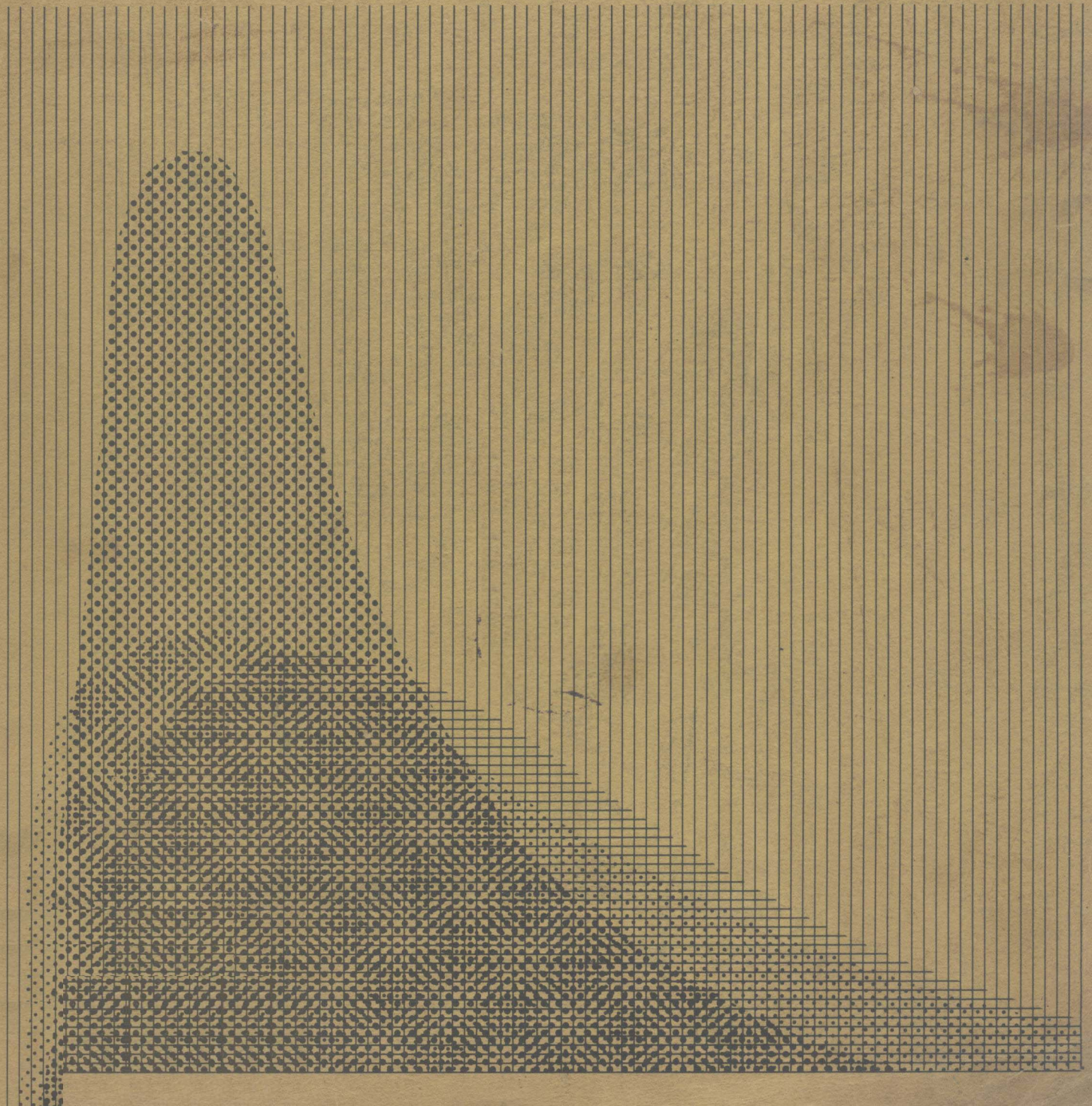# Polymer
Reactor
Engineering

POLYMER REACTOR ENGINEERING

A symposium sponsored jointly by the Macromolecular

Sciences Division of the Chemical Institute of Canada

and the Canadian Society for Chemical Engineering at

the 55th Chemical Conference and Exhibition of the

Chemical Institute of Canada, Quebec City, Quebec,

June 4 - 7, 1972

SYMPOSIUM ON

POLYMER REACTOR ENGINEERING

Laval University, Quebec City

Monday, June 5, 1972

PROGRAMME:

Morning Session

A. POLYMERIZATION KINETICS - Chairman : K. F. O'Driscoll
                                            University of Waterloo

9.00   Mathematical Modelling Techniques   : W. H. Ray
                                                   State University of New York
                                                   at Buffalo

9.30   Branch Formation During Polymerization   : W. W. Graessley
                                                   Northwestern University

10.00 Copolymerization   : K. F. O'Driscoll
                                                   University of Waterloo

10.30 Mechanism of Emulsion Polymerization   : J. L. Gardon
                                                   M & T Chemicals Inc.
                                                   Rahway, N.J.

11.00 Gel Effect in Vinyl Polymerization   : A. E. Hamielec
                                                   McMaster University

Afternoon Session

B. REACTOR DESIGN, SIMULATION AND OPTIMIZATION -

                                 Chairman   : A. E. Hamielec
                                                McMaster University

1.30   Mixing in Polymer Reactors   : E. B. Nauman
                                                 Union Carbide Corp.
                                                 Bound Brook, N.J.

2.00   Polymerization in Tubular Reactors   : J. A. Biesenberger
                                                 Stevens Institute
                                                 Hoboken, N.J.

2.30   Continuous Emulsion Polymerization   : G. W. Poehlein
                                                 Lehigh University

3.00   Design of Polymer Reactors   : B. Brasie,
                                                 Dow Chemical Co.
                                                 Midland, Michigan

3.30   Optimization of Polymer Reactors   : C. M. Crowe
                                                 McMaster University

"Mathematical Modelling Techniques"

W. Harmon Ray
Department of Chemical Engineering
State University of New York at Buffalo
Buffalo, New York, 14214

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Chapter 5   Some Practical Examples

5.1 Introduction

5.2 The Polycondensation of A-B Type Monomer

5.3 The Free Radical Polymerization of Styrene

5.4 Some Other Applications

5.5 Concluding Remarks

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Chapter 1 Introduction

As commercially produced polymers become more of a commodity
product, rather than a speciality product, there is a growing
need for a more detailed understanding of the phenomena taking
place in the polymer reactor. One quantitative form of this pro-
cess understanding is the mathematical model, which can represent
the detailed behaviour of a polymer reactor. The mathematical
model is an invaluable tool for developing the optimal design
and optimal control system for these reactors.

Because polymerization reactions are usually very complex in
nature, a reasonable amount of mathematical sophistication is re-
quired for detailed modelling. This paper will be devoted to re-
viewing some of the mathematical techniques which prove useful in
constructing these models.

The second chapter deals with methods of producing the molecular
weight distribution (MWD) of both homopolymer and copolymer systems
by analysis of the kinetic mechanism. The third chapter discusses
the less detailed characterization of the polymer available through
MWD moments, and develops straightforward methods for deriving the
moment equations. Chapter four considers the prediction of co-
polymer composition distributions and chain sequence distributions
from the kinetic scheme. A number of practical examples are given
in Chapter five in order to emphasize to the reader that all of
these mathematical manipulations are in fact practical. Finally,
a number of more complicated polymerization reactor systems -
some of which require further work to produce an adequate model
are discussed.

Chapter 2   Techniques for the Calculation of Differential Molecular Weight Distributions

2.1 Differential Distributions

The distribution of molecular weights in a polymeric material may be represented as a density function or "differential" distribution. For example, the comcentration of polymer of chain length n, P_n is shown as a discrete differential distribution in Figure 2-1. Although there are no values of P_n except for integer values of n, a smooth curve results from the numerous points on the graph. Thus we shall use a continuous graph to represent the differential distributions in this paper.

There are a number of differential distributions which fall under the generic title "molecular weight distributions". The plot of P_n vs n shown in Figure 2-1 is more precisely the "number chain length distribution" (NCLD), because it represents the chain length distribution with respect to the number of molecules (per unit volume). Similarly, the "weight chain length distribution" (WCLD), shown in Figure 2-2, represents the chain length distribution with respect to the weight of molecules (per unit volume), nwP_n. There is also a "number molecular weight distribution" (NMWD), shown in Figure 2-3, in which the number of molecules/ unit volume, P_n, is given as a function of molecular weight. Finally, the "weight molecular weight distribution" (WMWD) is shown in Figure 2-4.

These distributions become rather more complicated for co-polymerization systems where there are two or more chain lengths
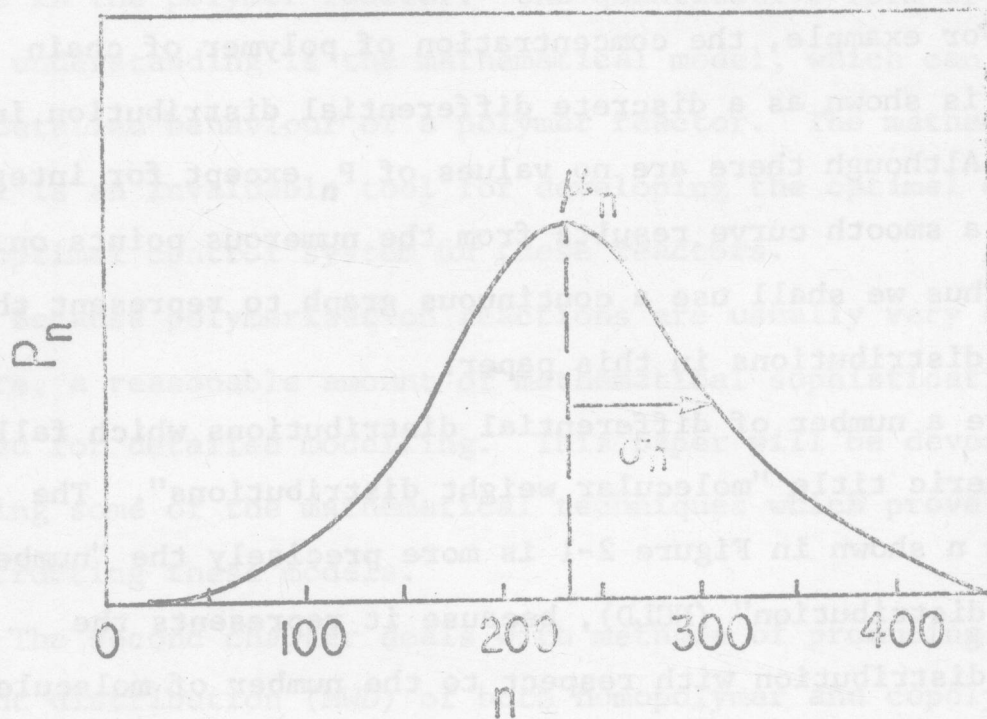
P_n

μ_n

σ_n

0   100   200   300   400

n

Figure 2.1 The number chain length distribution (NCLD)

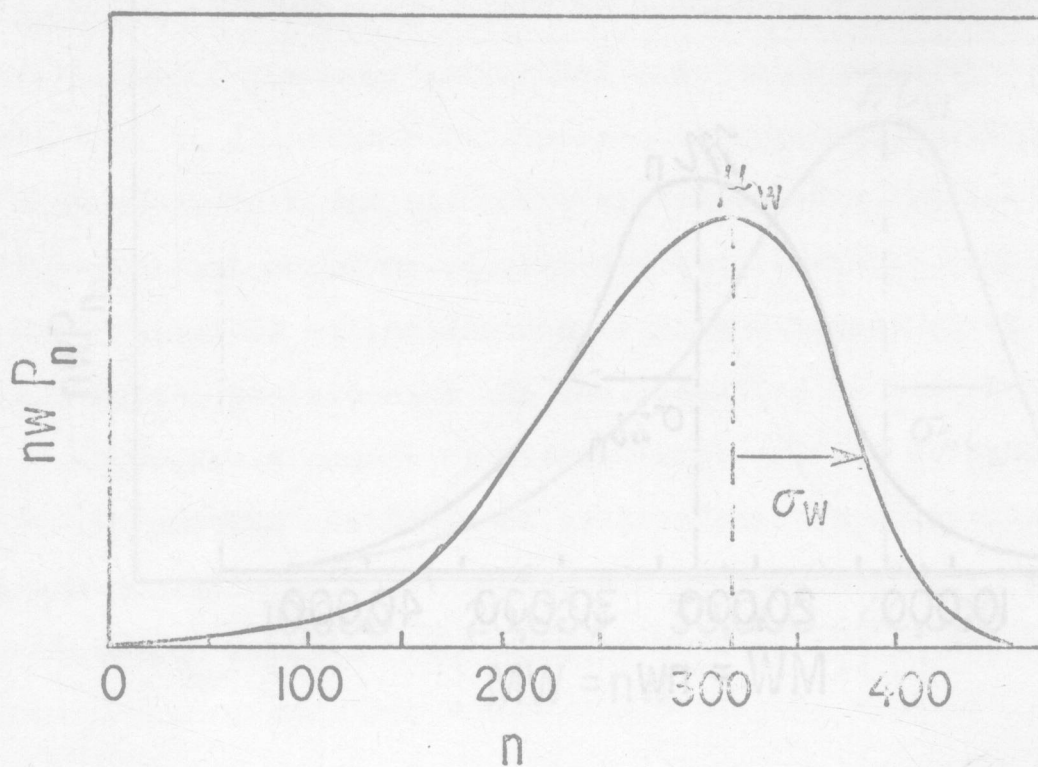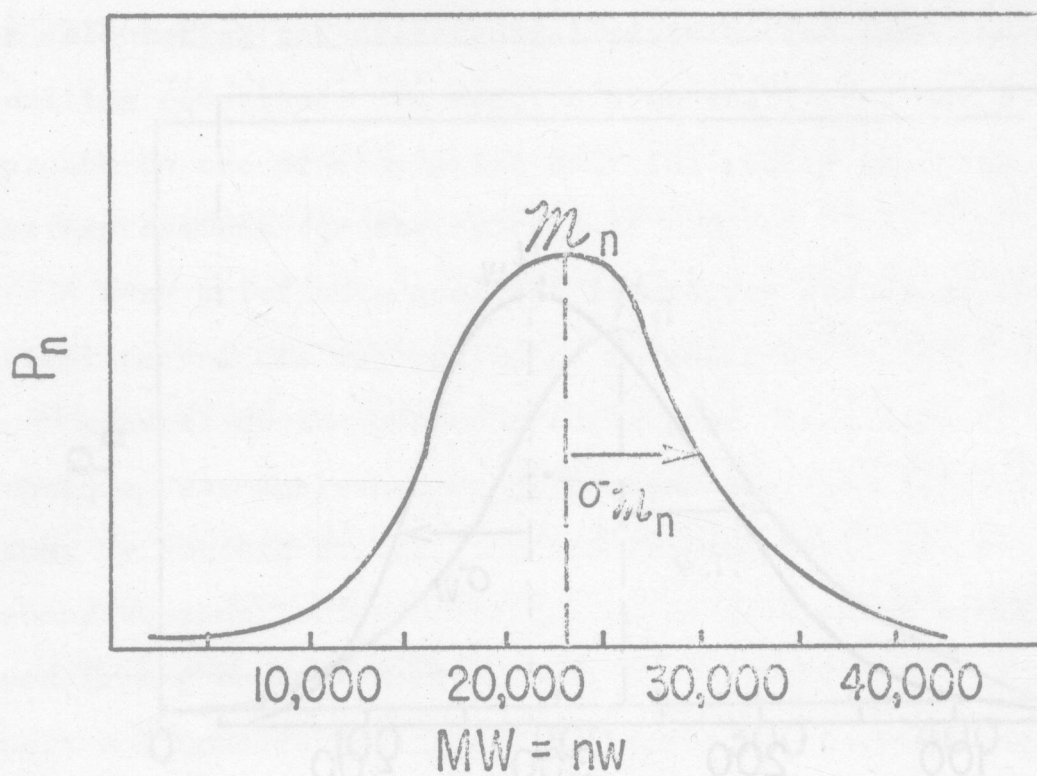Figure 2.2   The weight chain length distribution (WCLD)

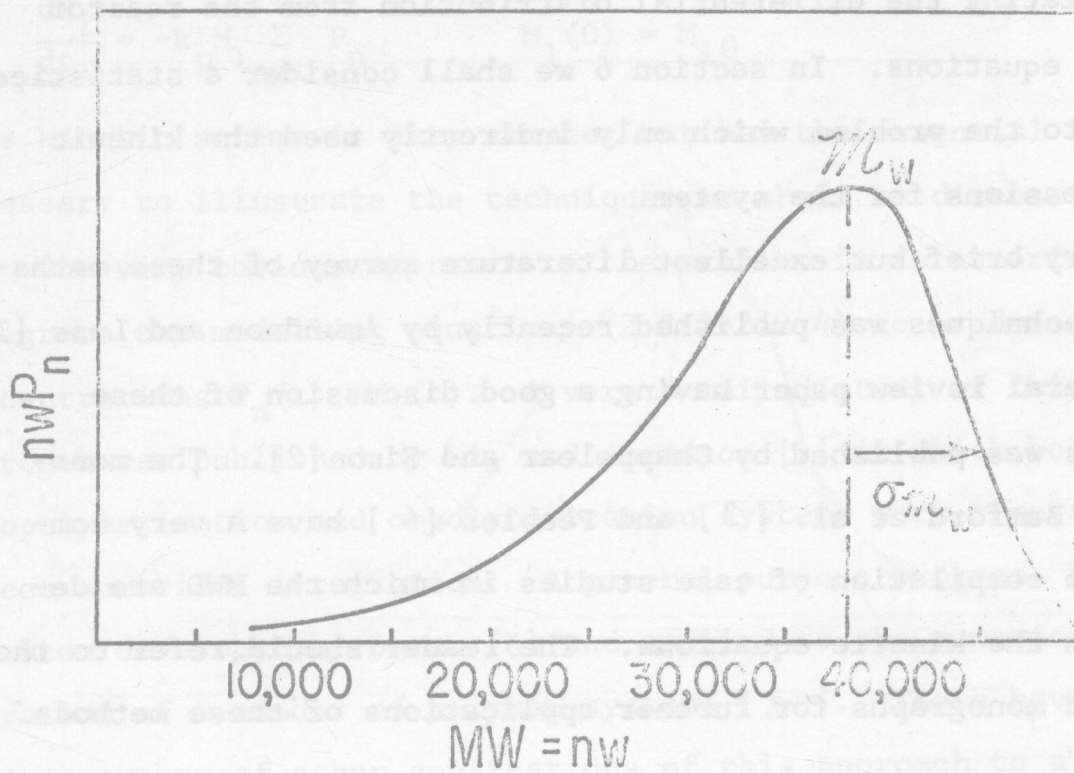Figure 2.3 The number molecular weight distribution (NMWD)

Figure 2.4 The weight molecular weight distribution (WMWD)

and molecular weights of interest. These systems will be discussed in more detail in section 7 of this chapter.

The next few sections will deal with a number of techniques for calculating the differential distribution from the reactor modelling equations. In section 6 we shall consider a statistical approach to the problem which only indirectly used the kinetic rate expressions for the system.

A very brief but excellent literature survey of these mathamatical techniques was published recently by Amundson and Luss [1]. A more general review paper having a good discussion of these techniques was published by Chappelear and Simon [2]. The monographs by Bamford et al. [3] and Peebles [4] have a very comprehensive compilation of case studies in which the MWD are derived from the kinetic equations. The reader should refer to these papers and monographs for further applications of these methods.

2.2 Numerical Integration

Let us consider the very simple mechanism which might arise in anionic polymerization with very rapid initiation.

$$P_n + M_1 \xrightarrow{k_p} P_{n+1} \qquad n = 1,2... \qquad (2.2.1)$$
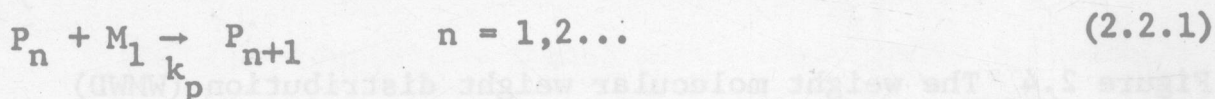
where P_n represents the growing polymer chain and M_1 is the monomer. The polymer material balances for a batch reactor yield the equations

$$\frac{dP_1}{dt} = -k_p M_1 P_1 \qquad P_1(0) = P_{10} \qquad (2.2.2)$$

$$\frac{dP_n}{dt} = -k_p M_1 (P_n - P_{n-1}) \qquad P_n(0) = 0 \qquad (2.2.3)$$

with the additional monomer balance

$$\frac{dM_1}{dt} = -k_p M_1 \sum_{n=1}^{\infty} P_n \qquad M_1(0) = M_{10} \qquad (2.2.4)$$

This kinetic scheme is very simple, but has the essential features necessary to illustrate the techniques we shall be discussing.

One very obvious approach to the problem is to numerically integrate the modelling equations (2.2.2-2.2.4) to produce the concentrations $P_n(t)$, $M_1(t)$. A very detailed study of this approach was published by Liu and Amundson [5] in which both homopolymerization and copolymerization systems were simulated by direct numerical integration. A general purpose program, REMECH, has been developed by Detar [6] and applied to the numerical integration of a number of polymer systems [7-8]. There have been a large number of other applications of this approach to a wide variety of polymer systems (eg; 9-11).

A simplication arises when Eq'ns 2.2.2-2.2.3 are summed to produce

$$\frac{dP}{dt} = 0 \qquad (2.2.5)$$

where $P = \sum_{n=1}^{\infty} P_n$. Thus for this problem $P = P_{10}$ at all times. The fact that P can be determined independently means that Eqn's (2.2.2-2.2.3) can now be solved sequentially rather than requiring simultaneous solution. This type of simplification can be applied to most polymerization systems and has been overlooked in a number of the papers cited above.

Another transformation which is useful is the stretching of the time variable by the relation

$$\tau = \int_0^\tau k_p M_1 dt \qquad (2.2.6)$$

This reduces 2.2.2-2.2.3 to

$$\frac{dP_1}{d\tau} = -P_1 \qquad P_1(0) = P_{10} \qquad (2.2.7)$$

$$\frac{dP_n}{d\tau} = -(P_n - P_{n-1}) \qquad P_n(0) = 0 \qquad n \geq 0 \qquad (2.2.8)$$

which can be solved in terms of the stretched variable τ. The influence of monomer changes, temperature variations, etc. only appear in the relationship (2.2.6) between τ and batch time, t.

One could now solve Eq'ns (2.2.7,2.2.8) sequentially for n as large as desired. A detailed example of this approach will be given in Chapter 5.

2.3. Generating Functions

An approach which has wide use in polymer kinetics and which can be used to produce the differential MWD is the generating function technique. Scanlan [12] appears to be the first to suggest it's use in polymer systems. Bamford and Jenkins [13] and Liu and Amundson [14] give rather good discussions of its application to polymerization.

Let us consider the system (2.2.7,2.2.8) written in terms of t (we suppress the tau for the moment).

$$\frac{dP_1}{dt} = -P_1 \qquad P_1(0) = P_{10} \tag{2.3.1}$$

$$\frac{dP_n}{dt} = -P_n + P_{n-1} \qquad P_n(0) = 0 \quad n \geq 2 \tag{2.3.2}$$

The generating function for this system is defined as

$$G(s,t) = \sum_{n=1}^{\infty} s^n P_n(t) \tag{2.3.3}$$

The equations for $G(s,t)$ in the batch reactor for the simple system (2.3.1-2) can be gotten by multiplying each equation by s^n and summing over n to yield

$$\frac{dG(s,t)}{dt} = (s-1) \ G(s,t) \ ; \quad G(s,0) = sP_{10} \tag{2.3.4}$$

This can be immediately solved to yield
$$G(s,t) = \exp(-t) \ sP_{10} \ \exp(st) \tag{2.3.5}$$

which when expanded in a power series in s gives

$$G(s,t) = P_{10} \exp(-t) \sum_{n=1}^{\infty} \frac{(t)^{n-1}}{(n-1)!} s^n \tag{2.3.6}$$

by comparison of this with the definition (2.3.3) one gets

$$P_n(t) = P_{10} \exp(-t) \frac{(t)^{n-1}}{(n-1)!} \ ; \ n \geq 1 \tag{2.3.7}$$

It is not always necessary to expand $G(s,t)$ in a power series to get the solution $P_n(t)$ because a table of generating functions and their inverses can be found in Erdelyi [15].

A number of recent papers have used generating functions to generate the differential distribution [eg. 16-17]. Some further applications of this technique will be discussed later in this paper.

2.4. Z Transforms

A technique which is nearly identical to the generating function technique involves the use of Z transforms [18] which are defined as

$$F(z) = \sum_{n=o}^{\infty} P_n z^{-n} \tag{2.4.1}$$

and which can be applied in the same way as the generating function. If we consider again the simple example (2.3.1-2), then by taking the Z-transform one obtains

$$\frac{dF(z,t)}{dt} = \left(\frac{1}{z} - 1\right) F(z,t) \; ; \quad F(z,0) = \frac{P_{10}}{z} \tag{2.4.2}$$

whose solution is

$$F(z,t) = \frac{P_{10}}{z} \exp(-t) \exp\left(\frac{t}{z}\right) \tag{2.4.3}$$

expanding into a power series in $1/z$

$$F(z,t) = P_{10} \exp(-t) \sum_{n=1}^{\infty} \frac{(t)^{n-1}}{(n-1)!} z^{-n} \tag{2.4.4}$$

and comparing coefficients, one obtains the differential distribution

$$P_n(t) = P_{10} \exp(-t) \frac{(t)^{n-1}}{(n-1)!} \; ; \quad n \geq 1 \tag{2.4.5}$$

One possible advantage of Z-transforms over the generating function is the existence of more extensive tables of the Z-transform and inverses [18]. Abraham [19-20] and Kilkson [21-22] have applied this method to a number of practical problems. The most interesting recent application of this method was reported by Chen and Spencer [23]. Their work shows that it is possible to extract numerical