The synthesis and crystallisation of narrow-distribution polymers of tetrahydrofuran

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THE SYNTHESIS AND CRYSTALLISATION

OF NARROW DISTRIBUTION POLYMERS

OF TETRAHYDROFURAN

by

T. G. CROUCHER

Supervisors: Dr. R. E. WETTON
Dr. D. S. BROWN

A doctoral thesis submitted in partial fulfilment of
the requirements for the award of the Degree of
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ORIGINALITY

The work presented in this thesis has been carried out by the author, except where otherwise acknowledged, and has not previously been submitted to this University or any other Institution for a higher degree.
ABSTRACT

Tetrahydrofuran (THF) may be polymerised cationically by suitable initiators via a ring-opening mechanism to give linear, high molecular weight products which normally have a broad molecular weight distribution. Factors affecting the molecular weight distribution are discussed, and pertinent kinetic experiments are described, which allow the formulation of a procedure of synthesising monodisperse polymers of THF. It was found that the major causes of broadening were propagation - depropagation equilibria, chain transfer to polymer oxygen and slow initiation.

When p-chlorophenyl diazonium hexafluorophosphate was used as initiator, a high initiation temperature followed by rapid quenching to a low propagation temperature, together with low conversion gave the required monodispersity. Kinetics of propagation were investigated over a wide temperature range, -10\(^\circ\)C to 80\(^\circ\)C, and the variation of \(k_p\) with temperature found to follow an Arrhenius expression with an activation energy of 51 kJ mol\(^{-1}\). When using triethyloxonium hexafluorophosphate as initiator, no separate initiation stage was necessary, the reaction proceeding at -5\(^\circ\)C to yield monodisperse polymers directly at low conversions.

A series of monodisperse, low molecular weight samples were studied under isothermal crystallisation conditions at 16\(^\circ\)C and 24\(^\circ\)C by several techniques. Dilatometry followed the specific volume change of a sample during crystallisation, polarising optical microscopy was used to evaluate growth rates and the morphological features of crystallites, and differential thermal analysis to investigate the melting points and heats of fusion of the samples. Wide angle and small angle X-ray diffraction techniques have
been employed, wide angle to give a measure of the weight fraction of crystallinity, and small angle to provide much detailed information on the structural parameters of the semi-crystalline polymers. In particular by matching the experimental correlation function derived from the small angle scattering curve with a theoretical correlation function generated from a lamellar model, the volume fraction of crystallinity, the crystalline lamellar thickness, the amorphous region thickness and the distributions of these thicknesses were obtained.

The degree of crystallinity (\(\phi\)) was generally found to be high (\(\phi = 0.70\)) for molecular weights below 5300, decreasing sharply at higher molecular weights to a more constant region (\(\phi = 0.55\)). Also \(\phi\) increased with time under isothermal conditions, but secondary crystallisation at different temperatures for long times (4 weeks) achieved similar \(\phi\) values. The lamellar thickness (\(c\)) was high (e.g., 90 \(\AA\)) below 5300 molecular weight, decreasing sharply above this molecular weight (e.g., 80 \(\AA\)) followed by a slow increase. As with the degree of crystallinity, \(c\) increased with secondary crystallisation, but unlike \(\phi\) it attained higher values with decreasing supercooling (e.g., higher crystallisation temperatures).

Growth rates at constant crystallisation temperature were found to increase with increasing molecular weight, pass through a maximum at molecular weight approximately 7000 after which they slowly declined. Melting points were found to increase with increasing lamellar thickness, and estimates of \(T_m^0\) (thermodynamic melting point of an infinitely thick crystal) and \(\sigma_e\) (end surface free-energy of a crystal) were made; both were found to increase with increasing molecular weight.
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CHAPTER 1. INTRODUCTION
Semi-crystalline polymers such as poly(ethylene) and poly(propylene) play an increasingly important role as engineering materials, and as such, any fundamental process affecting the properties of these polymers requires detailed investigation to permit the necessary understanding of the mechanism. Such a process in these materials is crystallisation, where certain polymer chains or portions thereof aggregate in some manner to give rise to a two-phase system comprising crystalline and amorphous regions. Not only is it necessary to perceive the development of the original crystallites, but also to discover the effect upon them of such variables as time, temperature, pressure and molecular weight.

The conception of polymeric crystals has changed over the years with technological developments giving new and more sophisticated methods of gathering even more accurate experimental data. When the macromolecular nature of polymers became accepted, a model based on the fringed micelle (1) enjoyed popularity for some time, (see Figure 2.3.1), because it gave a simple understanding of certain properties of polymers, such as mechanical strength due to the strong bonding between the crystalline and amorphous regions. However, the formation of ringed spherulites from a polymer melt, coupled with the discovery that spherulites are complex structures of almost macroscopic lamellae, (thin ribbons of crystalline material), suggested it was no longer sufficient to treat the observed broadening of polymer X-ray diffraction patterns as being due solely to small crystallite size (2), rather that a defected lattice structure was present.

The discovery of polymer single crystals grown from solution, independently reported in 1957 by Keller, Fischer and Till (3, 4, 5), was an important step in recognising the nature of crystallinity in polymers.
Electron microscope studies showed the crystals to be thin, flat platelets about 100 Å thick, but much larger in their other dimensions, and these structures are known as lamellae. It was noted from the electron diffraction studies that the polymer chains (at least 1000 Å long) were oriented normally to the plane of the lamellae (about 100 Å thick). This was explained by Keller (3) as signifying that the chains were folded back upon themselves. The recognition from electron diffraction work that polymers crystallised from the melt were composed of similar structures, lamellae, which in turn make up spherulites, is now universally accepted as the mode of bulk crystallisation of all flexible polymers (1).

A consequence of the chain folding model of crystallisation which remains controversial is the nature of the surface of the lamellae, that is whether sharp chain folding with adjacent re-entry or 'switchboard' (large folds with non-adjacent re-entry) models apply. For single crystals grown from solution it is now widely accepted (6), from evidence such as Moire fringes, that the sharp chain folding model is correct. In bulk crystallisation however such a generalisation is not permissible. Such models are discussed in detail later in the text where they are seen to be relevant to the work accomplished for this thesis. It has also been reported that polymers may crystallise from the melt in the form of chain-extended crystals (7, 8) where the crystal thickness approximately equals the extended chain length. This phenomenon is dependent upon conditions of crystallisation, such as temperature and pressure, and is also assumed to be attained more easily by low molecular weight polymers.

Theoretical treatment of the crystallisation based on kinetics of surface nucleation, following Lauritzen and Hoffman (9), allow predictions of initial lamellar thickness (C*) and growth rate (G),
which agree reasonably well with experimentally determined values. Detailed derivations and symbol definitions are given in Section 2.3, but qualitatively it may be noted that both $C^*$ and $G$ depend upon $1/\Delta T$, where $\Delta T$ is the degree of supercooling. This proportionality has been determined experimentally from studies on the growth of single crystals of poly(ethylene) from different solvents (10). However estimation or even definition of the true $T_m^0$ value itself is often difficult and poorly achieved in published work.

Much work has been performed upon crystallising poly(ethylene), (e.g., 3, 4, 5, 10), and these studies form the basis for the theory of crystallisation previously mentioned. Poly(ethylene) attains a high degree of crystallinity, 0.7 to 0.95 (11), whereas the subject of the present study, poly(tetrahydrofuran) = P(THF) = only attains values of up to 0.5 for high molecular weight polymer. Thus it was thought to be worthwhile to investigate the crystallisation behaviour of low molecular weight P(THF) with time, temperature and molecular weight as variables. This study forms the basis of the crystallisation work presented herein.

Synthesis of samples of low molecular weight P(THF) was first necessary, and as molecular weight itself was intended to be a variable, it was desired to produce samples having a narrow molecular weight distribution, e.g., $M_n/M_w \leq 1.1$. Tetrahydrofuran has been shown to polymerise cationically (12), and had also been shown to be a 'living' polymerisation
under rigorous conditions. In principle then, by analogy with anionic systems, it should have been straightforward to produce low molecular weight monodisperse samples of P(THF). However, it was found to be an exacting task requiring detailed study of reaction conditions to enable complicating factors, which do not significantly contribute to anionic systems, to be singled out and removed (or minimised) from the system prior to the preparation of the required polymers. Although discussed in more detail in Section 2.1, the factors found to cause molecular weight broadening in the polymerisation of THF were briefly:

1. Equilibrium effects caused by the reversible nature of the polymerisation.

2. Chain transfer reactions, notably to in-chain oxygen atoms.

3. Slow rate of initiation compared to propagation.

Two initiators were used for polymerisations, p-chlorophenyldiazonium hexafluorophosphate, whose complex initiation reaction is not fully understood, (initiator 'P'), and triethyloxonium hexafluorophosphate, whose initiation reaction is simple, (initiator 'T'). Samples prepared from these initiators carry the suffix P or T, to demonstrate from which compound they were prepared, and the sample numbers indicate their number average molecular weights, $M_n \times 10^{-3}$, i.e., T/3.3 represents triethyloxonium salt initiator having $M_n = 3300$. Using initiator P it was necessary to employ special reaction schemes to obtain monodisperse samples.
CHAPTER 2.  THEORY
2.1 THE POLYMERISATION OF TETRAHYDROFURAN

The polymerisation of tetrahydrofuran (THF) was first reported by Meerwein (14, 12) in 1939, since then it has been recognised as an equilibrium living polymerisation - no termination reactions being present under appropriate experimental conditions. Evidence for this lack of termination has been summarised by Dreyfuss and Dreyfuss (13), and a demonstration of the dependence of the position of equilibrium on temperature has recently been given by Leonard and Maheux (15).

Following the treatment of Dainton and Ivin for reversible addition polymerisation (16,17), it is found that the overall rate of polymerisation, which is assumed equal to the rate of disappearance of monomer, depends upon the rates of propagation and depropagation.

Propagation Reaction
\[ M_j^* + M_1 \xrightarrow{k_p} M_{j+1}^* \]  \hspace{1cm} 2.01

Depropagation Reaction
\[ M_j^* \xrightarrow{k_d} M_{j-1}^* + M_1 \]  \hspace{1cm} 2.02

where \( M_1 \) represents monomer,
\( M_j^* \) represents the active polymer species, and
\( k \) represents the reaction rate constant.

If \[ [P^*] = \sum_{j=1}^{\infty} [M_j^*] \]  \hspace{1cm} 2.03

(the total concentration of active chain-ends)
then the rate of propagation is given by:
\[ R_{pr} = k_p [M_1] [P^*] \]  \hspace{1cm} 2.04

and the rate of depropagation is given by:
\[ R_{dp} = k_d [P^*] \]  \hspace{1cm} 2.05

Combining these expressions yields the overall rate of polymerisation:
\[
\frac{-d[M_n]}{dt} = R_{pr} - R_{dp} = (k_p [M_1] - k_d) [P^*]
\]

since

\[
k_d = k_p [M_1]_e
\]

equation 2.06 becomes

\[
\frac{-d[M_n]}{dt} = k_p ([M_1] - [M_1]_e) [P^*]
\]

which upon integration yields

\[
\ln \frac{[M_1]_{t2}}{[M_1]_{t1}} = k_p \int_{t1}^{t2} [P^*] \, dt
\]

A method of determining \(\int_{t1}^{t2} [P^*] \, dt\) has been developed by Saegusa et al (18) who have used equation 2.09 to describe the polymerisation kinetics using several different initiators. If \(\int_{t1}^{t2} [P^*] \, dt\) is not available the assumption is generally made that the concentration of living chain-ends equals the concentration of initiator which has reacted,

\[
\int_{t1}^{t2} [P^*] \, dt = ([I]_{t1} - [I]_{t2}) (t_2 - t_1)
\]

If \(t_1 = 0\) and initiation is rapid then at \(t_2 = t\)

\[
\int_{0}^{t} [P^*] \, dt = [I]_0 t
\]

where \([I]_0\) is the concentration of initiator charged.

Upon rearrangement equation 2.09 now becomes:

\[
2.303 \log \frac{[M_1] - [M_1]_0}{[M_1]_t - [M_1]_e} = k_p t
\]

and a plot of the LHS against time should yield a straight line of slope \(k_p (1 \text{ mol}^{-1} \text{ sec}^{-1})\). Many workers have presented results in this form
using different initiators and at different temperatures (19). It is apparent that at a given temperature $k_p$ for bulk polymerisation is reasonably independent of counter-ion. If the variation of $k_p$ with temperature is examined via an Arrhenius expression (section 2.1.2), an activation energy of approximately 50 kJ mol$^{-1}$ is obtained (20).

### 2.1.1 The Ceiling Temperature

Thus the polymerisation of THF is an equilibrium reaction:

$$
M_j^* + M_j \xrightarrow{k_p} M_{j+1}^* - \xrightarrow{k_d}
$$

and

$$
\frac{k_p}{k_d} = K = \frac{[M_{j+1}^*]}{[M_j^*][M_j]} = \frac{[P^*]}{[M_j][P]}
$$

where $K$ is the equilibrium constant for the reaction, and $[M_j^*]_{eq}$ is the equilibrium monomer concentration, (the concentration of monomer which must remain unreacted at equilibrium). The equilibrium monomer concentration varies with temperature as described by the equation:

$$
[M_j^*]_{eq} = \exp \frac{\Delta G_p^o}{RT}
$$

where $\Delta G_p^o$ is the free energy change upon the conversion of 1 mol of monomer in solution to 1 base-mol of polymer in solution, the monomer concentration being 1 M.

For equilibrium at a given reaction temperature the overall rate of disappearance of monomer is zero, and we have high polymer in equilibrium with a given concentration of monomer - this concentration being $[M_j^*]_{eq}$. 
at that temperature. If the initial concentration of monomer is below $[M_1]$ for that temperature then conversion to high polymer cannot occur. Similarly if the monomer concentration is maintained constant (eg. as in bulk polymerisation) and the temperature is raised, eventually $[M_1]$ increases to equal $[M_1]$ initial. At this critical temperature (the ceiling temperature) and above, conversion to high polymer is not possible, (eg. all the monomer present in the system prefers to remain as monomer rather than polymer). The ceiling temperature for the bulk polymerisation of THF is $85 \pm 2^\circ C$ (13). Since at equilibrium the overall rate of polymerisation is zero, we have:

$$\frac{d[M_1]}{dt} = 0 \quad \Rightarrow \quad R_p = R_d$$  \hspace{1cm} (2.17)

and

$$k_p [M_1] = k_d$$  \hspace{1cm} (2.18)

where $[M_1]$ has become $[M_1]$ for that temperature. Since polymerisation ceases at the ceiling temperature the change in free energy for the process ($\Delta G_p$) has changed from a negative value (allowing polymerisation to occur) to zero, above the ceiling temperature $\Delta G_p$ becomes positive. Thus:

$$\Delta G_p = \Delta H_p - T\Delta S_p$$  \hspace{1cm} (2.19)

Since $\Delta G_p = 0$ then $T_c = \frac{\Delta H_p}{\Delta S_p}$  \hspace{1cm} (2.20)

where $T_c$ is the ceiling temperature, and the states of the thermodynamic functions are defined by the prevailing experimental conditions. When $\Delta H_p$ and $\Delta S_p$ are both negative then the above situation will occur giving rise to a ceiling temperature. If $\Delta H_p$ and $\Delta S_p$ are both positive, then the reverse effect occurs - polymerisation only occurs above a certain minimum 'floor temperature'. When $\Delta H_p$ is positive and $\Delta S_p$ is negative no polymerisation is possible under any conditions, and if $\Delta H_p$ is negative and $\Delta S_p$ is positive polymerisation may occur at all temperatures.
2.1.2 Variation of Rate Constants with Temperature

At low reaction temperatures, and hence low \([M_1]_e\) values, the position of equilibrium is well to the right in equation 2.13, (e.g. 75% conversion to polymer (21) at 25°C), but as the temperature is raised the position of equilibrium shifts further and further left until, at \(T_c\), it moves completely to the left where no polymerisation can occur, and equation 2.17 is obeyed. At low temperatures and in the early stages of the reaction before equilibrium is approached, \(k_p[M_1]\) is greater than \(k_d\), giving a finite overall reaction rate. As the temperature is increased however \(k_d\) increases more rapidly than \(k_p[M_1]\) until, at the ceiling temperature, \(k_p[M_1] = k_d\), i.e. equilibrium is reached immediately and is completely to the left of equation 2.13.

**FIGURE 2.1.1**

![Diagram](image)

Figure 2.1.1 shows a typical plot of the variation of either the overall rate of polymerisation or the per cent conversion with temperature (17), from which it may be seen that at low temperatures \(k_p[M_1]\) is the main contributor to the overall rate, but as the temperature increases \(k_d\) increases more rapidly until the overall rate passes through a maximum and falls to zero at \(T_c\).
The variation of the rate constants with temperature may be expressed by Arrhenius equations:

\[
\begin{align*}
    k_p &= A_p \exp \left( -\frac{H_{pr}}{RT} \right) \quad 2.21 \\
    k_d &= A_d \exp \left( -\frac{H_d}{RT} \right) \quad 2.22
\end{align*}
\]

where \( H_{pr} \) and \( H_d \) are activation energies for the reaction (see Figure 2.1.2) and \( A \) is a constant of integration.

FIGURE 2.1.2

Also

\[
H_{pr} - H_d = \Delta H_p \quad 2.23
\]

where \( \Delta H_p \) is the enthalpy of polymerisation. Since \( \Delta H_p \) is usually negative (polymerisation reactions are usually exothermic) and larger than \( H_{pr} \), it follows that \( H_d \) is larger than \( H_{pr} \) and thus \( k_d \) will increase faster with temperature than \( k_p \).

2.1.3 Thermodynamics of THF Polymerisation

The variation of \( T_c \) with \([M_1]\) is given by equation 2.24 (17)

\[
T_c = \frac{\Delta H_p}{R \ln (A_p [M_1]/A_d)} \quad 2.24
\]

where \( \Delta H_p \) is the change in enthalpy of polymerisation under the prevailing experimental conditions, and \( A_p \) and \( A_d \) are constants of integration.

Also at \( T_c \) the free energy change is zero and equation 2.20 is valid,

\[
T_c = \frac{\Delta H_p}{\Delta S_p} \quad 2.20
\]

where \( \Delta S_p \) is the entropy change under the prevailing experimental conditions.

Comparing 2.24 and 2.20 gives
$\Delta S_p = R \ln \left( \frac{\alpha_p}{\alpha_d} \right) + R \ln [M_1]$  

$\Delta S_p^o = \Delta S_p + R \ln [M_1]$  

where $\Delta S_p^o$ is in the standard state of concentration of 1 mol $l^{-1}$.

$\therefore \quad T_c = \frac{\Delta H_p}{(\Delta S_p^o + R \ln [M_1])}$  

From rearranging equation 2.16, we have

$\Delta G_p^o = RT \ln [M_1]$  

where $\Delta G_p^o$ is the standard state free energy change when $[M_1] = 1$ mol $l^{-1}$.

At the ceiling temperature

$\Delta G_p^o = RT_c \ln [M_1]_e$  

substituting in 2.27 gives

$T_c = \frac{\Delta H_p}{(\Delta S_p^o + \frac{\Delta G_p^o}{T_c})}$  

and so

$\Delta G_p^o = \Delta H_p - T_c \Delta S_p^o$  

Thus a monomer at concentration $[M_1]$ has a ceiling temperature $T_c$ - this may also be expressed by saying that at a temperature $T$ the monomer concentration in equilibrium with long chain polymer is $[M_1]_e$, where

$T = T_c$ and $[M_1]_e = [M_1] = \exp \frac{\Delta G_p^o}{RT}$.  

Therefore equation 2.30 becomes

$\frac{\Delta G_p^o}{RT} = \frac{\Delta H_p}{RT} - \frac{\Delta S_p^o}{R} = \ln [M_1]_e$  

and a plot of $\ln [M_1]_e$ against $1/T^oK$ should give a straight line of slope $\Delta H_p/R$ and intercept $\Delta S_p^o/R$. Typical values obtained by this method are those of Dreyfuss and Dreyfuss (13) for bulk polymerisation at 25$^oC$ where

$\Delta H_p = -19.14 \text{ kJ mol}^{-1}$

$\Delta S_p^o = -73.99 \text{ J K}^{-1} \text{ mol}^{-1}$
Since the ceiling temperature is known (85 ± 2°C), it is possible using equation 2.20 to calculate $\Delta S_p$ - the change in entropy under the prevailing experimental conditions,

$$\Delta S_p = -53.5 \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1}.$$  

From these figures it is possible, from equation 2.19, to estimate $\Delta G_p$ for that reaction temperature:

$$\Delta G_p^{298} = -3.34 \, \text{kJ} \, \text{mol}^{-1}$$

so that THF is only just able to polymerise at room temperature on thermodynamic grounds.

However equation 2.31, and hence the above method, is valid only if the mixture of monomer and polymer behaves ideally over the range of compositions covered by the experiment. Leonard and Ivin (22,23,24) have proposed a method of estimating the free energy change which includes an allowance for non-ideal mixing based on the Flory-Huggins theory.

$$\Delta G_{lc} = \Delta G_m - \Delta G_p$$

where $\Delta G_{lc}$ is the free energy change for conversion of 1 mol of liquid monomer to 1 base-mol of amorphous polymer of infinite chain length, $\Delta G_m$ is the partial molar free energy of the monomer (per mol) in the equilibrium mixture relative to that of pure liquid monomer, and $\Delta G_p$ is the partial molar free energy of the polymer (per base-mol) in the equilibrium mixture relative to that of the pure amorphous polymer.

Using the Flory-Huggins expression it can be shown that (23, 24)

$$\frac{\Delta G_{lc}}{RT} = \ln \phi_m + 1 + \phi_s (\chi_{ms} - \chi_{sp} \frac{V_m}{V_s}) + \phi_p (\phi_s - \phi_m)$$

where $\phi_m$ is the equilibrium volume fraction of monomer in the presence of a volume fraction of polymer equal to $\phi_p$, $V_m$ and $V_s$ are the molar volumes of monomer and solvent respectively, and $\chi_{ms}, \chi_{mp}$ and $\chi_{sp}$ are three interaction parameters where the subscripts m, p and s denote monomer,
polymer and solvent respectively. For the case of THF this expression reduces to (22)

\[
\frac{\Delta G_{lc}}{RT} = \ln \phi_m + 1 + \chi_{mp} (\phi_p - \phi_m)
\]

2.34

The best value of \( \chi_{mp} \) was found to be 0.3, and if this is used to calculate values of \( \frac{\Delta G_{lc}}{RT} \) which are then plotted against \( \frac{1}{T_0K} \), a straight line should result yielding \( \Delta H_{lc}/R \) from the slope and \( \Delta S_{lc}/R \) from the intercept. Results from this method may be summarised:

\[
\begin{align*}
\Delta H_{lc} & (\text{kJ}\cdot\text{mol}^{-1}) & \Delta S_{lc} & (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\
\text{Ivin & Leonard (22)} & -12.4 & -40.8 \\
\text{Dreyfuss & Dreyfuss (13)} & -13.8 & -44.7
\end{align*}
\]

It should be noted however that the ceiling temperature cannot be calculated from \( \Delta H_{lc} \) and \( \Delta S_{lc} \), eg.

\[
T_c \neq \frac{\Delta H_{lc}}{\Delta S_{lc}}
\]

2.35

because these terms do not include the partial molar free energies of the monomer and polymer.

The polymerisability of the homologous series of cyclic ethers has been shown to be a function of ring size or substitution (17). If the main contributor to \( \Delta G_p \) is considered to be \( \Delta H_p \) then the value for THF (5-membered ring) is only just negative (approximately \(-21\) kJ mol\(^{-1}\)). The 4- and 3-membered rings have progressively more negative \( \Delta H_p \) values, whilst tetrahydropyran (6-membered ring) has a positive \( \Delta H_p \) and thus does not polymerise. Many substituents on the THF ring cause \( \Delta H_p \) to become positive and thus prevent polymerisation.
2.1.4 Initiation of Bulk THF Polymerisation

A summary of useful initiators for the cationic polymerisation of THF, in bulk and in suitable solvents, has been given recently by Ledwith and Sherrington [25]. In general, to be an effective initiator for this polymerisation, a material must be capable of generating a cation on some part of a monomer molecule. This is often achieved via two reactions, a pre-initiation equilibrium giving rise to an active charged species together with its counter-ion, followed by addition of this pair to the monomer molecule:

\[
\begin{align*}
\text{solvent} & \quad \xrightarrow{\text{SLOW}} \quad X^+ + Y^- \\
X^+ + Y^- & \quad \xrightarrow{\text{monomer}} \quad X^+ \text{M} + Y^- \\
\end{align*}
\]

Cationic initiators for THF polymerisation may be classified as follows [25]:

1. Oxonium Salts
   - eg. \( \text{Et}_3\text{O}^+ \text{PF}_6^- \)
2. Protonic Acids
   - " \( \text{HSO}_3^- \)
3. Carboxonium Ion Salts
   - " \( \text{CH}_3\text{OCH}_2\text{Cl} + \text{AlCl}_3 \)
   (from organic molecule with labile H atoms + suitable Lewis Acid)
4. Acylium Ion Salts
   - " \( \text{CH}_3\text{COCl} + \text{AlCl}_3 \)
   (acid chloride + suitable Lewis Acid)
5. Stable Carbonium Ion Salts
   - " \( \text{Ph}_3\text{C}^+ \text{SbCl}_6^- \)
   (trityl salts)
6. Aryl Diazonium Salts
   - " \( \text{Cl Ph N=N}^+ \text{PF}_6^- \)
   (p-chlorophenyl diazonium hexafluorophosphate)
7. Friedel-Crafts Halides
   - " \( \text{PF}_5 \)
Initiators from two of these classes, 1 and 6, have been used throughout this work, and these reactions will be considered in more detail.

1. Oxonium Ion Salts

Trialkyl oxonium salts of the type \( R_3O^+ \) may be regarded as ether-solvated cations, i.e., \( R_2O + R^+ \rightleftharpoons R_3O^+ \)

and are thus powerful alkylating agents. The reaction with THF monomer has been shown (26) to be a straight forward alkyl exchange:

\[
(CH_3CH_2)_3O^+BF_4^- + O(CH_3CH_2) + \rightarrow CH_3CH_2 - O(CH_3CH_2)_2BF_4^- + \]

after which propagation occurs by nucleophilic attack of a fresh monomer molecule. However the production of the parent ether may be a disadvantage since this can act as a transfer agent, with also the rate of initiation slower than the rate of propagation.

Trialkyl oxonium salts are sufficiently stable to be used directly as preformed initiators, as in this work. A study of the effects of varying the counter-ion in a series of triethyl oxonium salts has been presented (27) where it was found that the order of stability of the counter-ions was

\[
PF_6^- > SbF_6^- > BF_4^- > SbCl_6^- 
\]

6. Aryl Diazonium Salts

A salt of this type, p-chlorophenyl diazonium hexafluorophosphate, was first reported to be an effective initiator for THF polymerisation by Dreyfuss (28) in 1966, where it was recognised that the inherent stability of the \( PF_6^- \) counter-ion meant that a living system capable of producing very high molecular weight polymers was present. The mechanism of initiation is not fully understood, but is thought to proceed as follows
(29) for both trityl and diazonium salts (groups 5 and 6):

\[
\text{Cl}(\text{N=N})_2 + \text{PF}_6^- + \text{O} \rightarrow \text{Cl} + \text{O} + \text{H} + \text{N}_2
\]

\[
\downarrow \text{fast}
\]

followed by

\[
\text{OH} - - - \text{O} + \text{O} \rightarrow \text{HO-(CH}_2\text{)}_2\text{O} + \text{O}
\]

Dehydrogenation of THF to a furan or dihydrofuran occurs, along with the formation of the free acid of the counter-ion (HPF₆⁻), which is stabilised by complexing with monomer. HPF₆⁻ is normally found as its diethyl-ether complex HPF₆.2(CH₃CH₂)₂O. The acid complex then reacts slowly with additional monomer to form the propagating species, which should have an hydroxyl end-group. However Ledwith (25) has pointed out that the initiation mechanism could equally well follow from the homolytic decomposition of the aryl diazonium salt (group 6 only) which would yield α-alkoxy radicals from the THF.

b. 1. \(\text{ArN}_2^+ + (X) \rightarrow \text{Ar}^+ + \text{N}_2\)

2. \(\text{Ar}^+ + \text{O} \rightarrow \text{O} + \text{ArH}\)

This type of free-radical may undergo facile electron transfer with the aryl diazonium cation to give the THF cation, necessary for propagation, together with an aryl radical which may react as in b.2 above.

3. \(\text{O} + \text{ArN}_2^+ \rightarrow + \text{Ar}^+ + \text{N}_2\)

\(\downarrow \text{propagation}\)

4. (see 2) \(\text{Ar}^+ + \text{O} \rightarrow \text{O} + \text{ArH}\)

Thus a chain reaction is set up for the initiation process whereby 2 molecules of initiator are required to give 1 molecule of 'living ends',
but after the first cycle, only 1 mol of initiator is required to give 1 mol of 'living ends', ie., reactions b.3 and b.4, once started, are self-supporting. This method of initiation will produce a polymer having an aldehydic end group:

\[
\begin{align*}
\text{PF}_6^- + \text{O} & \quad \rightarrow \text{H}_2\{\text{CH}_2\}_3\text{O} + \text{PF}_6^- \\
\end{align*}
\]

Use of this initiator gives rise to intense purple colouration of the reaction medium during the initiation reaction; this has also been noted with trityl salts (30). One explanation, put forward by Dreyfuss (29), suggests that the furans or dihydrofurans formed in reaction a. would tend to polymerise under the strongly acidic conditions, producing highly coloured polymers which have never been characterised. Since no colouration at all is produced when using \(\text{Et}_3\text{O}^+\text{PF}_6^-\) at low temperature (-5°C), the colour is seen not to be a characteristic of the polymer chain or its growing end. It must therefore either be an impurity as suggested above, or some chemical function of the initiated chain-end, and some work was performed to try and clarify this situation.

2.1.5 Propagation and Termination in Bulk THF Polymerisation

The propagation reaction is the repetitive addition reaction responsible for producing long chain molecules, and is considered to use the bulk of the available monomer such that the rate of monomer consumption may be assumed equal to the overall rate of polymerisation. In the polymerisation of THF, the depropagation reaction is also important, and we have an equilibrium polymerisation mechanism. Propagation is known (13) to proceed by nucleophilic attack of monomer oxygen upon a cyclic oxonium ion:
Termination in ionic polymerisations is unlikely to involve a mutual termination reaction due to the repulsion of chain-ends carrying a similar charge, and in the case of THF polymerisations in this work a linear mechanism was employed where the terminating species was either acetic acid or sodium ethoxide:

a) \[
\begin{align*}
\text{[O-(CH}_2\text{)_4]}_n &+ \text{CH}_3\text{C}=\text{O}^- & \rightarrow & \text{[O-(CH}_2\text{)_4]}_{n+1} + \text{CH}_3\text{C}=\text{O}^- \\
\text{PF}_6^- &\quad & & \text{PF}_6^- 
\end{align*}
\]

b) \[
\begin{align*}
\text{[O-(CH}_2\text{)_4]}_n &+ \text{OCH}_2\text{CH}_3^- & \rightarrow & \text{[O-(CH}_2\text{)_4]}_{n+1} + \text{OCH}_2\text{CH}_3^- \\
\text{PF}_6^- &\quad & & \text{PF}_6^- 
\end{align*}
\]

2.1.6 Broadening of the Molecular Weight Distribution

One of the major challenges of this work was to produce 'monodisperse' samples (i.e. where the ratio \(\overline{M}_w/\overline{M}_n \leq 1.10\)) of poly(THF), in an analogous manner to the anionic polymerisation of styrene, where this is an extremely facile reaction. There are many fundamental differences between anionic and cationic systems, one of the most important being the relative stability of the carbanion which may be explained by considering the electronic structure of both carbanion and carbenium ion:
With anionic systems, the stability of the carbanion affords the following consequences in polymerisation:

1. Termination reactions are absent, (with pure systems), giving a living system.
2. Transfer to monomer does not occur due to the high energy barrier.
3. Molecular weight prediction is easy, \( \bar{DP} = \frac{[M_0]}{[I_0]} \)
4. Narrow molecular weight distributions (MWD's) are easily attainable, if the rate of initiation is fast compared with the rate of propagation.
5. Novel block and graft copolymers may be synthesised.
6. The nature of the intermediates can be readily established.

Recognition of these factors, together with the knowledge that THF undergoes a reversible, equilibrium polymerisation allows discussion of several factors which may contribute to molecular weight broadening in this system.

a) Equilibrium Effects

Living P(THF) chains eventually reach an equilibrium between monomer and polymer where the rates of propagation and depropagation become equal.
The effect of having competing forward and backward reactions is, in due course, to spread the distribution of molecular weights until it reaches the Flory distribution \( \bar{M}_w/\bar{M}_n = 2 \). Miyake and Stockmayer (31) have calculated that for the anionic polymerisation of styrene it will take 80 years to reach this polydispersity. Dreyfuss and Dreyfuss (27) quote a corresponding value of 20 days for P(THF) at 30°C. Since broadening is observed even at low temperatures and to a higher degree than predicted, the propagation-depropagation effect cannot be solely responsible.

b) **Chain Transfer Reactions**

When using p-chlorophenyldiazonium hexafluorophosphate initiator, and assuming a very low level of impurities in our rigorous system, the most likely chain transfer agents present are in-chain oxygens and counter ions.

\[
\begin{align*}
\text{PF}_6^- & \quad [(\text{CH}_2)_4\text{O}]_x \\
\text{O} & \quad [(\text{CH}_2)_4\text{O}]_y \\
\text{PF}_6^- & \quad [(\text{CH}_2)_4\text{O}]_x \\
\end{align*}
\]

This example shows chain transfer to polymer oxygen, which is really a special case of a dialkyl ether. Dreyfuss (28) has shown dialkyl ethers to be effective chain transfer agents, and as can be seen from the above scheme this reaction leads to a randomisation of molecular weights with no decrease in the rate of polymerisation, and no decrease in the number average molecular weight. Rosenberg (32) has suggested that in the later stages of polymerisation when monomer is becoming scarce, species I increases.
in concentration leading to a very large rise in viscosity, although association of active ends would cause a similar effect. Problems of this type will grow in severity as the concentration increases so most of this work was performed with conversions below 10%.

With many systems, reaction of the growing end with counter-ion is a termination reaction, and this becomes a difficult problem when relatively unstable counter-ions, such as \( \text{BF}_4^- \) and \( \text{SbCl}_6^- \), are used. With \( \text{PF}_6^- \) as counter-ion, however, this being a far more stable species (27), the reaction between them is envisaged as follows (13):

\[
-O+ + \text{PF}_6^- \rightarrow -O(\text{CH}_2)_3\text{CH}_2\text{F} + \text{PF}_5
\]

The \( \text{PF}_5 \) itself may act as an initiator (33) and thus a transfer, rather than termination, reaction occurs. The effect of such a transfer will again be to broaden the distribution of molecular weights, but in this case with a delay in the chain reaction and an alteration of the counter-ion.

With triethyloxonium hexafluorophosphate initiator, a further possibility for chain transfer is introduced. Consideration of the initiation mechanism, equation 2.36, shows that a product of the alkyl exchange reaction is diethyl ether, and as previously mentioned, dialkyl ethers are effective chain transfer agents (28),

\[
\text{PF}_6^- \rightarrow -O-\text{CH}_2\text{CH}_3 + -O(\text{CH}_2)_4 - O + \text{CH}_2\text{CH}_3
\]
in an analogous mechanism to the reaction with in-chain oxygen, equation 2.45, except that in this case the number average molecular weight will be reduced.

c) **Slow Initiation Reactions**

The currently accepted mechanism of initiation by diazonium salts, as summarised by equations 2.37 and 2.38, shows the presence of a slow, rate-determining step, in line with the observed slow initiation at temperatures where the rate of propagation is reasonably fast. Similarly it has been noted (19) that the rate of initiation by triethyloxonium salts is slower than the rate of propagation, (since the cyclic trialkylloxonium ion is considered to be more reactive than \( \text{Et}_3\text{O}^+ \) towards the THF monomer), thus with both initiators slow initiation reactions will be a prime cause of molecular weight broadening, since centres initiated early in the reaction may grow to much longer chain lengths than those initiated later.

d) **Ion Pair Structure**

Whenever ions are present in solution their local environment will largely determine their rate of reaction. The following general scheme for the ions \( R^- \) and \( X^+ \) in solution has been proposed (34):

\[
\begin{align*}
\text{Free solvated ions} & \quad \Leftrightarrow \quad \text{Loose ion pairs} \\
\text{Solvent separated ion pairs} & \quad \Leftrightarrow \quad \text{Tight ion pairs (or clusters)}
\end{align*}
\]

and their order of reactivity is expected to be:

Free solvated ions \( \geq \) Loose ion pairs \( \geq \) Tight ion pairs

Thus if a certain proportion of growing chain-ends exist as free solvated ions or loose ion pairs, while the remainder exist as tight ion pairs, then the former could be expected to react (ie. propagate) faster than the latter, so spreading the MWD. However at the low reaction temperatures employed in this work, the addition of monomer takes place at an approximate rate of 1 monomer unit per 60 seconds (at \(-10^\circ\text{C}\)). Thus in the time taken
to achieve a high DP every chain end will fluctuate statistically between the various possible structures. Every chain will thus propagate at the same overall statistical rate and differences in ion pair structure will not lead to broadening of the MWD.

e) Macroion - Macroester Equilibrium

Although not affecting either of the initiators employed in this work, a further complication arises when using initiators which are capable of forming covalent bonds with the growing chain-end (35) such as simple halide ions, perchlorate ions and sulphonate ions. With these initiator systems another equilibrium is set up between the so called 'macroion' and 'macroester'.

\[
\text{Macroion} \quad \leftrightarrow \quad \text{Macroester}
\]

\[\text{Only the macroion is capable of propagation, the macroester remaining dormant, thus if this equilibrium is present it will give rise to a broadening of the MWD, the amount of which will be determined by the position of equilibrium. Solvent polarity largely determines this position, eg, in CH}_2\text{Cl}_2 \text{ the concentration of macroion approximately equals that of the macroester. In CCl}_4 \text{ the macroester form predominates (96%) while in CH}_3\text{NO}_2 \text{ the macroion form predominates (92%).}\]
2.2 GEL PERMEATION CHROMATOGRAPHY

The technique of Gel Permeation Chromatography (GPC) has gained wide popular acceptance since its inception in 1964 (36) as a rapid, reliable method of determining the average molecular weights of polymer samples varying from $5 \times 10^2$ to $10^6$. The method gives as much information in a single experiment as previously required at least three time-consuming separate investigations, a time reduction factor of at least 10. In essence the GPC experiment consists of introducing a solution of polymer to the solvent stream directly prior to this stream entering a column containing a swollen, cross-linked gel, usually a styrene-divinylbenzene copolymer. The gel contains pores of known size and distribution, these being controlled by the copolymerisation conditions, into and from which the solvent may freely diffuse. Small polymer molecules contained in the solvent may also diffuse in and out of these pores, but large molecules tend to be excluded from the smaller pores, thus having a small internal volume (i.e., inside the pores) available to them. As a result of this the large molecules elute first from the column, while the small molecules are retained longer and elute later.

The column eluant is monitored by a detector system, preferably one in which the detector response is directly proportional to solute concentration. The system typically fitted to commercial instruments detects the difference in refractive index between pure solvent and the column eluant, the response being linear with solute concentration over a wide range, and also the response is linear with molecular weight when the molecular weight exceeds a value of approximately 10,000. Below this value the effect of chain-ends must be considered.

The result of the experiment is, therefore, an elution curve (the chromatogram) showing detector response (proportional to polymer concentration
versus elution volume. From this curve, together with a suitable calibration curve (see section 2.2.2), it is a simple, though tediously repetitive, mathematical exercise to calculate the various molecular weight averages, and a computer programme has been written to perform these calculations following the method of Pickett (37), see section 2.2.5. A useful review of GPC has recently been published (38).

2.2.1 Theory of Separation

The principle mechanism of separation in GPC is now accepted as being by steric exclusion (39, 40), thus the retention of solutes is governed by

\[ V_R = V_o + K_d V_i \] 2.50

where

- \( V_R \) is the retention volume,
- \( V_o \) is the total volume of mobile phase (interstitial volume)
- \( V_i \) is the total volume of stationary phase (solvent volume within the gel)
- \( K_d \) is the distribution coefficient which determines the fraction of internal volume accessible to a solute of given size.

For molecules which are larger than the pore size, \( K_d = 0 \), while for molecules which are much smaller than the pore size, \( K_d = 1 \). Molecules which lie between these extremes have \( K_d \) values in the range 0 to 1. As will be discussed shortly, hydrodynamic volume is the size parameter upon which the steric exclusion mechanism is based (section 2.2.2), and from this Anderson and Stoddart (41) have derived

\[ K_d = -A \log [\eta] M + B \] 2.51

where

- \( A \) and \( B \) are constants and
- \([\eta] M\) is the hydrodynamic volume.

It has recently been shown (42 to 45) that under certain circumstances
ste. ric exclusion is not the primary mechanism of separation. For particular polymer-solvent systems, if the value of a in the Mark-Houwink equation

\[ [\eta] = K M^a \]

falls below 0.65, i.e., the solvent is either a poor or a theta solvent, then solute-gel interactions become important giving rise to a partition mechanism (where solutes have a different solubility in the mobile phase compared to the stationary phase) or an absorption mechanism (when the stationary phase is regarded as the surface area within the gel pores). Equation 2.50 then becomes

\[ V_R = V_o + K_d K_p V_i \]

where \( K_p \) is the distribution coefficient for solute-gel interaction effects, assumed independent of molecular weight. When a good solvent for a polymer is used (\( a \geq 0.65 \)) then \( K_p = 1 \), but for poor or theta solvents (\( 0.65 > a > 0.5 \)) \( K_p \) is greater than 1.

2.2.2 Calibration

GPC is not an absolute technique and calibration is required prior to the determination of molecular weights. A series of commercially available polystyrene standards (46) of known molecular weight and narrow MWD are normally employed for calibration, a plot of log. peak molecular weight versus elution volume being constructed. This plot is satisfactory for determining the molecular weights of further polystyrene samples, but if the molecular weights of different polymer samples are required, then a method of universal calibration is necessary.

Benoit et al (47) have proposed a universal calibration procedure based upon the hydrodynamic volume, \([\eta] M\), of a polymer molecule in solution such that a plot of log. \([\eta] M\) versus elution volume will be the
same for all polymers, \([\eta]\) being the intrinsic viscosity (equation 2.52). Thus conversion from one calibration curve to another is made via the equation

\[
\log [\eta]_p M_p = \log [\eta]_{ps} M_{ps}
\]

where \(ps\) denotes polystyrene
\(p\) denotes unknown polymer.

This method requires the extra experimental determination of \([\eta]\) as a function of elution volume. It is possible, however, to produce a universal calibration from a quantity related to the hydrodynamic volume, namely the unperturbed rms end-to-end distance \((\bar{r}_o^2)^{1/2}\), (48), from the Flory-Fox equation (49).

\[
[\eta] = \phi \left[\frac{\bar{r}_o^2}{M}\right]^{3/2} \alpha M^{1/2}
\]

where \(\phi\) is the universal viscosity constant
\(\alpha\) is the expansion coefficient describing polymer-solvent interactions.

Substitution of \([\eta]\) from 2.55 into equation 2.54 yields

\[
\frac{M_p}{M_{ps}} = \left[\frac{\bar{r}_o^2}{M}\right]_{ps} \left[\frac{\alpha_{ps}}{\alpha_p}\right]^{2}
\]

Assuming \([\alpha_{ps}/\alpha_p] \approx 1\) for the solvent used, as proposed by Dawkins (50), and by taking literature values (51) for the \([\bar{r}_o^2/M]\) terms, a conversion factor may be calculated to determine the absolute molecular weight from the 'polystyrene equivalent' molecular weight at a given elution volume. For the case of \(P(THF)\) we calculate the value 0.592 as the conversion factor, i.e.,

\[
M_{P(THF)} = 0.592 M_{ps}
\]

at a given elution volume. The determination of \(M_{P(THF)}\) enables absolute molecular weights to be evaluated from the chromatogram.
2.2.3 Determination of Molecular Weights

Determination of the average molecular weights of a polymer sample by GPC first necessitates the computation of its true molecular weight distribution curve. Ideally this could be achieved by merely substituting log. molecular weight for elution volume on the chromatogram, as defined by the calibration curve. It has been shown however (37, 52, 53) that this approach is oversimplified and can produce erroneous results. Instead it is necessary to take into account the variation in slope of the calibration curve \( \frac{d(\log. M)}{dv} \), and this method is used in our calculations, where the differential weight distribution, \( w(M) \), as a function of molecular weight, \( M \), is related to the chromatogram by

\[
w(M) = \frac{d I(v)}{dv} \cdot \frac{dv}{d(\log. M)} \cdot \frac{d(\log. M)}{dM} \tag{2.57}
\]

where \( I(v) \) is the weight fraction of polymer eluted up to elution volume \( v \).

\( \frac{d I(v)}{dv} \) is the ordinate of the chromatogram, i.e., the height \( h(v) \).

\( \frac{d(\log. M)}{dM} \) is \( \frac{1}{M} \).

Thus knowing the height of the curve, the molecular weight \( (M) \) and the slope of the calibration curve at corresponding elution volumes, the differential weight distribution \( w(M) \) may be computed and changed from co-ordinates of elution volume \( (v) \) to molecular weight \( (M) \) by equation 2.57.

From this true MWD curve the average molecular weights may be calculated (50) from:

\[
\bar{M}_n = \frac{1}{M_0 \int_{M_1}^{M_0} \left( \frac{1}{M} \right) w(M) dM} \tag{2.58}
\]
\[ \overline{M}_v = \left[ \int_{m_1}^{m_0} M^a \, w(M) \, dM \right]^{1/a} \]

\[ \overline{M}_w = \int_{m_1}^{m_0} M \, w(M) \, dM \]

\[ \overline{M}_z = \frac{\int_{m_1}^{m_0} M^2 \, w(M) \, dM}{\int_{m_1}^{m_0} M \, w(M) \, dM} \]

\[ \overline{M}_{z+1} = \frac{\int_{m_1}^{m_0} M^3 \, w(M) \, dM}{\int_{m_1}^{m_0} M^2 \, w(M) \, dM} \]

Also the peak average \((\bar{M}_p)\) molecular weight and the polydispersity ratio, which do not depend on \(w(M)\) may be calculated from the above:

\[ \overline{M}_p = (\overline{M}_n \times \overline{M}_w)^{1/2} \]

Polydispersity Ratio \[\frac{\overline{M}_w}{\overline{M}_n}\]

The computer programme written to calculate the molecular weight averages is based on that of Pickett et al (37), and is listed and described in the Appendix. As well as the molecular weight averages the programme also plots the true differential and cumulative weight distributions as a function of molecular weight, and a differential histogram of the cumulative weight distribution. The conversion factor described in section 2.2.2 is employed to correct the molecular weight data given, for the calibration curve, in terms of polystyrene, to those of the polymer under analysis.
Correction for Machine Broadening

A complication to this technique arises from the spreading of the molecules inherent in any chromatographic process. A solution of a monomeric substance, having a single molecular weight, and examined after passage through a Gel Permeation Chromatograph, will appear as a Gaussian distribution rather than a single line. When this degree of spreading is superimposed upon a polymer sample containing a range of molecular weights then this machine broadening must be considered - for samples of \( \frac{M_w}{M_n} \) ratio > 2 however it may generally be ignored. Several mathematical approaches have been put forward (54, 55) to remove the effect of spreading from the data before it is analysed as detailed in section 2.2.3, but none of these procedures have been adopted in this work. Instead a more empirical approach has been used based on the values of the polydispersity ratio given with the polystyrene standards. The data from their chromatograms is analysed as previously discussed and the computed values of the polydispersity ratios are compared with the 'known' values (ie, the values given by the manufacturer) as a function of molecular weight. It is found that the computed \( M_n \) values are too low while the computed \( M_w \) values are too high, and a percentage correction may be determined (as a function of molecular weight) to achieve the correct \( \frac{M_w}{M_n} \) ratio. If these values are plotted as log. \( M_n \) (or log. \( M_w \)) versus percentage correction then the latter may be determined at any intermediate value of \( M_n \) (or \( M_w \)), both corrections being necessary (ie, to \( M_n \) and \( M_w \)) to give the required polydispersity ratio.
2.3 INTRODUCTION TO POLYMER CRYSTALLISATION

The acceptance of the macromolecular nature of polymeric molecules made the concept of polymer crystallinity difficult to visualise. A popular early model was the fringed micelle, see Figure 2.3.1, where small lengths of polymer chains are aligned over small regions - the crystals - before returning to their random, amorphous manner.

![Figure 2.3.1](image)

Thin films of bulk polymers, when viewed through a polarising microscope, were observed to crystallise as spherulites. These are spherical three-dimensional bodies which appear as discs when growth is allowed in two dimensions only - as in a thin film. Growth is seen to commence from a point source of nucleation and advances radially, the rate of radial growth being linear. The phenomenon of ringed spherulites could not be explained by the fringed micelle.

The isolation of polymer single crystals from dilute solution (e.g. polyethylene (3, 4, 5)) proved to be an important step forward in the understanding of polymer crystallisation, for upon examination of these crystals by electron diffraction (e.g. polyethylene (56)) it was found that
although the crystals were only some 100-200 Å thick (being very large in the other two dimensions) the polymer chains were oriented practically perpendicularly to the basal surface. Since the length of the polymer chains greatly exceeded this thickness dimension, it was shown that the chains in the crystal are folded. The nature of the fold surface however is still not fully understood, and Figure 2.3.2 shows some of the possible alternatives from the tight loops of the adjacent re-entry model to the loose folds of the switchboard model. It has been proposed (57) that for polyethylene single crystals the fold surface is irregular (loose folds and non-adjacent re-entry) and this accounts for the small fraction of amorphous material present, although the view of single crystals having sharp chain-folds is widely held at present.

The most important factors which any theoretical treatment of crystallisation must necessarily predict are twofold, these being:

1. The crystalline fold length is directly dependent on 1/supercooling, not 1/(crystallisation temperature). This has been shown for polyethylene crystallised from different solvents (10).
2. The fold length is independent of the size of the crystal formed earlier (58, 59).

Having observed the folded nature of polymer single crystals, it was also found that bulk crystallised polymers contained similar crystalline units (60), these being incorporated within the previously mentioned spherulite structures as ribbons of lamellae interposed with amorphous material. Evidence supporting this model has come from electron microscopy, small-angle X-ray scattering, nitric acid etching, T_g determination on the amorphous phase etc. The lamellae grow outwards from the nucleation point maintaining a linear radial growth rate and the overall spherical nature. The exact mechanism of this process is not known but it is thought that
sharp chain fold, adjacent re-entry

statistical fold, adjacent re-entry

switchboard
branching of the lamellae must occur.

Between the polymer chains leaving the crystal and entering the amorphous layer, there is an intermediate region of high energy allowing the chains to separate from the close packing of the crystal to the random nature of the amorphous layer. This intermediate region also contains any large loops associated with chain folds. The annealing (thickening) effect shown by lamellae at or above the crystallisation temperature may be attributed to the lowering of the total free energy by the reduction of the surface area of the intermediate region. It has been suggested from Small Angle X-ray Scattering (SAXS) determinations (61) that the intermediate region is some 5-20 Å thick. The nature of the fold surface may be characterised by the end-surface free energy, $\sigma_e$, although in practice it is difficult to obtain experimentally. It has been suggested (62, 63), however, that the $\sigma_e$ defined by the lamellar growth rate should be distinguished from that found after growth, i.e., by melting experiments, where $\sigma_e$ may decrease by up to three times (64, 65).

Polymer crystallisation, when studied by dilatometry (change in specific volume), shows two distinct regions following an induction period, the primary (rapid decrease) and secondary (slower decrease) stages. Comparable polarising microscopy shows that the changeover point between these regions corresponds to impingement of spherulites, after which no further changes are observed. This suggests that secondary crystallisation is undertaken in the amorphous regions within the spherulites, which may occur either by lamellar thickening as in polyethylene, or by the formation of new lamellae in the amorphous regions as in isotactic polystyrene (66).

Lamellar thickening has been widely observed for polymers and is thought to arise from translation of chains through the lattice, either by
the movement of single defects (67) or by a jump mechanism of a complete chain segment (68). A further possible cause of lamellar thickening suggests (69) the re-arrangement of chains within the lamellae to allow folds to be pulled into and through the lattice, eventually doubling the fold length.

2.3.1 Background to Polymer Crystallisation Theory

Two basic theories of polymer crystallisation have been proposed, the equilibrium and kinetic theories. The equilibrium theory as suggested by Peterlin (70, 71, 72) calculates the free energy of a polymer chain crystal lattice by combining terms for the surface energy, the entropy of the chains in the crystal and the intermolecular forces. Although the theory predicts an increase in lamellar thickness with increasing temperature, it does not account for its precise variation with supercooling \( \Delta T = T^o_m - T^o_d - T_c \), where \( T^o_d \) is the dissolution temperature) as shown by polyethylene single crystals (10). Similarly, although the theory explains lamellar thickening or annealing as the temperature is raised above \( T_c \) (the crystallisation temperature), it does not account for isothermal thickening at \( T_c \) without either (a) requiring the surface energy to increase relative to the surface energy associated with crystal formation, or (b) that the original crystal is formed under kinetic control. The latter is now widely accepted (9) as being the case, the nucleation and initial growth of lamellae being kinetically controlled, while isothermal annealing is thermodynamically controlled, the driving force arising from a desire to decrease the high surface energy associated with thin crystals.

Certain information necessary for the kinetic analysis, to be described, is available from thermodynamic considerations of the melting point. For a lamellar crystal, having a fold period \( C \) and large dimensions
Figure 2.3.3, the free energy of formation of the crystal is given by

\[ \Delta G = 4xC \sigma_s + 2x^2 \sigma_e - x^2 C(\Delta f) \]  

where \( \sigma_s \) and \( \sigma_e \) are the side-surface and end-surface free energies respectively, and \( (\Delta f) \) is the free energy difference between the supercooled liquid and the crystalline states which, near the melting point, is given by:

\[ (\Delta f) = \frac{\Delta H_f \Delta T}{T_m^o} \]  

where \( \Delta H_f \) is the heat of fusion per unit volume of crystal (assumed independant of \( T \) at low supercooling), \( T_m^o \) is the melting point of a perfect, infinitely thick crystal, and \( \Delta T = T_m^o - T \).

At the melting point of the crystal, \( \Delta G = 0 \), and if \( x \gg C \), then

\[ T_m = T_m^o \left[ 1 - \frac{2 \sigma_e}{\Delta H_f C} \right] \]  

Rearrangement of equation 2.67 yields an equation for the minimum possible lamellar thickness
when \( \Delta G \) is zero. However \( \Delta G \) must be negative for crystallisation to proceed, thus \( C \) must in practice assume a value greater than this minimum thickness. This is accounted for by the addition of the term \( \Delta C \), representing a small fraction of \( C \), the minimum fold length, yielding \( C^* \)

\[
C^* = \frac{2 \sigma_e T_m^o}{\Delta H_f} \frac{\sigma_e T_m^o}{\Delta T} + \Delta C
\]

where \( \Delta C \) is usually in the range \( 10^{-4} \text{ to } 10^{-3} \text{ m}^3 \). Thus from determinations of melting point and lamellar thickness \( (C) \), both \( T_m^o \) and \( \sigma_e \) may be determined via 2.67, providing \( \Delta H_f \) is known, from a plot of \( T_m \) versus \( 1/C \). A value of \( \sigma_e \) for polyethylene determined by this method (73) is \( 93 \pm 8 \text{ mJ m}^{-2} \).

The model chosen to represent the kinetic crystallisation theory, after Lauritzen and Hoffman (9), is the simplest model to give reasonable agreement with experimental results. Those authors envisage adjacent re-entry of chains thus producing a chain-folded surface, but this is not central to the treatment. The end-surface free energy is then given by

\[
\sigma_e = \frac{q}{2a \sigma_o b_o} + \sigma_{e_0}
\]

where \( 2a b_o \) is the surface area produced by the fold, \( q \) is the work required to form the fold (from the bending of the chain), and \( \sigma_{e_0} \) is the value of \( \sigma_e \) when \( q = 0 \), i.e. no work is required to form the fold, and is thus a 'surface tension' term. This value \( \sigma_{e_0} \) will be smaller than \( \sigma_e \) and is expected to approximate to the value of \( \sigma_s \), the side-surface free energy, which is generally 5 to 10 times smaller than \( \sigma_e \). Values of \( q \) calculated in this way (74) give good agreement with those found from \( \sigma_e \) via equation 2.67, \([4 \text{ to } 5 \text{ kcal (mol of folds)}^{-1}]\), thus it is seen that the
major contribution to $\sigma_e$ comes from $q$ - the work done in forming the fold.

In equation 2.66 it was assumed that $\Delta H_f$, the heat of fusion, is independent of temperature. This is true for low supercoolings, but at high supercoolings $\Delta H_f$ decreases with decreasing temperature, and at these higher supercoolings the equation

$$
(\Delta f) = \frac{\Delta H_f(\Delta T)}{T_m} f
$$

should be used (75) where

$$
f = \frac{2T}{T_m + T}
$$

thus $f < 1$ for low supercoolings, but reduces $(\Delta f)$ considerably in the vicinity of the glass transition temperature, $T_g$.

2.3.2 Kinetic Theory of Polymer Crystallisation

This treatment, following Lauritzen and Hoffman (9), is the simplest theory allowing prediction of lamellar thickness and growth rate over a wide range of supercooling which gives good comparison with experimental results. It is based on surface nucleation theory, as are all those yielding lamellar thickness and growth rate (76-80), and does not consider fluctuations in the fold period. Those which do consider fluctuations are considerably more complicated (79, 81) but do give superior comparisons between theory and experiment. The model for this theory is shown in Figure 2.3.1:
The growth of the crystal proceeds in the G direction, increasing by steps of a monomolecular thickness. The deposition of the first element is under surface nucleation control, followed by the further deposition of segments along the crystal face in the g direction. This is followed by the deposition of a further surface nucleation step upon the newly formed crystal face, which then again grows along the g direction and so on. The polymer molecule is assumed to have a cross-section area $a_0 b_0$, the lamellar thickness is maintained at $C$, and $\sigma_s$ and $\sigma_e$ represent the side-surface and end-surface free energies respectively.

After $n$ folds have formed, the free energy of formation is given by

$$\Delta G = 2 \eta a_0 b_0 \sigma_e + 2b_0 C \sigma_s - \eta a_0 b_0 (\Delta f)$$ \hspace{1cm} (2.73)$$

or

$$\Delta G = 2b_0 C \sigma_s + a_0 b_0 \eta \left[ 2 \sigma_e - C(\Delta f) \right]$$ \hspace{1cm} (2.74)$$
The folding back of the chain forming the first element represents the maximum free energy of the surface nucleus i.e., when $\eta = 1$. As the number of folds increases so the free energy lowers until a region of stability is reached, thus this is a nucleation controlled process having an initial high energy barrier, (from the creation of new surfaces), which subsequently decreases. Two rate processes are thus attributable to each fold, the forward and backward rates, i.e:

\[ \eta = 0 \xrightarrow{A_0} \eta = 1 \]

\[ \xrightarrow{B_1} \]

and each fold may be represented by the occupation number $N_0, N_1, N_2 \ldots$ for the folds $\eta = 0, 1, 2 \ldots$

It is now required to obtain a general steady state expression for the rate at which this barrier to nucleation (the free energy maximum) is overcome - the general nucleation rate $'S'$. This represents the net flow of polymer from sites in the liquid ($\eta = 0$) to the first element in the nucleus ($\eta = 1$) of a new layer:

\[ S = N_0 A_0 - N_1 B_1 \]

Upon reaching the surface a segment of the chain has to re-arrange before it can take up its crystallographic position and attach to the crystal. The mechanism of this re-arrangement is not known, although it is probably very complex involving many intermediate steps. To permit some characterisation of these steps it is useful to apportion $\varphi$ - a fraction of the free energy of fusion - to the activation free energy of the forward reaction, and the remainder to the backward reaction, (77, 79), see Figure 2.3.5.
The formation of the first element creates two new surfaces having a lateral surface energy of $2b C_o$ less that portion of the free energy of crystallisation which occurs simultaneously, $\beta a b C(\Delta f)$. The rate constants $A_0$ and $B_0$ may now be defined:

$$A_0 = \beta \exp \left[ -2b C_o / kT + \beta a b C(\Delta f) / kT \right]$$

$$B_0 = \beta \exp \left[ -(1-\beta) a b C(\Delta f) / kT \right]$$

where $\beta$ is the retardation factor governing the rate of transport of polymer molecules, or their sections, to the crystallisation site. At high supercoolings the polymer melt becomes extremely viscous so that the retardations represented by $\beta$ are the controlling feature of the surface nucleation rate. To maintain the continuity of the theory $\beta$ will be discussed in more detail later.

Subsequent deposition of elements (i.e., growth in the $g$ direction)
corresponding to \( \eta = 1, 2, 3 \ldots \) forms no new lateral surfaces, but free energy is required to form each fold at a cost of \( 2a_o b_o \sigma \) less the free energy of fusion \( \phi a_o b_o C(\Delta f) \). Assuming \( \Delta f \) is apportioned as for the first step, then the rate constants for these subsequent steps (A and B) are given by:

\[
A = \beta \exp \left[ -\frac{2a_o b_o \sigma}{kT} + \frac{\phi a_o b_o C(\Delta f)}{kT} \right]
\]

\[
B = \beta \exp \left[ -(1-\phi) \frac{a_o b_o C(\Delta f)}{kT} \right]
\]

For a more generalised model the value of \( \phi \) for the first step \( \eta = 0 \) to \( \eta = 1 \) could be denoted \( \phi_0 \), and that for all subsequent steps \( \eta = 1 \) to \( \eta = 2, 3, 4 \ldots \), denoted \( \phi_1 \) where \( \phi_0 \neq \phi_1 \). However the nucleation rate and lamellar thickness depend almost entirely on \( \phi_0 \), and little on \( \phi_1 \), and so for practical purposes the case \( \phi = \phi_0 = \phi_1 \) may be used, where the \( \phi \) value associated with the first step governs the behaviour of the model. If the steady state assumption is now applied, \( dN/\eta/dt = 0 \), to the effect that the nucleation rate of each step is the same as for the initial step, then \( S \) is shown (9) to be:

\[
S = \gamma N_\eta \exp \left[ -\frac{2a_o b_o \sigma}{kT} + \frac{\phi a_o b_o C(\Delta f)}{kT} \right] - \gamma N_{\eta+1} \exp \left[ -(1-\phi) \frac{a_o b_o C(\Delta f)}{kT} \right]
\]

also, since each occupation number depends upon its neighbours, the nucleation rate may be expressed (9) as:

\[
S = N_{\eta+1} (A-B)/(A-B+B_1)
\]

Since the portion of the free energy of fusion contributing to the backward reaction rate has been assumed equal for each step, then the net rate of formation of nuclei of the length \( C \) is:

\[
S(C) = \gamma N_0 \exp \left[ (-2b_o C_o \sigma + \phi a_o b_o C(\Delta f))/kT \right]
\]

\[
(1 - \exp \left[ (-a_o b_o C(\Delta f) + 2a_o b_o \sigma_e)/kT \right])
\]
The total surface nucleation rate, $S_T$, may be found by summing equation 2.82 over all possible values of $C$, and since $C$ will be an increment of $C_R$, the repeat unit length, then the summation may be replaced by the integral:

$$S_T = \frac{1}{C_R} \int_0^\infty S(C) \frac{dC}{2\sigma_0/(\Delta f)}$$  \hspace{1cm} 2.83

thus

$$S_T = N_0 (\beta/C_R) P \exp \left[ \frac{2a b \sigma_0 e}{kT} \right] \exp \left[ -\frac{4b \sigma_0 e}{(\Delta f)kT} \right]$$  \hspace{1cm} 2.84

where

$$P = \frac{kT}{2b \sigma_0 - a b (\Delta f) \beta} - \frac{kT}{2b \sigma_0 + (1 - \beta) a b (\Delta f)}$$  \hspace{1cm} 2.85

$S_T$ then has the dimension surface nuclei sec$^{-1}$. The main contribution to $S_T$ at low supercoolings is given by the last exponential term in 2.84, thus for a process obeying a first order dependence on the surface nucleation rate, the overall crystal growth rate will be proportional to $\exp \left[ -\frac{4b \sigma_0 e}{(\Delta f)kT} \right]$.

2.3.3 Initial Lamellar Thickness

Since no fluctuations in fold length are permitted, the initial fold length ($C^*$) will equal the average fold length ($C_{av}$), which may be calculated from the surface nucleation rate:

$$C_{av} = C^* = \frac{1}{C_R} \int_0^\infty \frac{C S(C) \ dC}{2\sigma_0/(\Delta f)}$$  \hspace{1cm} 2.86

which reduces to (9)

$$C_{av} = \frac{2\sigma_0}{\Delta f} + \frac{kT}{2b \sigma_0} \left[ \frac{[2+(1-2\beta) a o (\Delta f)/2\sigma_0]}{[1-a o (\Delta f) \beta/2\sigma_0][1+a o (\Delta f)(1-\beta)/2\sigma_0]} \right]$$  \hspace{1cm} 2.87

The first term on the right hand side is the main contributor at low super-
coolings, while the second term increases in importance with increasing supercooling. Equation 2.87 may be compared with equation 2.69,

\[ C^* = \frac{2\sigma}{e_m} \frac{T_m^0}{\Delta H_f \Delta T} + \Delta C \]  \hspace{1cm} 2.69

where \((\Delta f) = \frac{\Delta H_f \Delta T}{T_m^0}\)  \hspace{1cm} 2.66

The last term in equation 2.87 is dependent on \(\phi\), and upon assigning values to \(\phi\), the following expressions result:

When \(\phi = 1\), \((78)\), \(\Delta C = \frac{kT}{2b \sigma_s} \left[ \frac{(4\sigma_s/a_o) - (\Delta f)}{(2\sigma_s/a_o) - (\Delta f)} \right] \) \hspace{1cm} 2.88

When \(\phi = 0\), \(\Delta C = \frac{kT}{2b \sigma_s} \left[ \frac{(4\sigma_s/a_o) + (\Delta f)}{(2\sigma_s/a_o) + (\Delta f)} \right] \) \hspace{1cm} 2.89

When \(\phi = 1\), it may be seen that \(\Delta C\) becomes infinite when:

\[ \Delta T = 2\sigma_s T_m^0 / \Delta H_f a_o \] \hspace{1cm} 2.90

however, no such '\(\Delta C\) catastrophe' has been recorded in any experimental investigation, instead a gradual decrease in \(C^*\) with increasing supercooling is found, which is predicted by taking the value of \(\phi = 0\).

For certain systems, when conditions of high molecular mobility are met, the lamellae are able to undergo isothermal thickening or annealing. As previously mentioned this effect is thought to be thermodynamic in origin resulting from a desire to decrease the end-surface free energy latent in the folded surface structure by decreasing its ratio of crystal. The previous equations for \(C^*\) do not apply in the case of annealing, but only to the kinetically controlled initial formation of lamellae, assuming the supercooling is such that this initial thickness can be measured before annealing occurs. The existence of these chain folded crystals together with the above theory, shows the dominance of kinetic control in determining the
2.3.4 The Growth Rate (G)

Before discussing the calculation of the growth rate from the nucleation rate, it is necessary to consider the retardation factor $\beta$. For bulk polymers capable of undergoing high supercooling it is possible to apply the jump rate appropriate to local motions which may be expressed (82):

$$\beta = \frac{(kT/h)J_1 \exp \left[-U^*/R(T - T_\infty)\right]}{p}$$

2.91

The exponential term largely controls the temperature dependence of $\beta$, and will be discussed in detail shortly. The factor $J_1$ is included to account for any barriers not explicitly accounted for by the exponential term, and is expected to be of the order $10^{-2}$ to $10^{-5}$. Also its temperature dependence will be small compared to the exponential term, so $J_1$ will generally act as a pre-exponential factor which simply reduces $\beta$.

After nucleation at the rate $S_T$, the strip of length $L$ and thickness $b_0$ is assumed to be rapidly completed before a further nucleation act occurs. Then $G$ is given by:

$$G = b_o S_T \frac{n_s}{N} = \frac{b_o L S_T}{a_o N} \quad \text{where } n_s = \frac{L}{a_o}$$

2.92

or

$$G = G_o \exp \left[-\frac{U^*}{R(T - T_\infty)}\right] \exp\left[-4b_o \sigma_S \sigma_e / (\Delta f) kT\right]$$

2.93

where $G$ is in cms. sec$^{-1}$, $G_o$ is the pre-exponential term containing non-temperature dependent factors, $-U^*$ is the activation energy for transport of a chain to the crystal face, $T_\infty$ is a hypothetical temperature, related to the glass transition temperature $T_g$, where all motion associated with viscous flow ceases, and the second exponential term contains the free energy necessary to form a nucleus of critical size.
Similarly, if the strip is completed more slowly, such that further nucleation may occur before completion, (leading to a ragged growth front), then:

\[ G = G_0 \exp \left[ -\frac{U^*}{R(T - T_\infty)} \right] \exp \left[ -\frac{2b \sigma_0 \varepsilon_0}{(\Delta f)kT} \right] \tag{2.94} \]

Both possibilities are described by the general equation:

\[ G = G_0 \exp \left[ -\frac{U^*}{R(T - T_\infty)} \right] \exp \left[ -\frac{K g}{T(\Delta T) f} \right] \tag{2.95} \]

where \( f \) is given by equation 2.72, and

\[ K_g = \frac{4b \sigma_0 \varepsilon_0}{\Delta H_f k} \quad \text{rapid completion} \tag{2.96} \]

or

\[ K_g = \frac{2b \sigma_0 \varepsilon_0}{\Delta H_f k} \quad \text{slow completion} \tag{2.97} \]

The form of the first exponential term (the transport term) in 2.95 is indicated from the temperature dependence of viscosity of high polymers shown by the Williams-Landel-Ferry relation (82, 83, 84) where an expression of the form \( \exp \left[ -\frac{U^*}{R(T - T_\infty)} \right] \) is accurately obeyed between \( T_g \) and \( T_g + 100 \) K. The "universal" constants \( U^* \) and \( T_\infty \) are assigned the values \( U^* = 4120 \text{ cal. mol}^{-1} \) and \( T_\infty = T_g - 51.6 \) K, although considerable fluctuations from these values are known.

If the growth rate variation with temperature, \( G(T) \), is examined, it is found that as the temperature decreases from \( T_m \), \( G \) first increases, passes through a maximum, and then decreases again, see Figure 2.3.6.
The rise of $G$ with decreasing temperature is largely controlled by the free energy, or second exponential, term in 2.95, the fall at still lower temperature being largely controlled by the transport, or first exponential, term. A method of comparing theory and experiment has been suggested by Kovacs (85). This method requires an estimation of $U^*$ and $T_\infty$, using these to calculate $\log G + U^*/[2.3 R(T - T_\infty)]$, and fitting this to a linear relation in $1/T(\Delta T)$. This method yields a value of $G_0$ and $K_g$ for each set of $U^*$ and $T_\infty$ values, and the precision of the fit may be expressed by a correlation coefficient. The estimated $U^*$ and $T_\infty$ values are then varied to maximise the correlation coefficient, a value of 0.98 and above representing a good fit of the data.

Good agreement between $G(T)$ as measured and $G(T)$ as predicted by 2.95 is given when the values $U^* \approx 1300 \pm 300 \text{ cal. mol}^{-1}$ and $T_\infty \approx T_g - 30 \text{ K}$ are used for the crystallisation of isotactic polystyrene, whereas from fluidity measurements the same values (85) are $3830 \text{ cal. mol}^{-1}$ and $T_g - 60.9 \text{ K}$ respectively. The smaller "universal" parameters associated with the crystallisation process have also been shown to apply over a wide
temperature range (i.e., either side of the maximum) for poly(tetramethyl-p-silphenylene) - siloxane (86) and poly(propylene oxide) (87). Over a narrow temperature range, the following polymers also give good agreement with the smaller "universal" parameters: trans-1,4-poly(isoprene), poly(methylene oxide), polyethylene, poly(ethylene oxide) and poly(butene-1).

The reason for the crystallisation parameters being smaller in value than those from viscosity measurements is thought to be (9) a result of the physically adsorbed yet mobile surface layer of molecules on the growing surface of the crystal. Such a layer may be expected to have a higher effective glass transition than the bulk phase, while a lower activation energy may be associated with motion within this layer. Thus the method of estimating the activation energy $\Delta F^*$, in the modified equation (88)

$$G = G_0 \exp \left[ -\frac{\Delta F^*}{RT} \right] \exp \left[ -\frac{K}{T(\Delta T)^g} \right]$$

directly from the modified WLF expression (82)

$$\Delta F^* = \frac{4120}{51.6 + T - T_g}$$

is shown to give rather poor fits of the data at temperatures below the maximum $G(T)$, when the transport term is more important. Best fits between $G(T)$ experimental and $G(T)$ theoretical are given by the values $U^* = 1300 \pm 300$ cal. mol$^{-1}$ and $T_\infty = T_g - 30$ K, which give correlation coefficients of the order 0.995 to 0.998. Values of the correlation coefficient obtained when using the bulk polymer viscosity parameters ($U^* = 4120$ cal. mol$^{-1}$ and $T_\infty = T_g - 51.6$ K) are of the order 0.90 to 0.95.

The value of $K_g$ found by this method is usually not very sensitive to changes in $U^*$ and $T_\infty$, being generally about $1 \times 10^5$ K$^2$, while $G_0$
(cms sec\(^{-1}\)) is very sensitive. Once a value of \(K\) has been obtained, then the product \(\sigma_s \sigma_e\) may be found via equations 2.96 or 2.97, assuming the constants \(b_0, T_m^0\) and \(\Delta H_f^0\) are known. A value of \(\sigma_e\) may also be found from a plot of \(T_m\) versus \(1/C\) (equation 2.67), thus enabling \(\sigma_s\) to be determined.

2.3.5 **Effect of Molecular Weight**

The preceding derivation has shown that \(G(T)\), for moderate to high molecular weight (\(\geq 5 \times 10^4\)) polymers, passes through a maximum with decreasing temperature, and \(C'(T)\) - the variation of \(C^*\) with temperature - falls smoothly with decreasing temperature. However, low molecular weight polymers have a correspondingly higher percentage of chain ends, and the theory requires modification to allow for this.

For the approximation requiring the restriction of chain ends to the fold surface, and for a monodisperse sample of low molecular weight (89), the \(C'(T)\) curve is no longer smooth, but might be expected to fall in steps from \(T_m\) corresponding to extended chain, once folded chain, etc., crystals. The plot of \(G(T)\) also shows discontinuities in slope at the points corresponding to the steps in \(C'(T)\). When the number of folds in the crystal exceeds 4 or 5, the theory converges to that given previously, thus these effects are not shown for moderate to high molecular weight polymers. This behaviour has been shown to occur for poly(ethylene oxide) by Kovacs (90).
2.4 THEORY OF POLYMER MELTING

The concept of $T_m^0$, the melting point of an infinitely thick, perfect crystal, and its estimation from equation 2.67 have been referred to previously,

$$ T_m = T_m^0 \left[ 1 - \frac{2\sigma C}{\Delta H_f C} \right] $$  \hspace{1cm} 2.67

from a plot of $T_m$ versus $1/C$. However an alternative, when isothermal annealing of the lamellae at $T_x$ (crystallisation temperature) occurs such that

$$ C = \gamma C^* $$  \hspace{1cm} 2.100

where

$$ C^* = \frac{2\sigma T_m^0}{\Delta H_f \Delta T} + \Delta C $$  \hspace{1cm} 2.69

and assuming $\left[ 2\sigma T_m^0 / \Delta H_f \Delta T \right] > \Delta C$, then substituting 2.100 and 2.69 into 2.67 yields the expression (82)

$$ T_m = T_m^0 \left[ 1 - \frac{1}{\gamma} \right] + \frac{T_x}{\gamma} $$  \hspace{1cm} 2.101

Thus a plot of $T_m$ versus $T_x$, extrapolated to the line $T_m = T_x$ (i.e., equivalent to extrapolation to infinite $C$), gives $T_m^0$ with the slope being $\gamma$. This value has been found (91) to be approximately 2.

The $T_m$ of a polymer is not a characteristic value, as in most substances, but is found to depend on the supercooling, (equation 2.67). This arises from the co-existence of the crystalline and amorphous phases which are not in thermodynamic equilibrium, but that the phase transition (melting) occurs between 2 metastable states providing neither of the states is changing within itself. The range of temperature over which melting occurs may be explained by the existence of lamellae of different thicknesses, those of lower $C$ melting at a lower temperature than those of higher $C$. 
A theoretical study of melting has been proposed by Flory (92) for a fringed micelle model where the free energy of fusion ($\Delta G_f$) is given by:

$$\Delta G_f = \Delta H_f - T\Delta S_f$$

where

$$\Delta H_f = \Delta H_f^1 + \Delta H_m$$

($\Delta H_f^1$ from melting of crystallites and $\Delta H_m$ from the heat of mixing)

and from which Flory obtains

$$\frac{\Delta G_f}{xN} = (1 - \lambda) (\Delta H_u - T\Delta S_u) + \frac{RT}{\lambda} \left[ \frac{1}{x} \ln (\lambda) + \frac{1 - \lambda}{\rho} \left( \ln(D) + \ln\left(\frac{x - 2 + 2}{x}\right) \right) \right]$$

where

- $1 - \lambda$ is the degree of crystallinity,
- $\rho$ is the length of the crystal in chain units,
- $D$ is a nucleation constant given by $\ln(D) = -2\sigma_e/RT$,
- $\sigma_e$ is the end-surface free energy,
- $\Delta H_u$ and $\Delta S_u$ are the heat and entropy of fusion per monomer unit,
- $N$ is the number of polymer molecules and
- $x$ is the length of a monodisperse polymer expressed in chain units.

Since $T_m$ is defined as the temperature at which the last trace of crystallinity disappears, the conditions

$$\left[ \frac{\partial (\Delta G_f)}{\partial \lambda} \right]_\rho = 0 \text{ and } \lambda = 1$$

may be imposed from which

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \frac{1 + b}{x}$$

where

- $b = \left[ 1 - (\rho_e - 1)/x \right]^{-1}$

and $\rho_e$ is the equilibrium length of the crystallite.
For the most probable molecular weight distribution (i.e. \( \bar{M}_w/\bar{M}_n = 2 \)) then

\[
\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{2R}{x \Delta H_u}
\]

where \( x \) is the number fraction of molecules of length \( x \) units.

Although this derivation is based on a fringed micelle model, it has been suggested that the main conclusions will not be altered significantly for a chain folded lamellar system (93).

The melting of polyethylene has been studied by considering the melting points of long chain n-alkanes (94). If the number of carbon atoms in the molecule is \( n \), then

\[
\Delta H_n = n \Delta H + \Delta H_e
\]
\[
\Delta S_n = n \Delta S + \Delta S_e
\]

where \( \Delta H \) and \( \Delta S \) are the enthalpy and entropy of fusion of a repeat unit, and \( \Delta H_e \) and \( \Delta S_e \) allow for chain end effects. Thus when the free energy of fusion is zero,

\[
T_m = \frac{\Delta H}{\Delta S} = \frac{\Delta H (n+a)}{\Delta S (n+b)}
\]

where \( a = \frac{\Delta H_e}{\Delta H} \) and \( b = \frac{\Delta S_e}{\Delta S} \).

Since \( T_m^0 = \frac{\Delta H}{\Delta S} \) then

\[
T_m = T_m^0 \left( \frac{n+a}{n+b+R \ln(n)} \right)
\]

This expression has been modified by Flory and Vrij (95) to allow for the unpairing of chain ends in the melt:

\[
T_m = T_m^0 \left( \frac{n+a}{n+b+R \ln(n)} \right)
\]

Much work has been performed on the melting points of extended chain crystals of monodisperse polymers on the basis of the Flory and Flory-Vrij treatments.
(96 - 100), where the latter has been shown (100) to lead to

$$T_m = T_m^o \left[ 1 - 2 \sigma_e / \Delta H_u \rho \right] / \left[ \left( 1 - R T_m^o \ln(I) / \Delta H_u \rho \right) \right]$$  \hspace{1cm} 2.113

The numerator of 2.113 is equation 2.67, while the denominator contains terms specifically due to the finite chain length. The melting point of 2.113 is that of a lamellar crystal of thickness $\rho$ chain units composed of chains which traverse the crystal on average $t$ times. The parameter $I$ allows for the various possible states of order in the crystal. If chain ends are paired then

$$I = 1/x$$  \hspace{1cm} 2.114

where $x$ is the chain length of a monodisperse polymer. Because of the chain length distribution in a real polymer fraction, chain ends are not normally paired, thus for a monodisperse polymer forming a regularly folded-chain crystal, $I$ may be expressed:

$$I = (x - S\rho + 1)/x$$  \hspace{1cm} 2.115

where $S$ is the number of sequences chosen consecutively from a given molecule, and $S\rho \ll x$.

Beech and Booth (98) have extended the original Flory treatment to evaluate the melting points of low molecular weight poly(ethylene oxide) having narrow molecular weight distributions. They obtain the expression

$$\frac{\Delta G_f}{xN} = (1-\lambda)(\Delta H_u - T\Delta S_u) + RT \left[ \frac{1}{x} \ln(\lambda) + \frac{1 - \lambda}{\rho} \left( \ln(D) + \ln(I) \right) \right]$$  \hspace{1cm} 2.116

which is similar to the Flory equation 2.104, where $I = S(x - S\rho + 1)/x$ for a monodisperse polymer giving a chain-folded crystal. From 2.116 they found

$$T_m = T_m^o \left[ 1 - 2 \sigma_e / \Delta H_u \rho \right] / \left[ \left( 1 + (RT_m^o / \Delta H_u \rho) \lambda(1/x) - \ln(I)/\rho \right) \right]$$  \hspace{1cm} 2.117

Values of $T_m$ calculated by 2.117 were compared with the experimental
values to give the end-surface free energy \( \sigma_e \) which was found to pass through a maximum with molecular weight at \( \bar{M}_n \approx 6 \times 10^3 \).
2.5 SMALL ANGLE X-RAY SCATTERING

The theory of Small Angle X-ray Scattering (SAXS) has recently been reviewed in detail by Warner (11). A two-phase model is assumed for semi-crystalline polymers where the scattered intensity is proportional to the square of the electron density difference between these phases. Since this difference is usually small the scattered intensity is low, and methods of maximising the intensity are required. Long exposure times, and the provision of a vacuum path between sample and detector are necessary, but the most important factor is the type of collimation system used. With pinhole collimation long exposure times are required, but no correction for collimation errors is necessary. If a slit system is employed the intensity is increased, and counter detection may be used. However, use of slits causes a collimation error resulting in smearing of the data which must be corrected for prior to any structural interpretation.

Superimposed upon the ideal two-phase scattering is the background scattering, comprising:

1. Natural background radiation and electrical noise.
2. Parasitic scattering from slit edges.
3. Liquid or amorphous scattering.
4. Scattering from foreign particles (dust, additives).

Parts 1 and 2 are removed experimentally by re-scanning over the same angular range, and for high molecular weight polymers parts 3 and 4 may also be removed by repeating all the experimental measurements with the samples molten. However this was not possible with the low molecular weight polymers due to their low viscosity when molten, thus corrections were not applied for the removal of 3 and 4 in this work.

There are several important definitions of scattering angle used in SAXS theory, and these will be discussed in relation to Figure 2.5.1,
For monochromatic radiation of wavelength $\lambda$, we may now define:

$$2\theta = \text{angle of scattering}$$

$$s = \frac{2 \sin \theta}{\lambda} = \frac{2\theta}{\lambda} \quad \text{(for small angles)}$$

$$S = 2\pi s = \frac{4\pi \sin \theta}{\lambda} = \frac{4\pi \theta}{\lambda} \quad \text{(for small angles)}$$

$$m = 2a \sin \theta = 2a\theta = a\lambda s \quad \text{(for small angles)}$$

The units of $s$ and $S$ are $\lambda^{-1}$, while $m$ is in cms.

In this work, slit collimation with counter detection was used, the data being desmeared via computer programme, as outlined below.
When pinhole collimation is used a circular diffraction pattern results: a slit may be considered as a series of pinholes (Figure 2.5.2) and thus the scattering profile will be the sum of those from the individual pinholes. According to Guinier (101) and Vonk (102) the desmeared intensity \( I(m_j) \) is related to the smeared intensity \( \bar{I}(m) \) by equation 2.121.

\[
I(m_j) = \frac{-1}{\pi C} \int_0^\infty \frac{d\tilde{I}(m)}{dm} \cdot \frac{dm}{(m^2 - m_j^2)^{1/2}} \tag{2.121}
\]

where \( C \) is a constant, and \( m \) and \( m_j \) define the angle \( \Theta \) at which that intensity \( \bar{I}(m) \) was measured.

The smeared curve is not integrated immediately but is first matched by fitting a Fourier Series to it, this smoothed curve \( I_f(m) \) being represented by:

\[
I_f(m) = \frac{1}{2A_0} + \sum_{m=1}^{m_{\text{max}}} A_m \cos \left( 2\pi m \left[ \frac{m - m_{\text{min}}}{2(m_{\text{max}} - m_{\text{min}})} \right] \right) \tag{2.122}
\]

the coefficients \( A \) being given by

\[
A_m = \frac{2}{m_{\text{max}} - m_{\text{min}}} \int_{m_{\text{min}}}^{m_{\text{max}}} \bar{I}(m) \cos \left( 2\pi m \left[ \frac{m - m_{\text{min}}}{2(m_{\text{max}} - m_{\text{min}})} \right] \right) \, dm \tag{2.123}
\]

The integration is then carried out as in equation 2.121 with \( m_{\text{min}} \) and \( m_{\text{max}} \) being the lower and higher limits respectively, this giving the desmeared curve.

The desmeared curve for many semi-crystalline polymers shows a broad maximum, see Figure 2.5.3, which represents the order between layers oriented in three dimensions. It is possible to extract from this information that which represents order in the direction perpendicular to the layers by the use of the Lorentz Factor, \( 4\pi s^2 \) (11), where \( s \) is a function of
crude smeared data
after desmearing
after Lorentz correction

ARBITRARY INTENSITY

Figure 2.5.3

2θ°
scattering angle. This shifts the broad maximum to higher angles, see Figure 2.5.3, but will not affect sharp diffraction peaks such as those found in Wide Angle X-ray Scattering (WAXS). Multiplying the desmeared curve by the Lorentz Factor means each 'd' spacing will have equal probability, and Bragg's Law may be applied to the angle at which the desmeared, Lorentz corrected maximum occurs to give a characteristic 'd' spacing - in this case the distance being the repeat period $l$, where $l = C + A$, of the crystalline and amorphous layers, see Figure 2.5.4. However, due to the range of d values present, and the form of Bragg's Law, this 'Bragg' spacing is neither the average nor the most probable repeat period.

FIGURE 2.5.4

Bragg's Law is given by:

$$ n\lambda = 2d \sin \theta \tag{2.124} $$

where $n$ is the order of diffraction,

$\lambda$ is the x-ray wavelength,

$d$ is the interplanar spacing $(C + A)$

and $2\theta$ is the scattering angle.

If the volume fraction of crystallinity ($\phi_{SV}$) is known, the lamellar thickness $C$ may be calculated from the repeat period by $C = l x \phi_{SV}$.

To determine $\phi_{SV}$ and the widths of the crystalline and amorphous distributions, $\beta_c$ and $\beta_a$ respectively, we have used the correlation function approach.

2.5.1 The Correlation Function

So far only an approximate repeat period, $l$, has been obtained from
the SAXS data. The scattering curve however contains much more structural information, and to obtain this it is necessary to propose a model and calculate how this model will scatter x-rays. If we then compare the experimental with the theoretical scattering curves, we may deduce that the structural parameters used in building the model are representative of those in the original sample. The process of fitting the experimental and theoretical curves is eased if the correlation functions, as defined by Debye (103,104) and Porod (105), are used instead:

\[ \gamma(x) = \frac{\langle \Delta \eta_A \Delta \eta_B \rangle}{\langle \Delta \eta^2 \rangle} \]

where \( \Delta \eta_A \) and \( \Delta \eta_B \) are the local deviations of the electron density from the average value \( \langle \eta \rangle \) at positions A and B separated by distance r, see Figure 2.5.5. The Fourier Transform of the correlation function is proportional to the scattering curve.

Thus in the case of semi-crystalline polymers the one-dimensional correlation function may be visualised (106) as a rod AB of length r perpendicular to the layers of lamellae and moving in the direction x. The product of the electron density deviations at A and B is averaged over all positions and divided by the average at \( x = 0 \) (i.e. \( \langle \Delta \eta^2 \rangle \)), thus the
one dimensional correlation function is given by:

\[
\gamma(x) = \frac{\int_{0}^{\infty} \Delta \eta(x+r) \Delta \eta(x) \, dx}{\int_{0}^{\infty} \Delta \eta(x)^2 \, dx}
\]

To obtain the one-dimensional experimental correlation function we require the Fourier Transform of the desmeared scattering curve which may be calculated as (102)

\[
\gamma(x) = \frac{\int_{0}^{\infty} s^2 I(s) \cos 2\pi rs \, ds}{\int_{0}^{\infty} s^2 I(s) \, ds}
\]

Experimental correlation functions obtained in this work are shown in Chapter 4, but may be schematically represented, see Figure 2.5.6, as

\[\text{FIGURE 2.5.6}\]

\[\begin{array}{c}
\gamma(x) \\
1.0 \\
-1.0
\end{array}\]

a series of maxima and minima of decreasing height.

The theoretical correlation function is based on a two-phase model of alternating layers of high (crystalline) and low (amorphous) electron densities. The basic theory has been described by Vonk and Kortleve (102) and modified by Warner (11). A spread of thicknesses is allowed for each
layer such that these thicknesses, \( r_c \) and \( r_a \) for crystalline and amorphous respectively, are distributed around their average values of \( C \) and \( A \) as shown by the normalised functions \( P_c(r_c) \) and \( P_a(r_a) \):

\[
\int_0^\infty P_c(r_c) \, dr = \int_0^\infty P_a(r_a) \, dr = 1
\]

2.128

The volume fraction of crystallinity \( \phi_{SV} \) may be found from \( C \) and \( A \), where

\[
\phi_{SV} = \frac{C}{C + A}
\]

2.129

From Figure 2.5.5, if the end \( A \) is in a crystalline layer, the probability of end \( B \) also being in a crystalline layer is \( P_{cc} \); similarly the probabilities \( P_{ca}, P_{ac} \) and \( P_{aa} \) may be defined. For a two-phase model:

\[
P_{cc} + P_{ca} = 1
\]

2.130

\[
P_{ac} + P_{aa} = 1
\]

\[
\phi_{SV} P_{ca} = (1 - \phi_{SV}) P_{ac}
\]

It can now be shown (102)

\[
\gamma(x) = \frac{\phi_{SV}}{1 - \phi_{SV}} \left[ \frac{1}{\phi_{SV}^2} \int_0^\infty (r_c - r) P_c(r_c) \, dr_c \right. \\
\left. + P_{cac} + P_{cacac} + \ldots \right] - 1
\]

2.131

where the subscripts of \( P \) denote the layers traversed by the rod \( AB \). As previously mentioned \( P_c \) and \( P_a \) are distribution functions for the crystalline and amorphous layers, and in this work \( P_c \) and \( P_a \) have been evaluated as Gaussian distributions:

\[
P(r) = \frac{1}{\beta(2\pi)^{1/2}} \exp \left[ -\frac{(r - \phi_{SV})^2}{2\beta^2} \right]
\]

2.132

where \( \beta \) is a width parameter representing the standard deviation. Other types of distribution are possible, e.g. log. normal, square, and these are built in to the computer programme used to calculate the theoretical
correlation functions.

When large values of $\beta$ or low values of $\phi_{SV}$ (or $1 - \phi_{SV}$) are used, the Gaussian curve becomes asymmetric with a certain area cut off - see Figure 2.5.7:

![Figure 2.5.7](image)

A method of correcting for this has been introduced by Warner (107), where the average value of $x$ should equal $\phi_{SV}$, i.e.

$$
\bar{x} = \phi_{SV} = \frac{\int_{0}^{\infty} x P_{c}(x)dx}{\int_{0}^{\infty} P_{c}(x)dx}
$$

or

$$
\bar{x} = (1 - \phi_{SV}) = \frac{\int_{0}^{\infty} x P_{a}(x)dx}{\int_{0}^{\infty} P_{a}(x)dx}
$$

The curves $P_{c}$ and $P_{a}$ are calculated such that these equations apply and are then divided by the scale factor, (the total area of the curve $P_{c}$ or $P_{a}$ versus $x$ from 0 to $\infty$). In the computer programme this process is performed such that the curves $P_{c}$ or $P_{a}$ are positioned correctly on the axis and the scale factor then calculated. The first curve of $P_{c}$ versus $x$ is calculated with its peak at $\phi_{SV}$, then the average $\bar{x}$ is found from the above equations.
and the curve shifted by \((\vec{x}_c - \phi_{SV})\). Because this shift alters the cut-off area, the curve is recalculated and a new value of \(\vec{x}_c\) found - this process being repeated a stipulated number of times until no significant change occurs from one value to the next.

Figure 2.5.8 shows the effect of \(\phi_{SV}\) on the theoretical correlation function for infinitely sharp distributions, i.e. \(\beta_c = \beta_a = 0\).

Fitting of theoretical to experimental correlation functions may be rationalised by defining three parameters of the experimental correlation functions:

1. The depth of the first minimum \(\gamma_{\text{min}}\)
2. The height of the first maximum \(\gamma_{\text{max}}\)
3. The ratio of the position of the first minimum to the first maximum.

Now a large number of theoretical correlation functions are computed at reasonable intervals of \(\phi_{SV}\), \(\beta_c\) and \(\beta_a\), characterised into the above three parameters, and set down in a series of tables showing the variations with \(\beta_c\) and \(\beta_a\) at successive values of \(\phi_{SV}\). To fit an experimental correlation function, these three parameters are matched as well as possible from the tables, using trends between the available values etc., after which it is possible to generate more theoretical correlation functions in the required region to obtain the best fit. Final matching is always done by direct comparison of the two correlation functions.

The characteristic repeat period calculated by application of the Bragg equation to the de smeared Lorentz corrected maximum has already been mentioned. We may also determine the most probable thicknesses, \(C_p\) and \(A_p\), from the position of the first maximum in the experimental correlation functi,
Theoretical Correlation Functions

\( \beta_c = \beta_a = 0 \)
(C + A)_p, then:

\[ C_p = \phi_{SV} (C + A)_p \]

\[ A_p = (1 - \phi_{SV}) (C + A)_p \]

The limitation of this approach is that it applies to an ideal two-phase system. The theory can be modified to take into account diffuse interphase boundaries and density fluctuations within phases (102, 108), but it was not possible to make these corrections in this work due to the mobility of the samples when molten.
CHAPTER 3. EXPERIMENTAL
3.1 **SYNTHESIS**

High vacuum techniques were employed throughout this work, a pressure of $10^{-5}$ torr being generally obtained in a greaseless vacuum system. Glass reaction vessels were used after cleaning with chromic acid, drying and flaming, and treating with dichlorodimethyl silane. Two initiators for the cationic bulk polymerisation of THF were used; p-chlorophenyl-diazonium hexafluorophosphate, with which a detailed study of the kinetics of polymerisation was carried out, and triethyloxonium hexafluorophosphate, which was used to produce poly(THF) without studying the kinetics in detail.

3.1.1 **Purification of Reagents**

Tetrahydrofuran (Fisons SLR Grade) was fractionally distilled under nitrogen, a middle cut taken and stored over calcium hydride under vacuum for at least 24 hours. Living poly($\alpha$-methylstyrene) tetramer was prepared anionically (109) by the reaction of a sodium/potassium alloy, (1gm:0.3gm, melted together under vacuum) upon $\alpha$-methylstyrene (1.5mls). THF was vacuum distilled onto this complex producing a deep wine-red colour upon standing. This reaction effected a rigorous degree of purity on the monomer by removing all protonic or other species capable of causing the termination of a living anionic system. THF was left on this complex for a minimum of 24 hours before use.

Phosfluorogen A, the trade name of p-chlorophenyl(diazonium) hexafluorophosphate, is obtainable commercially (110) but requires purification before use by the method of Dreyfuss (28). Phosfluorogen A (5gms) is added to distilled water (350mls) at $30^\circ C \pm 2^\circ C$ and stirred vigorously for 10 minutes. The mixture is filtered rapidly using a glass sinter to remove any undissolved material, and the resulting clear solution is placed in an ice bath. The purified initiator crystallises as white platelets (M. Pt. $252^\circ C$) which are removed by filtration and dried at room
temperature under vacuum for several days. The product could be stored under vacuum for several weeks before use with no visible deterioration.

Triethyloxonium hexafluorophosphate is obtainable commercially (111) and also requires purification before use. The initiator (1gm) is dissolved in dry methylene dichloride (25mls) and filtered if necessary. The solution is poured into dry diethyl ether (50mls) thus causing the precipitation of the triethyloxonium salt. The liquid is decanted and the product washed twice with dry diethyl ether. The remaining ether is evaporated under a stream of nitrogen and the product dried further under vacuum, ideally for use within 2 or 3 days. Initially the above procedure was carried out in a nitrogen filled dry box, but it was later found sufficient if performed rapidly under a nitrogen stream.

Sodium ethoxide was prepared by the reaction of sodium metal upon ethanol in diethyl ether solution (112), other reagents being used as supplied.

3.1.2 P-chlorophenyl diazonium Hexafluorophosphate

The experiments performed using this initiator may be grouped into two broad classifications; (a) to determine the most favourable initiation conditions for production of monodisperse polymers, and (b) to investigate the effect of reaction temperature on the polymerisation kinetics. The results of these two sets of reactions enabled conditions to be chosen to give a predicted conversion to polymer of known molecular weight and narrow molecular weight distribution (MWD).

All experiments followed the same basic reaction scheme which is outlined below, detailed variations will be discussed were appropriate. A known amount of initiator (to give a concentration of approximately
2 x 10^{-2} \text{ mol. l}^{-1}) was weighed into a clean, dry reactor, returned to the vacuum line and evacuated for several hours. Dry THF was vacuum distilled from the complex into a measuring vessel and from there into the reactor. This was maintained at liquid nitrogen temperature while being sealed off from the line under vacuum, and was stored in liquid nitrogen until used—normally within 2 hours of sealing.

After removal of the helical reactor from liquid nitrogen, and prior to initiation, the vessel was allowed to equilibrate in the following manner to give standardisation between runs. The reactor was held at room temperature for 4 minutes, by which time the monomer had melted. It was then transferred to a methanol bath at -10^\circ C for 6 minutes, being held at an angle of 45^\circ, and being turned continuously to ensure homogeneous mixing of the reactants. After the initiation and propagation reactions described later, termination was achieved by freezing the reactants in liquid nitrogen, opening the reactor, and transferring the contents to a suitable terminating solution.

The effect of time on initiation was studied, in straight tube reactors, at two initiation temperatures. Reactions were performed at 40^\circ C and 60^\circ C for 7.5, 15 and 30 minute periods before transferring to a bath at 0^\circ C for 30 minutes. The effect of temperature on initiation was studied at temperatures of 85^\circ C, 90^\circ C and 95^\circ C for 7.5 minutes, and 95^\circ C and 100^\circ C for 5 minutes before transferring to a bath at 0^\circ C for 30 minutes. It was shown from these results that the best initiation conditions for production of monodisperse polymers were 95^\circ C for 4 minutes, followed by rapid quenching to a low reaction temperature for propagation.

These most favourable initiation conditions were then used for a series of kinetic experiments, using helical glass reactors (Figure 3.1.1).
FIGURE 3.1.1

Helical Glass Reactor
After initiation the reactor was quenched in a bath at $-10^\circ$C (15 seconds) and in liquid nitrogen (15 seconds) before transferring to a bath at the required reaction temperature. Reactions were performed for various times (from 0.5 to 8.0 hours) at several temperatures ($-10^\circ$C, $0^\circ$C and $20^\circ$C). Acetic acid solution in THF (10% v.v) was most commonly employed for termination. Sodium ethoxide ($5 \times 10^{-2}$ mol. $l^{-1}$) solution in THF was also used, but a wider MWD suggested a poorer termination reaction was occurring.

A further set of experiments was performed in straight tube reactors to study the polymerisation kinetics at higher propagation temperatures, while still using the most favourable initiation conditions. After initiation reactors were transferred directly to baths set at $50^\circ$, $60^\circ$, $70^\circ$ and $80^\circ$C for 10 minutes, followed by termination.

It should be noted that, using this initiator, an intense purple colour develops during the initiation reaction which persists upon termination, in contrast to, for example, the characteristic red colour of living anionic polystyrene, which disappears upon termination. The recovered polymer exhibits a decrease in the intensity of colour as molecular weight increases, samples of very high molecular weight (150,000) appearing pale brown.

3.1.3 Triethyloxonium Hexafluorophosphate

Experiments using this initiator were easier to carry out practically owing to the less complicated reaction scheme, i.e., the initiation stage is very rapid, and does not require induction through temperature-jump techniques. After purification and drying, the initiator was weighed into a reactor such that its concentration would be $1$ to $2 \times 10^{-2}$ mol. $l^{-1}$ of monomer. Reactors employed breakseals to separate the initiator from the monomer until required, and were either small or large volume, Figures 3.1.2a
and 3.1.2b respectively.

**FIGURE 3.1.2**

The reaction temperature of $-5^\circ C$ was used for all experiments with this initiator, the reactor being placed in the methanol bath at this temperature for 15 minutes to allow equilibration before opening the breakseal (by means of a P.T.F.E. coated magnetic stirrer bar) and mixing the reactants. The vessel was maintained in the bath for its required reaction time, after which termination was achieved by opening the side-arm breakseal into a solution of acetic acid in THF (10% v.v). With this initiator no colouration of the reactants occurred either during reaction or upon termination; the solution remained colourless throughout. The polymers, when recovered, were colourless when amorphous and white and opaque when crystalline regardless of molecular weight.
3.1.4 Purification of Polymers

Completion of the termination reaction, regardless of initiator, leaves a dilute solution of dead polymer in THF together with any by-products of initiation and any unreacted initiator. To separate these from the polymer the following technique was used in all cases. An equal volume of distilled water was added to the solution, and the THF evaporated under a stream of nitrogen to leave the bulk of the polymer floating on the surface. The product was then extracted with de-oxygenated benzene at least 3 times, the benzene upper layer being decanted off each time and evaporated to dryness under a stream of nitrogen. This was followed by several days of drying under vacuum to remove all traces of solvent.

Even after this procedure, those polymers prepared using p-chlorophenylidazanium hexafluorophosphate were still highly coloured, and a more sophisticated technique was employed to purify them further before use.

3.1.5 Column Chromatography

A preparative scale Gel Permeation Chromatograph was set up according to the procedure of Mulder (113). Columns were set up using Bio-Rad SX-1 (high molecular weight) or SX-8 (low molecular weight) gels in toluene as solvent. The system used a gravity feed solvent flow from a 2.5 l constant pressure reservoir, the gel being contained in columns 1 m. long by 2 cms. diameter, giving an internal volume of 200 mls. Samples (normally 5% w/v in toluene) were introduced by syphon using a Hamilton 3-way valve, and the column effluent was passed through a flow-through cell mounted in an infra-red spectrometer containing solvent in the reference beam. The i.r. spectrometer was set to absorb at 1120 cm\(^{-1}\), (C-O-C), the output from the spectrometer being monitored by a time-base recorder. Ultra-violet and infra-red spectroscopy were performed on a
sample before and after its passage through the column.

In each case the gel was chosen so that its exclusion limit was below the molecular weight of the polymer, thus the polymer was contained in the excluded volume and eluted straight through, while any lower molecular weight impurities could diffuse into the gel and be retained and hence separated.

3.2 MOLECULAR WEIGHT CHARACTERISATION

Molecular weight averages and the molecular weight distribution (MWD) were determined by Gel Permeation Chromatography (GPC) using a Waters Associates ALC/GPC 501 liquid chromatograph. THF was used as solvent at room temperature upon 4 commercially available styragel columns. The instrument was calibrated using the familiar narrow MWD polystyrene standards (46), and a conversion factor calculated as indicated previously (Section 2.2.2) to enable absolute molecular weights of poly(THF) samples to be determined from the polystyrene calibration.

Solutions (0.2% w/v) were made up using fresh THF drawn off from the instrument's solvent reservoir, filtered through a fibreglass filter mat and injected. The solvent was pumped at a flow rate of 2.5 mls. min\(^{-1}\), and the total elution time for each sample was 80 mins. The column effluent was monitored by a refractive index detector, from which the output was connected to a time-base recorder running at 1 cm. min\(^{-1}\), thus a 5 ml. volume increment (count) was equivalent to 2 cms. on the chromatogram. A computer programme, based on the method of Pickett et al (37), was written to calculate the various molecular weight averages and to plot the true MWD.
3.3 DILATOMETRY

A dilatometer of special design, as shown in Figure 3.3.1, was required in this work owing to the low viscosity of the low molecular weight polymers when molten.

![Diagram of dilatometer](image)

**FIGURE 3.3.1**

**FIGURE 3.3.2**

Samples (about 0.25 gm) were moulded into a cylindrical shape using the evacuable equipment shown in Figure 3.3.2. The apparatus is evacuated and placed in hot water (60°C), at which temperature the sample melts and flows into shape. Bubbles in the samples were removed by successive filling of the apparatus with nitrogen and re-evacuating. After crystallisation of the sample in the mould under vacuum (usually at 20°C) the sample was removed and weighed directly.

The inner thimble of the dilatometer was filled with silicone rubber and degassed under high vacuum for several days. The polymer sample plug was placed inside the silicone rubber and re-evacuated. When no new bubbles formed in the rubber, the thimble was joined to the stem, (made from 0.05 cm internal diameter veridia tubing). The whole dilatometer was then evacuated for several hours prior to filling with mercury.
Each dilatometer was melted in a water bath at 60°C for 10 mins, followed by rapid transfer to a Townson and Mercer X27M thermostated water bath at the required temperature (±0.01°C). After allowing 2 mins for thermal equilibrium, the drop in height of the mercury was followed with a cathetometer. Temperature-jump experiments were similar except that after primary crystallisation the dilatometer was re-positioned in a bath at 20°C (±0.01°C) to study the secondary process as a function of primary crystallisation conditions.

3.4 DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analysis (DTA) was used to measure polymer melting points and heats of fusion upon a Dupont 900 Thermal Analyser together with a Dupont DSC cell (Catalogue No. 900600). A diagram of the cell is shown in Figure 3.4.1.

![Diagram of Differential Thermal Analyser Cell]

An aluminium pan is placed above each thermocouple, one containing the sample and the second being the reference. A heating block supplies heat at a constant rate to both pans, this rate being adjustable, and the thermocouples monitor the temperatures of each. With the cell used in this way the temperature difference between the pans, ΔT is
proportional to $C_p$ and is plotted against reference temperature.

Each run was calibrated on the temperature axis by a small amount of mercury placed in the reference pan, the melting point of mercury being $-38.9^\circ C$ (114). Sample weights were accurately measured to about 1.5 mgs, the samples being sealed in aluminium pans, melted under vacuum at $60^\circ C$ for 10 minutes, and set to crystallise under vacuum at $16^\circ$ or $24^\circ C$. Duplicate runs were performed at the end of primary crystallisation, after 2 weeks and again after 4 weeks. After crystallisation the sample was placed in the cell together with the reference, cooled to $-100^\circ C$ by liquid nitrogen, and then heated at $15^\circ C$ min$^{-1}$ to at least $50^\circ C$. With sample weights of 1.5 mg no temperature lag is observed at this heating rate. The melting point must be reduced by $\Delta T^\circ C$ to allow for the difference between sample and reference temperature during melting, where $\Delta T^\circ C$ is the height of the peak above the baseline in $^\circ C$.

Heat of fusion ($\Delta H$) measurements with this cell require calibration with a substance of known $\Delta H$ which melts close to the melting point of the polymer samples. In this case gallium was used, melting point $29.8^\circ C$ (114), having a heat of fusion of $79.9$ J gm$^{-1}$ (115). When run under the same conditions as the polymer samples, then the calibration coefficient, $E$, in equation 3.1 may be calculated from the sample weight ($M$) and the area under the melting peak ($A$).

$$\Delta H = \frac{E \cdot A}{M} \tag{3.1}$$

The calibration coefficient varies over the temperature range of the instrument, thus the standard must melt close to the sample under observation. Once $E$ is known, then $\Delta H$ for each sample may be calculated from the sample weight and peak area.
3.5 SMALL ANGLE X-RAY SCATTERING

Small angle X-ray scattering (SAXS) has been used to obtain detailed information on the lamellar structure of the semi-crystalline samples. A Rigaku Denki camera (Catalogue No. 2202) with slit optics was used, the source of X-rays being a fine focus copper target tube mounted on a Phillips PW 1010 1 kilowatt generator, and the detector being a Nuclear Enterprise DMI-2 sodium iodide scintillation counter used in conjunction with a Laben 100 spectroscope. Copper Kβ radiation was selectively removed by a nickel filter prior to collimation. Automatic step scanning at intervals of 0.01° x n, where n is an integer from 1 to 9, was available which, together with the 100 channel facility of the spectroscope, enabled the desired angular range to be studied for the selected counting time. In this work the samples were scanned from 0.055° to 3.025°, in intervals of 0.03°, for 100 second counts. The spectroscope enabled pulse height discrimination to be used to achieve monochromatic measurements. The slit system of the camera is depicted schematically in Figure 3.5.1. Slits S1 and S2 collimate the X-ray beam, and slit S3, being of adjustable width, is used to reduce the parasitic scattering from S2. The sample is placed behind S3, and the scattered radiation passes through a vacuum chamber, (to reduce loss of intensity) through the detector slits S4 and S5 and into the detector.

Samples could be thermostated on the instrument by locating them in a perspex cell, with mylar windows, and passing dry nitrogen gas at a controlled temperature over the sample. The nitrogen temperature was controlled by first passing through a copper cooling coil immersed in Drikold (solid carbon dioxide) and methanol, and then through a dewar tube containing a nichrome heating element. A copper-constantan thermocouple together with a digital voltmeter were used to measure the sample temperature which could be controlled to ±0.5°C.
Due to the mobility of the polymer samples when molten, it was not possible to measure their amorphous scattering. This is normally subtracted from the crystalline scattering and reduces the errors arising from liquid and foreign particle scattering. Sample holders, as shown in Figure 3.5.2 were made, with a mylar window, of known dimensions to contain the polymer.

**FIGURE 3.5.2**

The crystalline sample was placed gently in the sample chamber, and the holder heated to 60°C under vacuum for 10 minutes. Upon melting the polymer flowed down to fill the sample chamber, flushing with nitrogen and re-evacuating ensured removal of bubbles from the sample. The sample holder was then placed in a desiccator, under nitrogen, suspended in a T and M water bath set at either 16°C or 24°C. SAXS runs were performed at the end of primary crystallisation, as determined by dilatometry, and again after 4 weeks.

The slit dimensions and interslit distances used were those found to be the optimum by Dr. Warner (11) for this camera. The alignment procedure adopted was as suggested by the Rigaku-Denki manual except for slit $S_3$, for which the method of Warner was employed (11).
Semi-crystalline samples were placed behind slit $S_3$ in the thermostated temperature cell, and the scattering measured over the range 0.055° to 3.025°. The parasitic scattering was then measured by either:

a) Placing the sample in an absorbing position (ie, behind slit $S_5$) and rescanning over the same angular range, or

b) Rescanning over the same range without the sample absorbing, and reducing the scattered intensity data by the attenuation factor of the sample. This factor was measured separately by scanning without the sample present, then repeating the same range with the sample absorbing. An average figure covering the whole range could then be established by comparison of these data, allowing for natural background.

Method (a) is preferable, since it is carried out immediately following the sample scattering thus reducing any errors from different values of parasitic scattering which may occur at different instrument alignments, and was used wherever possible.

To extract the important structural information from the scattering data a computer programme is necessary. This was kindly supplied by Dr Vonk, (DSM, Holland) and modified by Dr Warner (11). The information made available to the programme consisted of a smoothed curve of the sample scattering minus the parasitic scattering - these component curves coming directly from the instrument prior to smoothing. This subtracted curve, known as the smeared curve due to the smearing effect of the slits, was given in interpolated values of 0.025°.

Other information was necessary for further calculations to be performed: the number of Fourier coefficients involved in fitting the smeared curve over the angular range up to 2.5° was 25. The point from which Porod's law was assumed to be obeyed was estimated for each sample.
from a plot of $1M^3$ vs $M$. The programme now produces the following information:

1. Desmeared scattering curve
2. Lorentz corrected desmeared curve
3. 1- and 3-dimensional correlation functions
4. Smeared scattering total integral.

Application of Bragg's Law to the Lorentz corrected desmeared curve, (the correction allows for scattering from lamellae in all orientations), allows calculation of a repeat period of the amorphous-crystalline regions. The fitting of the 1-dimensional experimental correlation function to a theoretical model, the theoretical correlation function, allows the most probable repeat period, the volume fraction of crystallinity $\phi_{SV}$, and the distribution widths of the crystalline and amorphous phases, $\beta_c$ and $\beta_a$ respectively, to be found. The most probable thickness of the crystalline regions may now be determined from:

$$C = \text{most probable repeat period} \times \phi_{SV}$$

where $C$ is the lamella thickness.

3.6 **WIDE ANGLE X-RAY SCATTERING**

Wide angle X-ray scattering (WAXS) may be used to determine the state of crystallographic order in the polymer samples, and to detect any phase changes in the crystal structure. It may, for high molecular weight samples, also be used to measure the weight fraction of crystallinity, $\phi_{ww}$. Because of the low viscosity of these low molecular weight polymers when molten, this measurement could not be performed satisfactorily.

The instrument used incorporated a Phillips PW1050 diffractometer, a Phillips PW1051/3 analysis unit with pulse height discrimination (PW4082) and a proportional counter. Nickel filtered copper radiation was used (as
in SAXS measurements), the diffractometer scanning rate was 1.0° minute⁻¹, and the diffracted intensity was plotted as a function of angle on a chart recorder. The angular range normally scanned was from 8° to 40°.

FIGURE 3.6.1

Sample holders of the type shown in Figure 3.6.1 were used to contain the samples which were melted under vacuum at 60°C for 10 minutes. The samples were then set to crystallise, under nitrogen, at 25°C for 4 weeks, after which they were scanned as detailed on the diffractometer. The sample temperature could be thermostated during measurement to ±0.5° by blowing nitrogen over the sample as detailed in section 3.5.

The weight fraction of crystallinity could be determined by scanning the crystalline sample, then melting the polymer in situ (by blowing hot nitrogen over it) and re-scan the same angular range. Comparison of the amorphous halo of the crystalline ($A_c$) and amorphous ($A_a$) samples allows calculation of $\phi_{ww}$:

$$\phi_{ww} = \frac{A_a - A_c}{A_a}$$  \hspace{1cm} (3.3)

but the high degree of mobility of the molten samples made this determination difficult. In view of this difficulty, $\phi_{ww}$ was estimated by measuring the
areas under the crystalline $A_c^1$ and amorphous peaks $A_a^1$, and assuming the total area was 100% of the total scattering. The percentage of either the crystalline or amorphous phases could then be calculated from equation 3.4

$$\phi_{ww} = \frac{A_c^1}{A_a^1 + A_c^1} \times 100\%$$

3.7 POLARISING OPTICAL MICROSCOPY

The primary region of crystallisation of the samples could be studied by polarising optical microscopy by use of a thermostatic temperature cell, designed by the author, a Leitz Diulux-Pol polarising microscope and a Leica M1 camera.

FIGURE 3.7.1

The temperature cell, shown in Figure 3.7.1 was connected to a T & M thermostatic bath with an external circulation facility, the temperature within the water bath being maintained to ±0.01°C. No difference could be detected between the bath water temperature and the cell water temperature by a copper-constantan thermocouple inserted directly in the water flow of the cell by a Solartron LM 1604 DC digital volometer reading to ±0.001 mv, or by a potentiometer also reading to ±0.001 mv. The design of the cell allowed the water flow to come into intimate contact with the underside of the
glass cover slip bearing the polymer film to achieve good thermal contact.

The films were cast from benzene solution (6 to 12% w:v) onto circular glass cover slips, 19 mms diameter and 0.3 mms thick. Upon evaporation of the benzene the cover slips were carefully removed from the dish, any polymer found on the underside of the cover slips being removed, and the films dried under vacuum for at least 24 hours before use. Film thicknesses of approximately 10 μ were estimated by weighing.

When required the sample film on the cover slip was melted in the cell by water at 60°C for 5 minutes. The cell was connected to the water bath at the required temperature and the water flow opened, the time of crystallisation being started from this point. As soon as it was possible to focus the polarising microscope, i.e., as soon as any crystallites started to appear, a photograph was taken and the time noted. Photographs were then taken at frequent intervals throughout the crystallisation to enable radial growth rates to be determined. The absolute size of the crystalline entities could be measured by reference to a scale etched on a glass slide which was photographed under the same conditions as the sample.
4.1 SYNTHESIS OF POLY(TETRAHYDROFURAN)

The synthesis of low molecular weight polymers of tetrahydrofuran having a narrow molecular weight distribution has been investigated by the use of two initiators. The first, p-chlorophenyldiazonium hexafluorophosphate (abbreviated to 'P'), has been used in a detailed kinetic investigation of the polymerisation at a series of temperatures following an initial study to determine the effects of initiation and propagation conditions upon the molecular weight distribution of the product. The second, triethyloxonium hexafluorophosphate (abbreviated to 'T'), has been used only at a single propagation temperature, where conditions were found to give low molecular weight distributions. The polymerisation kinetics were studied over a range of reaction times.

4.1.1 Synthesis using p-Chlorophenyldiazonium Hexafluorophosphate

The effect of initiation time at a series of temperatures was investigated, other conditions being maintained constant as follows:

- concentration of initiator: $2.0 \times 10^{-2} \text{ mol l}^{-1}$
- propagation temperature: $0^\circ \text{C}$
- propagation time: 30 mins.

The initiation temperatures investigated were $40$ and $60^\circ \text{C}$, while initiation times at each temperature were 7.5, 15 and 30 mins. Typical results—those obtained at $60^\circ \text{C}$—are shown in Figure 4.1.1, these being the GPC molecular weight distributions for each initiation time at $60^\circ \text{C}$, followed by propagation at $0^\circ \text{C}$ for 30 mins. A similar pattern results for initiation at $40^\circ \text{C}$.

The effect of initiation temperature, for short initiation times, followed by propagation at $0^\circ \text{C}$ for 30 mins, has also been investigated, the results being shown in Figure 4.1.2—these being the GPC molecular weight distributions at various temperatures for either 5 or 7.5 mins.
Molecular Weight Distributions by GPC,

Initiation at 60°C

Initiation times:
- 30 mins
- 15 mins
- 7.5 mins

Molecular Weight (Elution Volume Counts)
Interpretation of this data leads empirically to the adoption of the 'clean' initiation conditions shown by Figure 4.1.2d, e.g. 95°C for 5 mins. Other combinations of initiation conditions are seen to yield broad or distorted molecular weight distributions, whereas the clean conditions yield a narrow distribution, $M_w/M_n = 1.08$. Accordingly all further work with this initiator was performed using the clean conditions, e.g. initiation at 95°C for 5 mins., followed by rapid quenching to the required propagation temperature. Three propagation temperatures were investigated, -10, 0 and 20°C, for a series of reaction times at each temperature, the initiator concentration being a constant $2 \times 10^{-2} \text{ mol l}^{-1}$. The percentage conversions obtained under these conditions are listed in Table 4.01.

**TABLE 4.01**

<table>
<thead>
<tr>
<th>REACTION TEMPERATURE (°C)</th>
<th>-10</th>
<th>0</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIME (hrs)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% CONVERSION</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TIME (hrs)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% CONVERSION</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TIME (hrs)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% CONVERSION</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.83</td>
<td>1.98</td>
<td>1.98</td>
</tr>
<tr>
<td>4</td>
<td>2.85</td>
<td>3.22</td>
<td>3.43</td>
</tr>
<tr>
<td>6</td>
<td>3.97</td>
<td>3.43</td>
<td>3.43</td>
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<tr>
<td>8</td>
<td>5.16</td>
<td>4.69</td>
<td>4.69</td>
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<tr>
<td>1</td>
<td>1.98</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>4.43</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>1.50</td>
<td>11.16</td>
<td>11.16</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>6.38</td>
<td>8.91</td>
<td>8.91</td>
</tr>
<tr>
<td>3</td>
<td>13.80</td>
<td>13.80</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>8.18</td>
<td>8.18</td>
<td></td>
</tr>
</tbody>
</table>

Products from the previous reactions were analysed by Gel Permeation Chromatography to obtain their molecular weight averages and polydispersity ratios. The variation of $M_w$ with propagation time for two reaction temperatures is shown in Figure 4.1.3, while the equivalent polydispersity ratios are given in Table 4.02.
FIGURE 4.1.3

Variation of $N_n$ with Time

- $0^\circ C$
- $-10^\circ C$

Time - Hours

Variation of $N_n$ with Time
As previously mentioned, a series of reactions was performed at various propagation temperatures for a fixed time, 10 mins., following the clean initiation conditions. The percentage conversions to polymer in this fixed reaction time are shown in Table 4.03.

Purification of samples prepared using this initiator was performed using preparative scale GPC as described in Section 3.1.5. Ultra-violet and infra-red analysis of samples was performed both before and after this treatment, the recorded spectra being shown in Figures 4.1.4a and 4.1.4b respectively.
FIGURE 4.1.4

(a) Ultra-Violet Spectra

1: Crude Polymer
2: Purified Polymer

(b) Infra-Red Spectrum
4.1.2 Synthesis using Triethyloxonium Hexafluorophosphate

Reactions using triethyloxonium hexafluorophosphate did not require a separate initiation stage as did reactions using the previous initiator. In this case a breakseal reactor was used such that when equilibrium was reached at the required reaction temperature, -5°C in all cases, the solid initiator was mixed as rapidly as possible with the monomer. Polymerisation was allowed to proceed and after the required reaction time, the reactor was opened and the polymerisation terminated. The initiator concentration varied between 1 and $2 \times 10^{-2}$ mol l$^{-1}$ but was generally held at the lower limit. The data obtained from these reactions are given in Table 4.04.

<table>
<thead>
<tr>
<th>REACTION TIME (HOURS)</th>
<th>$[I_0]$ (mol l$^{-1}$)</th>
<th>PERCENT. CONVERSION</th>
<th>POLYDISPERSY RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.142</td>
<td>0.010</td>
<td>0.29</td>
<td>1.06</td>
</tr>
<tr>
<td>0.333</td>
<td>0.015</td>
<td>1.71</td>
<td>1.09</td>
</tr>
<tr>
<td>0.500</td>
<td>0.0187</td>
<td>2.23</td>
<td>1.18</td>
</tr>
<tr>
<td>0.500</td>
<td>0.010</td>
<td>0.99</td>
<td>1.10</td>
</tr>
<tr>
<td>0.721</td>
<td>0.010</td>
<td>3.11</td>
<td>1.08</td>
</tr>
<tr>
<td>1.000</td>
<td>0.023</td>
<td>4.47</td>
<td>1.09</td>
</tr>
<tr>
<td>1.120</td>
<td>0.010</td>
<td>4.19</td>
<td>1.09</td>
</tr>
<tr>
<td>1.500</td>
<td>0.021</td>
<td>13.81</td>
<td>1.11</td>
</tr>
<tr>
<td>1.500</td>
<td>0.013</td>
<td>9.21</td>
<td>1.09</td>
</tr>
<tr>
<td>1.500</td>
<td>0.010</td>
<td>8.52</td>
<td>1.11</td>
</tr>
<tr>
<td>1.780</td>
<td>0.010</td>
<td>8.50</td>
<td>1.09</td>
</tr>
<tr>
<td>2.500</td>
<td>0.010</td>
<td>14.00</td>
<td>1.05</td>
</tr>
<tr>
<td>3.000</td>
<td>0.010</td>
<td>18.33</td>
<td>1.07</td>
</tr>
<tr>
<td>3.750</td>
<td>0.010</td>
<td>24.35</td>
<td>1.07</td>
</tr>
<tr>
<td>4.500</td>
<td>0.010</td>
<td>33.65</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Reaction Temperature = -5°C

Molecular weight averages were again determined by GPC, and the variation
of $M_n$ with reaction time for these polymerisations is shown in Figure 4.1.5.
Molecular Weight versus Time, Initiator T

\[ \bar{M}_n \times 10^{-3} \]

Reaction Time (Hours)
4.2 **GEL PERMEATION CHROMATOGRAPHY**

Gel Permeation Chromatography (GPC) allows rapid determination of polymer molecular weight averages and hence polydispersity ratios. It is not an absolute technique and requires a calibration curve, usually obtained from a series of polystyrene standards of known molecular weight averages and distribution. A calibration technique is required, based usually on hydrodynamic volume, to enable conversion from "polystyrene equivalent" molecular weights to absolute sample molecular weights, see Section 2.2.2.

A typical calibration curve obtained is shown in Figure 4.2.1 as a plot of log peak molecular weight against elution volume. The steps involved in proceeding from a raw sample chromatogram to absolute molecular weight averages via the calibration curve are explained in detail in Section 2.2.3. A further correction required by this data is to allow for machine-broadening of the sample elution curves. This effect has been estimated in this work by considering the broadening of the molecular weight distribution of the polystyrene standards obtained on the instrument compared to their known values. A percentage correction may then be applied to the data as a function of molecular weight. This data is given in Table 4.05.
### TABLE 4.06

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>INITIATOR</th>
<th>$\overline{M}_n$</th>
<th>$\overline{M}_w$</th>
<th>$\overline{M}_{w}/\overline{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>T</td>
<td>3300</td>
<td>3600</td>
<td>1.09</td>
</tr>
<tr>
<td>T/5.3</td>
<td>T</td>
<td>5300</td>
<td>5700</td>
<td>1.08</td>
</tr>
<tr>
<td>P/8.4</td>
<td>P</td>
<td>8400</td>
<td>9100</td>
<td>1.08</td>
</tr>
<tr>
<td>P/13.4</td>
<td>P</td>
<td>13400</td>
<td>15000</td>
<td>1.12</td>
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<tr>
<td>T/22.8</td>
<td>T</td>
<td>22800</td>
<td>24400</td>
<td>1.07</td>
</tr>
<tr>
<td>Lesser Used Samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T/7.8</td>
<td>T</td>
<td>7800</td>
<td>8400</td>
<td>1.08</td>
</tr>
<tr>
<td>T/10.7</td>
<td>T</td>
<td>10700</td>
<td>11700</td>
<td>1.09</td>
</tr>
</tbody>
</table>

After the synthesis work producing monodisperse polymers of THF of differing molecular weights, various samples were selected to enable studies of their crystallisation behaviour to be carried out. The samples chosen, together with their initiator species, molecular weight averages and polydispersity ratios are shown in Table 4.06.
4.3 AMORPHOUS DENSITY DETERMINATIONS

Measurements of refractive index of all the samples produced using triethylloxonium hexafluorophosphate initiator were made using an Abbe Refractometer, thermostatted at 50°C, and adjusted to the sodium D-line. By using the Lorenz-Lorentz equation:

\[ R_m = \frac{2}{n^2 + 2} \frac{M}{\rho} \]

where \( R_m \) is the molar refraction, \( n \) is the refractive index, \( M \) is the molecular weight of the repeat unit, and \( \rho \) is the density,

and calculating a value of \( R_m \) for a polymer repeat unit, the density may be calculated from refractive index measurements. Using data from the literature (116) a value of \( R_m = 20.231 \) has been calculated, and the corresponding densities - subsequently used for dilatometry results - listed in Table 4.07. However previous work (117) has measured the extrapolated amorphous density of a high molecular weight sample of P(THF) \( (M_n \approx 200,000) \) as 0.985 at 20°C. To bring these density values in line with this latter sample, an \( R_m \) value of 20.508 is necessary, and density values calculated using this figure are also listed in Table 4.07.

The selected temperature of operation was above the melting points of the samples to ensure measurement of the amorphous density. A plot of amorphous density versus \( 1/M_n \) is illustrated in Figure 4.3.1, for densities calculated using \( R_m = 20.231 \).
## Table 4.07 Refractive Index Data

<table>
<thead>
<tr>
<th>$\frac{1}{\overline{M}_n}$</th>
<th>$1/\overline{M}_n \times 10^{-4}$</th>
<th>$n$</th>
<th>$\frac{n^2 - 1}{n^2 + 2}$</th>
<th>$\rho$ with $R_m = 20.231$</th>
<th>$\rho$ with $R_m = 20.508$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>8.333</td>
<td>1.45295</td>
<td>.270262</td>
<td>.96322</td>
<td>.95021</td>
</tr>
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<td>3300</td>
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<td>1.45615</td>
<td>.271911</td>
<td>.96910</td>
<td>.95601</td>
</tr>
<tr>
<td>3640</td>
<td>2.747</td>
<td>1.45590</td>
<td>.271782</td>
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<td>.95556</td>
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<td>5300</td>
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<td>.971667</td>
<td>.95854</td>
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<td>7460</td>
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<td>1.45785</td>
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<td>.972215</td>
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<tr>
<td>7770</td>
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<tr>
<td>11200</td>
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<td>.972857</td>
<td>.95972</td>
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<td>10700</td>
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<td>.972764</td>
<td>.95963</td>
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<td>11400</td>
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<td>11550</td>
<td>0.8811</td>
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<td>.95999</td>
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<td>17800</td>
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<td>.96080</td>
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<td>1.45895</td>
<td>.273350</td>
<td>.974229</td>
<td>.96107</td>
</tr>
</tbody>
</table>
Amorphous Density versus Molecular Weight

Amorphous Density $\rho_a$ (g·m$^{-1}$)

$\frac{1}{\bar{M}_n} \times 10^4$

0.975
0.970
0.965
0.975
0.970
0.965

0.975
0.970
0.965

0
1.0
2.0
3.0
4.0

0
1.0
2.0
3.0
4.0
4.4 CRYSTALLISATION STUDIES

The crystallisation behaviour of the P(THF) samples listed in Table 4.06 has been studied by various techniques comprising: dilatometry, polarising microscopy, differential thermal analysis (DTA), wide-angle X-ray scattering (WAXS), and small-angle X-ray scattering (SAXS); each sample, in general, having been measured by each technique after crystallisation at a minimum of two temperatures for various crystallisation times.

4.4.1 Dilatometry

This technique measures the drop in height of a mercury column corresponding to the change in volume of the sample upon crystallisation. A knowledge of the amorphous density enables the specific volume of the sample to be calculated (118) and plotted against time. Results of such measurements on the five major samples, at various crystallisation temperatures between 16 and 24°C, for crystallisation times of up to approximately 10,000 mins., are given in Figures 4.4.1 to 4.4.5.

Relative rates of crystallisation have been estimated from dilatometry by measuring the time taken to complete a given fraction of the overall crystallisation. Here it was found that little difference arose in the trends of the results between measurements allowing for the induction period or not, and whether the fraction of crystallinity chosen was either 1/4 or 1/2 of the total. The results chosen to illustrate these trends were therefore the so-called \( t_{1/2} \) values (time to reach 50% specific volume change of the primary process) after allowing for the induction period. These results are recorded in Table 4.08, and a plot of \( \log t_{1/2} \) versus \( M_n \) is shown in Figure 4.4.6.
Sample T/3.3

Specific Volume

Log Time (mins)

16°C

24°C

0.92

0.94

0.96

0.98

1.00

1.02
Sample P/8.4

![Graph showing specific volume over log time for different temperatures (15°C, 20°C, 24°C).]
Half-Lives ($t_{1/2}$) versus Molecular Weight

- $t_{1/2}$ in log scale
- Molecular Weight ($\overline{M}_n$ x $10^{-3}$)
- Temperature: 24°C and 16°C
TABLE 4.08

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>AMORPHOUS DENSITY (50°C) (gms. cc⁻¹)</th>
<th>16 1/2 (mins)</th>
<th>Log 16 1/2</th>
<th>24 1/2 (mins)</th>
<th>Log 24 1/2</th>
<th>AVRAMI EXPONENT (n)</th>
<th>16°</th>
<th>24°</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>0.96910</td>
<td>8.8</td>
<td>0.95</td>
<td>2598</td>
<td>3.41</td>
<td>1.2</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>T/5.3</td>
<td>0.97167</td>
<td>4.7</td>
<td>0.67</td>
<td>180</td>
<td>2.25</td>
<td>1.5</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>P/8.4</td>
<td>0.97250</td>
<td>10.1</td>
<td>1.01</td>
<td>1123</td>
<td>3.05</td>
<td>1.8</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>P/13.4</td>
<td>0.97329</td>
<td>8.7</td>
<td>0.94</td>
<td>376</td>
<td>2.58</td>
<td>1.8</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>T/22.8</td>
<td>0.97359</td>
<td>6.7</td>
<td>0.82</td>
<td>80</td>
<td>1.90</td>
<td>1.5</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

One sample of these five, sample P/13.4, was selected for temperature-jump studies, where primary crystallisation was followed as usual by dilatometry at various temperatures, but once primary crystallisation was complete the dilatometer was withdrawn from the original thermostat bath and rapidly transferred to another - maintained at a single constant temperature - to follow the secondary crystallisation. Plots of specific volume against log. time are shown for the primary region - at different temperatures - in Figure 4.4.7, and for the secondary region - at a single constant temperature - in Figure 4.4.8. Measurement of the slope of the secondary crystallisation plots at specific times allows a comparison of the relative rates of secondary crystallisation (at one temperature) as a function of the temperature of primary crystallisation; these results being recorded in Table 4.09.
Sample P/13.4, Temperature Jump Dilatometry.

Primary Crystallisation

Specific Volume

Log Time (mins)

16°C  18°C  20°C  24°C
Sample P/13.4, Temperature Jump Dilatometry.

Secondary Crystallisation

Primary at 16°C

18°C

20°C

24°C

Log Time (mins)

Specific Volume

FIGURE 4.4.8
### Table 4.09 Rates of Secondary Crystallisation

<table>
<thead>
<tr>
<th>T_c (at 20)</th>
<th>dV/dlogt</th>
<th>V_0</th>
<th>V_∞</th>
<th>q (at T_c)</th>
<th>q (at 20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0.00355</td>
<td>1.0032</td>
<td>0.9450</td>
<td>0.0876</td>
<td>0.0610</td>
</tr>
<tr>
<td>18</td>
<td>0.00395</td>
<td>1.0050</td>
<td>0.9480</td>
<td>0.0868</td>
<td>0.0693</td>
</tr>
<tr>
<td>20</td>
<td>0.00495</td>
<td>1.0065</td>
<td>0.9472</td>
<td>0.0835</td>
<td>0.0835</td>
</tr>
<tr>
<td>24</td>
<td>0.00525</td>
<td>1.0092</td>
<td>0.9450</td>
<td>0.0709</td>
<td>0.0818</td>
</tr>
</tbody>
</table>

#### 4.4.2 Polarising Microscopy

When thin films (approx. 10μ) of polymer are allowed to crystallise under controlled conditions such that the film may be viewed through a polarising microscope, then spherulites are usually seen to develop in the film, commencing as small pinpoints and gradually increasing in size, their rate of radial growth being linear with time. Two samples of low molecular weight, T/3.3 and T/5.3 were investigated by this method at a series of temperatures within the range 16 to 24°C. Photographs of the resulting structures were taken at noted time intervals, and the diameter of these crystalline entities measured as a function of time. At each temperature the radii of several structures were measured at each time interval, the slopes calculated from linear regression and averaged to give the radial growth rate, Gr.

The results at each temperature, shown as plots of spherulite
diameter versus time, are illustrated in Figures 4.4.9 and 4.4.10 for samples T/3.3 and T/5.3 respectively, while the radial growth rates are shown as plots of log Gr against temperature in Figure 4.4.11.

4.4.3 Wide-Angle X-ray Scattering (WAXS)

Due to the mobility of these low molecular weight samples when molten the usual method of WAXS analysis based on relative amorphous areas could not be used in this work. In consequence the less reliable method (described in Section 3.6) was employed based on the ratio of crystalline to amorphous scattering to obtain results on four samples, but the larger than usual error inherent in these must be taken into consideration. The estimated error in these crystallinity measurements is of the order of ±5%, the results being given in Table 4.10. Comparative measurements on a high molecular weight sample by both methods yielded μ values which varied by 5%.

**Table 4.10**

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TIME AT 25°C (days)</th>
<th>PERCENT. CRYSTALLINITY</th>
<th>TIME AT 25°C (weeks)</th>
<th>PERCENT. CRYSTALLINITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/5.3</td>
<td>7</td>
<td>63.1</td>
<td>4</td>
<td>70.3</td>
</tr>
<tr>
<td>T/7.8</td>
<td>4</td>
<td>61.1</td>
<td>4</td>
<td>64.5</td>
</tr>
<tr>
<td>T/10.7</td>
<td>7</td>
<td>62.6</td>
<td>4</td>
<td>68.8</td>
</tr>
<tr>
<td>T/22.8</td>
<td>4</td>
<td>58.5</td>
<td>4</td>
<td>62.6</td>
</tr>
</tbody>
</table>
Sample T/3.3, Optical Microscopy

![Graph showing the relationship between sample size and time at different temperatures.]

- **0.6**
- **0.5**
- **0.4**
- **0.3**
- **0.2**
- **0.1**

**Temperature and Time**
- 16°C
- 17°C
- 18°C
- 19°C
- 20°C
- 21°C

**Y-axis**: Size (cm) X 100
**X-axis**: Time (mins x 10^-2)

**Legend**
- ○ 16°C
- □ 17°C
- ● 18°C
- □ 19°C
- ○ 20°C
- □ 21°C

**Figure 4.4.9**
Optical Microscopy, Radial Growth Rates

log $G_r$

$\times 400$

Temperature ($^\circ C$)
4.4.4 Differential Thermal Analysis (DTA)

DTA has been used extensively to provide measurements of melting point and heat of fusion, the data for samples having undergone crystallisation at 16°C and 24°C being recorded in Tables 4.11 and 4.12 respectively. The heats of fusion are recorded under \( \Delta H^1 \), as measured from the area under the melting peak. However, certain samples exhibit the phenomenon of double melting peaks - see Figure 4.4.12 - and for these cases, values of \( \Delta H \) for the highest temperature melting peaks only are recorded under \( \Delta H^1 \), while values from the total area under both peaks are recorded under \( \Delta H^2 \). Thus a blank entry under \( \Delta H^2 \) signifies a single melting transition.

FIGURE 4.4.12

![DTA traces for sample T/3.3 (24°C)](image)

The \( \Delta H \) results are calculated from the corresponding \( \Delta H \) data using a value for the heat of fusion of pure crystalline P(THF) of 200 J gm\(^{-1}\) (117). Plots illustrating the variation of melting point (highest temperature melting peak for double melting samples) with molecular weight are given in Figures 4.4.13 to 4.4.15 for different crystallisation conditions.
## TABLE 4.11

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TIME AT 16°C</th>
<th>MELTING POINT (°C)</th>
<th>$\Delta H^1$ (J gm$^{-1}$)</th>
<th>$\beta^1 \Delta H$</th>
<th>$\Delta H^2$ (J gm$^{-1}$)</th>
<th>$\beta^2 \Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>50 mins.</td>
<td>29.0</td>
<td>71.5</td>
<td>0.36</td>
<td>116.7</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>4 wks.</td>
<td>34.5</td>
<td>126.9</td>
<td>0.64</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T/5.3</td>
<td>50 mins.</td>
<td>31.7</td>
<td>97.4</td>
<td>0.49</td>
<td>135.3</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>2 wks.</td>
<td>37.0</td>
<td>102.8</td>
<td>0.51</td>
<td>107.9</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>4 wks.</td>
<td>38.4</td>
<td>125.8</td>
<td>0.63</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P/8.4</td>
<td>180 mins.</td>
<td>34.7</td>
<td>113.4</td>
<td>0.57</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2 wks.</td>
<td>36.9</td>
<td>122.3</td>
<td>0.61</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4 wks.</td>
<td>37.4</td>
<td>125.4</td>
<td>0.63</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P/13.4</td>
<td>100 mins.</td>
<td>33.9</td>
<td>96.2</td>
<td>0.48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2 wks.</td>
<td>39.2</td>
<td>132.2</td>
<td>0.66</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4 wks.</td>
<td>39.3</td>
<td>120.7</td>
<td>0.60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T/22.8</td>
<td>110 mins.</td>
<td>35.7</td>
<td>55.5</td>
<td>0.28</td>
<td>89.0</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>2 wks.</td>
<td>41.4</td>
<td>85.5</td>
<td>0.43</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4 wks.</td>
<td>42.5</td>
<td>96.9</td>
<td>0.49</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

## TABLE 4.12

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TIME AT 24°C</th>
<th>MELTING POINT (°C)</th>
<th>$\Delta H^1$ (J gm$^{-1}$)</th>
<th>$\beta^1 \Delta H$</th>
<th>$\Delta H^2$ (J gm$^{-1}$)</th>
<th>$\beta^2 \Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>192 hrs.</td>
<td>36.6</td>
<td>86.1</td>
<td>0.43</td>
<td>131.3</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>2 wks.</td>
<td>37.0</td>
<td>93.3</td>
<td>0.47</td>
<td>102.2</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>4 wks.</td>
<td>36.9</td>
<td>96.8</td>
<td>0.48</td>
<td>106.0</td>
<td>0.53</td>
</tr>
<tr>
<td>T/5.3</td>
<td>24 hrs.</td>
<td>37.9</td>
<td>81.4</td>
<td>0.41</td>
<td>98.1</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>2 wks.</td>
<td>40.8</td>
<td>103.3</td>
<td>0.52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4 wks.</td>
<td>41.4</td>
<td>121.1</td>
<td>0.61</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P/8.4</td>
<td>50 hrs.</td>
<td>39.5</td>
<td>104.8</td>
<td>0.52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2 wks.</td>
<td>40.6</td>
<td>130.3</td>
<td>0.65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4 wks.</td>
<td>42.0</td>
<td>127.9</td>
<td>0.64</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P/13.4</td>
<td>24 hrs.</td>
<td>40.7</td>
<td>123.0</td>
<td>0.62</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2 wks.</td>
<td>42.6</td>
<td>140.4</td>
<td>0.70</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4 wks.</td>
<td>42.9</td>
<td>132.8</td>
<td>0.66</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T/22.8</td>
<td>4.5 hrs.</td>
<td>39.7</td>
<td>97.7</td>
<td>0.49</td>
<td>99.1</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>2 wks.</td>
<td>46.1</td>
<td>100.9</td>
<td>0.51</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4 wks.</td>
<td>47.1</td>
<td>93.7</td>
<td>0.47</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Melting Point versus Molecular Weight

(1) End of Primary

$\overline{M_n} \times 10^{-3}$
Melting Point versus Molecular Weight

(2) After 2 weeks

![Graph showing the relationship between Melting Point and Molecular Weight at 16°C and 24°C after 2 weeks. The graph includes data points for molecular weights ranging from 5 to 25, with Melting Point values ranging from 35°C to 45°C. The graph indicates a positive correlation between molecular weight and melting point.]
Melting Point versus Molecular Weight

(3) After 4 weeks

Melting Point (°C)

$\bar{M}_n \times 10^{-3}$
4.4.5 Small Angle X-ray Scattering (SAXS)

Before documenting the SAXS data, it is useful to know the extended chain lengths of the samples under investigation - these may be calculated as follows:

The bond lengths and bond angles are known, e.g.,

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>C-C</th>
<th>1.541 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C-O</td>
<td>1.43 Å</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>C-C-C</th>
<th>109.5°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C-O-C</td>
<td>110.0°</td>
</tr>
</tbody>
</table>

from which it may be found that \( r = 6.12 \) Å. The molecular weight of a repeat unit \( = 72 \), thus the extended chain length of any molecular weight sample is given by:

\[
\text{Extended Chain Length} = \frac{\bar{M}_n \times 6.12}{72} \text{ Å}
\]

Values calculated for the samples used in this work are given in Table 4.13
Typical scattering curves, after parasitic scattering has been removed, are shown in Figures 4.4.17 to 4.4.21. After desmeasuring and applying the Lorentz correction, the Bragg repeat period is determined and the experimental correlation function calculated. Fitting this with a theoretical correlation function allows appropriate values of the model to be assigned, these data being recorded as follows.

Tables 4.14 and 4.15 contain results of $\phi_{SV}$, $(C+A)_a$ (average repeat period), $C$ (lamella thickness), $A$ (amorphous thickness), and the number of folds, where:

$$\text{Number of folds} = \frac{\text{Extended Chain Length}}{C}$$

for crystallisation temperatures of $16^\circ C$ and $24^\circ C$ respectively.

Tables 4.16 and 4.17 contain results of $\beta_a$ and $\beta_c$, (the amorphous and crystalline distribution widths), $\Delta A$ and $\Delta C$, (the absolute spread of chain lengths in $\AA$ from the distributions $\beta_a$ and $\beta_c$), for crystallisation temperatures of $16^\circ C$ and $24^\circ C$ respectively.
Scattering Curve, Sample T/3.3, 24°C, 7 days

Intensity (c.p.)

Angle (degrees)
Scattering Curve, Sample T/5.3, 16°C, 5 weeks
Scattering Curve, Sample T/7.8, 16°C, 18 hours

![Scattering Curve Diagram]
Scattering Curve, Sample T/11.4, 16°C, 2.5 days

Intensity (c.p.100g)

Angle (degrees)
Scattering Curve, Sample T/22.8, 24°C, 4 weeks
### TABLE 4.14 Structural Parameters from SAXS

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TIME AT 16°C</th>
<th>$\phi_{SV}$</th>
<th>(C+A)$_a$</th>
<th>C (°A)</th>
<th>A (°A)</th>
<th>No. of FOLDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>35 min</td>
<td>0.59</td>
<td>133</td>
<td>79</td>
<td>54</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>2 wks</td>
<td>0.63</td>
<td>137</td>
<td>86</td>
<td>51</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.69</td>
<td>135</td>
<td>93</td>
<td>42</td>
<td>2.0</td>
</tr>
<tr>
<td>T/5.3</td>
<td>60 min</td>
<td>0.56</td>
<td>135</td>
<td>76</td>
<td>59</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>5 wks</td>
<td>0.70</td>
<td>130</td>
<td>91</td>
<td>39</td>
<td>4.0</td>
</tr>
<tr>
<td>T/7.8</td>
<td>16 hrs</td>
<td>0.51</td>
<td>132</td>
<td>67</td>
<td>65</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>19 days</td>
<td>0.60</td>
<td>133</td>
<td>80</td>
<td>53</td>
<td>7.3</td>
</tr>
<tr>
<td>T/11.4</td>
<td>2.5 days</td>
<td>0.51</td>
<td>138</td>
<td>70</td>
<td>68</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.58</td>
<td>136</td>
<td>79</td>
<td>57</td>
<td>11.3</td>
</tr>
<tr>
<td>P/13.4</td>
<td>80 min</td>
<td>0.64</td>
<td>136</td>
<td>87</td>
<td>49</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.78</td>
<td>145</td>
<td>113</td>
<td>32</td>
<td>9.1</td>
</tr>
<tr>
<td>T/22.8</td>
<td>40 min</td>
<td>0.50</td>
<td>143</td>
<td>72</td>
<td>71</td>
<td>25.9</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.56</td>
<td>145</td>
<td>81</td>
<td>64</td>
<td>22.9</td>
</tr>
</tbody>
</table>

### TABLE 4.15 Structural Parameters from SAXS

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TIME AT 24°C</th>
<th>$\phi_{SV}$</th>
<th>(C+A)$_a$</th>
<th>C (°A)</th>
<th>A (°A)</th>
<th>No. of FOLDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>7 days</td>
<td>0.64</td>
<td>157</td>
<td>101</td>
<td>56</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>5 wks</td>
<td>0.67</td>
<td>160</td>
<td>107</td>
<td>53</td>
<td>1.6</td>
</tr>
<tr>
<td>T/5.3</td>
<td>16 hrs</td>
<td>0.60</td>
<td>151</td>
<td>91</td>
<td>60</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.72</td>
<td>148</td>
<td>107</td>
<td>41</td>
<td>3.2</td>
</tr>
<tr>
<td>T/7.8</td>
<td>2.5 days</td>
<td>0.57</td>
<td>150</td>
<td>86</td>
<td>64</td>
<td>6.7</td>
</tr>
<tr>
<td>P/13.4</td>
<td>24 hrs</td>
<td>0.67</td>
<td>158</td>
<td>106</td>
<td>52</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.76</td>
<td>170</td>
<td>129</td>
<td>41</td>
<td>7.8</td>
</tr>
<tr>
<td>T/22.8</td>
<td>4 hrs</td>
<td>0.52</td>
<td>160</td>
<td>83</td>
<td>77</td>
<td>22.4</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.56</td>
<td>165</td>
<td>92</td>
<td>73</td>
<td>20.0</td>
</tr>
</tbody>
</table>
Typical correlation functions, both experimental and theoretical, are shown in Figures 4.4.22 to 4.4.26.

**TABLE 4.16** Distribution widths from SAXS

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TIME AT 16°C</th>
<th>( \beta_a )</th>
<th>( \beta_c )</th>
<th>( \Delta A ) (Å)</th>
<th>( \Delta C ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>35 min</td>
<td>0.15</td>
<td>0.11</td>
<td>39.5</td>
<td>29.5</td>
</tr>
<tr>
<td></td>
<td>2 wks</td>
<td>0.12</td>
<td>0.08</td>
<td>33.1</td>
<td>21.8</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.12</td>
<td>0.08</td>
<td>32.5</td>
<td>21.6</td>
</tr>
<tr>
<td>T/5.3</td>
<td>60 min</td>
<td>0.23</td>
<td>0.03</td>
<td>61.7</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>5 wks</td>
<td>0.15</td>
<td>0.10</td>
<td>39.0</td>
<td>26.0</td>
</tr>
<tr>
<td>T/7.8</td>
<td>18 hrs</td>
<td>0.20</td>
<td>0.10</td>
<td>53.1</td>
<td>26.3</td>
</tr>
<tr>
<td></td>
<td>19 days</td>
<td>0.16</td>
<td>0.14</td>
<td>42.4</td>
<td>37.3</td>
</tr>
<tr>
<td>T/11.4</td>
<td>2.5 days</td>
<td>0.23</td>
<td>0.04</td>
<td>63.8</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.20</td>
<td>0.12</td>
<td>54.3</td>
<td>32.7</td>
</tr>
<tr>
<td>P/13.4</td>
<td>80 min</td>
<td>0.26</td>
<td>0.26</td>
<td>70.8</td>
<td>70.7</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.28</td>
<td>0.24</td>
<td>81.5</td>
<td>69.5</td>
</tr>
<tr>
<td>T/22.8</td>
<td>40 min</td>
<td>0.28</td>
<td>0.03</td>
<td>79.5</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.23</td>
<td>0.07</td>
<td>66.9</td>
<td>20.3</td>
</tr>
</tbody>
</table>

**TABLE 4.17** Distribution widths from SAXS

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TIME AT 24°C</th>
<th>( \beta_a )</th>
<th>( \beta_c )</th>
<th>( \Delta A ) (Å)</th>
<th>( \Delta C ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>7 days</td>
<td>0.17</td>
<td>0.11</td>
<td>52.9</td>
<td>34.7</td>
</tr>
<tr>
<td></td>
<td>5 wks</td>
<td>0.21</td>
<td>0.06</td>
<td>67.5</td>
<td>19.2</td>
</tr>
<tr>
<td>T/5.3</td>
<td>16 hrs</td>
<td>0.18</td>
<td>0.12</td>
<td>54.0</td>
<td>36.4</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.13</td>
<td>0.12</td>
<td>38.1</td>
<td>35.7</td>
</tr>
<tr>
<td>T/7.8</td>
<td>2.5 days</td>
<td>0.16</td>
<td>0.11</td>
<td>47.6</td>
<td>33.2</td>
</tr>
<tr>
<td>P/13.4</td>
<td>24 hrs</td>
<td>--0.24</td>
<td>0.26</td>
<td>75.6</td>
<td>82.3</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.22</td>
<td>0.24</td>
<td>75.2</td>
<td>81.5</td>
</tr>
<tr>
<td>T/22.8</td>
<td>4 hrs</td>
<td>0.32</td>
<td>0.005</td>
<td>102.7</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>4 wks</td>
<td>0.25</td>
<td>0.08</td>
<td>83.0</td>
<td>26.3</td>
</tr>
</tbody>
</table>
Correlation Functions, Sample T/3.3, 24°C, 7 days

- Theoretical
- Experimental

$\gamma(x)$

$\mathbf{x} (\mathbf{R})$
Correlation Functions, Sample T/5.3, 16°C, 5 weeks

- Theoretical
- Experimental

$\gamma(x)$

$x(\lambda)$
Correlation Functions, Sample T/7.8, 16°C, 18 hours

- Theoretical
- Experimental
Correlation Functions, Sample T/11.4, 16°C, 2.5 days

- Theoretical
- Experimental

\( \gamma(x) \)

\( x(\lambda) \)
Correlation Functions, Sample T/22.8, 24°C, 4 weeks

Theoretical

Experimental

\( \gamma(x) \)
5.1 SYNTHESIS

The polymerisation of THF was first reported by Meerwein in 1939 (14), but this work did not become generally available until 1960 (119). A review of this field was published by Dreyfuss and Dreyfuss in 1967 (13), and more recent reviews have also appeared (19,21,25,120). The polymerisation was soon realised to be reversible, such that only a limiting conversion could be obtained at a given temperature due to an equilibrium between monomer and polymer being reached. The variation of this equilibrium position with temperature has been demonstrated (15,28). The theory of reversible addition polymerisation, proposed by Dainton and Ivin (17), defines the concept of a ceiling temperature (Section 2.1.1) such that for any given monomer concentration, a critical temperature (the ceiling temperature) exists above which polymerisation to high polymer cannot occur. Similarly at a constant temperature a critical monomer concentration exists such that this must remain as monomer - hence only a limiting conversion is possible. The ceiling temperature may be estimated by plots of either equilibrium conversion or rate of polymerisation versus temperature, \( T_c \) being the point at which the curve cuts the temperature axis. The accepted value of the ceiling temperature for bulk THF polymerisation obtained in this way is \( 84 \pm 2^\circ C \) (28).

The polymerisation of THF occurs only by a cationic mechanism, and it is now widely accepted (28,121,122) that the propagating species is the tertiary oxonium ion (1), growth of

\[
\begin{align*}
\{0 - \text{\CH}_2 - \text{\CH}_2 - \text{\CH}_2 - \text{\CH}_2 \}_n & \xrightarrow{2} \text{\CH}_2 \\
\{0 - \text{\CH}_2 - \text{\CH}_2 - \text{\CH}_2 - \text{\CH}_2 \}_{n+1} & \xrightarrow{0}
\end{align*}
\]
which occurs via nucleophilic attack by monomer oxygen upon carbon atoms 2 or 3 (i.e. \( \alpha \)- to the oxygen). Attack upon carbon 1 results in the substitution of one oxonium ion for another, thus there is no net change. Since propagation occurs only cationically, initiators for the polymerisation are generally either strong or Lewis acids or their salts, resulting finally in the species (II) which may then

\[
\begin{align*}
\text{R} & \quad \text{O}^+ \\
\text{II}
\end{align*}
\]

be attacked by monomer. Termination may occur with impurity species, such as water, oxygen, amines, acids etc., and as with all ionic polymerisations great care is necessary to remove such species prior to polymerisation. Apart from impurities the most likely cause of termination is by reaction with the counter-ion. Evidence has been put forward (27) to show that although this does occur with less-stable counter-ions, when \( \text{PF}_6^- \) is used no termination occurs and a true living system results. The order of stability of counter-ions with respect to termination was found to be:

\[
\text{PF}_6^- \approx \text{SbF}_6^- > \text{BF}_4^- \geq \text{SbCl}_6^-
\]

Other evidence supporting a living system when using \( \text{PF}_6^- \) counter-ion comes from the additional polymerisation of a second batch of monomer (either THF or other suitable monomer) (28,123), and from the polymerisation - depolymerisation - repolymerisation experiments in the presence of \( \text{PF}_6^- \) ions (15, 28).

With a living system it should be straightforward, by analogy with anionic polymerisations, to control the molecular weight, and its distribution, of the product. However, although molecular weight may be predicted fairly readily, many factors contribute to broadening of the molecular weight distribution which do not occur in the anionic case.
These factors have been discussed in detail in Section 2.1.6, and may be summarised as relative stabilities of carbanion versus carbenium ion, equilibrium effects, chain transfer, slow initiation, ion/ion-pair equilibria and macroion-macroester equilibria.

Much work has been undertaken to study the kinetics of THF polymerisation using different initiators (13,19,124). Polymerisation with initiators which react rapidly to produce a constant number of growing centres fit the rate equation 2.12;

\[
\frac{2.303}{[1]_o} \log \left( \frac{[M_1]_o - [M_1]_e}{[M_1]_t - [M_1]_e} \right) = k_p t
\]

2.12

Triethylaloxonium salts are reported (21) to initiate polymerisations which fit this equation. Other initiators do not rapidly produce a constant number of active centres, and polymerisations with these initiators follow equation 2.09;

\[
\ln \frac{[M_1]_{t1} - [M_1]_e}{[M_1]_{t2} - [M_1]_e} = k_p \int_{t1}^{t2} [P^*] \, dt
\]

2.09

Equation 2.12 is derived from 2.09 by assuming that the concentration of active chain-ends \([P^*]\) is equal to the concentration of initiator reacted. The phenoxy-endcapping method, developed by Saegusa et al. (18) enables \([P^*]\) to be determined directly, and these workers have examined the kinetics of polymerisation initiated by different initiators using equation 2.09 (19). They show that for systems where \([P^*]\) increases with time, a plot of

\[
\ln \left( \frac{[M_1]_{t1} - [M_1]_e}{[M_1]_{t2} - [M_1]_e} \right)
\]

against time is not linear, whereas if the former is plotted against
\[
\int_{t_1}^{t_2} [P^*] \, dt \quad \text{a straight line results, see Figure 5.1.1.}
\]

**FIGURE 5.1.1**

\[ [P^*] \quad \text{t} \quad \ln \left( \frac{[M]_{t_2}}{[M]_{t_1}} \right) \quad \int_{t_1}^{t_2} [P^*] \, dt \]

### 5.1.1 Clean Initiation Conditions

Initiation of THF polymerisation by p-chlorophenyl diazonium hexafluorophosphate has been studied in detail during this work to elucidate reasons for the broad molecular weight distributions normally obtained, and to evolve a method of producing monodisperse polymers.

Figure 4.1.1 shows the effect of increasing initiation time (other conditions remaining constant) upon the molecular weight and its distribution at 60°C. The molecular weight is seen to increase with initiation time, as is the molecular weight distribution. Similarly, Figure 4.1.2 shows the results of maintaining a short initiation time (5 or 7.5 mins.) at a series of temperatures close to and above the ceiling temperature, (other conditions remaining constant). Only one critical initiation temperature, 95°C, is found to give a narrow, undistorted molecular weight distribution, when initiation is performed.
These results may be explained by considering the initiation reaction in detail. Basically initiator molecules react by some mechanism (see Section 2.1.4) with monomer molecules to form an active centre capable of growth by the addition of further monomer. If the initiation reaction rate is comparable to or slower than the polymerisation rate, then those active centres formed early will polymerise while new centres are still being formed, thus polymerisation will occur during initiation. At a constant initiation temperature, the molecular weight and its distribution will both increase with time because polymerisation is occurring concurrently. The constant propagation conditions will add the same molecular weight interval to each sample, thus the increasing initiation time is reflected by the increase in molecular weight parameters.

As the ceiling temperature is approached, the overall rate of polymerisation passes through a maximum and then decreases, due to increasing depropagation, whereas the initiation rate will increase with increasing temperature. As a result a critical temperature will be reached when the initiation rate becomes faster than the overall propagation rate, leading to a sharpening of the molecular weight distribution. In fact it is found that above the ceiling temperature (i.e. at 95°C) propagation is reduced sufficiently to allow the formation of active centres without any accompanying polymerisation. If this active system is now quenched rapidly to a suitable reaction temperature, we are effecting instantaneous initiation by allowing all the active sites to propagate simultaneously, any unused initiator being prevented from reacting by the low polymerisation temperature. Thus the kinetics of this system may be expected to follow equation 2.12 (see Section 5.1), and as shown in Figure 5.1.3, (Section 5.1.2), plots of
against time are linear at low reaction temperatures.

$\frac{2.303}{[I_0]} \log \left( \frac{[M_1]_e - [M_1]_o}{[M_1]_t - [M_1]_e} \right)$

The initiation conditions found necessary for the preparation of monodisperse samples, referred to as the clean initiation conditions, were 95°C for 5 mins. It was subsequently found that 4 mins. produced still sharper distributions, so these conditions were adopted for all further polymerisations with this initiator. The production of active centres at a high temperature introduces the problem of cooling the reactants rapidly to a low propagation temperature without causing polymerisation during the quenching process. A system of rapid cooling (15 sec at -10°C, 15 sec in liquid nitrogen) was adopted as standard which, when used with helical reactors (Figure 3.1.1) allowed rapid heat transfer to and from the reactants.

5.1.2 Kinetics of Propagation

After clean initiation and rapid quenching, propagation was investigated at a series of low reaction temperatures. The yields of products and their molecular weights were measured to enable a kinetic analysis of the data to be performed, these results being shown in Table 4.01 and Figure 4.1.3 respectively. The conversion data are shown plotted against reaction time in Figure 5.1.2 for each reaction temperature, where it is seen that the conversion increases linearly with time except at the higher temperature. The lines do not pass through the origin because the reaction time does not include the initiation and quenching times, where a certain amount of conversion (≈ 0.7%) occurs. Although the lines at -10°C and 0°C are linear, the corresponding plots of $M_n$ against time, Figure 4.1.3, show a linear variation at -10°C but at 0°C $M_n$ falls away
Conversion versus Reaction Time, Initiator P

- 20°C
- 0°C
- -10°C

Percent Conversion

Time (hours)
from a straight line suggesting that chain transfer processes are becoming significant at this temperature. Typical chain transfer processes, as shown below:

\[
\text{---P} \text{O} \text{---P} \xrightarrow{\text{t} \text{O/}} \text{O} \text{---P} \text{F} \_6 \xrightarrow{\text{---P} \text{F} \text{F} \_6 \xrightarrow{\text{---P} \text{F} \text{F} \_6 \xrightarrow{\text{---P} \text{F} \text{F} \_6}}
\]

are discussed in Section 2.1.6, where it is recognised that transfer will lead to broadening of the polydispersity ratio. This is confirmed by the results in Table 4.02, showing the polydispersity ratios as a function of reaction time at each temperature. Those at -10°C remain narrow, whilst those at 0°C broaden with time.

As detailed in Section 2.1, the rate of polymerisation, assuming a negligible quantity of monomer is consumed during initiation at the low reaction temperatures, may be represented by equation 2.08

\[
\frac{-d[M_1]}{dt} = k_p \left( [M_1] - [M_1]_e \right) [P^*]
\]

However not all of the initiator which decomposes necessarily starts a polymer chain, thus we may define \( n \):

\[
n = \frac{\text{mols initiator decomposed}}{\text{mol chains started}}
\]

(i.e., the number of initiators required to start one chain).
Integration and rearrangement of 2.08 yields

\[
\ln \left( \frac{[M_1]_o - [M_1]_e}{[M_1]_t - [M_1]_e} \right) = k_p \int_0^t [P^*] \, dt
\]

and following equation 2.10

\[
\int_0^t [P^*] \, dt = \frac{([I]_o - [I])}{n} \cdot t
\]

Substituting 5.03 into 5.02, and dividing by \([I]_o\) gives

\[
\frac{2.303 \log \left( \frac{[M_1]_o - [M_1]_e}{[M_1]_t - [M_1]_e} \right)}{[I]_o} = \frac{k_p}{n} \cdot t \cdot \frac{[I]_o - [I]}{[I]_o}
\]

Now

\[
\frac{[I]_o - [I]}{[I]_o} = f
\]

where \(f\) is the fraction of initiator decomposed at high temperature, thus

\[
\frac{2.303 \log \left( \frac{[M_1]_o - [M_1]_e}{[M_1]_t - [M_1]_e} \right)}{[I]_o} = \frac{f}{n} \cdot k_p \cdot t
\]

By plotting the L.H.S. of 5.06 against \(t\), the reaction time, the quantity \((f/n) k_p\) may be determined from the slope, and \(k_p\) is obtained from this value as follows:

\[
\text{Number of moles of chains started} = \frac{\text{Yield}}{n} \, (\text{mol} \, l^{-1})
\]

Thus from equation 5.01,

\[
n = \frac{([I]_o - [I])}{Yield} \frac{\overline{M_n}}{n}
\]

Combining this with equation 5.05 gives

\[
\frac{f}{n} = \frac{\text{Yield}}{\overline{M_n} \cdot [I]_o}
\]
which is a constant for these initiation conditions, and equals approximately 0.1.

The data are shown plotted as discussed above in the form of equation 5.06 in Figure 5.1.3. Data required for these plots are shown in Table 5.01, along with values of \( k_p \) determined as described above. The lower temperature data exhibit good straight lines whereas at 20°C the plot shows a slight positive deviation, suggesting that at 20°C concurrent initiation with propagation occurs causing this effect as shown in Figure 5.1.1 for a system where \([P^*]\) increases with time.

5.1.3 **High Temperature Propagation**

Propagation at higher temperatures was studied, after 'clean' initiation, for a constant reaction time at different temperatures, the results given in Table 4.03 being shown in Figure 5.1.4 as a plot of conversion against reaction temperature. The data was analysed kinetically using equation 5.06 by plotting the L.H.S. against \( t \). This gave only a single point (after 10 mins.) at each temperature, but using values of the intercept estimated from Figure 5.1.3, a straight line was drawn from which \((f/n) k_p\), and hence \( k_p \), was estimated. When these \( k_p \) values were substituted into equation 5.06, and the theoretical conversion calculated, good agreement was obtained with the experimental values as shown by the dotted line in Figure 5.1.4. The data required for the single point plots, together with the \( k_p \) values obtained, are given in Table 5.01. Figure 5.1.4 is essentially a plot of polymerisation rate, i.e., amount of polymer produced per 10 mins., against reaction temperature, and as such may be used to estimate the ceiling temperature - the point at which the polymerisation rate becomes zero, i.e., cuts the temperature axis (17). The data when extrapolated yields a value of 85 ± 3°C for the ceiling temperature, literature value 84 ± 2°C (28).
Kinetic Plot using Equation 5.06

\[
\frac{[M]_t}{[M]_0} = \frac{[M]_e}{[M]_0} - \frac{[M]_t}{[M]_0} e^{-k t}
\]

\( t \geq 0 \)

Temperature:
- 20°C
- 0°C
- -10°C
## TABLE 5.01 Kinetic Data, Initiator P

<table>
<thead>
<tr>
<th>TEMPERATURE (°C)</th>
<th>([M_1]_e) (mol (^{-1}))</th>
<th>([M_1]_o) (mol (^{-1}))</th>
<th>(k_p) ((1 \text{ mol}^{-1} \text{ sec}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>1.25</td>
<td>12.74</td>
<td>9.20 x 10^{-4}</td>
</tr>
<tr>
<td>0</td>
<td>1.70</td>
<td>12.60</td>
<td>2.20 x 10^{-3}</td>
</tr>
<tr>
<td>20</td>
<td>2.96</td>
<td>12.32</td>
<td>1.46 x 10^{-2}</td>
</tr>
<tr>
<td>50</td>
<td>5.93</td>
<td>11.90</td>
<td>1.29 x 10^{-1}</td>
</tr>
<tr>
<td>60</td>
<td>7.32</td>
<td>11.76</td>
<td>2.85 x 10^{-1}</td>
</tr>
<tr>
<td>70</td>
<td>8.94</td>
<td>11.63</td>
<td>5.19 x 10^{-1}</td>
</tr>
<tr>
<td>80</td>
<td>10.81</td>
<td>11.49</td>
<td>1.05 x 10^{-0}</td>
</tr>
</tbody>
</table>

* \([M_1]_e\) values from Ofstead (125)
Yield (per 10 mins) versus Propagation Temperature

- -- Experimental Points
- - - Calculated from 5.06

Percent Conversion

Temperature (°C)
5.1.4 Propagation Rate Constants

When the ln. \( k_p \) values are plotted against \( 1/T \) K as an Arrhenius expression (equation 2.21), as in Figure 5.1.5, a straight line results from the slope of which an activation energy of 51.3 kJ.mol\(^{-1}\) may be calculated. This agrees well with the value of 50.2 kJ.mol\(^{-1}\) quoted by Saegusa (19) for bulk THF polymerisations initiated by BF\(_3\)-epichlorohydrin and by Al Et\(_3\) - H\(_2\)O (2:1) - epichlorohydrin. Also this plot shows good agreement between the \( k_p \) values determined at low reaction temperatures and those calculated from the single point determinations at high reaction temperatures.

5.1.5 Triethyloxonium Hexafluorophosphate Initiator

Polymerisation of THF initiated by triethyloxonium hexafluorophosphate has also been studied at a single reaction temperature, conversions and molecular weight averages having been determined as previously discussed. These data are given in Table 4.04 and Figure 4.1.5 respectively.

Polymerisations using this initiator did not require a separate initiation stage, as for p-chlorophenyldiazonium hexafluorophosphate, but initiation occurred rapidly upon mixing with monomer and the reaction time was taken from the point of initial mixing. Since the separate initiation reaction was not required, we may use equation 2.12 directly to analyse the data, rather than equation 5.06.

\[
2.303 \log \frac{[M_1]^t}{[M_1]^o} = k_p t
\]

A plot of the L.H.S. against \( t \) is shown in Figure 5.1.6, where the result is a curve showing a positive deviation from the straight lines previously obtained for similar plots. Also Figure 4.1.5 shows \( \bar{M} \) to increase linearly with time, except at high conversions (30%), which suggests chain transfer is not occurring to any significant extent agreeing with the
$\ln k_p$ versus $1/\text{Propagation Temperature}$

- High Temperature
- Low Temperature
- Initiator T

$(1/T) \times 10^3$
Kinetic Plot using Initiator T at -5°C

○ Experimental Data
□ Data Corrected for Slow Initiation

Reaction Time (hours)
conditions of low temperature and low conversion found previously to reduce chain transfer.

Previously it was suggested that this type of positive deviation in a kinetic plot was caused by an increasing concentration of active centres, as demonstrated in Figure 5.1.1, the curvature being removed if $t$ is replaced by $\int_{t_1}^{t_2} [P^*] \, dt$ as the independent variable. In the absence of $\int_{t_1}^{t_2} [P^*] \, dt$ data, other evidence will be examined to determine the cause of this deviation.

In support of this slow initiation scheme we may consider the work of Tobolsky (26) using $^{14}$C labelled triethyl oxonium tetrafluoroborate initiator for the solution polymerisation of THF in dichloroethane. The conversion of initiator throughout the reaction was determined, and is shown plotted against monomer conversion, see Figure 5.1.7. Plots of $[P^*]$ versus time for the same initiator in bulk THF have been shown to be similar (19). From Figure 5.1.7, and knowing the monomer conversion, it is possible to estimate $[I]_e$, the concentration of initiator effective in starting chains, and to use this value instead of $[I]_o$, the concentration of initiator charged, in equation 2.12. These values are given in Table 5.02, and the recalculated values of the L.H.S. of equation 2.12 are shown plotted on the same axis in Figure 5.1.6.
Rate of Initiator Consumption, from (26)
Although this recalculated plot is less curved, it still carries a noticeable positive deviation. It must also be remembered that the estimated slowness of initiation as shown in Figure 5.1.7, i.e., initiator not totally consumed until some 30% of monomer has reacted - about 4 hours, could not be tolerated in this system and still yield narrow distribution polymers. The polydispersity ratios are, as shown in Table 4.04, all close to 1.10 or less, which is not consistent with initiation still proceeding up to 4 hours after mixing.

The initiator used in Tobolsky's work, $\text{Et}_2\text{O}^+\text{BF}_4^-$, in dichloroethane solution, must therefore react more slowly than $\text{Et}_2\text{O}^+\text{PF}_6^-$ in bulk THF. This is reasonable since not only is the $\text{PF}_6^-$ counter-ion more stable, but reaction in solution will follow different kinetics from reaction in bulk. Thus the straightening effect on the kinetic plot from slow initiation is an overestimate, and an alternative mechanism is required to explain the
positive deviation at higher conversions.

The phenomenon of auto-acceleration is well known in free radical polymerisation, where the increasing viscosity of the medium slows down the movement of the growing chain-ends and allows them to react with more monomer than previously before meeting another radical and terminating. Also the concentration of radicals increases due to lack of termination. This has the effect of a positive deviation on the rate of free-radical polymerisation at higher conversions. In ionic polymerisations, mutual termination does not occur, but rather the opposite, i.e., the growing chain-ends are thought to remain in clusters associated with their counter-ions (126). As monomer conversion increases, the chains become longer, and they too will tend to be affected by the increasing viscosity of the medium. By analogy with the free-radical case, increasing viscosity, chain entanglements etc., tend to keep chain-ends apart, thus breaking down the ionic clusters to their more reactive ion-pairs. This enables the chain-ends to 'see' more monomers than they would while clustered, and so both conversion and molecular weight will increase. A combination of both effects, slow initiation and increasing viscosity, combine to explain the positive deviation obtained in the kinetic plot. Slow initiation cannot be the only cause since very narrow distribution polymers are obtained. The variation of molecular weight with time, Figure 4.1.5, at low conversions - below 15% - yields a straight line indicating the absence of chain transfer. However at higher conversions chain transfer to polymer oxygen will become increasingly important, leading to a negative deviation from a straight line as shown in Figure 4.1.3 for reaction at 0°C. This will be in competition with the cluster breakdown effect discussed previously which gives a positive deviation. It is apparent from the slight positive deviation in Figure 4.1.5 at higher
conversions - above 15% - that the accelerating effect caused by the breakdown of ionic clusters is dominant, although reduced by the onset of chain transfer.

The value of $k_p$ is similar from both plots in Figure 5.1.6, being $1.8 \times 10^{-3}$ mol$^{-1}$ sec$^{-1}$ at $-5^\circ$C. This is seen to compare well with values of $k_p$ determined using initiator $P$ by including this point on the Arrhenius plot in Figure 5.1.5, ln. $k_p$ versus $1/T K$, where it is seen to fall close to the straight line obtained for the previous initiator.
5.2 MOLECULAR WEIGHT DISTRIBUTIONS

Several theoretical expressions for the molecular weight distributions obtained during polymerisation reactions have been proposed (127), some of these being shown graphically in Figure 5.2.1. The most probable or Flory distribution is commonly attained in condensation polymerisations giving linear chain molecules (128), where the ratio $\frac{M_w}{M_n} = \frac{x}{x_n} = 2$.

With free radical polymerisations, if restricted to low conversion, and if termination is by disproportionation (or transfer), then the resulting distribution is again the most probable or Flory, with $\frac{M_w}{M_n} = 2$.

Termination by combination is more complex, but if chain transfer is absent then $\frac{M_w}{M_n} = 1.5$ (1). If the polymerisation is allowed to proceed to high conversions, $x_n$ (instantaneous) decreases and $\frac{M_w}{M_n}$ increases as conversion increases, due to the decreasing monomer concentration. This may be seen from equation 5.10 (1) for the kinetic chain length $\eta$, (with no chain transfer),

$$\eta = \frac{k_p}{2(f k_d k_t)} \frac{[M]^{1/2}}{[I]^{1/2}}$$

where $k_p$ is the propagation rate constant,

$k_d$ is the initiation rate constant,

$k_t$ is the termination rate constant,

$f$ represents the fraction of radicals successful in initiating chains,

$[M]$ is the monomer concentration,

$[I]$ is the initiator concentration and

$x_n = \eta$ for termination by disproportionation or $x_n = 2\eta$ for termination by combination.

As $[M]$ decreases so will $\eta$ and hence $x_n$, which will lead to $\frac{M_w}{M_n}$ approaching infinity as a limit. In practice however, typical values for high conversion free radical polymerisations rarely exceed 5.
Molecular Weight Distributions

- Flory
- Exponential
- Schulz
- Log Normal
- Normal
- Poisson

Arbitrary Units

Figure 5.2.1
Polymers formed by monomer addition where termination is absent often have very narrow molecular weight distributions. Such systems are found readily in anionic living polymerisations, such as the preparation of polystyrene using n-Butyl Lithium initiator in hydrocarbon solvents, but less readily in cationic systems. Reasons for broadening of the $\frac{M_w}{M_n}$ ratio in THF polymerisation have already been discussed in detail (see Section 2.1.6). However in principle a Poisson distribution of molecular weights should result in the early stages of an ionic, living polymerisation (1). The $\frac{M_w}{M_n}$ ratio for a Poisson distribution may be found from equation 5.11,

$$\frac{M_w}{M_n} = 1 + \frac{1}{x_n}$$  \[5.11\]

Values of $\frac{M_w}{M_n}$ calculated from equation 5.11 for various values of $x_n$ are given in Table 5.03:

<table>
<thead>
<tr>
<th>$x_n$</th>
<th>$M_n$</th>
<th>$P($THF$)$</th>
<th>$\frac{M_w}{M_n}$ (Poisson)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>72</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>144</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>360</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>720</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1440</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>3600</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>7200</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>72000</td>
<td>1.001</td>
<td></td>
</tr>
</tbody>
</table>

from which it may be seen that as $x_n$ increases, so $\frac{M_w}{M_n}$ becomes sharper. Other factors intervene to increase $\frac{M_w}{M_n}$, such as slow initiation, chain transfer, termination etc., so that even the 'monodisperse'
polystyrene standards for GPC calibration usually have polydispersity ratios between 1.05 and 1.10.

The monodisperse P(THF) samples prepared in this work generally have a polydispersity ratio of 1.07 to 1.10, and although this is very narrow in relation to the normal $M_w/M_n$ values obtained for P(THF), inspection of the widths of distributions at half the peak height, (henceforth referred to as the half-width), serves to give a measure of the absolute spread of molecular weights. For the most probable distribution given in Figure 5.2.1, having $\bar{x}_n = 100$, (equivalent $\bar{M}_n$ for P(THF) = 7200) the molecular weight limits cover the range 1700 to 19400, thus the absolute spread at the half-width is 17700. A distribution of P(THF) having $\bar{M}_n = 7500$ and $M_w/M_n = 1.09$, see Figure 5.2.2 for example, has a half width of 5000 to 9800 = 9800, almost half the value from the most probable distribution. The Poisson distribution shown in Figure 5.2.1, also having a P(THF) equivalent $\bar{M}_n$ of 7200, has a half-width of 6480 to 7920 = 1440. From Table 5.03, for $\bar{x}_n = 100$ (i.e., $\bar{M}_n$ for P(THF) = 7200), then $M_w/M_n$ for a Poisson distribution = 1.01, thus if $\bar{M}_n = 7200$, $M_w = 7272$. Obviously the distributions attained by these polymers are not sharp enough for Poisson distributions, but they are still very narrow by normal standards and are certainly much sharper than the most probable distributions. Table 5.04 compares some theoretical (Poisson) polydispersity ratios with the experimental values for polymers prepared with triethyloxonium hexafluorophosphate initiator:
FIGURE 5.2.2

Experimental Molecular Weight Distribution

\[ \frac{M_w}{M_n} = 1.09 \]

\[ M_n = 7500 \]
It is apparent that in general the experimental polydispersity ratio is broader than the theoretical value, only in the very early stages of the reaction - at less than 0.3\% conversion - does the experimental ratio agree with the theoretical. This supports the suggestion that if initiation is rapid and no termination occurs, then a Poisson distribution of molecular weights is formed in the very early stages of polymerisation, but the distribution then tends to broaden to about 1.1 instead of becoming still sharper. Reasons for this limited degree of broadening are the same as those previously discussed (Section 2.1.6), but because they are being controlled by a suitable choice of reaction conditions, their effects are minimised.

It should also be noted that although the polydispersity ratios for all the samples used in the crystallisation studies are low, around 1.1, there will be an increase in the absolute spread of molecular weights for a given sample as $\bar{M}_n$ increases. Thus for the 2 samples T/3.3 and T/22.8 in Table 5.05:
it is seen that although the polydispersity ratio sharpens from 1.09 to 1.07, the absolute spread of molecular weights (given in this case by $\bar{M}_w - \bar{M}_n$) increases from 300 to 1600.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>$\bar{M}_w/\bar{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T/3.3$</td>
<td>3300</td>
<td>3600</td>
<td>1.09</td>
</tr>
<tr>
<td>$T/22.8$</td>
<td>22800</td>
<td>24400</td>
<td>1.07</td>
</tr>
</tbody>
</table>
5.3 CRYSTALLISATION AND MELTING

The most basic parameter pertaining to experimental studies of polymer crystallisation is $\phi$, the fraction of crystallinity. In this work all techniques for studying crystallisation, except polarising optical microscopy, yield a value of $\phi$, although these values will not be identical for the same sample because the different methods actually measure different crystallisation parameters. WAXS, for example, measures the weight fraction of lattice structures, $\phi_{\text{WW}}$:

$$\phi_{\text{WW}} = \frac{\text{Weight of polymer in crystalline lattice}}{\text{Total weight of polymer}} \quad 5.12$$

whereas SAXS measures the volume fraction of crystalline lamellae, $\phi_{\text{SV}}$:

$$\phi_{\text{SV}} = \frac{\text{Volume of lamellae}}{\text{Total volume of polymer}} \quad 5.13$$

The weight fraction of lamellae, $\phi_{\text{SW}}$, rather than the weight fraction of crystallinity, $\phi_{\text{WW}}$, may be calculated from $\phi_{\text{SV}}$ if the crystal density, $\rho_c$, is known:

$$\phi_{\text{SW}} = \frac{\phi_{\text{SV}} \rho_c}{(1 - \phi_{\text{SV}}) \rho_a + \phi_{\text{SV}} \rho_c} \quad 5.14$$

Dilatometry yields a density fraction of crystallinity, $\phi_{\text{dil}}$, which is an averaged weight fraction of regions with the ideal crystal volume

$$\phi_{\text{dil}} = \frac{\rho_x - \rho_a}{\rho_c - \rho_a} \quad 5.15$$

where $\rho$ is the density, and $c$, $a$ and $x$ refer to pure crystalline, pure amorphous, and the value at the time of measurement respectively. Melting point determinations by DTA allow computation of $\Delta H$, the enthalpy of fusion per gram of sample, from the area under the melting curve. If $\Delta H$ for pure crystalline polymer is known, then a weight fraction value of $\phi_{\Delta H}$ based on $\Delta H$ may be calculated,
A value of $\Delta H$ for pure crystalline P(THF) has been extrapolated (117) as 200 J gm.\(^{-1}\). Thus we have four different methods for obtaining parameters describing the degree of crystallinity of a polymer sample, the results of which will be discussed in section 5.3.1.

The crystallisation of poly(ethylene) (PE) has been studied in detail, and it is generally considered that high density (linear) PE achieves a very high fraction of crystallinity, (greater than 0.90), where the amorphous phase is found only at the crystal boundaries. Secondary crystallisation in PE occurs mainly by lamellar thickening (129,130) but in isotactic polystyrene growth of new lamellae within the amorphous regions has been observed (66). The structure of P(THF) is similar to PE, with the oxygen atom of the former being sterically similar to a methylene carbon of PE, and both polymers crystallise in a similar zig-zag conformation, as opposed to the helical structure of poly(ethylene oxide), (PEO). P(THF) crystallises with a face centred monoclinic unit cell (131,132), the unit cell of PEO is monoclinic (133), while PE crystallises with an orthorhombic unit cell (134). The unit cell and its dimensions for P(THF) are shown in Figure 5.3.1.

The fraction of crystallinity attained by high molecular weight P(THF) is much lower, around 0.3 to 0.5, than that of PE, and the secondary process accounts for a relatively higher proportion of the total degree of crystallinity. It has been shown by SAXS (135) that high molecular weight P(THF) crystallises in a sandwich-like structure of alternating crystalline and amorphous layers. During the primary process, nucleation and radial growth of lamellae occur yielding a spherulitic structure. The lamellae grow within a sharp distribution of thicknesses (C) but there is a wide
FIGURE 5.3.1
distribution of amorphous thicknesses (A) (136). Secondary crystallisation arises from slow isothermal thickening and increase in density of the lamellae through the removal of defects (136).

Studies of the crystallisation of low molecular weight poly(ethylene oxide) show a series of steps in plots of log. G versus crystallisation temperature (90). These are interpreted, together with SAXS information, as discrete jumps in the lamellar thickness which correspond to the lamellae changing from chain-extended crystals (no chain folds) to once-folded, twice-folded etc. crystals. As the molecular weight increases, to 150,000 for example, no steps occur and the plot is a smooth curve. This type of approach has been used in the present work and will be discussed later.

The melting point of a high polymer may be defined as the point at which the last trace of crystallinity disappears, and for DTA measurements this is taken as the temperature at which the high temperature side of the peak returns to the baseline, see I on Figure 5.3.2. However in this study we wish to compare the melting point with the corresponding lamellar thickness (C) from SAXS, which when measured from the correlation function will give a most probable value of C. Thus all melting points quoted here are those found from the peak position of the $\Delta C_p$ curve, point II on Figure 5.3.2, which should correspond most nearly to the melting point of
lamellae with the most probable C.

5.3.1 Trends in Crystallinity with Molecular Weight

Before considering the results from the various techniques in detail, it is worth examining the general picture at this stage to allow better appreciation of the discussion to follow.

Values of the fraction of crystallinity measured by different techniques are summarised in Table 5.06, from their respective tables*, for well crystallised samples (generally about 4 weeks) which had been treated isothermally.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\phi_{\text{dil}}$ (16°C)</th>
<th>$\phi_{\text{SV}}$ (16°C)</th>
<th>$\phi_{\Delta H}$ (16°C)</th>
<th>$\phi_{\text{dil}}$ (24°C)</th>
<th>$\phi_{\text{SV}}$ (24°C)</th>
<th>$\phi_{\Delta H}$ (24°C)</th>
<th>$\phi_{\text{WW}}$ (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>0.696</td>
<td>0.69</td>
<td>0.64</td>
<td>0.545</td>
<td>0.67</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>T/5.3</td>
<td>0.718</td>
<td>0.70</td>
<td>0.63</td>
<td>0.636</td>
<td>0.72</td>
<td>0.61</td>
<td>0.70</td>
</tr>
<tr>
<td>T/7.8</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>P/8.4</td>
<td>0.564</td>
<td>(0.63)</td>
<td>0.544</td>
<td>(0.64)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T/11.4</td>
<td>0.58</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P/13.4</td>
<td>0.587 (0.78)</td>
<td>(0.60)</td>
<td>0.549 (0.76)</td>
<td>(0.66)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T/22.8</td>
<td>0.563 0.56</td>
<td>0.49</td>
<td>0.582 0.56</td>
<td>0.47</td>
<td>0.63</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Drawn from Table* (5.08) (4.14) (4.11) (5.08) (4.15) (4.12) (4.10)

Similar values for a high molecular weight sample of P(THF) isothermally crystallised at 20°C (11) may be included for comparison, see Table 5.07.
TABLE 5.07

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\phi_{\text{dil}}$</th>
<th>$\phi_{SV}$</th>
<th>$\phi_{\Delta H}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/150.0</td>
<td>0.376</td>
<td>0.465</td>
<td>0.494</td>
</tr>
</tbody>
</table>

Trends in these results become clearer when the data is depicted graphically, see Figure 5.3.3 for example. Typically it is apparent that crystallinity commences at a certain value which increases as molecular weight increases from 3300 to 5300, but then falls suddenly by some 10-15% as the molecular weight increases from 5300 to 7800. After this point $\phi$ remains approximately constant over the range 7800 to 22800, with a further gradual decline up to 150000. The dilatometry data is measured at log. time 4.0 (1 week) rather than at log. time 4.6 (4 weeks) - log. time in minutes. Thus all $\phi_{\text{dil}}$ values will be slightly lower than if measured after 4 weeks.

Data from SAXS at both 16°C and 24°C follow the pattern from dilatometry very closely, see Figure 5.3.3, where $\phi_{SV}$ increases initially, passes through a maximum at molecular weight 5300, and drops suddenly by some 10% to a plateau between 8000 and 23000 molecular weight. The results of $\phi_{SV}$ for sample P/13.4 are thought to be erroneously high, due to the presence of an impurity, and have not been included in these trends. Further discussion of this feature is given in Section 5.3.10.

Results of $\phi_{\Delta H}$ from DTA also follow this overall trend with molecular weight assuming the values for samples P/8.4 and P/13.4 are incorrect due to the presence of some impurity, see Section 5.3.10. Also $\phi_{\text{WW}}$ results from WAXS, although more limited in number and having a larger degree of error, tend to follow this pattern. Thus in summarising the data of degree
Variation of $\phi$ with Molecular Weight

- $\phi_{\text{dil}}$ at 16°C
- $\phi_{\text{dil}}$ at 24°C
- $\phi_{\text{SV}}$ at 16°C

$M_n \times 10^{-3}$

Figure 5.3.3
of crystallinity from all available sources, its variation with molecular weight is as shown in Figure 5.3.3, passing through a maximum with molecular weight 5300 and decreasing suddenly thereafter to a more constant lower value with increasing molecular weight.

5.3.2 Dilatometry

A number of parameters have been measured in this work, but the most general from the point of view of crystallinity levels and kinetics are specific volume measurements. The $\phi_{dil}$ values discussed in the previous section were calculated from the isothermal specific volume plots, Figures 4.4.1 to 4.4.5, using the density data given in Table 5.08,

$$
\begin{array}{|c|c|c|c|}
\hline
\text{Sample} & \rho_a & \rho_x & \phi_{dil} \\
\hline
T/3.3 & 0.9920 & 1.0811 & 0.696 \\
T/5.3 & 0.9946 & 1.0846 & 0.718 \\
P/8.4 & 0.9952 & 1.0655 & 0.564 \\
P/13.4 & 0.9964 & 1.0689 & 0.587 \\
T/22.8 & 0.9967 & 1.0661 & 0.563 \\
\text{T} = 16^\circ C & & & \\
T/22.8 & 0.9852 & 1.0333 & 0.357 \\
\text{T} = 20^\circ C & & & \\
P/150.0 & & & \\
\text{T} = 24^\circ C & & & \\
\hline
\end{array}
$$

where $T_c$ is the crystallisation temperature, and $\phi_{dil}$ is calculated from equation 5.15.

The relative rates of crystallisation from dilatometry may be found by measuring the time taken to reach 0.5 of the specific volume change upon primary crystallisation, the so-called half-life ($t_{1/2}$). The trends present are not significantly affected by choice of smaller fractional
life times. Because very long induction times are present in certain samples, notably those crystallised at 24°C, it is necessary to subtract these times from the total $t_{1/2}$ to obtain the half life for the growth stage only. Corrections were made to the data by finding the point at which primary crystallisation commences (a deviation from the initial constant volume) and measuring the half-life time from this point and not from time $t = 0$. Results measured in this way are given in Table 4.08, and shown plotted as a function of molecular weight in Figure 4.4.6. A small amount of a sample of P(THF) of $M_n = 1200$ was prepared in this work, and although no quantitative crystallisation studies were performed with this sample, it was noticed that, while it would crystallise at a temperature of approximately -30°C, it would melt rapidly to an oil at room temperature. Thus it is apparent that crystallisation of this sample at either 16°C or 24°C would be very slow, and this is the basis of the extrapolation (dotted line) to low molecular weight shown in Figure 4.4.6.

This gives rise to a maximum in the rate of crystallisation (e.g. a minimum in the $t_{1/2}$ values) in the region of molecular weight 5300, which corresponds to the maximum in the data of fraction of crystallinity versus molecular weight, e.g. Figure 5.3.3. Thus not only does this sample attain the highest degree of crystallinity, it also achieves it at a faster rate than any of its neighbours. At 24°C, sample T/22.8 does crystallise at a faster rate than T/5.3, although it attains a lower $\phi$ value, which suggests that the rate of T/5.3 is faster than its neighbours because it is attaining a higher degree of crystallinity, and not the converse - that it attains a higher $\phi$ because of its faster rate. Data for samples P/8.4 and P/13.4 must be treated with care, see Section 5.3.10.

Table 4.08 gives data for the Avrami (137) exponent, $n$, obtained
from the slope of a plot of the LHS of the Avrami equation, 5.17:

$$\ln \left[ \frac{(v_\infty - v_t)/(v_\infty - v_0)}{\rho} \right] = -kt^n$$ 5.17

against time, where the subscripts $\infty$, $t$ and $0$ have their usual meanings. Such plots were good straight lines, as shown in Figure 5.3.4 for sample T/5.3 at 16°C, but the values of the exponents do not generally turn out to be the whole numbers required by the theory. Different whole number values of $n$ should signify different mechanisms of crystallisation based on the growth geometry and the type of nucleation, see Table 5.09. In practice integral values of $n$ are rarely found and this guide must be treated with caution.

**TABLE 5.09**

<table>
<thead>
<tr>
<th>Growth Geometry</th>
<th>Type of Nucleation</th>
<th>Avrami Exponent (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rods</td>
<td>Predetermined</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Sporadic</td>
<td>2</td>
</tr>
<tr>
<td>Discs</td>
<td>Predetermined</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Sporadic</td>
<td>3</td>
</tr>
<tr>
<td>Spherulites</td>
<td>Predetermined</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Sporadic</td>
<td>4</td>
</tr>
</tbody>
</table>

Avrami exponents for polymer spherulites are expected to be either 3 or 4 depending upon whether nucleation is heterogeneous (predetermined) or homogeneous (sporadic) respectively. The values given in Table 4.08, which lie between 1 and 2, are not suggestive of a spherulitic regime of crystallisation, but more of either rods or discs. Values between 2 and 3 have previously been reported for high molecular weight $P$(THF) (138). The types of entities observed during crystallisation of low molecular weight samples will be considered in Section 5.3.6.
Avrami Analysis, Sample T/5.3, 16°C

\[ \ln \left( \frac{\ln \left( \frac{A_t}{A_\infty} \right)}{V_t^2} \right) \]

\[ \ln t \]

Figure 5.3.4
5.3.3 Rates of Secondary Crystallisation

The relative rates of secondary crystallisation \( q \) may be estimated from the specific volume plots, Figures 4.4.1 to 4.4.5, using equation 5.18.

\[
q = \frac{-dV/d \log t}{V_0 - V_\infty}
\]

where \(-dV/d \log t\) is the slope of the curve, and \(V_0\) and \(V_\infty\) are the specific volumes at the beginning and end of primary crystallisation respectively.

The denominator in equation 5.18 is necessary to normalise the rate for the number of lamellae present, assuming that secondary crystallisation proceeds by a lamellar based process such as thickening. The slope was estimated by drawing the best straight line through the points in the early stages of secondary crystallisation, since these plots all exhibit some curvature. The relative rates measured thus are given in Table 5.10.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_c ) (°C)</th>
<th>( dV/d \log t )</th>
<th>( V_0 )</th>
<th>( V_\infty )</th>
<th>( q )</th>
<th>( \ln q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>16</td>
<td>0.0064</td>
<td>1.0080</td>
<td>0.9385</td>
<td>0.0921</td>
<td>-2.3850</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>0.0102</td>
<td>1.0138</td>
<td>0.9415</td>
<td>(0.1411)</td>
<td>(-1.9583)</td>
</tr>
<tr>
<td>T/5.3</td>
<td>16</td>
<td>0.0113</td>
<td>1.0058</td>
<td>0.9349</td>
<td>0.1594</td>
<td>-1.8363</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>0.0070</td>
<td>1.0110</td>
<td>0.9375</td>
<td>0.0952</td>
<td>-2.3518</td>
</tr>
<tr>
<td>P/8.4</td>
<td>16</td>
<td>0.0051</td>
<td>1.0043</td>
<td>0.9485</td>
<td>0.0905</td>
<td>-2.4024</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.0048</td>
<td>1.0073</td>
<td>0.9470</td>
<td>0.0788</td>
<td>-2.5408</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>0.0041</td>
<td>1.0100</td>
<td>0.9440</td>
<td>0.0621</td>
<td>-2.7790</td>
</tr>
<tr>
<td>P/13.4</td>
<td>16</td>
<td>0.0051</td>
<td>1.0032</td>
<td>0.9450</td>
<td>0.0876</td>
<td>-2.4350</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>0.00495</td>
<td>1.0050</td>
<td>0.9480</td>
<td>0.0868</td>
<td>-2.4442</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.00495</td>
<td>1.0065</td>
<td>0.9472</td>
<td>0.0835</td>
<td>-2.4832</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>0.00455</td>
<td>1.0092</td>
<td>0.9450</td>
<td>0.0709</td>
<td>-2.6465</td>
</tr>
<tr>
<td>T/22.8</td>
<td>16</td>
<td>0.0055</td>
<td>1.0032</td>
<td>0.9490</td>
<td>0.1015</td>
<td>-2.2877</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>0.0050</td>
<td>1.0089</td>
<td>0.9438</td>
<td>0.0768</td>
<td>-2.5667</td>
</tr>
</tbody>
</table>

It is apparent from the \( q \) values that the rate decreases with increasing temperature for a given sample, while the variation of \( q \) with molecular weight is shown, in Figure 5.3.5, to increase with increasing \( M_n \) initially, but then to drop sharply to a fairly constant value.
Rates of Secondary Crystallisation (q) versus Molecular Weight

FIGURE 5.3.5

\[ q \]

\[ M_n \times 10^3 \]
The secondary crystallization of high molecular weight P(THF) has been shown (136) to consist of lamellar thickening and densification of both phases. If the driving force for secondary crystallization is considered to be the reduction in surface to bulk free energy by lamellar thickening, then it is possible to treat the effect more quantitatively. If the rate of lamellar thickening is controlled by a nucleation barrier, with no overall increase in the degree of crystallinity, as proposed by Hirai et al (139), then

$$\frac{dc}{dt} = A \exp \left( -\frac{BC}{kT} \right)$$

where $A$ is a constant and

$$B = 2d \frac{\sigma_s^2}{\sigma_e}$$

d is the height of the surface nucleus and $\sigma_s$ and $\sigma_e$ are the side surface and end surface free energies respectively. Peterlin has shown (68, 140) that if a diffusion controlled rate determining step exists for the mass transport of a chain segment through a crystal lattice, then

$$\frac{dc}{dt} = A^1 \exp \left( -\frac{CE_m}{d_o kT} - 4d_o \frac{\sigma_s^2}{\sigma_e} T_m^o / \Delta H \Delta T \right)$$

where $A^1$ is a constant considered independent of $C$ (68). The first part of the exponential term is due to diffusion control and the second part is due to nucleation control. The diffusion mechanism is considered as a series of collective translations of the whole straight chain segment by a distance $d_o$, the energy barrier between consecutive equilibrium lattice positions is $E_m$ and the activation energy of the collective jump is $CE_m / d_o$. Such a mechanism suggests that the rate $q$ should be, for a completely sharp chain folded model, extremely dependent upon molecular weight. However, for molecular weights in the range 8000 to 23000 $q$ has been shown to be fairly constant, and indeed if a value of $q$ for high molecular weight P(THF) at $16.7^\circ C$ of 0.117 is included it is clear that there is no significant
dependence of q with molecular weight over this range. This indicates either a non-sharp chain folded model of crystallisation in this range, where a crystalline segment of a chain may jump independently of another attached segment because they are joined by a statistical fold, or alternatively that the process is nucleation controlled.

Comparison of the q values in Table 5.10 with similar data for high molecular weight P(THF), Table 5.11, shows a fundamental difference.

<table>
<thead>
<tr>
<th>Tc</th>
<th>q</th>
<th>Secondary rates for</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.7</td>
<td>0.117</td>
<td>P(THF), M_n = 150,000</td>
</tr>
<tr>
<td>20.0</td>
<td>0.154</td>
<td>(polydisperse) (11)</td>
</tr>
<tr>
<td>23.7</td>
<td>0.196</td>
<td></td>
</tr>
</tbody>
</table>

The results in Table 5.10 show q decreasing with increasing temperature, while those for the high molecular weight sample increase with increasing temperature. This phenomenon may be explained with a reference to equation 5.20 and Figure 5.3.6 showing schematically the variation of primary and secondary crystallisation rates with supercooling.
In both cases the slopes to the left (high supercooling) of the maxima exhibit a diffusion controlled dependence, while those to the right are nucleation dependent. It is apparent that for low molecular weight samples, which have a low $T_m^o$ and hence low $\Delta T$ for a given crystallisation temperature, the rates of both primary and secondary crystallisation are nucleation controlled, and both will increase as supercooling increases, position I. High molecular weight samples however having a high $T_m^o$ and hence higher $\Delta T$ for the same crystallisation temperature may still be nucleation controlled in primary, but now may be diffusion controlled in secondary, position II, and thus $q$ for high molecular weights may increase with increasing temperature (decreasing $\Delta T$) while $q$ for low molecular weights may decrease with increasing temperature. Figure 5.3.5 shows a maximum in the value of $q$ at $M_n = 5300$, while a similar plot of $1/t_1^{1/2}$ (a measure of the rate of primary crystallisation) shows a maximum at $M_n = 7000$, see Figure 5.3.27. This suggests that the maximum in the rate of primary will occur at higher $\Delta T$ than the rate of secondary, since higher molecular weights are at a larger $\Delta T$ for constant crystallisation temperature, which agrees with Figure 5.3.6.

Assuming $q \propto dC/dt$, as shown from the measured $C'$ values in Tables 4.14 and 4.15, then from equation 5.20 we may say

$$q = A^{11} \exp \left(-CE_m^o/kT\right) - \exp(4\sigma^2 d T_m^o/\Delta H_f \Delta T)$$  \hspace{1cm} 5.21

and

$$\ln q = \ln A^{11} - (CE_m^o/kT) - (4\sigma^2 d T_m^o/\Delta H_f \Delta T)$$  \hspace{1cm} 5.22

If the rate of thickening is diffusion controlled then a plot of $\ln q$ versus $1/T$, which ignores the nucleation term, should be a straight line of slope equal to $(CE_m^o/dk)$. This mechanism is thought to be correct at high molecular weights where the larger $\Delta T$ will reduce the contribution of the nucleation term. Figure 5.3.7 shows such a plot of $\ln q$ versus $1/T$, \hspace{1cm}
the results being shown schematically in Figure 5.3.8.

At high molecular weights the rate decreases as T decreases, suggesting a diffusion controlled mechanism applies and from the slope of this line the activation energy for diffusion control, $E_m/d_o$, may be estimated if C is known. The lines for lower molecular weights slope the opposite way showing $q$ increasing as $T$ decreases, however, and the slope increases with decreasing $M_n$. This suggests that, at lower supercoolings, the nucleation term becomes pre-dominant in equation 5.20, while the diffusion term remains as previously determined from the high molecular weight sample.

From rearranging equation 5.22,

$$\ln q + \frac{(CE_m/d_o kT)}{T_m} = \ln \Lambda^{11} - (4\sigma_s^2d_o T_m^o \Delta H_f^o / \Delta T)$$

thus a plot of $\ln q + (CE_m/d_o kT)$ against $T_m^o/\Delta T$ should yield a straight line of slope $- (4\sigma_s^2d_o \Delta H_f^o)$. The required data, contained in Table 5.12, are shown plotted in Figure 5.3.9 as $\ln q + (CE_m/d_o kT)$ versus $T_m^o/\Delta T$. 

FIGURE 5.3.8
FIGURE 5.3.9

\[ \ln q + \left( \frac{C_p}{dV} \right) \text{ versus } T_m \frac{\partial}{\partial T} \]

\[ (I \times \frac{m}{2C}) + b \ln \]

Values:
- 3300
- 5300
- 8400
- 13400
- 22800
It is apparent from Figure 5.3.9 that the points lie on a series of good straight lines having different slopes, these slopes increasing with increasing molecular weight. Extrapolation to $T_m^0/\Delta T = 0$ gives the intercept ($= \ln A_{11}$) which is seen to be fairly constant. The line for sample T/3.3 is estimated from a single point together with this intercept value. Since the slope varies with molecular weight, another parameter in equation 5.23 which contributes to the slope must be molecular weight dependent.

The side surface free energy, $\sigma_s$, should remain constant for a polymer with a given lamellar structure, but $\Delta H_f$ may vary with molecular weight. From the measured values of $\Delta H$, the heat of fusion per gram of sample, it is possible to calculate $\Delta H_f$, the heat of fusion per gram of lamellae, from equation 5.24:

$$\Delta H_f = \Delta H/\varphi_{SW}$$  \[5.24\]

where $\varphi_{SW}$ is defined in equation 5.14 as the weight fraction of lamellae.
These data are summarised in Table 5.12, and listed completely in Table 5.17 (Section 5.3.7), where it is seen that if the values for samples P/8.4 and P/13.4 are disregarded (due to impurity considerations, Section 5.3.10) then in general $\Delta H_f$, after secondary crystallisation, does decrease with increasing molecular weight. As shown in Table 5.13, however, this decrease is not sufficient to completely explain the increase in slope, because $\sigma_s^2 d_o$ continues to increase with $\overline{M}_n$.

**TABLE 5.13**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slope</th>
<th>$\Delta H_f$</th>
<th>$\sigma_s^2 d_o$</th>
<th>$d_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>0.503</td>
<td>177</td>
<td>22.2</td>
<td>1.40</td>
</tr>
<tr>
<td>T/5.3</td>
<td>0.585</td>
<td>167</td>
<td>24.4</td>
<td>1.53</td>
</tr>
<tr>
<td>P/8.4</td>
<td>0.705</td>
<td>165</td>
<td>29.1</td>
<td>1.82</td>
</tr>
<tr>
<td>P/13.4</td>
<td>0.775</td>
<td>163</td>
<td>31.6</td>
<td>1.98</td>
</tr>
<tr>
<td>T/22.8</td>
<td>0.985</td>
<td>160</td>
<td>39.4</td>
<td>2.46</td>
</tr>
</tbody>
</table>

The values of $d_o$ are calculated assuming a constant $\sigma_s$ value of $4\text{mJ.m}^{-2}$ (e.g. 5-10% of $\sigma_s$ for high molecular weight P(THF)), thus the absolute values of $d_o$ are not really meaningful, but they do show an upward trend when they might be expected to remain constant. It is likely that the assumption made previously is not strictly valid, thus the terms from nucleation and diffusion control cannot be separated out so readily. A decreasing contribution from diffusion with decreasing $\overline{M}_n$ would tend to increase the slopes at lower molecular weights which may remove the upward trend in $d_o$.

Thus when the data are analysed assuming a diffusion controlled mechanism only, as in Figure 5.3.7, the points do not fit on very good straight lines, and although a trend in slopes is apparent (Figure 5.3.8)
the absolute values for sample T/5.3 are out of step. The high molecular weight sample however does appear to fit a diffusion controlled mechanism.

If the data are examined for nucleation control, assuming a constant contribution from the diffusion term (estimated from the high molecular weight sample), then as shown in Figure 5.3.9, good straight lines result sharing a common intercept, but which show a molecular weight dependence of slope. This may be caused by a decrease in $\Delta H_f$ with increasing molecular weight, or by a decreasing contribution from diffusion with decreasing $M_n$. This is strong evidence to support the suggestion that the rate of thickening of low molecular weight P(THF) is nucleation controlled in the temperature range of the present measurements.

The temperature jump study performed on sample P/13.4 has also been analysed in terms of $q$. These data have been recorded in Table 4.09, and are now shown graphically in Figure 5.3.10. The smooth curve gives $q$ values obtained for isothermal crystallisation at $T_c$. When only primary crystallisation is allowed at $T_c$ followed by jumping to another temperature (in this case 20°C), then $q$ alters as shown by the arrows. It is seen that $q$ decreases following a jump to an increased temperature (e.g. from 10°C or 18°C to 20°C), while $q$ increases following a reduction in temperature from primary at 24°C to secondary at 20°C. This temperature dependence is indicative of a nucleation controlled process, supporting the suggestion contained in equation 5.20 and in Figure 5.3.6, where the rate of thickening decreases as temperature increases at low supercoolings.
Temperature Jump Dilatometry, Secondary Growth Rates

- Jumped to 20°C
- Isothermal Secondary Crystallisation

Crystallisation Temperature

FIGURE 5.3.10
A typical scattering curve for P(TiIF) in the wide angle region is shown in Figure 5.3.11 over the angular range measured in this work. The area due to the amorphous scattering is shown bounded by a dotted line. The WAXS reflections, as reported by Bowman (138), are given in Table 5.14, together with their crystallographic assignment, interplanar d spacing and relative intensity.

<table>
<thead>
<tr>
<th>Angle (2theta)</th>
<th>Assignment</th>
<th>d (Å ± 0.05 Å)</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.2</td>
<td>020</td>
<td>4.40</td>
<td>S</td>
</tr>
<tr>
<td>24.7</td>
<td>110</td>
<td>3.60</td>
<td>S</td>
</tr>
<tr>
<td>38.0</td>
<td>130</td>
<td>2.37</td>
<td>W</td>
</tr>
<tr>
<td>41.2</td>
<td>040</td>
<td>2.19</td>
<td>VW</td>
</tr>
<tr>
<td>43.65</td>
<td></td>
<td>2.07</td>
<td>W</td>
</tr>
<tr>
<td>45.7</td>
<td>220</td>
<td>1.99</td>
<td>VW</td>
</tr>
<tr>
<td>50.5</td>
<td>200</td>
<td>1.81</td>
<td>W</td>
</tr>
</tbody>
</table>

The determination of \( \phi_{WW} \) from WAXS is usually carried out by measuring the area under the amorphous halo for the crystalline scan, melting the sample and rescanning, and then measuring the area due to the wholly amorphous scattering. Comparison of these two areas then allows calculation of \( \phi_{WW} \), the weight fraction of crystallinity. With the low molecular weight samples however, this accepted technique could not be used due to the extreme mobility of the samples when molten - they would run out of the sample holder while the scan was in progress. An alternative method was therefore necessary to allow \( \phi_{WW} \) to be measured, and this was performed by assuming that the total crystalline plus amorphous scattering area was equal to the amorphous area for the molten sample. The crystalline area was then expressed as a percentage of the total of the crystalline plus...
WAXS of Poly(tetrahydrofuran)
amorphous areas. It was recognised that this method would not give the accuracy of the accepted method, but a compromise was necessary to achieve the results. A comparison of both methods on a high molecular weight sample yielded the following values:

<table>
<thead>
<tr>
<th></th>
<th>Wholly Amorphous</th>
<th>Crystalline plus Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_{WW}$</td>
<td>0.417</td>
<td>0.465</td>
</tr>
</tbody>
</table>

from which it may be seen that the results agree to within 5%, with the second method yielding the higher figure.

The $\phi_{WW}$ values obtained by WAXS are recorded in Table 4.10 for 4 samples crystallised for various times at $25^\circ$C, the sample T/10.7 was not used for any other measurements. For both long and short times it is apparent that $\phi_{WW}$ generally decreases as molecular weight increases, in a similar fashion to other $\phi$ results quoted in Table 5.06. Without data for sample T/3.3 it is not quite so clear if there is a sudden decrease in $\phi_{WW}$ between samples T/5.3 and T/7.8, as there is with the other $\phi$ values. The possible error in these results inherent in the method of measurement, in the order of ±5%, means that not a great deal of emphasis should be attributed to them, just that the trend in $\phi_{WW}$ agrees reasonably well with the trend in other $\phi$ values.

5.3.5 Small Angle X-ray Scattering (SAXS)

The SAXS from P(THF) has been shown by previous work in these laboratories to be completely consistent with a lamellar morphology. Alternating layers of crystalline and amorphous regions are assumed to have large in-plane dimensions and overall random arrangements of these lamellar stacks. Using this as the basis of a model enables considerable structural data to be interpreted from the SAXS curve. The calculation of
the 1 dimensional correlation function (ECF), and the fitting of this with a theoretical correlation function (TCF) calculated from the model, permits measurement of the volume fraction of crystallinity, $\phi_{SV}$, and the most probable repeat period, $(C+A)_p$. In addition the most probable crystalline and amorphous thicknesses, $C$ and $A$, can be computed together with the width parameters (standard deviations for Gaussian distributions) for the crystalline and amorphous regions, $\beta_C$ and $\beta_A$ respectively. SAXS runs were generally performed at the same two temperatures common to all previous measurements, 16°C and 24°C, after two crystallisation times, viz. end of primary and $\frac{1}{4}$ weeks, for each sample. The crystallisation time for the end of primary run was estimated from dilatometry.

The raw scattering curve, after correction to remove parasitic scattering, should also be treated to remove amorphous scattering followed by a correction (108) to account for deviations from Porod's Law before further analysis. In this work it was not possible to measure the amorphous scattering due to the mobility of the molten samples, the same problem was also found for WAXS measurements. The amorphous scattering contributes to the tail of the scattering curve, i.e., above 1°, which is the region where Porod's Law, or a deviation from it, applies. Since the amorphous scattering could not be removed, no correction for deviations from Porod's Law was applied. It has been shown previously in the case of high molecular weight P(THF) that a negative deviation from Porod's Law results, signifying a diffuse boundary between the crystalline and amorphous phases (11). The thickness of this diffuse boundary has been estimated, using the Ruland correction as shown in Table 5.15 (11, 108).
It was also shown that making a suitable correction for this deviation had little effect upon the structural parameters obtained from SAXS, typical results being compared in Table 5.16 (11).

**TABLE 5.15**

<table>
<thead>
<tr>
<th>Time at 20°C</th>
<th>Diffuse Boundary Layer Thickness ((\bar{X}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 days</td>
<td>14.4 ± 4</td>
</tr>
<tr>
<td>47 days</td>
<td>18.7 ± 4</td>
</tr>
</tbody>
</table>

In view of the small effect of the correction upon these parameters, it was felt that data obtained without using it would be sufficiently accurate, in view of the extreme experimental difficulties of the required measurements for the present samples.

Data obtained from SAXS measurements as previously described is given in Tables 4.14 to 4.17 in Section 4.4.5. The two most important parameters derived in this way are \(C\), the lamellar thickness, and \(\phi_{SV}\), the volume fraction of crystallinity. Trends in \(C\) are shown in Figures
5.3.12 and 5.3.13 for results at 16°C and 24°C respectively. At 16°C, for short crystallisation times, where C corresponds to the thickness of the crystal 'as grown', it is found that there is a sharp drop in C (by some 10%) as molecular weight increases from very low values to above approximately 6000. After this drop C tends to increase linearly with molecular weight over a wide range, (up to 150,000, see inset). The results following isothermal crystallisation for 4 weeks show the same trend with $\bar{M}_n$ as did the short time values, except that it may be seen that the increase in C at higher molecular weights (20,000) is less than that at low molecular weights. This means that lower molecular weight samples, having a lower $\Delta T$, isothermally anneal more following the trend shown previously that the rate of thickening is higher for low molecular weight samples, see Figure 5.3.5.

At 24°C, the data follows the same pattern with $\bar{M}_n$ except for one point, sample T/5.3 for short time, however this point after secondary crystallisation is seen to fall on a line having the same shape as before. Also at 24°C the 'as grown' lamellar thicknesses (short time) are larger than their equivalents at 16°C as predicted by surface nucleation theory.

Similar determinations of the amorphous thickness, A, are shown in Figures 5.3.14 and 5.3.15 at 16°C and 24°C respectively. In all cases a trend of increasing A with increasing molecular weight is noted, (up to 150,000, see inset), except for the value of sample T/5.3, long time at 24°C. As noted previously the C spacing for this sample increases markedly during secondary crystallisation, and this is coupled with a dramatic decrease in A for this point. Secondary crystallisation is synonymous with an increase in C, and we now see that this increase is completely at the expense of the amorphous thickness, which decreases with crystallisation
Lamellar Thickness ($C$) versus Molecular Weight at $16^\circ C$
Lamellar Thickness (C) versus Molecular Weight at 24°C

Figure 5.3.13
Variation of Amorphous Thickness (A) with $M_n$ at 16°C

Short Time

Long Time

$A(\lambda)$

$M_n \times 10^{-3}$

$M_n \times 10^{-4}$
Variation of Amorphous Thickness ($A$) with $M_n$
time. For the short time values of $A$, however, there is little dependence upon temperature as shown in Figure 5.3.15 where both sets of points for $A$ at $16^\circ C$ and $24^\circ C$ lie on the same curve. This is not the case for the secondary crystallised samples of course, because $C$ has been shown to thicken at different rates depending on temperature, thus $A$ will decrease at correspondingly different rates.

The contribution of $C$ and $A$ together may be expressed in the repeat period or $(C+A)_p$ values also given in Tables 4.14 and 4.15. It has been shown above that thickening of the lamellae occurs completely at the expense of $A$, thus it is expected that $(C+A)_p$ will not alter significantly with secondary crystallisation, and generally this is what is found, see Figures 5.3.16 and 5.3.17. The repeat period however, is seen to increase with increasing temperature. As previously discussed, $C$ 'as grown' increases with $1/\Delta T$ (hence increasing temperature), but $A$ remains independent of temperature for short crystallisation times, so the increase of $(C+A)_p$ with temperature is due to an increase of $C$.

At short crystallisation times $(C+A)_p$ displays a linear dependence with molecular weight, (up to $M_n = 150,000$, see inset). This trend is caused by the amorphous thickness increasing with $M_n$ as in Figure 5.3.15, while $C$ drops initially and then slowly increases, Figure 5.3.12. After secondary crystallisation however, there appears to be a decrease in $(C+A)_p$ at very low molecular weights between 3300 and 5300 before the linear trend with $M_n$ is resumed. This suggests that the decrease in $A$ after secondary crystallisation for sample T/5.3, where points at both $16^\circ C$ and $24^\circ C$ lie below the line, may be real (because the $(C+A)_p$ values of T/5.3 and above lie on a good straight line) and that the $A$ value for T/3.3 after secondary is too high. This effect may be due to the ability of
Variation of $(C+A)_p$ with Molecular Weight, Short Time
Variation of $(C+A)_p$ with Molecular Weight, Long Time

$\bar{M}_n \times 10^{-3}$

Figure 5.3.17
sample T/5.3 to achieve larger C values (and $\phi$ values) after secondary crystallisation than the other samples, thus giving a reduced A with constant $(C+A)_p$.

As pointed out in Section 2.5, the repeat period derived from the application of Bragg's Law to the maximum in the scattering curve, $(C+A)_{\text{Bragg}}$, is not a reliable measure of the periodicity because of the nature of equation 2.124:

$$n \lambda = 2d \sin \theta$$

where d is equivalent to the repeat period.

If all the d spacings were identical, this approach would be satisfactory, but due to the reciprocal dependence of d upon $\sin \theta$, the peak position will be biased towards lower angles and hence higher spacings when a distribution of d values is present. This effect is observed experimentally, and may be seen from the data in Table 5.17.

**TABLE 5.17**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time at $16^\circ C$</th>
<th>$(C+A)_{\text{Bragg}}$</th>
<th>$(C+A)_p$</th>
<th>Time at $24^\circ C$</th>
<th>$(C+A)_{\text{Bragg}}$</th>
<th>$(C+A)_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>35 min</td>
<td>135</td>
<td>133</td>
<td>7 day</td>
<td>157</td>
<td>157</td>
</tr>
<tr>
<td></td>
<td>2 wk</td>
<td>134</td>
<td>137</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 wk</td>
<td>134</td>
<td>135</td>
<td>5 wk</td>
<td>169</td>
<td>160</td>
</tr>
<tr>
<td>T/5.3</td>
<td>60 min</td>
<td>141</td>
<td>135</td>
<td>16 hr</td>
<td>158</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>5 wk</td>
<td>132</td>
<td>130</td>
<td>4 wk</td>
<td>151</td>
<td>148</td>
</tr>
<tr>
<td>T/7.8</td>
<td>18 hr</td>
<td>139</td>
<td>132</td>
<td>2.5 day</td>
<td>158</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>19 day</td>
<td>136</td>
<td>133</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T/11.4</td>
<td>2.5 day</td>
<td>148</td>
<td>138</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 wk</td>
<td>142</td>
<td>136</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P/13.4</td>
<td>80 min</td>
<td>164</td>
<td>136</td>
<td>24 hr</td>
<td>160</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>4 wk</td>
<td>150</td>
<td>145</td>
<td>4 wk</td>
<td>165</td>
<td>170</td>
</tr>
<tr>
<td>T/22.8</td>
<td>40 min</td>
<td>150</td>
<td>143</td>
<td>4 hr</td>
<td>182</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>4 wk</td>
<td>151</td>
<td>145</td>
<td>4 wk</td>
<td>183</td>
<td>165</td>
</tr>
</tbody>
</table>
Comparison with Tables 4.16 and 4.17, which contain the size distribution width data, shows generally that the difference between $(C+A)_{Bragg}$ and $(C+A)_p$ increases as the distribution width of the periodicity increases.

The variation of the volume fraction of crystallinity, $\phi_{SV}$, with molecular weight was considered in Section 5.3.1 for samples having undergone secondary crystallisation at $16^\circ C$. These data are replotted in Figure 5.3.18, together with the short time data. It is seen that secondary crystallisation generally increases $\phi_{SV}$ by some 8%, except for sample T/5.3 where a much larger change upon secondary crystallisation occurs giving the unusual 'stepped' plot discussed previously. The inset shows the gradual reduction of $\phi_{SV}$ up to molecular weight 150,000. If the shape of the stepped curve is assumed to apply at $24^\circ C$ also, the data after secondary crystallisation at this temperature also fit this pattern as shown in Figure 5.3.19. The lack of definitive points means this plot must be regarded with caution. Samples at $24^\circ C$ after short crystallisation times lie on a gradually declining curve, as do those at $16^\circ C$, showing that once again sample T/5.3 undergoes a greater degree of secondary crystallisation. The values at short times are higher at $24^\circ C$ than at $16^\circ C$ by some 4%, but after secondary crystallisation at both temperatures the $\phi_{SV}$ values become very similar.

Tables 4.14 and 4.15 show the theoretical maximum number of folds a polymer chain of known length would have to make to be completely contained within a crystal of known thickness, assuming the chain axis is perpendicular to the major lamellar surface. These values may be meaningful at very low molecular weights, but as we shall see later, it is thought unlikely with P(THF) that chains requiring say 20 or more passes through a given crystal would form sharp-folded, adjacent re-entry lamellae. These data are shown
Variation of $\phi_{SV}$ with Molecular Weight at 16°C
Variation of $\phi_{SV}$ with Molecular Weight at 24°C
for completeness in Figures 5.3.20 and 5.3.21, but are not thought to be meaningful at higher molecular weights. If these plots are extrapolated to number of folds = 0, we may predict the molecular weight at or below which chain-extended or non-folded crystals will form under these crystallisation conditions. These values are 1400 and 1600 at 16°C and 24°C respectively, short crystallisation times.

The standard deviations of the Gaussian distributions of C and A, being $\beta_c$ and $\beta_a$, are recorded in Tables 4.16 and 4.17, and the variations with molecular weight are typically as shown in Figures 5.3.22 and 5.3.23 for $\beta_c$ and $\beta_a$ respectively. In general $\beta_c$ decreases with increasing molecular weight, this trend once again agreeing with data reported previously (136) for high molecular weight P(THF), where very low values of $\beta_c$ were found, see Table 5.16 for example. Conversely $\beta_a$ is found to increase with molecular weight, Figure 5.3.23, also agreeing high molecular weight data. The absolute distribution width of crystalline thicknesses, as characterised by $\Delta C(\bar{x})$, therefore remains approximately constant with increasing molecular weight, whereas the absolute distribution width of amorphous thicknesses, $\Delta A(\bar{x})$, increases continually with molecular weight, see Tables 4.16 and 4.17. There does not appear to be any marked temperature dependence of $\beta_c$ or $\beta_a$, results at both crystallisation temperatures being very similar, see Tables 4.16 and 4.17.

Secondary crystallisation does have an effect upon the width parameters however, where $\beta_c$ increases with time and $\beta_a$ decreases with time. This observation is consistent with a model proposed previously (136) for the secondary crystallisation of high molecular weight P(THF), comprising a system of lamellae which exhibit small angle ($<1^0$) branching, thus giving rise to triangular amorphous regions. The lamellae will thicken
Figure 5.3-20

Number of Folds versus Molecular Weight, Short Time

Number of Folds

$\overline{M}_n \times 10^{-3}$

$16^\circ C$

$24^\circ C$
Number of Folds versus Molecular Weight, Long Time

Figure 5.3.21
Variation of $\beta_c$ with Molecular Weight at 16°C

Long Time

Short Time

$\overline{\theta_n} \times 10^{-3}$
Variation of $\beta_a$ with Molecular Weight at 16°C

Short Time

Long Time

$M_n \times 10^{-3}$
preferentially into the larger amorphous regions. Some lamellae therefore remain in the 'as grown' state, while others may thicken giving an increasing $\beta_c$. On the other hand, since the small amorphous thicknesses (i.e., those close to the lamellae branch points) will remain, while the larger spacings will be reduced by the ingrowing crystals, the overall distribution of amorphous thicknesses will decrease.
5.3.6 **Optical Microscopy**

Optical microscopy on thin films of P(THF) has been performed to determine the rate of growth of the crystallites as a function of crystallisation temperature. Previous work on high molecular weight P(THF) has shown that crystallisation occurs in the form of ringed spherulites (138) where the size of spherulite, radial growth rate and ring-spacing are all dependent on the crystallisation temperature. The spherulite radii grow linearly until they totally impinge, which corresponds to the end of primary crystallisation. In the present work, samples T/3.3 and T/5.3 were examined over the temperature range 16°C to 24°C, photographic recording of the crystallites at known time intervals being used to provide a measurement of the growth dimension.

Neither of these samples crystallised as true spherulites at any of the temperatures considered. Sample T/3.3 formed crystallites as depicted in Figure 5.3.24. Initially small specks were observed which tended to grow preferentially along one axis, I. Thickening of these axialites to sheaves occurred, II, followed in some cases by a second growth at an angle, not necessarily 90°, to the first giving a 'cross' effect, III. As further growth ensued, the area between the arms of the cross was filled in to give, albeit sometimes distorted, a spherical body with ragged, sheaf-like edges, IV. Total impingement was not always attained, usually one or two gaps (estimated at 5% of the total space) remained after growth had ceased, and this is thought to be due to thickness effects. If the film thickness was increased, obscuring of the crystallites followed because a second layer would crystallise over the subjects. If the thickness was reduced, very large gaps were left between crystallites when growth ceased. This suggests that when thin films are employed, the growing crystals tend to pull in crystallisable
material from the melt, thus eventually leaving gaps between them due to depletion of amorphous polymer. A compromise was evolved to obtain the maximum film thickness reducing the residual gaps to a minimum without causing a second layer of crystals to overlap the first. This scheme is shown photographically for sample T/3.3 crystallised at 20°C in Figure 5.3.25. As the temperature of crystallisation increased, nucleation decreased allowing the smaller number of crystallites formed to grow larger before impinging than those crystallised at lower temperatures.

Measurements of the sizes of these crystallites were generally taken along the growth direction of at least 3 or 4 of the original axialites, and plots of these distances against time, having been found to be linear, were measured to yield the slopes. These slopes were then averaged to give the growth rate $Gr$, see Figures 4.4.9 and 4.4.10. Measurements taken along the 'secondary' growth axialites were also found to vary linearly with time, and to exhibit the same growth rate as the original axialites. Crystallisations of sample T/5.3 tended to be very similar to the above
pattern, except that the crystallites tended to be more sharply defined, less ragged and sheaf-like at the edges.

When log \( G_r \) was plotted against crystallisation temperature, as in Figure 4.4.11, it was found that sample T/3.3 gave a curve with a pronounced discontinuity occurring between 18\(^o\)C and 19\(^o\)C. Sample T/5.3 did not show this effect, but there is a suggestion that such a discontinuity may be about to show itself towards slightly higher temperatures. This phenomenon has been shown to occur readily in poly(ethylene oxide) fractions (90) and is attributed in that case to a large change in lamellar thickness, as indicated by SAXS, where the lamellae form as chain-extended crystals at higher temperatures, i.e. the lamellar thickness, \( C \), equals the extended chain length. As temperature decreases to the low side of the discontinuity, the lamellar thickness changes to one half of its former value, indicating that a single chain-fold is occurring in the crystal. At still lower temperatures, a further discontinuity may be found, where SAXS shows the lamellar thickness changing to one third of the extended chain length, giving a twice-folded crystal, and so on. It is believed that these changes in crystal structure are responsible for the changes in the growth rate plots.

Analysis of SAXS results from sample T/3.3 at 16\(^o\)C and 24\(^o\)C, short crystallisation times, indicate the lamellar thicknesses to be 79\(\AA\) and 101\(\AA\) respectively. It may be seen from the ensuing discussion that these data are consistent with a sharp chain folded crystal structure at very low molecular weight.
At 24°C the lamellar thickness is too large to allow more than 2 passes through a crystal, see Figure 5.3.26. As ΔT increases (crystallisation temperature decreases) C becomes less, as observed experimentally and predicted from equation 2.69, assuming σ_e and ΔH_f are constant.

At a certain critical C spacing (which for this chain length would be 93.5 Å) the chain may fit completely into the crystal by forming 3 passes. According to Kovacs (90) the surface free energy, σ_e, will increase as the ratio of chain folds to non-folded chains on the crystal surface increases, thus lamellae containing twice folded chains will have a higher σ_e than those containing once folded chains. This means that as T_c decreases from 24°C, σ_e remains essentially constant (for once folded lamellae) while C decreases. At a certain temperature, however, a structural transition will occur to twice folded lamellae having a larger C spacing and larger σ_e. This unfavourable increase in surface free energy will be overshadowed by an increased negative contribution to the free energy of crystallisation, ΔG_c, from the free energy of fusion, Δf, which arises from a greater amount of a chain being contained within the crystal at lower temperature as shown in Figure 5.3.26. If we consider the following model structure for crystalline P(THF), we may derive an explanation for this structural transition in terms of free energy of crystallisation, see Figure 5.3.27.
As shown in Section 2.3, the free energy of crystallisation for a wholly crystalline polymer is given by the relation

$$\Delta G_c = -\Delta f x^2 + 4\sigma_s x C + 2\sigma_e x^2$$

where $\Delta G_c$ must be negative for crystallisation to occur. The major contribution to $\Delta G_c$ is from the negative free energy of fusion, $\Delta f$, which is the energy given up by an amorphous chain upon crystallisation, with an unfavourable positive free energy required to form the crystal surfaces. The term $4\sigma_s x C$ is considered trivial and ignored. Let us now consider a strip of unit cross section area and length 1 passing through many lamellae (see Figure 5.3.27). The volume of such a strip $= 1 \times 1 \times 1 = 1$, while the number of lamellae passed through by the strip $= 1/(C+A)$. Then for a partially crystalline polymer,

$$\Delta G_{c(PC)} = - \left( \frac{C}{C+A} \Delta f 1 \right) + \frac{1}{C+A} 2\sigma_e$$

where $\Delta G_{c(PC)}$ is the free energy of crystallisation of a partially
crystalline polymer for a strip of volume 1, and C/(C+A) is the volume fraction of crystallinity. We may now determine $\Delta G_c(\text{PC})$ per unit volume

$$\Delta G_c(\text{PC}) = -\left[\frac{C}{C+A} \Delta f\right] + \frac{2\sigma_e}{C+A}$$

5.26

If we now consider a given chain crystallising in a folded lamellar structure, as in Figure 5.3.26, the volume fraction of crystallinity term becomes the volume fraction per chain,

$$\Delta G_c(\text{PC}) = -\left[\frac{(n+1)C}{L} \Delta f\right] + \frac{2\sigma_e(n+1)}{L}$$

5.27

per chain

where (n+1) is the number of chain passes per lamella, and L is the extended chain length.

From equation 2.69, $C \propto 1/(\Delta T)$ for a constant $\sigma_e$, i.e., for the once folded model at 24°C with low $\sigma_e$ and for the twice folded model at 16°C with high $\sigma_e$, assuming $T_m^o$ and $\Delta H_f$ constant. Values of $C$ calculated for both models are listed in Table 5.18, and shown plotted against $T_c$ in Figure 5.3.28. Calculations of $\Delta G_c(\text{PC})$ per chain for both models from equation 5.27 are also listed in Table 5.18 and shown in Figure 5.3.28.

<table>
<thead>
<tr>
<th>$T_c$</th>
<th>$C (1)$</th>
<th>$C (2)$</th>
<th>$\Delta f \times 10^{-9}$</th>
<th>$-\Delta G_c(\text{PC}) (1) \times 10^{-9}$</th>
<th>$-\Delta G_c(\text{PC}) (2) \times 10^{-9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>101 *</td>
<td>105</td>
<td>8.2</td>
<td>2.58</td>
<td>- **</td>
</tr>
<tr>
<td>22</td>
<td>92</td>
<td>97</td>
<td>8.3</td>
<td>2.17</td>
<td>- **</td>
</tr>
<tr>
<td>20</td>
<td>86</td>
<td>90</td>
<td>8.4</td>
<td>1.87</td>
<td>2.31</td>
</tr>
<tr>
<td>18</td>
<td>80</td>
<td>84</td>
<td>8.5</td>
<td>1.57</td>
<td>1.86</td>
</tr>
<tr>
<td>16</td>
<td>75</td>
<td>79 *</td>
<td>8.6</td>
<td>1.32</td>
<td>1.49</td>
</tr>
</tbody>
</table>

* measured values of $C$

** cannot physically fit 3 chain passes into lamellae of these thicknesses.
FIGURE 5.3.28

Estimated Variation of $C$ and $\Delta G_c$ (PC) with $T_c$
Values of $\Delta f$ may be determined from the heat of fusion, $\Delta H_f$, from equation 2.66

$$\Delta f = \frac{\Delta H_f \Delta T}{T_m^0}$$

As shown by these data, when it becomes possible for a chain to physically fit 3 passes into a crystal, it may do so with an overall negative contribution to $\Delta G_c (PC)$, despite the increased $\sigma_e$, leading to an energetically more favourable system. The data do not predict the temperature at which this transition would occur, only that it must be at or below the temperature at which $C(2) = 93.5^\circ$.

An increase in $\sigma_e$ implies that the growth rate, $G$, should decrease on the low temperature side of the transition, since from equation 2.95:

$$G = G_o \exp \left( -\frac{4b_0 \sigma_s T_c^0}{k \Delta H_f \Delta T} \right)$$

leading to the observed discontinuity in the plot of log $G$ versus $T_c$ (Figure 4.4.11). As the temperature decreases further, $\sigma_e$ remains essentially constant at its increased value, and $G$ therefore increases once again.

Similar considerations for sample T/5.3, where no discontinuity in $G$ is observed within the temperature range studied, suggest that the number of passes of a given chain within a crystal increases from 5 to 6 as $T_c$ drops from 24°C to 16°C. The corresponding increase in $\sigma_e$ from this structural change, where the ratio of folds to ends changes from 4 : 2 at 24°C to 5 : 2 at 16°C, is not sufficient to alter the growth rate (or the lamellar thickness) sufficiently to cause a discontinuity. As found previously for poly(ethylene oxide) (90), when the number of passes of a
given chain exceeds about 4, no discontinuity occurs.

The development of the crystallites, as shown in Figures 5.3.24 and 5.3.25, is very reminiscent of the description of the initial growth of a true polymer spherulite (141), where the formation of an axialite, followed by growth of sheaves, and finally a completely spherical body which then grows equally in all directions is envisaged. The early stages of growth prior to spherulite formation are not normally seen with an optical microscope, for the present system however, it would appear that these species are the preferred structure for crystallisation under the prevailing conditions. The lack of tie molecules (prohibited by the short length of the chains) in the circumferential direction could be the cause of the absence of spherical symmetry.

The variation of growth rate with molecular weight was investigated at 24°C, the log G values being compared with corresponding log \((1/t_{1/2})\) from dilatometry in Figure 5.3.29. Values for samples P/8.4 and P/13.4 from dilatometry are slow compared with log G values (microscopy) on samples T/7.8 and T/11.4 (similar molecular weights), suggesting interference from impurities (Section 5.3.10). The decrease in growth rate with decreasing molecular weight (at constant temperature) will be due in part to the increase in \(1/Tm\), since \(T_m^0\) increases at higher molecular weights. In the following section on melting (5.3.7) where \(T_m^0\) is derived, the actual \(\Delta T\) values can be calculated, and values of G inferred at any temperature from a plot of log G against \(1/T\Delta T\) for certain samples. This graph (Figure 5.3.9) may then be replotted at constant \(\Delta T\) to remove the effect of supercooling and allow the true influence of molecular weight to be seen, see Figure 5.3.35.
Growth Rate Variation with $\bar{M}_n$ at 24°C by Microscopy (G) and Dilatometry ($t_{1/2}$)

- Optical Microscopy
- Dilatometry

$\log G$ (cm$^3$ min$^{-1}$) vs. $\bar{M}_n \times 10^{-3}$

Figure 5.3.29
5.3.7 Melting

The melting points \( T_m \) and heats of fusion \( (\Delta H, \text{ J g}^{-1} \text{ sample}) \) measured by DTA are recorded in Tables 4.11 and 4.12, after the necessary corrections, described in Section 3.4, had been performed. The variations of \( T_m \) with molecular weight are shown in Figures 4.4.13 to 4.4.15, where \( T_m \) generally increases with \( M_n \) for the same crystallisation conditions.

The DTA scans of certain samples are complicated by the presence of double melting peaks, as shown in Figure 4.4.12. Samples prepared using initiator P did not show this effect. It has been shown \( (11) \) for high molecular weight P(THF) that a broad, low melting region is present below the main peak on DTA scans, and this was shown to be due to extra crystallinity induced in the inter-lamellar regions by cooling the sample to low temperature in the instrument prior to melting. It is thought that the low melting peak in low molecular weight samples is also induced by the cooling process, since it diminishes in area as secondary crystallisation proceeds as in the high molecular weight case. This is caused by lamellae thickening into the amorphous region. The low melting peak is sharper than in the high molecular weight case which is due to the smaller amorphous thickness available for inter-lamellar crystallisation. This means that the range of inter-lamellar crystals will not be so broad as in for high molecular weights, so the melting peak will be sharper. Samples P/8.4 and P/13.4 do not exhibit this effect, which is thought to be due to the presence of an impurity in these samples \( (\text{Section 5.3.10}) \) which is rejected to the inter-lamellar region suppressing any induced crystallinity.

In all cases where double melting peaks occur, the melting point has been measured from the high temperature peak, since it is probable that the low temperature peak results from the cooling procedure. No evidence was found from SAXS measurements to support the presence of two crystalline
regions of different thicknesses in isothermally crystallised samples.
Similarly, the $\Delta H$ results are taken from the areas of the high melting peaks, because these represent melting of the structures formed isothermally.

As derived in Section 2.4, the melting point of a polymer crystal will be related, through the Flory equation 2.107, to the number of chain ends present:

$$\frac{1}{T_m} - \frac{1}{T_m} = \frac{2R}{\Delta H_U x_n}$$

thus as molecular weight decreases, the melting point will be depressed by the increasing number of chain ends per unit volume of crystal. If the data from Tables 4.11 and 4.12 are analysed using equation 2.107, it is found that for a given set of crystallisation conditions, a plot of $1/T_m$ versus $1/x_n$ is a good straight line. These data are listed in Table 5.19 and the plots are shown in Figure 5.3.30, but results from samples P/8.4 and P/13.4 are not included due to interference from impurities.

### Table 5.19 Data required to test Flory Relation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time at 16°C</th>
<th>$T_m$ (K)</th>
<th>$10^3$</th>
<th>Time at 24°C</th>
<th>$T_m$ (K)</th>
<th>$10^3$</th>
<th>$10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>short</td>
<td>302.0</td>
<td>3.311</td>
<td>short</td>
<td>309.3</td>
<td>3.233</td>
<td>2.182</td>
</tr>
<tr>
<td></td>
<td>long</td>
<td>307.5</td>
<td>3.252</td>
<td>long</td>
<td>309.9</td>
<td>3.227</td>
<td></td>
</tr>
<tr>
<td>T/5.3</td>
<td>short</td>
<td>304.7</td>
<td>3.282</td>
<td>short</td>
<td>310.9</td>
<td>3.217</td>
<td>1.359</td>
</tr>
<tr>
<td></td>
<td>long</td>
<td>311.4</td>
<td>3.211</td>
<td>long</td>
<td>314.4</td>
<td>3.181</td>
<td></td>
</tr>
<tr>
<td>T/22.8</td>
<td>short</td>
<td>308.7</td>
<td>3.239</td>
<td>short</td>
<td>312.7</td>
<td>3.198</td>
<td>0.316</td>
</tr>
<tr>
<td></td>
<td>long</td>
<td>315.5</td>
<td>3.170</td>
<td>long</td>
<td>320.1</td>
<td>3.124</td>
<td></td>
</tr>
</tbody>
</table>

The dependence of melting point upon molecular weight, for low molecular weight P(THF), is thus shown to agree with the Flory relation for given crystallisation conditions. The slope of these plots yields $\Delta H_U$, the heat of fusion per monomer unit, which should be a constant, the slope at 24°C,
To Show Variation of $1/T_m$ versus $1/x_n$
short time, is however different, thus the application of the Flory relation may not be justified for very low molecular weight polymers. A more complete description could possibly be obtained by application of the Flory-Vrij treatment, i.e. equation 2.117, as detailed in Section 2.4.

For certain points in the ensuing discussion the derivation of $\Delta H_f$ (heat of fusion per gram of lamellae) from the experimental value of $\Delta H$ (heat of fusion per gram of sample) is required. This may be calculated from

$$\Delta H_f = \Delta H / \phi_{SW}$$  \hspace{1cm} (5.24)

where $\phi_{SW}$ is the weight fraction of lamellae determined from $\phi_{SV}$ (volume fraction of crystallinity from SAXS) via equation 5.14:

$$\phi_{SW} = \frac{\phi_{SV} \rho_c}{(1-\phi_{SV}) \rho_a + \phi_{SV} \rho_c}$$  \hspace{1cm} (5.14)

where $\rho_c$ and $\rho_a$ are the crystalline and amorphous densities respectively. Assuming a value of $\rho_c = 1.12 \text{ g cm}^{-3}$ \hspace{1mm} (11), the necessary data and the calculated $\Delta H_f$ results are listed in Table 5.20. This data was used previously in Section 5.3.3 to summarise any variation in $\Delta H_f$ with molecular weight.
TABLE 5.20 Calculation of $\Delta H_f$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time at $16^\circ C$</th>
<th>$\Delta H$ ($J g^{-1}$)</th>
<th>$\phi_{SV}$</th>
<th>$\phi_{SW}$</th>
<th>$\rho_a$ (g cm$^{-3}$)</th>
<th>$\Delta H_f$ ($J g^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3 short</td>
<td>71.5</td>
<td>0.59</td>
<td>0.62</td>
<td>0.9783</td>
<td>114.9</td>
<td></td>
</tr>
<tr>
<td>T/3.3 long</td>
<td>126.9</td>
<td>0.69</td>
<td>0.72</td>
<td>176.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T/5.3 short</td>
<td>97.4</td>
<td>0.56</td>
<td>0.59</td>
<td>0.9809</td>
<td>164.4</td>
<td></td>
</tr>
<tr>
<td>T/5.3 long</td>
<td>125.8</td>
<td>0.70</td>
<td>0.73</td>
<td>173.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P/8.4 short</td>
<td>113.4</td>
<td>0.52*</td>
<td>0.53</td>
<td>0.9817</td>
<td>205.2</td>
<td></td>
</tr>
<tr>
<td>P/8.4 long</td>
<td>125.4</td>
<td>0.60*</td>
<td>0.63</td>
<td>198.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P/13.4 short</td>
<td>96.2</td>
<td>0.50*</td>
<td>0.53</td>
<td>0.9827</td>
<td>180.6</td>
<td></td>
</tr>
<tr>
<td>P/13.4 long</td>
<td>120.7</td>
<td>0.57*</td>
<td>0.60</td>
<td>200.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T/22.8 short</td>
<td>55.5</td>
<td>0.50</td>
<td>0.53</td>
<td>0.9829</td>
<td>104.2</td>
<td></td>
</tr>
<tr>
<td>T/22.8 long</td>
<td>96.9</td>
<td>0.56</td>
<td>0.59</td>
<td>163.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Time at $24^\circ C$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time at $24^\circ C$</th>
<th>$\Delta H$ ($J g^{-1}$)</th>
<th>$\phi_{SV}$</th>
<th>$\phi_{SW}$</th>
<th>$\rho_a$ (g cm$^{-3}$)</th>
<th>$\Delta H_f$ ($J g^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3 short</td>
<td>86.1</td>
<td>0.64</td>
<td>0.67</td>
<td>0.9729</td>
<td>128.1</td>
<td></td>
</tr>
<tr>
<td>T/3.3 long</td>
<td>96.8</td>
<td>0.67</td>
<td>0.70</td>
<td>138.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T/5.3 short</td>
<td>81.4</td>
<td>0.60</td>
<td>0.63</td>
<td>0.9756</td>
<td>128.7</td>
<td></td>
</tr>
<tr>
<td>T/5.3 long</td>
<td>121.1</td>
<td>0.72</td>
<td>0.75</td>
<td>162.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P/8.4 short</td>
<td>104.8</td>
<td>0.56*</td>
<td>0.59</td>
<td>0.9764</td>
<td>176.6</td>
<td></td>
</tr>
<tr>
<td>P/8.4 long</td>
<td>127.9</td>
<td>0.62*</td>
<td>0.65</td>
<td>196.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P/13.4 short</td>
<td>123.0</td>
<td>0.54*</td>
<td>0.57</td>
<td>0.9773</td>
<td>214.4</td>
<td></td>
</tr>
<tr>
<td>P/13.4 long</td>
<td>132.8</td>
<td>0.58*</td>
<td>0.61</td>
<td>216.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T/22.8 short</td>
<td>97.7</td>
<td>0.52</td>
<td>0.55</td>
<td>0.9775</td>
<td>176.4</td>
<td></td>
</tr>
<tr>
<td>T/22.8 long</td>
<td>93.7</td>
<td>0.56</td>
<td>0.59</td>
<td>158.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* $\phi_{SV}$ estimated from Figures 5.3.18 and 5.3.19

Application of the general melting equation, 2.67, as detailed in Section 2.4 permits estimation of $T_m^0$ - the melting point of an infinitely thick crystal having the same degree of perfection as the lamellae actually grown.

$$T_m = T_m^0 - \frac{2\sigma}{C_m} \frac{T_m^0}{\Delta H_f C}$$

2.67

A plot of $T_m$ against $1/C$ should be a straight line of slope $(2\sigma T_m^0/\Delta H_f)$
and intercept, when $1/C = 0$, of $T_m^0$. For these low molecular weight polymers however the effect of maximum crystal thickness from fully extended chain length must be taken into account, thus we have not taken $T_m^0$ as the point where $1/C = 0$, but where $1/C = 1/(\text{extended chain length})$. When the value of $T_m^0$ is known it may be used in equation 2.67 to calculate $\sigma_e$, the end surface free energy. The data necessary to determine $T_m^0$ are listed in Table 5.21, the plots of $T_m$ versus $1/C$ are shown in Figure 5.3.31, and the extrapolated values of $T_m^0$, together with the calculated results of $\sigma_e$, are listed in Table 5.22.

**TABLE 5.21 Evaluation of $T_m^0$**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time at $16^\circ C$</th>
<th>$1/C \times 10^{-8}$</th>
<th>$T_m$</th>
<th>Time at $24^\circ C$</th>
<th>$1/C \times 10^{-8}$</th>
<th>$T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>35 min</td>
<td>1.266</td>
<td>302.0</td>
<td>7 day</td>
<td>0.990</td>
<td>309.6</td>
</tr>
<tr>
<td></td>
<td>2 wk</td>
<td>1.163</td>
<td>307.7</td>
<td>5 wk</td>
<td>0.935</td>
<td>309.9</td>
</tr>
<tr>
<td></td>
<td>4 wk</td>
<td>1.075</td>
<td>307.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T/5.3</td>
<td>60 min</td>
<td>1.316</td>
<td>304.7</td>
<td>16 hr</td>
<td>1.099</td>
<td>310.9</td>
</tr>
<tr>
<td></td>
<td>5 wk</td>
<td>1.099</td>
<td>311.4</td>
<td>4 wk</td>
<td>0.935</td>
<td>314.4</td>
</tr>
<tr>
<td>P/13.4</td>
<td>80 min</td>
<td>1.149</td>
<td>306.9</td>
<td>24 hr</td>
<td>0.943</td>
<td>313.7</td>
</tr>
<tr>
<td></td>
<td>4 wk</td>
<td>0.885</td>
<td>312.3</td>
<td>4 wk</td>
<td>0.775</td>
<td>315.9</td>
</tr>
<tr>
<td>T/22.8</td>
<td>40 min</td>
<td>1.389</td>
<td>308.7</td>
<td>4 hr</td>
<td>1.205</td>
<td>312.7</td>
</tr>
<tr>
<td></td>
<td>4 wk</td>
<td>1.235</td>
<td>315.5</td>
<td>4 wk</td>
<td>1.087</td>
<td>320.1</td>
</tr>
</tbody>
</table>
Extrapolation of $1/C$ versus $T_m$ to find $T_m$.

- $T/3.3$
- $P/13.4$
- $T/5.3$
- $T/22.8$

FIGURE 5.3.31
The values of $T_m^0$ are thus shown to increase with increasing molecular weight, see Figure 5.3.32 from which the results $(T_m^0)_*$ in Table 5.22 are estimated. The variation of $1/T_m^o$ with $1/x_n$ is also shown in Figure 5.3.30, where agreement with the Flory relation is also indicated. This plot yields a value of $T_m^0$, for an infinitely long polymer chain, of 361 K from the intercept when $1/x_n = 0$. From Figure 5.3.33 it may be seen that $\sigma_e$ increases in the same manner with molecular weight, while $\sigma_e M_n$ is shown to increase linearly with $M_n$. 

The general melting expression, equation 2.67, predicts that if $T_m^0$, $\Delta H_f$ and $\sigma_e$ remain constant, then an increase in melting point will be caused by an increase in lamellar thickness, $C$. For a given molecular weight $T_m^0$ will remain constant, and Table 5.23 lists the predicted values of $C$ assuming $2\sigma_e/\Delta H_f$ remains constant - as suggested by the plots of $T_m$.
Variation of $T_m^o$ with Molecular Weight

$T_m^o$ vs $\bar{M}_n \times 10^{-3}$
Variation of Surface Free Energy ($\sigma_\infty$) with Molecular Weight

![Graph showing variation of surface free energy with molecular weight.](image-url)
against 1/C in Figure 5.3.3.

**TABLE 5.23** Prediction of C from increase in $T_m$ with constant $\sigma_e$ and $\Delta H_f$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$</th>
<th>Time</th>
<th>$T_m$ (K)</th>
<th>C (actual)</th>
<th>C (theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>16</td>
<td>2 wk</td>
<td>307.7</td>
<td>86</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>long</td>
<td>307.5</td>
<td>93</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>short</td>
<td>309.6</td>
<td>101</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>long</td>
<td>309.9</td>
<td>107</td>
<td>104</td>
</tr>
<tr>
<td>T/5.3</td>
<td>16</td>
<td>short</td>
<td>304.7</td>
<td>76</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>long</td>
<td>311.4</td>
<td>91</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>short</td>
<td>310.9</td>
<td>91</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>long</td>
<td>314.4</td>
<td>107</td>
<td>107</td>
</tr>
<tr>
<td>P/8.4</td>
<td>16</td>
<td>short</td>
<td>307.7</td>
<td>67</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>long</td>
<td>310.4</td>
<td>80</td>
<td>73</td>
</tr>
<tr>
<td>P/13.4</td>
<td>16</td>
<td>short</td>
<td>306.9</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>long</td>
<td>312.2</td>
<td>79</td>
<td>79</td>
</tr>
<tr>
<td>T/22.8</td>
<td>16</td>
<td>short</td>
<td>308.7</td>
<td>72</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>long</td>
<td>315.5</td>
<td>81</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>short</td>
<td>312.7</td>
<td>83</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>long</td>
<td>320.1</td>
<td>92</td>
<td>94</td>
</tr>
</tbody>
</table>

The theoretical values are calculated from 2.67 assuming $2\sigma_e/\Delta H_f$ is constant, and in general it is found that C (theoretical) agrees reasonably with C (actual), suggesting that any changes which occur in $\sigma_e$ and $\Delta H_f$ on secondary crystallisation, or on primary crystallisation at different temperatures, tend to balance out. Thus the variation in melting point is due primarily to changes in lamellar thickness.

As mentioned in the previous section when discussing growth rates from optical microscopy, it is now possible to determine the actual supercooling ($\Delta T$) applied to the samples at a particular crystallisation temperature ($T_c$), since

$$\Delta T = T_m^0 - T_c$$
where $T_m^\circ$ has been determined experimentally. Application of 5.29 to the samples whose growth rates were measured at $24^\circ C$ reveals the supercooling levels to be:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m^\circ$ (K)</th>
<th>$\Delta T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/3.3</td>
<td>321.2</td>
<td>24.2</td>
</tr>
<tr>
<td>T/5.3</td>
<td>333.2</td>
<td>36.2</td>
</tr>
<tr>
<td>T/7.8</td>
<td>339.5</td>
<td>42.5</td>
</tr>
<tr>
<td>T/10.7</td>
<td>344.3</td>
<td>47.3</td>
</tr>
<tr>
<td>T/22.8</td>
<td>356.7</td>
<td>59.7</td>
</tr>
</tbody>
</table>

Samples T/3.3 and T/5.3 were examined at a series of temperatures and the corresponding growth rates determined, thus from a plot of $\log G$ versus $1/\Delta T$ (following equation 2.95), we should be able to predict the growth rate at any desired supercooling. The necessary data for this approach is given in Table 5.25 for samples T/3.3 and T/5.3.

<table>
<thead>
<tr>
<th>Sample T/3.3, $T_m^\circ = 321.2K$</th>
<th>$T_c$ (K)</th>
<th>$\log G$ (cm min$^{-1}$)</th>
<th>$\Delta T$ (K)</th>
<th>$1/\Delta T \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>289</td>
<td>-1.3372</td>
<td>32.2</td>
<td>10.746</td>
<td></td>
</tr>
<tr>
<td>290</td>
<td>-1.4260</td>
<td>31.2</td>
<td>11.052</td>
<td></td>
</tr>
<tr>
<td>291</td>
<td>-1.8844</td>
<td>30.2</td>
<td>11.379</td>
<td></td>
</tr>
<tr>
<td>292</td>
<td>-2.1163</td>
<td>29.2</td>
<td>11.728</td>
<td></td>
</tr>
<tr>
<td>293</td>
<td>-2.1772</td>
<td>28.2</td>
<td>12.103</td>
<td></td>
</tr>
<tr>
<td>294</td>
<td>-2.5901</td>
<td>27.2</td>
<td>12.505</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample T/5.3, $T_m^\circ = 333.2K$</th>
<th>$T_c$ (K)</th>
<th>$\log G$ (cm min$^{-1}$)</th>
<th>$\Delta T$ (K)</th>
<th>$1/\Delta T \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>-1.1334</td>
<td>43.2</td>
<td>7.9821</td>
<td></td>
</tr>
<tr>
<td>291</td>
<td>-1.3072</td>
<td>42.2</td>
<td>8.1432</td>
<td></td>
</tr>
<tr>
<td>292</td>
<td>-1.4895</td>
<td>41.2</td>
<td>8.3696</td>
<td></td>
</tr>
<tr>
<td>293</td>
<td>-1.6904</td>
<td>40.2</td>
<td>8.4900</td>
<td></td>
</tr>
<tr>
<td>294</td>
<td>-2.1431</td>
<td>39.2</td>
<td>8.6769</td>
<td></td>
</tr>
<tr>
<td>295</td>
<td>-2.2147</td>
<td>38.2</td>
<td>8.8739</td>
<td></td>
</tr>
<tr>
<td>296</td>
<td>-2.5901</td>
<td>37.2</td>
<td>9.0817</td>
<td></td>
</tr>
<tr>
<td>297</td>
<td>-3.3420</td>
<td>36.2</td>
<td>9.3011</td>
<td></td>
</tr>
</tbody>
</table>
When this data is plotted as in Figure 5.3.34, log G at the desired supercooling can be estimated. A value of $\Delta T = 42.5K$ was chosen - this being the degree of supercooling of sample T/7.8 at 24°C. Results of log G for samples T/3.3 and T/5.3 at $\Delta T = 42.5K$ were estimated from Figure 5.3.34, while values for samples T/10.7 and T/22.8 were calculated using equation 2.95. Thus a plot of log G against $\bar{M}_n$ at constant supercooling may now be made, as shown in Figure 5.3.35, where it is apparent that log G decreases dramatically as $\bar{M}_n$ increases, but at higher molecular weights (above 7800) attains a more constant value. This means that crystallisation of short chains involves a faster nucleation rate than that for longer chains, suggesting that the critical nucleus is formed more easily for the shorter chains. This favours the idea of a molecular nucleation model, where a complete chain is necessary to form the nucleation step.
Estimation of Log $G$ at Constant $\Delta T$
Variation of Log G with Molecular Weight

Log G
x 400

\( \bar{M}_n \times 10^{-3} \)

Constant \( T_c \)

Constant \( \Delta T \)
5.3.8 Crystallisation Models

It has previously been shown (11, 135) using SAXS that high molecular weight, polydisperse P(THF) crystallises isothermally in a sandwich type structure comprising alternate crystalline and amorphous layers. The crystalline regions are made up of regularly aligned chains with fold surfaces which were deduced to largely consist of statistical loops rather than sharp folds. Certain chains pass from one crystal, through the amorphous region to another crystal forming tie molecules, however, the majority of chains, once they commence crystallisation, are thought to remain within a given lamella, such chains being necessarily folded.

The nature of the fold surface for bulk crystallised lamellae has been the subject of much recent discussion to determine whether sharp chain folds with adjacent re-entry or statistical loops with random re-entry are the pre-dominant structure. In the case of solution grown single crystals it is now thought that the sharp chain fold model is correct (6). It is now clear (11) that for high molecular weight P(THF), having a diffuse boundary region of up to 18 Å between the crystalline and amorphous regions, a statistical loop rather than sharp chain fold surface is present. The secondary crystallisation process for high molecular weight P(THF) comprises lamellar thickening together with densification of both phases. The lamellae thicken by tightening up the large loops leading to an increase in $\sigma_e$, the end surface free energy.

Crystallisation of low molecular weight, monodisperse P(THF) is expected to differ from that of high molecular weight polymer due to the increased mobility of the short chains, the higher proportion of end-groups, and the inability to form inter-crystal tie molecules or long re-entrant loops at short chain lengths. Once a segment of a chain commences...
crystallisation the behaviour will tend to be independent of molecular weight until the presence of an end-group is felt. Thus the same chain, once it begins to crystallise, will be statistically more probable to re-enter adjacently, especially if it is adsorbed onto the growth face.

Typical models of folded chain crystals are shown in Figure 2.3.2, from sharp chain fold with adjacent re-entry to the switchboard model of statistical loops with random re-entry. The fringed micelle structure, shown in Figure 2.3.1, is included at this point for completeness, but is not thought to apply to semi-crystalline P(THF). The high degree of fit between experimental and theoretical correlation functions, calculated on the basis of a two-phase sandwich structure, suggests a model of the type shown in Figure 2.3.2 applies, it being necessary to determine the nature of the crystal surface. The possible model structures are summarised in Figure 5.3.36, and experimental data will be considered in detail to delineate that which applies to low molecular weight P(TIIF).

Models A and $A^1$ are based on the sharp chain fold surface, with $A$ being energetically more favoured due to lack of defects.

FIGURE 5.3.36
Model B is based on the statistical loop structure with adjacent re-entry. The chain length of very low molecular weight polymers largely precludes the formation of non-adjacent re-entry surfaces, especially for sample T/3.3, but they may well form at higher molecular weights. Model C is an extension of B where the loop crosses an amorphous region to enter another lamella forming a tie molecule.

Analysis of data from SAXS for sample T/3.3, extended chain length 280.5 Å, is summarised in Table 5.26. Model C must be rejected because the chain length only barely allows the chain to cross from one lamella.
to another, with the amorphous segment practically straight. The consequent loss of configurational entropy would make such structures thermodynamically unfavourable for short chain lengths.

The dependence of model structure on crystallisation temperature as shown in Table 5.26 shows that model A undergoes a fundamental transition, from 2 passes at 24°C to 3 passes at 16°C, while model B shows no such variation. As mentioned in Section 5.3.6 it is possible to explain the discontinuity in the curve of growth rate versus temperature on the basis of a change in the ratio of folds to ends per chain affecting...
Model A demonstrates this dependence, and was discussed in this context in Section 5.3.6. Model B would have no such effect on the growth rate since its ratio of folds to ends per chain is constant.

In each case, the crystallinity per chain for model A is higher than the measured value $\phi_{SV}$, which suggests that some complete chains which are missed by the growing lamellae are relegated to the amorphous region. It was noted previously in Section 5.3.7 that the amorphous thickness remained essentially independent of crystallisation temperature, while $C$ increased with increasing temperature at a given molecular weight. If whole chains remain in the amorphous region, they might be expected to adopt a random coil configuration in which the root mean square end-to-end distance, $(r_e^2)^{0.5}$, is proportional to $(M_n)^{0.5}$. A plot of the amorphous thickness $(A)$ against $(M_n)^{0.5}$ is shown in Figure 5.3.37, where it is seen that $A$ increases linearly with $(M_n)^{0.5}$ at both crystallisation temperatures up to $M_n = 11,400$, with the data lying on one line.

**FIGURE 5.3.37**

![Graph showing variation of amorphous thickness (A) with $(M_n)^{0.5}$](image)

This strongly suggests that at low molecular weights, certain chains are found completely in the amorphous region, where they adopt a random
coil configuration, thus lowering the value of $\phi$ per chain to that found for $\phi_{SV}$, and explaining the dependence of the amorphous thickness on molecular weight but not crystallisation temperature. Model B shows an inconsistency in this respect since although at 24°C $\phi$ per chain is higher than $\phi_{SV}$ (thus requiring some completely amorphous chains) at 16°C $\phi$ per chain approximately equals $\phi_{SV}$ indicating the absence of completely amorphous chains.

After secondary crystallisation at both temperatures, the lamellar thickness $C$ has been shown to increase at the expense of the amorphous thickness $A$, Section 5.3.5. Both models account for the increase in $C$ by lamellar thickening, a process which will tend to draw amorphous chains into the crystal thus explaining the corresponding decrease in $A$. Similar considerations for sample T/5.3 follow exactly similar trends as those outlined above.

Further criteria upon which the choice of a model may be based are:

1. Effect of secondary crystallisation on the double melting peaks.

2. Variation of the rate of secondary crystallisation with molecular weight.

3. Variation of $\sigma_e$ with molecular weight.

As mentioned previously the low molecular weight samples exhibit double melting peaks by DTA, where the low temperature melting peak is caused by lamellae grown in the amorphous regions upon cooling the samples. Careful analysis of these traces shows that in general, the effect of secondary crystallisation is as depicted schematically in Figure 5.3.38, from data given in Figure 4.4.12.
The low melting peak decreases in size and in melting point, which is consistent with a model involving thickening of the isothermally grown lamellae, thus reducing the melting point of the inter-lamellar crystals. Removal of chains from the amorphous region to the crystal will decrease the material available for inter-lamellar crystallisation. Since the amorphous thickness is reduced by secondary crystallisation, the available thickness for inter-lamellar crystals is reduced, thus their melting point will decrease.

If the rate of secondary crystallisation was diffusion controlled, then for a sharp chain folded model A structure, the rate would be strongly dependent on molecular weight since translation of a complete chain through the lattice would be necessary. However we have already shown (Section 5.3.3) that the rate of secondary crystallisation is nucleation controlled at low molecular weights, and although it is diffusion controlled at high molecular weight for the same crystallisation temperature, the frequent presence of statistical folds in the surface
means that the rate is not particularly dependent on molecular weight. This has been found to be the case experimentally, supporting the type A model at low molecular weights.

Kovacs (90) has proposed that for poly(ethylene oxide) the average surface free energy $\sigma_e (n)$ for a crystal having $n$ folds per chain will be given by

$$\sigma_e (n) = \frac{\sigma_{e, e}}{1+n} (1 + \frac{\sigma_{e, f}}{\sigma_{e, e}} n)$$

where $\sigma_{e, e}$ is the free energy associated with a chain end, and $\sigma_{e, f}$ that associated with a sharp chain fold. This is discussed further in Section 5.3.9, but equation 5.30 reduces to

$$\sigma_e (n) = \sigma_{e, e} \frac{1+\rho n}{1+n}$$

where $\sigma_{e, e} = \rho \sigma_{e, f}$. Since $\rho$ is assumed constant, and for a given crystal size $(1+n)$ is proportional to molecular weight, a plot of $\sigma_e \overline{M}_n$ against $\overline{M}_n$ should be linear if a sharp chain fold model applies. Such a plot is shown in Figure 5.3.33 (Section 5.3.7) and is indeed found to be linear at low molecular weights suggesting sharp chain folding is occurring. As molecular weight increases however this plot becomes less meaningful since we are plotting $\sigma_e$ (small number) times $\overline{M}_n$ (becoming very large) against $\overline{M}_n$, thus at high molecular weights a straight line is to be expected.

To summarise the data so far presented, it is strongly suggested that at molecular weights below approximately 6000, crystallisation occurs in the form of sharp chain fold, adjacent re-entry lamellae, model A. At molecular weights above this level, the number of possible passes for a given chain starts to become large, e.g. more than $\approx 8$, and so it will
become more probable that statistical loops will occur giving rise to a model, type B, with at least a proportion of loops rather than sharp chain folds which is known to be the case at high molecular weights.

The trends previously discussed for $\beta_c$ and $\beta_a$ with secondary crystallisation (Section 5.3.5) may be explained by the preferential thickening of lamellae into wider amorphous spaces; since the lamellae are thought to exhibit small angle branching (136), as shown in Figure 5.3.39.

![Small Angle Branching of Lamellae](image)

This gives triangular regions of amorphous material into which lamellae may only thicken when the amorphous region exceeds a certain critical thickness. Thus $\beta_c$ will increase due to certain lamellae thickening and not others, while $\beta_a$ will decrease because the small values of $\Delta$ remain untouched, while the larger values are reduced by thickening of the lamellae.

The trends in $\phi$ and C with molecular weight all show a step down from fairly high values at a molecular weight of approximately 6000, as shown in Figure 5.3.40.

![Trends of $\phi$ and C with $M_n$](image)
These trends may now be explained on the basis of the crystallisation models proposed earlier. At very low molecular weights, sharp chain folding with adjacent re-entry, model A, occurs yielding high crystallinities. As the chain length increases, at a given lamellar thickness, the number of passes per chain increases, and so does the chance of a non-adjacent re-entry structure, model B. Thus the sudden drop in $\mathcal{C}$ and $\mathcal{C}$ at a particular molecular weight may be explained by the change from a completely sharp chain folded surface to one comprising at least some statistical loops at molecular weight approximately 6000. The trends then continue linearly up to very high molecular weight, suggesting the predominance of the statistical loop model at these molecular weights.

5.3.9 Comparison with Poly(ethylene oxide)

Much work has recently been performed on the crystallisation and melting of low molecular weight, monodisperse poly(ethylene oxide) - PEO - samples, (90, 98/9, 142/3). The chemical structure of PEO is midway between poly(ethylene) - PE - and P(THF), as shown:

\[
\begin{align*}
\text{PE} & \quad \left[ \begin{array}{c}
\text{C} \text{-C} \\
\end{array} \right]_n \\
\text{PEO} & \quad \left[ \begin{array}{c}
\text{C} \text{-C-O} \\
\end{array} \right]_n \\
\text{P(THF)} & \quad \left[ \begin{array}{c}
\text{C} \text{-C-C-O} \\
\end{array} \right]_n
\end{align*}
\]

but it crystallises in a helical rather than the zig-zag conformation attained by PE and P(THF). Equivalent extended chain lengths for the same molecular weights of PEO and P(THF) are given in Table 5.27.
<table>
<thead>
<tr>
<th>$M_n$</th>
<th>Extended Chain Lengths</th>
<th>PEO ($\bar{x}$)</th>
<th>P(THF) ($\bar{x}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>63.3</td>
<td>85.0</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>126.6</td>
<td>170.0</td>
<td></td>
</tr>
<tr>
<td>4000</td>
<td>253.2</td>
<td>340.0</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>379.8</td>
<td>510.0</td>
<td></td>
</tr>
</tbody>
</table>

It is seen that the crystalline extended chain length of P(THF) is some 34% greater than that of PEO for an equivalent molecular weight. Studies of crystallisation and melting (142) of PEO give the following general results.

Isothermal crystallisation (at constant supercooling or $\Delta T$) by dilatometry, optical microscopy and calorimetry show the variation of crystallisation rate with $M_n$ to be of the form shown in Figure 5.3.41.

FIGURE 5.3.41

Variation of Log G with $M_n$ for PEO and P(THF)

The initial decrease in rate with $M_n$ is similar to that found for P(THF),
Figure 5.3.35, but the sudden increase in rate for PEO is caused by the ability of the chains to form chain-folded crystals, PEO having a much larger lamellar thickness (200-400 Å). It is apparent from Figure 5.3.41 that at higher molecular weights, (> 10,000), PEO having ΔT = 10°, crystallises faster than P(THF) having a much larger ΔT of 42.5°.

The onset of chain folding at constant ΔT has been predicted theoretically by Sanchez and Dimarzio (144) for solution crystallisation of poly(ethylene). The following equation is derived:

\[
C_c(L) = \frac{2\sigma_e/\Delta G}{1 + 2\sigma_e/L\Delta G} = \frac{C_c(\infty)}{1 + C_c(\infty)/L}
\]

where \( C_c(L) \) is the minimum crystal thickness for which molecules of extended length L can form folded chain crystals, \( C_c(\infty) \) is the minimum crystal thickness for an infinite chain which has the same equilibrium dissolution temperature (\( T_d^\circ \)) as the chain of length L. The temperature \( T_d^\circ \) is analogous with \( T_m^\circ \) as defined previously, but applies to crystallisation from solution. Since \( T_m^\circ \) and \( T_d^\circ \) depend on molecular weight, \( C_c(\infty) \) can also vary with \( M_n \). This equation permits evaluation of the minimum supercooling, \( \Delta T_{\text{min}} \), necessary for folded crystal growth. For a chain of length L the maximum possible thickness for a folded chain crystal is \( L/2 \), and substituting this into 5.32, and knowing

\[
\Delta G = [\Delta H T_m^\circ + \Delta h] (\Delta T/T_d^\circ)
\]

where \( \Delta G \) is the free energy difference per mol of monomer between polymer solution and crystal, and \( \Delta h \) is the partial molar (per mol of monomer) heat of solution of liquid polymer and solvent, they obtain

\[
\Delta T_{\text{min}} = (2\sigma_e/\Delta H L) T_d^\circ
\]

When supercooling is less than \( \Delta T_{\text{min}} \) (i.e. near to the melting point) then
non-folded chain crystallisation occurs. The variation of $\Delta T_{\text{min}}$ with molecular weight, as predicted by 5.3.4, is shown in Figure 5.3.42. For poly(ethylene) of molecular weight 3000, a supercooling of $12^\circ$ or less would result in non-folded chain crystallisation, while for P(THF) similar calculations using experimentally determined values shows a supercooling of some $4^\circ$ or less is necessary for non-folded chain crystallisation.

**FIGURE 5.3.42**

Onset of Chain Folding with $\overline{M}_n$ at Constant $\Delta T$

Hence at a constant $\Delta T$, a critical $\overline{M}_n$ will be reached above which chain folded crystals may form, but below which only extended-chain or other non-folded lamellae are permitted.

Crystallisation studies by dilatometry (142) yield fractional values of $n$, the Avrami exponent, in the range of $2.0 \pm 0.6$, very similar to those found in this work for P(THF), Table 4.08.

The rate of crystallisation of P(THF) found from microscopy (G), varies with molecular weight as shown in Figure 5.3.35 at constant temperature. If these data are corrected to constant $\Delta T$ as shown in Section 5.3.7 log G is shown to decrease smoothly with molecular weight as also shown in Figure 5.3.35. There is no indication of a minimum at low molecular
weights such as occurs for PEO, Figure 5.3.41.

Melting points of isothermally crystallised PEO fractions have been shown (142) to increase with increasing molecular weight as predicted by the Flory relation, equation 2.107. The melting data presented here have also been shown to obey this equation for given crystallisation conditions, see Figure 5.3.30.

Analysis of growth rates of PEO have been made (90, 142) using equation 2.93:

\[ G = G_0 \exp \left(-\frac{U}{RT} - \frac{U}{RT_m} \right) \exp \left[-\frac{4b_0 \sigma \cdot T^0}{k_{\text{BT}} \Delta T} \right] \]

Plots of log G (cm min⁻¹) against 1/\Delta T have been made (90) from corresponding plots of log G against T (T is crystallisation temperature) showing discontinuities in the curves as shown in Figures 5.3.43 and 5.3.44.

Corresponding data for P(THF) samples T/3.3 and T/5.3 have been presented in the form of Figure 5.3.43 (see Figure 4.4.11) where one such discontinuity is apparent for sample T/3.3, but not for sample T/5.3.
If this data is analysed via equation 2.93, the plots shown in Figure 5.3.3 result. The scatter on the points for T/3.3 make it difficult to decide on the best line through them - i.e. whether straight or kinked - while all the T/5.3 data lie on a good straight line apart from the point at the highest temperature.

The discontinuities in Figure 5.3.43, and the changes of slope in Figure 5.3.44, have been explained for PEO on the basis of lamellar thickness data from SAXS, where it has been shown that the crystals change from fully extended-chain to once-folded chain, or from once-folded to twice-folded chain etc., on either side of a break. Morphological evidence has also been presented (90, 142) to support this idea. Theoretical justification of this phenomenon has been put forward by Kovacs (90) as follows.

Equation 2.93 predicting the variation of growth rate was derived for a polymer chain of infinite length. Low molecular weight polymers however must have a higher proportion of chain ends which will make a different contribution to \( \sigma_e \) than chain folds. If \( \sigma_{e,e} \) and \( \sigma_{e,f} \) \((= \rho \sigma_{e,e})\) are the contributions to \( \sigma_e \) from chain ends and chain folds respectively, then for a crystal involving \( n \) folds per chain (i.e., \( C = \) extended chain length/ \( 1+n \)) and assuming additivity, to a first approximation:

\[
\sigma_e(n) = \frac{\sigma_{e,e}}{1+n} \left( 1 + \frac{\sigma_{e,f}}{\sigma_{e,e}} n \right)
\]

\[
= \left( \frac{1+\rho n}{1+n} \right) \sigma_{e,e}
\]

providing all the chain-ends remain on the surface of the crystals. Thus for a once-folded crystal,
\[ \sigma_e (1) = (1+p) \frac{\sigma_{e,e}}{2} \]

and if \( p \) is greater than 1, then equation 2.93 will yield a discontinuous increase of the negative slope of the \( \log G \) versus \( 1/\Delta T \) curve by a factor of \( \frac{\sigma_e (1)/\sigma_{e,e}}{2} = (1+p)/2 \) for a transition from extended chain to once-folded chain. Since the factors \( b_0, \sigma_s, \Delta H_f \) are essentially independent of molecular weight, a quantisation of \( \sigma_e (n) \), and hence \( C \), will occur as the number of folds increases.

PEO, having hydroxyl end-groups, will tend to gain a large negative contribution to \( \sigma_{e,e} \) during crystallisation due to hydrogen bonding between adjacent end-groups. This serves to lower \( \sigma_{e,e} \) and to produce no stearic constraints. The quantisation effect of lamellar thickness is explained because the chain-ends will always try and remain on the crystal surface to reduce the energy requirements. As \( \Delta T \) increases, however, growth may occur more rapidly by adopting a chain-folding mechanism, and once the end-groups are separated by more than a few lattice spacings, there is no longer any contribution to \( \sigma_e \) which then approaches \( \sigma_{e,f} \).

Estimation of \( \sigma_e \) by different authors (98, 99, 142) have shown a general increase of \( \sigma_e \) with molecular weight as found in this work for P(THF), see Figure 5.3.33. Plots of \( \sigma_e \) versus \( \bar{M}_n \) for PEO (99) show \( \sigma_e \) increasing with \( \bar{M}_n \), due to increasing polydispersity, up to the point where chain folding commences, i.e. to a once-folded crystal, when \( \sigma_e \) is reduced. After this \( \sigma_e \) continues to increase again with \( \bar{M}_n \) until the next quantised decrease of \( C \) occurs, after which it once again drops back.

To summarise the comparison of PEO with P(THF), it has been shown that low molecular weight PEO readily forms extended chain crystals,
while low molecular weight P(THF) shows no such tendency under the crystallisation conditions studied. This crystal structure leads to discontinuities in plots of log G against $1/T\Delta T$, and to a minimum in log G against molecular weight for PEO at constant $\Delta T$, explained by the morphology changing from extended chain to folded chain crystals. No significant minima are apparent for higher order transitions (e.g. once folded to twice folded chains) in plots of log G against $M_n$ for PEO. The growth rate of P(THF) at constant $\Delta T$ is shown to vary smoothly with $M_n$, showing no minimum. It is possible such a minimum would occur however, either at lower molecular weights, or higher $\Delta T$, where chain extended crystals would be formed.

A plot of log G versus $T_c$ for P(THF) sample T/3.3 does show a discontinuity which has been explained by the sharp chain folded crystal structure changing from once folded (higher $T_c$) to twice folded (lower $T_c$) crystals. The exact quantisation of lamellar thicknesses occurring in low molecular weight PEO is thought to be caused largely by the influence of hydrogen bonding on $\sigma_e$, the end surface free energy. The chain ends always try to remain on the crystal surface to reduce $\sigma_e$ by the energy involved in the hydrogen bonding. Such exact quantisation does not occur readily in low molecular weight P(THF) because the chain ends are not hydroxyl groups so this negative contribution to $\sigma_e$ will not exist.

5.3.10 Presence of Impurities

It has been noted in the text several times that results obtained with samples P/8.4 and P/13.4, prepared with p-chlorophenyldiazonium hexafluorophosphate initiator, have been out of step with samples of similar molecular weight prepared with triethyloxonium hexafluorophosphate initiator. With SAXS measurements for example, theoretical correlation
functions were difficult to fit for sample P/13.4, and impossible for sample P/8.4, using the same model which gives good fits with other samples. Melting points are shown to be low, and inter-lamellar crystallisation is suppressed. Growth rates for these samples from dilatometry are low, but the $\phi_{dil}$ values obtained do appear in good general agreement with $\phi$ determined by other methods. In consequence the majority of data gained from these samples, although included in Section 4, has been omitted from the discussion except to point out the unreliability.

It has been suggested that some impurity species must be present in these samples to cause the above mentioned discrepancies. This is difficult to understand in terms of extraneous residual material merely being mixed with the polymer, due to the rigorously pure conditions necessary for its synthesis, and also to the extreme care taken to remove any such impurities after polymerisation by precipitation, solvent extraction and preparative GPC. However the colour of these polymers is disturbing, and its removal by conventional techniques was not possible. Also the intensity of colour was noted to decrease with molecular weight - this was very apparent when equal concentration solutions were prepared - suggesting that the degree of colour is related to the number of chain ends. It was also shown that under equivalent growth conditions, living P(THF) chains initiated by triethylxonium hexafluorophosphate show no colouration whatever, thus it is proposed that the colour is chemically associated with the initiated end group. It is also suggested that the species causing the colour, being foreign to the polyether chain, is responsible for the disruption of experimental results as mentioned previously, and is thought to reside in the form of a complex end group.

It was suggested in Section 2.1.4 that the initiation reaction was though to proceed via the following mechanism,
leading to an hydroxyl end-group. The presence of the intense purple colour was explained (29) by the acid catalysed resinification of the furan or dihydrofuran - species I - to form highly coloured polymers of low molecular weight. This is thought to be unlikely in view of the preceeding comments. However an alternative mechanism to this was proposed by Ledwith (25) which involved the formation of an aryl radical by homolytic decomposition of the initiator which reacted with monomer producing the \(\alpha\)-alkoxy radical:

\[
\text{Ar} \cdot \text{N}^+ \xrightarrow{2.37} \text{Ar}^* + \text{N}_2
\]

\[
\text{Ar}^* + \text{O} \xrightarrow{2.38} \text{O} + \text{ArH}
\]

Species II then undergoes facile electron transfer with the initiator cation to yield the THF cation (III) which may propagate.

\[
\text{O} \xrightarrow{\text{III}} \text{O}^+ + \text{Ar}^* + \text{N}_2
\]

Species II however may also react with a further radical by combination:
Attack by a further radical followed by the electron transfer reaction would yield

\[
\begin{align*}
\text{II} & \quad + \text{Ar}^* & \quad \rightarrow & \quad \text{Ar} \\
\text{Ar} & \quad + \text{Ar}^* & \quad \rightarrow & \quad \text{Ar} \\
\text{Ar} & \quad + \text{ArN}_2^+ & \quad \rightarrow & \quad \text{Ar}^* + \text{N}_2 
\end{align*}
\]

which may then propagate:

\[
\begin{align*}
\text{Ar} & \quad + \cdot\text{O} & \quad \rightarrow & \quad \text{O-CH}_2-\text{CH}_2-\text{CH}_2-\text{C} = \text{O} \\
\text{Ar} & \quad + \cdot\text{O} & \quad \rightarrow & \quad \text{O-CH}_2-\text{CH}_2-\text{CH}_2-\text{C} = \text{O}
\end{align*}
\]

where \(\text{Ar} = \text{Cl-}\)

Such a system might be expected to be coloured, and could form a third phase disrupting the crystalline and amorphous regions and producing anomalies in the data. The high temperature required for the initiation reaction, 95°C, would tend to favour the rapid production of radicals \((\text{Ar}^*)\) from ions \((\text{ArN}_2^+)\), lending support to side reactions of this type due to their extreme reactivity.
CHAPTER 6. CONCLUSION
Synthetic methods have been developed for the preparation of low molecular weight, narrow distribution polymers of THF, using both p-chlorophenyldiazonium hexafluorophosphate (P) and triethyloxonium hexafluorophosphate (T) as initiators. The causes of broadening of the molecular weight distribution in these systems were found to be (a) equilibrium effects, (b) chain transfer to polymer oxygen, (c) slow and continuing initiation at moderate temperatures, and procedures were developed to minimise these. P required rapid heating to 95°C for 4 mins, followed by quenching to a low reaction temperature (e.g. -10°C), while for T no separate initiation stage was necessary. After initiation with P the kinetics of polymerisation were found to be first order in monomer, requiring an allowance for the equilibrium monomer concentration. After due analysis the rate constant for propagation over the temperature range -10°C to 80°C followed an Arrhenius expression with an activation energy of 51 kJ mol⁻¹. Initiation and propagation using T at -5°C gave a rate constant for propagation which agreed well with values obtained using P. At high conversions (> 20%) an acceleration in the rate occurs due to breakdown of ionic clusters.

Molecular weight averages of the products were determined by GPC, where a conversion factor of 0.592 was found necessary to transfer from a poly(styrene) calibration to P(THF) based on unperturbed dimensions.

The isothermal crystallisation and melting characteristics of P(THF) samples within the molecular weight range 3.3 x 10³ to 2.28 x 10⁴ were investigated. In general it was found that the per cent crystallinity and lamellar thickness were high at molecular weights below 6 x 10³, while above this value they drop sharply to a level which then varies linearly with molecular weight. This behaviour is explained on the basis
of kinetic crystallisation theory, with a change from a sharp chain folded adjacent re-entry lamellar model to a statistical loop model as the molecular weight exceeds $6 \times 10^3$. Longer chains may more easily be incorporated into a crystal at different positions, this is not possible for short chains.

The rate of primary crystallisation, $G$, was found to be proportional to $1/(T\Delta T)$, as predicted by kinetic theory. At constant crystallisation temperature $G$ passes through a maximum at molecular weight $6 \times 10^3$, while at constant supercooling $G$ decreases smoothly with molecular weight, but exhibits a change of slope at $6 \times 10^3$. The growth rate at $\overline{M_n} = 3.3 \times 10^3$ showed a discontinuity against crystallisation temperature at $18.5^\circ C$, where $G$ was reduced below normal kinetic theory predictions. This is explained by a transition from a once folded lamellar crystal at high crystallisation temperatures to a twice folded crystal at lower crystallisation temperatures corresponding to an increase in lamellar thickness. The increase in $\sigma_e$ from such a transition is overruled by the overall negative increase in free energy of crystallisation.

The rate of secondary crystallisation was shown to be under nucleation control, in contrast with high molecular weight P(THF). The lamellar thickness increased with time at constant temperature at the expense of the amorphous thickness, and there was an accompanying increase in the width parameter of the crystalline layers, $\beta_c$, while that of the amorphous regions, $\beta_a$, decreased. This is in accord with a model of small angle branched lamellae, where thickening occurs preferentially into the thicker amorphous regions.

The amorphous thickness was shown to increase linearly with $(\overline{M_n})^{0.5}$ up to $\overline{M_n} = 11 \times 10^3$, for samples after primary crystallisation, with points
from two temperatures lying on the same line. This suggests that whole chains remain in the amorphous regions where they adopt a statistical configuration.

Melting points for a given set of crystallisation conditions increased with molecular weight as predicted by the Flory equation. Upon cooling and subsequent melting samples exhibited two melting peaks, the lower melting transition being due to interlamellar crystallisation within amorphous regions caused by the cooling process.
5. Till, P.H., J Polymer Sci., 24, 301, (1957)
22. Ivin, K.J., and Leonard, J., Polymer, 6, 621, (1965)
38. Smith, W.V., Rubber Chemistry and Technology, 55, (3), 667, (1972)
43. " " " " " Die Makromol. Chemie, 176, 1795, (1975)
44. " " " " " Die Makromol. Chemie, 176, 1815, (1975)
46. Pressure Chemical Company, Pittsberg, U.S.A.,
49. Flory, P.J., and Fox, T.G., J. Am. Chem. Soc., 73, 1904, (1951)
64. Bassett, D.C., and Khalifa, B.A., Polymer, 14, 390, (1973)
68. Peterlin, A., Polymer, B 1, 279, (1963)
89. Lauritzen, Jr., J.I., Unpublished work.
J. Am. Chem. Soc., 64, 1712, (1942)
Ann. N.Y. Acad. Sci., 42, 1, (1942)
100. Ashman, P.C., and Booth, C., Polymer, 13, 495, (1972)
110. Ozark Mahoning Co., Tulsa, Oklahoma.
111. Cationics Inc., 653 Alpha Drive, Cleveland, Ohio 44143.
114. East, R.C., CRC Handbook of Chemistry and Physics (42nd Ed. 1972)
115. American Institute of Physics Handbook
140. Peterlin, A., Polymer, 6, 25, (1965)
141. Sharples, Introduction to Polymer Crystallisation, St. Martins, NY, (196)
1. Introduction

The technique of Gel Permeation Chromatography (GPC) has gained wide popular acceptance over the past decade as a rapid, reliable method of determining the average molecular weights of polymer samples varying from $5 \times 10^2$ to $10^6$. Experimentally, a solution of the polymer is introduced at the top of a column containing a swollen, cross-linked gel, usually a styrene-divinylbenzene copolymer. The cross-linked gel contains pores of known size and distribution, these being controlled by the copolymerisation conditions. The polymer molecules may diffuse in and out of these pores while following the general downward flow of solvent - the steric exclusion mechanism, see reference 1 for example. Chromatographic separation occurs because the smaller polymer molecules diffuse further into the gel, and are thus retained on the column longer than the larger molecules which are excluded from small pores. The column eluent is monitored by a suitable detector system, i.e. one in which the detector response is directly proportional to solute concentration, and a plot of solute concentration versus elution volume results, see figure 1.

The technique is not absolute, and calibration is required prior to the determination of molecular weights. A series of commercially available polystyrene standards$^2$ of known molecular weights and narrow molecular weight distributions are normally employed for calibration, yielding a plot of log peak molecular weight versus elution volume, see figure 2. This curve may be constructed for one polymer (e.g. polystyrene), but if used for the determination of molecular weights for the determination of molecular weights of a different polymer a method of universal calibration is required.

Benoit et al.$^3$ have proposed a universal calibration procedure based upon the hydrodynamic volume, $[\eta]M$, of a polymer molecule in solution such that a plot of log $[\eta]M$ versus elution volume will be the same for all polymers, $[\eta]$ being the intrinsic viscosity. Thus conversion from one calibration curve to another is made via equation I

$$\log [\eta]_P M_P = \log [\eta]_{PS} M_{PS}$$

where PS denotes polystyrene

and P denotes unknown polymer.

This method requires the extra experimental determination of $[\eta]$ as a function of elution volume. It is possible, however, to produce a universal
calibration from a quantity related to the hydrodynamic volume, namely the unperturbed root-mean-square end-to-end distance \((r_0^2)^{1/4}\) from the Flory-Fox equation\(^5\)

\[
\eta = \phi \alpha^3 \left[ \frac{r_0^2}{M} \right]^{3/2} M^{1/2}
\]

where \(\phi\) is the universal viscosity constant
and \(\alpha\) is the expansion coefficient describing polymer-solvent interactions.

Now the polystyrene calibration may be related to the unknown by

\[
\log M_P - \log M_{PS} = \log \left[ \frac{(r_0^2)}{M} \right]_{PS} \left[ \frac{M}{(r_0^2)} \right]_P
\]

where \([M]/(r_0^2)\) is a constant for a given polymer, requiring only a single experimental determination. This method, the Dawkins Method, has been shown to work well when the two polymers concerned have similar polymer-solvent interactions, i.e. their Mark-Houwink exponents \((a)\) are approximately equal, as is often the case when the GPC solvent is a good solvent for both polymers. Recently published work by Dawkins and Hemming\(^6-9\) has shown this method does not hold well for polystyrene in poor or theta solvents where solute-gel interactions, leading to partition and adsorption effects, may arise depending on the polarity of the eluent.

A further complication arises from the spreading of the molecules inherent in any chromatographic process. A solution of a monomeric substance, having a single molecular weight, injected through a Gel Permeation Chromatograph will appear as a Gaussian distribution rather than a single line.

When this degree of spreading is superimposed upon a polymer sample containing a wide range of molecular weights, chromatogram broadening becomes important. For samples of wide molecular weight distribution, having the polydispersity ratio \(\bar{M}_w/\bar{M}_n > 1.5\), it is usually ignored. Several mathematical approaches have been put forward to remove the effect of spreading from the data before it is analysed\(^\text{10}\), but the program detailed here does not take zone-spreading into account.

To compute the required molecular weight distribution from the available data, ideally it is necessary merely to substitute the molecular weight axis from figure 2 for the elution volume axis on figure 1. It has been shown however\(^\text{11,12}\) that this approach is oversimplified and can produce erroneous results. Instead it is necessary to take into account the variation in slope of the calibration curve, and this method is employed here. Also to allow the average molecular weights to be determined, it is first necessary
to calculate the molecular weight distribution, defined as the cumulative weight distribution, \( \bar{f}(M) \), or the differential weight distribution, \( W(M) \), as a function of molecular weight. This will be considered in more detail in section 3.

2. **Use of the Program**

a) **Data Input**

There are four types of data cards required to feed the necessary information into the program, further cards may be needed if extra plots are required.

1. **Problem Control Card** (see Table 1 and Figure 3)

**NA** Defines the number of equal increments on the calibration curve, which must be less than 50, thus there must be NA calibration data cards. When problems are batched, and NA = 0 (or blank), the previously entered calibration curve is used.

**NB** If the concentration data is measured from the 0% baseline, NB = 0, if it is measured from the 100% baseline, NB ≠ 0. Because most baselines have a linear drift superimposed on them, a linear function is subtracted from the concentration data so that the first and last points both equal 0.

**NC** Defines the number of concentration data cards entered, which must be less than 50. When problems are batched, and NC = 0 (or blank), the previously entered concentration data are used.

**EPS** The Mark-Houwink exponent (a) for the polymer-solvent system used. This is employed to calculate \( M_\alpha \) independently of the other molecular weight averages, and since \( M_\alpha < M_v < M_w \) this affords a check on the satisfactory operation of the program.

**H0** These together define the low molecular weight limit used for integration in the format \( U \times 10^V \) where \( H_0 = U, I = V \). \( U \) must = 1, 2 or 5.

**HI** These together define the high molecular weight limit used for integration in the format \( U \times 10^V \) where \( H_1 = U, J = V \). \( U \) must = 1, 2 or 5.

**KO** This determines the type of standard plot produced by the program. \( KO = 0 \) (or blank) gives a 'short' plot, occupying one page with the molecular weight axis across the page. \( KO ≠ 0 \) gives a 'long' plot, occupying two pages with the molecular weight axis down the page.

**HIPLT** When HIPLT and K both = 0 (or blank) only the standard plot will be produced. If a limit on molecular weight is set using HIPLT and K, in the format \( U \times 10^V \) where \( U = 1, 2 \) or 5, then an extra plot is produced where only the molecular weights up to HIPLT and K are plotted, but on full scale. Thus if the limit set by HIPLT and K falls say half way on the standard plot axis, then the extra plot will be a repeat of the first half of the standard plot spread out to cover the full scale. \( H_0, I < HIPLT, K < HI, J \).
ATT The attenuation setting of the Gel Permeation Chromatograph, used in the calculation of the reduced area.

C\textsubscript{NC} The concentration of solute in \(gm\) litre\(^{-1}\) of solution, used in the calculation of the reduced area.

WD The title of the particular data set, it is printed at the top of each page along with the page number.

2. **Constants Card** (see Table 2 and Figure 3)

\(C\textsubscript{FN}\) As discussed earlier, a method of universal calibration must be employed in order to calculate molecular weight averages of polymers other than those used for calibration. The method employed here is the Dawkins Method where comparison of the constants \([\frac{r^2}{M}]\) for the polymers concerned yields a value for \(C\textsubscript{FN}\) as defined by equation III. If the second polymer is the same as the calibration polymer, then \(C\textsubscript{FN} = 1\). If the required ratio is not known for the second polymer, then taking \(C\textsubscript{FN} = 1\) will yield the 'calibration standard equivalent molecular weight', although the ratio \(\bar{M}_w/\bar{M}_n\) will be the same.

If a different value of \(C\textsubscript{FN}\) is chosen within a batch of problems, then the calibration curve must be re-entered also (along with the requisite value of NA). This is because the calibration curve values are calculated using \(C\textsubscript{FN}\) and are then carried forward, so if \(C\textsubscript{FN}\) is changed, but NA= 0 (or blank) and no calibration data cards are included, then the calibration curve generated with the previous value of \(C\textsubscript{FN}\) will be used.

**NSMTH1** This is the number of times the subroutine SMOOTH is used to smooth the log molecular weights (in subroutine DERIV) before the derivative is calculated. Normally a value of 5 is satisfactory.

**NSMTH2** The number of times smoothing is applied (as for NSMTH1) to the derivative after it has been calculated (in subroutine DERIV). Normally a value of 5 is satisfactory.

**NSMTH3** The number of times smoothing is applied after interpolation (by subroutine INTERP) when calculating the cumulative molecular weight distribution. Normally a value of 2 is satisfactory.

**NSMTH4** The number of times smoothing is applied after interpolation when calculating the differential molecular weight distribution. Normally a value of 2 is satisfactory.

3. **Calibration Data Cards** (see Table 3 and Figure 3)

**AX** This is the elution volume axis of the calibration curve, given in counts where 1 count = 5 mls, or directly in elution volume (mls), at equal increments. Only one value, along with its corresponding **AZ** value, is punched per card, thus there will be as many calibration data cards as there are points taken from the calibration curve (=NA) at equal increments.

**AZ** This is the molecular weight corresponding to the count or elution volume on the calibration-curve given for AX.

**NOTE** If NA = 0, then no calibration data cards are required.
4. Concentration Data Cards (see Table 3 and Figure 3)

CX This is the elution volume axis of the concentration curve, given in counts or elution volume (as for AX) but not necessarily at equal increments. Only one value, along with its corresponding CY value, is punched per card, thus there will be as many concentration data cards as there are points taken from the concentration curve (= NC), though not necessarily at equal increments.

CY This is the concentration (e.g. height measured from either the 0% or 100% baseline) corresponding to the count or elution volume on the concentration curve given for CX.

NOTE If NC = 0, then no concentration data cards are required.

5. Extra Plot Cards (see Table 3 and Figure 3)

An extra plot card is detected by spaces 1 to 29 being left blank.

KO This determines the type of the extra plot, i.e. whether short or long, as in the Problem Control Card.

HIPLT K These together define the high molecular weight limit, in the format $U \times 10^V$, which will be plotted, as in the Problem Control Card. Thus a whole series of extra plots may be produced if desired where the molecular weight scale is controlled by HIPLT, K either on the Problem Control Card or upon the extra plot cards.

WD The title of the particular data set, it is printed at the top of each page along with the page number.


b) Program Output

PAGE 1

The title of the data set, WD, is printed at the top of the page, followed by a table listing the input data contained on the Problem Control Card, and the calibration constant CϕN.

A second table entitled Calculated Molecular Weight Averages also appears on page 1, listing all the computed average molecular weights, the polydispersity ratio and the reduced area.

PAGE 2

Two tables appear side by side on page 2, the first entitled Standard Calibration Curve lists the curve input via the calibration data cards. The elution volume (V) is shown directly, along with its corresponding log. molecular weight ($\ln GM$) and the differential of each point (D $\ln GM/DV$). There are as many values in this table as there are calibration data cards, i.e. NA. The second table entitled Concentration Data lists the curve (generally a peak) input via the concentration data cards. The elution volume (V) is shown directly, as is the concentration at each corresponding
point (READ). The data is then converted to 0% baseline readings if NB \neq 0 or blank and a linear function is calculated such that subtraction of this function from the concentration data points (READ) leaves the first and last values as zero (TRANSF). A third table, entitled Sample Calibration Curve, may be listed on page 2 under the Standard Calibration Curve table, or if NA > 25 it will be printed on the following page labelled page 2A. This table repeats the elution volumes (V) from the above table, but now the log molecular weights (L\log G M) are the L\log G M values from the above table multiplied by the calibration constant C\phi N. The third column lists the differential of each point (DL\log G M/DV).

PAGE 3

A table entitled Molecular Weight Distributions is listed, giving the molecular weight (M\log LT), the cumulative molecular weight distribution (CUM AMT), and the differential molecular weight distribution (D AMT/DM) over the molecular weight range covered by the sample. A minimum of 51 values always appears, but if NC > 51, then NC values will be listed. This may cause a throw to a new page which will be unlabelled.

PAGE 4

This shows the first of the plots to be drawn, the standard plot. The type of plot chosen is controlled by KO on the Problem Control Card as previously detailed. If a short plot is chosen, it is contained on a single page with the molecular weight axis across the bottom. The left hand ordinate gives the scale of C, the cumulative molecular weight distribution. It is assumed that the total amount of polymer is 1 gram so that C always covers the range 0 to 1. The values of C given on page 3 (CUM AMT) are plotted against molecular weight to give the typical 'S' shaped curve. The right hand ordinate gives the scale of D, the differential molecular weight distribution (the differential of C with respect to M). The values of D given on page 3 (D AMT/DM) are plotted against molecular weight to show the differential curve.

If a long plot is chosen, the same comments apply as for the short plot except that now the plot is spread over two pages, with the molecular weight axis being the ordinate, and with both C and D as abscissae across the top of the page. The second page used for a long plot is not labelled.

PAGE 5

This page shows a bar-chart or differential histogram representing the sample and computed from the cumulative molecular weight distribution in the
The highest molecular weight (M), in the form \( U \times 10^V \) where \( U = 1, 2 \) or 5, to be used in the histogram is chosen so that at least 90\% of the sample is contained below that molecular weight. The range 0-M is then divided into 20 equal increments, the mid-value of each increment being printed underneath. The ordinate is scaled in \( \text{m.gms. g}^{-1} \) of polymer. The range of M contained in the first increment is compared with the values of C given on page 3, and C', the value corresponding to the highest molecular weight is chosen and plotted. If C' is too small to register on the ordinate scale then a blank is left in that increment. Now the range of M contained in the second increment is compared with the values of C given on page 3, and C", the value corresponding to the highest molecular weight is chosen, and the quantity C"-C' is plotted in that increment, and so on until the 20 increments are completed. If no bar is more than 10\% larger than its previous bar, a further histogram is computed and plotted with the molecular weight range 0 to M reduced to 0.1 of its former value. This is continued until a peak is clearly visible in the histogram. Extra histograms will bear the same page label as the first histogram, i.e. page 5.

**Extra Plots**

The desired number of extra plots, either long or short, is stipulated by non-zero entries in HIPLT,K on the Problem Control Card or on Extra Plot Cards. In each case the value of HIPLT,K in the format \( U \times 10^V \) where \( U = 1, 2 \) or 5, is the highest molecular weight for which the cumulative and differential molecular weight distributions may be plotted. The same comments for both short and long plots apply as detailed for page 4, and any extra plots will bear the same page label as the standard plot, i.e. page 4.

**3. Theory**

a) **Description of the Program**

The method of inputting data to the program, and the way in which this data, and the calculated data, are printed out by the program have been dealt with in the previous section; now it is necessary to consider the detailed functions and calculations carried out within the program. A number of subroutines are employed for this purpose, and these will be considered later. The program initially reads the information stored on the Problem Control Card and the Constants Card, and then makes various decisions according to this information.

i) Checks whether concentration data measured from 0\% or 100\% baseline, and carries this information forward to the table of input data.
ii) Checks whether long or short plot indicated and carries this information forward to the table of input data.

iii) Checks the value of the low and high molecular weight limits for integration, and checks the value of HIPLT,K.

iv) Distinguishes between a Problem Control Card and an Extra Plot Card.

v) Prints the table of the input data.

vi) Checks whether a new calibration curve has been included, or the previously entered curve is to be re-used (if NA = 0 or blank).

vii) The calibration data cards are read, and then the molecular weights are multiplied by the calibration constant. Both sets of molecular weights (before and after multiplication by C\(MN\)) are logged, smoothed, differentiated and smoothed again.

viii) Checks whether new concentration data have been included, or the previously entered concentration data are to be re-used (if NC = 0 or blank).

ix) Checks again whether concentration data measured from 0% or 100% baseline.

x) Reads concentration data cards, and calculates TRANSF values. Also checks whether the range of the concentration data lies within the range of the calibration data. If it does not, then the message 'INSUFFICIENT CALIBRATION DATA' is printed and the program jumps to the next problem.

Note the program has obtained all the basic data made available to it, and the required calculations commence.

1. Reduced Area

This affords a further check on the satisfactory operation of the program by performing the calculation:

\[
\text{Reduced Area} = \frac{\text{Area under concentration curve}}{\text{Attenuation Setting} \times \text{Solute Concentration}}
\]

Values for different samples of a given polymer should only fluctuate by 10%.

2. Molecular Weight Distributions

Initially the function \(I(v)\) is defined, being the relative amount of polymer contained in the volume \(v_1\) to \(v\), as

\[
I(v) = \frac{\int_{v_1}^{v} I(v) \, dv}{\int_{V_0}^{v_1} I(v) \, dv}
\]

To change coordinates from \(v\) to \((\log.M)\) we require the function of the calibration curve, \(G\), such that

\[
G = (\log.M)/v
\]

\[
G^{-1} = v/(\log.M)
\]

then the cumulative molecular weight distribution in terms of \((\log.M)\) is
given by:

\[ I(\log M) = I(v) \cdot v = I(v) \cdot G^{-1}(\log M) \]

Now the differential molecular weight distribution in terms of \((\log M)\) is given by:

\[
w(\log M) = \frac{d}{dv} \left[ \int_{v_1}^{v} I(v) \, dv \right] \cdot \frac{d}{d(\log M)} G^{-1}(\log M)
\]

\[
= \frac{dI(v)}{dv} \cdot \frac{d}{d(\log M)}
\]

and in terms of \(M\):

\[
w(M) = \frac{dI(v)}{dv} \cdot \frac{d}{d(\log M)} \cdot \frac{d(\log M)}{dM}
\]

Similarly for the cumulative molecular weight distribution in terms of \(M\)

\[
I(M) = I(v) \cdot G^{-1}(\log M) \cdot \frac{d(\log M)}{dM}
\]

where \(d(\log M)/dM = 1/M\).

3. Molecular Weight Averages

The required molecular weight averages are now computed from the differential molecular weight distribution \(w(M)\) as follows:

\[
\overline{M}_n^{14.} = \frac{1}{\int_{M_1}^{M_0} (1/M) \, w(M) \, dM}
\]

\[
\overline{M}_v^{15.} = \left[ \int_{M_1}^{M_0} M^a \, w(M) \, dM \right]^{1/a}
\]

\[
\overline{M}_w^{3.} = \int_{M_1}^{M_0} M \, w(M) \, dM
\]

\[
\overline{M}_z = \frac{\int_{M_1}^{M_0} M^2 \, w(M) \, dM}{\int_{M_1}^{M_0} M \, w(M) \, dM}
\]

\[
\overline{M}_{z+1} = \frac{\int_{M_1}^{M_0} M^3 \, w(M) \, dM}{\int_{M_1}^{M_0} M^2 \, w(M) \, dM}
\]

Also the functions \(\overline{M}_p\) and the polydispersity ratio, which do not depend on \(w(M)\), are calculated:

\[
\overline{M}_p = (\overline{M}_n \overline{M}_w)^{1/2}
\]
Polydispersity Ratio = $\frac{M_w}{M_n}$

The computed molecular weight averages are now printed out in tabular form on page 1. Tables of the input calibration and concentration data are given on page 2, and on page 3 the values of $I(M)$ and $w(M)$ are printed out.

The program now considers the plots, first of all the standard plot. First a suitable molecular weight scale is calculated, and then the choice of short or long plot is examined, and the required plot computed. Similarly a suitable scale is chosen and then the differential histogram is computed, a check being made to see if further histograms are necessary. Finally the value of HIPLT.K is considered to check if any extra plots are required, if so then these are computed, if not then the program returns to start for the next problem.

b. Description of the Subroutines

1. DFRNTL

This subroutine is used to take $\log_{10}$ of the molecular weights input via the calibration data cards (both before and after multiplication by $C_N$), smooth the logged values using subroutine SMOOTH, calculate the derivative of each point by differences and smooth this derivative. The calling sequence is:

```fortran
CALL DERIV(X,Y,DT,N,N1,N2)
```

where

- $X$ contains $N$ values of the independent variable (e.g. elution volume) in equal increments in ascending order.
- $Y$ contains $N$ corresponding values of the dependent variable (e.g. molecular weights). The $\log_{10}$ of these values is found, and the values smoothed, the result in each case being stored in $Y$ (the original values being destroyed).
- $DY$ contains $N$ corresponding values of the computed derivative, these are smoothed and then stored in $DY$.
- $N$ is the number of data points contained in $X$, $Y$ and $DY$.
- $N1$ is the number of times smoothing is applied to the $\log_{10}$ molecular weights.
- $N2$ is the number of times smoothing is applied to the computed derivative.

2. SMOOTH

This subroutine will smooth a set of equally spaced points using Lagrangian smoothing formulae obtained by finding the least squares quadratic through five successive points. The calling sequence is:

```fortran
CALL SMOOTH(Y,N,K)
```
where \( Y \) contains \( N \) values of the ordinate requiring smoothing, the corresponding abscissae are assumed to be equally spaced but may be given in either ascending or descending order.

\( N \) is the number of values in \( Y \).

\( K \) is the number of times the smoothing formulae are applied to \( Y \). If \( K = 0 \) the subroutine will return.

The smoothed values are returned in \( Y \), the original values being destroyed.

3. **INTERP**

Use of this subroutine allows values of a given function to be interpolated at any set of specified points, in any order. Any point lying outside the range of the function is returned as zero. The calling sequence is

\[
\text{CALL INTERP}(X1,Y1,N1,X2,Y2,N2)
\]

where

- \( X1 \) contains the known abscissa values of the function. They are not required to be in any specific order.
- \( Y1 \) contains the corresponding ordinate values.
- \( N1 \) is the number of values defining the function, i.e. the number of entries in \( X1 \) or \( Y1 \).
- \( X2 \) contains the known abscissa values at which the interpolated values are desired. They are not required to be in any specific order.
- \( Y2 \) contains the interpolated ordinate values corresponding to the \( X2 \) abscissa.
- \( N2 \) is the number of interpolated values, i.e. the number of entries in \( X2 \).

4. **SUM**

This subroutine numerically evaluates the indefinite integral of a function given at a set of discrete points. A four-point quadratic Lagrangian formula for unequally spaced points is used, this being exact for cubics.

The formula is obtained by averaging the areas under the left and right portions, respectively, of 2 quadratics fitted at the points \( X_{-1}, X_0, X_1 \) and \( X_0, X_1, X_2 \) respectively, see figure 4. This gives the formula as

\[
\int_{X_0}^{X_1} y \, dx = \frac{C}{12} \left[ \frac{-C^2}{AB} y_2 + \left(4 + \frac{B}{A} + \frac{E}{D}\right) y_1 + \left(4 + \frac{A}{B} + \frac{D}{E}\right) y_0 - \frac{C^2}{DE} y_{-1} \right]
\]

where

- \( A = X_2 - X_1 \)
- \( B = X_2 - X_0 \)
- \( C = X_1 - X_0 \)
- \( D = X_1 - X_{-1} \)
- \( E = X_0 - X_{-1} \)
The calling sequence for SUM is,

\[
\text{CALL SUM}(X,Y,Z,C,N)
\]

where

- \(X(1)\) to \(X(N)\) are the independent variables.
- \(Y(1)\) to \(Y(N)\) are corresponding dependent variables.
- \(Z(1)\) to \(Z(N)\) are corresponding integrated values.
- \(C\) is the constant of integration.
- \(N\) is the number of points at which the function is entered.

5. **SIZE**

This function computes the scale required for LPL\(\Phi\)T, SPL\(\Phi\)T and HSGRAM by calculating the scale interval \(S\), and an initial scale point \(A\) from a set of points \(X = (x_1, \ldots, x_n)\) such that:

1. \(S = 1, 2, 3\) or 5 times a power of 10
2. \(A = KS\) for some integer \(K\)
3. \(A \leq x_i \leq A + 10S\) for each \(x_i\) of \(X\)
4. No smaller value of \(S\) satisfies these requirements.

The calling sequence for SIZE is

\[
\text{XSC} = \text{SIZE}(N, X, XS, IS, IF)
\]

where

- \(\text{XSC} = 10/S\)
- \(N = \text{Number of points in the set } X\)
- \(X = \text{vector of length } N \text{ holding values to be scaled}\)
- \(XS = 1.5 \cdot 10A\)
- \(IS = \text{vector of length } 11 \text{ holding the least set of integers such that } IS = 10^{IF}\) represents the scale marks.
- \(IF = \text{the integer exponent of the scale}\)

6. **LPL\(\Phi\)T**

This subroutine plots 2 dependent variables \(Y_1\) and \(Y_2\) against an independent variable \(X\) on a plot covering 2 pages of output on a grid 100 scale units, the independent variable being plotted down the paper. The accuracy of the dependent variables is twice that achieved in SPL\(\Phi\)T, but the output of pages is less convenient. The calling sequence for LPL\(\Phi\)T is

\[
\text{CALL LPL\(\Phi\)T}(M, W, N, X, Y_1, H_1, Y_2, H_2)
\]

where

- \(M\) is the number of 'words' in the heading vector \(W\)
- \(W\) contains the plot heading.
- \(N\) is the number of entries in \(X, Y_1\) and \(Y_2\) which require plotting.
- \(X\) contains the values of the independent variable.
Y1 contains values of the first dependent variable which must correspond, in order, to the X values.

H1 holds the character used to denote Y1 on the plot. It is set at C.

Y2 contains values of the second dependent variable which must correspond, in order, to the X values.

H2 holds the character used to denote Y2 on the plot. It is set at D.

7. SPLAT

As for LPLIT this subroutine plots 2 dependent variables against 1 independent variable, but this time on a grid 50 x 100 occupying only 1 page of output. The dependent variables are plotted down the page on the 50 side of the grid thus limiting their accuracy to about 2%. However the output is more convenient for storage, etc. The calling sequence is identical to that for LPLIT, except that if H2 (D in LPLIT) is set = BLANK, the second dependent variable does not plot.

8. HSGRAM

This subroutine is used to plot the histograms computed in the program. It produces 20 vertical bars scaled to represent mgms.gm⁻¹ of polymer. At the base of each bar is printed the average molecular weight represented by that bar, while the percentage of sample represented by the histogram is printed at the top of the chart, which occupies one page of output.

The calling sequence is

CALL HSGRAM(M,W,N,X,Y,IZ)

where

M is the number of 'words' in the heading vector W
W contains the heading for the plot
N ≤ 20 is the number of bars in the plot
X holds the molecular weights corresponding to the initial points of the intervals represented by the bars
Y holds the amount, in mgms.gm⁻¹ of polymer of the sample represented by the bars
IZ is the integer giving the percentage of sample represented by the histogram.
References

<table>
<thead>
<tr>
<th>NAME</th>
<th>PROGRAM TITLE</th>
<th>HTO1</th>
<th>DATE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**ADDRESS**

**PROBLEM CONTROL CARD**

| MANG | MCG | EPS | HS | IH | JO | ATT. | CPNC | WD |

**CONSTANTS CARD**

| CON   | NSMTH1 | NSMTH2 | NSMTH3 | NSMTH4 |

**CALIBRATION DATA CARDS**

| AX   | A2     |

**CONCENTRATION DATA CARDS**

| CX   | CY     |

**EXTRA PLOT CARD**

| KO   | KD     |
### 1. PROBLEM CONTROL CARD

<table>
<thead>
<tr>
<th>READ</th>
<th>FORMAT</th>
<th>COLUMNS</th>
<th>D.P. in COLUMN</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>I5</td>
<td>1-5</td>
<td></td>
<td>Number of calibration data cards, must be less than 50.</td>
</tr>
<tr>
<td>NB</td>
<td>I2</td>
<td>6-7</td>
<td></td>
<td>NB = 0 or 1 depending on whether concentration data measured from 0% or 100% baseline respectively.</td>
</tr>
<tr>
<td>NC</td>
<td>I5</td>
<td>8-12</td>
<td></td>
<td>Number of concentration data cards, must be less than 50.</td>
</tr>
<tr>
<td>EPS</td>
<td>F5.3</td>
<td>13-17</td>
<td>14</td>
<td>Mark-Houwink exponent (a) for polymer solvent system.</td>
</tr>
<tr>
<td>Hφ</td>
<td>F4.0</td>
<td>18-21</td>
<td>21</td>
<td>$Hφ$ and I together define the lower limit of molecular weight to be used for integration, in the format $U \times 10^V$ where $Hφ = U$ and $I = V$.</td>
</tr>
<tr>
<td>I</td>
<td>I2</td>
<td>22-23</td>
<td></td>
<td>$Hφ$ and I together define the lower limit of molecular weight to be used for integration, in the format $U \times 10^V$.</td>
</tr>
<tr>
<td>HI</td>
<td>F4.0</td>
<td>24-27</td>
<td>27</td>
<td>HI and J together define the higher limit of molecular weight to be used for integration, also in the format $U \times 10^V$.</td>
</tr>
<tr>
<td>J</td>
<td>I2</td>
<td>28-29</td>
<td></td>
<td>HI and J together define the higher limit of molecular weight to be used for integration, also in the format $U \times 10^V$.</td>
</tr>
<tr>
<td>KO</td>
<td>I2</td>
<td>30-31</td>
<td></td>
<td>Determines type of standard plot produced, KO = 0 gives short plot, KO = 1 gives long plot.</td>
</tr>
<tr>
<td>HIPLT</td>
<td>F2.0</td>
<td>32-33</td>
<td>33</td>
<td>HIPLT and K together define the highest molecular weight to be plotted on an extra plot. If HIPLT and K = 0 (or blank) no extra plot is produced.</td>
</tr>
<tr>
<td>K</td>
<td>I2</td>
<td>34-35</td>
<td></td>
<td>HIPLT and K together define the highest molecular weight to be plotted on an extra plot. If HIPLT and K = 0 (or blank) no extra plot is produced.</td>
</tr>
<tr>
<td>ATT</td>
<td>F5.0</td>
<td>36-40</td>
<td>40</td>
<td>Attenuation setting of Gel Permeation Chromatograph.</td>
</tr>
<tr>
<td>CN</td>
<td>F8.4</td>
<td>41-48</td>
<td>44</td>
<td>Solute concentration in gm litre$^{-1}$.</td>
</tr>
<tr>
<td>WD</td>
<td>4A8</td>
<td>49-60</td>
<td></td>
<td>Title of data set, to be printed at the top of each page.</td>
</tr>
</tbody>
</table>
### 2. CONSTANTS CARD

<table>
<thead>
<tr>
<th>READ</th>
<th>FORMAT</th>
<th>COLUMNS</th>
<th>D.P. in COLUMN</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(\phi)N</td>
<td>F10.5</td>
<td>1-10</td>
<td>5</td>
<td>C(\phi)N defines the calibration constant calculated from the ratios of ([-\gamma_0^2/\mu]) for the calibration polymer (poly-styrene) and the unknown by the Dawkins Method. If ratio is not known use C(\phi)N = 1.0.</td>
</tr>
<tr>
<td>NSMTH1</td>
<td>I10</td>
<td>11-20</td>
<td></td>
<td>NSMTH1 defines the number of times smoothing is applied to the log molecular weights (in DERIV) before the derivative is taken. (5 recommended.)</td>
</tr>
<tr>
<td>NSMTH2</td>
<td>I10</td>
<td>21-30</td>
<td></td>
<td>NSMTH2 defines the number of times smoothing is applied to the derivative (in DERIV). (5 recommended.)</td>
</tr>
<tr>
<td>NSMTH3</td>
<td>I10</td>
<td>31-40</td>
<td></td>
<td>NSMTH3 defines the number of times smoothing is applied after interpolation when calculating the cumulative molecular weight distribution. (2 recommended.)</td>
</tr>
<tr>
<td>NSMTH4</td>
<td>I10</td>
<td>41-50</td>
<td></td>
<td>NSMTH4 defines the number of times smoothing is applied after interpolation when calculating the differential molecular weight distribution. (2 recommended.)</td>
</tr>
<tr>
<td>READ</td>
<td>FORMAT</td>
<td>COLUMNS</td>
<td>D.P. in COLUMN</td>
<td>COMMENTS</td>
</tr>
<tr>
<td>------</td>
<td>---------</td>
<td>---------</td>
<td>----------------</td>
<td>----------</td>
</tr>
<tr>
<td>3. CALIBRATION DATA CARDS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AX</td>
<td>F10.5</td>
<td>1-10</td>
<td>5</td>
<td>'Counts' from calibration curve in equal increments of elution volume.</td>
</tr>
<tr>
<td>AZ</td>
<td>F10.5</td>
<td>11-20</td>
<td>11-20</td>
<td>Molecular weight corresponding to the above elution volume increment.</td>
</tr>
<tr>
<td>4. CONCENTRATION DATA CARDS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CX</td>
<td>F10.5</td>
<td>1-10</td>
<td>5</td>
<td>'Counts from concentration curve in increments of elution volume, equal spacing not necessary.</td>
</tr>
<tr>
<td>CY</td>
<td>F10.5</td>
<td>11-20</td>
<td>15</td>
<td>Concentration (e.g. height measured from the baseline) of the corresponding point on the concentration curve.</td>
</tr>
<tr>
<td>5. EXTRA PLOT CARDS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO</td>
<td>I2</td>
<td>30-31</td>
<td>-</td>
<td>Definitions as for Problem Control Card, other spaces to be left blank.</td>
</tr>
<tr>
<td>HIPLT</td>
<td>F2.0</td>
<td>32-33</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>I2</td>
<td>34-35</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>WD</td>
<td>4A8</td>
<td>49-80</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
MASTER GEL

THIS PROGRAM WRITTEN IN STANDARD FORTRAN

DIMENSION AX(50),AY(50),AZ(50),OZ(50)
DIMENSION CX(200),CY(200),CV(200),CX1R(200),CY1R(200),DCY1R(200)
DIMENSION OX1(200),OY1(200),OZ1(200),OZ2(21),OY2(21),OZ2(21)
DIMENSION OX(200),OM1(200),OM2(200),OM3(200),OM4(200),OM5(200)
DIMENSION XING(200),WD(4),X0(1),XI(1),YY(1),YYZ(1)
DIMENSION IPILOTS(2),IPLOTL(2),ITC(2)
DATA IPILOTS(1),IPILOTS(2)/4HSHOR,4HT /
DATA IPLOTL(1),IPLOTL(2)/4HLONG,4H /

READ PROBLEM CONTROL CARD
1 READ (1,2) NA, NR, NC, EPS, HO, I, H, J, K0, HIPLT, K, ATT, CONC, WD
C CHECK FOR TERMINATOR CARD WITH NA = -1
IF (NA.EQ.-1) GO TO 56
2 FORMAT (15,15,F5.3,2(F4.0,12),12,F2.0,12,F5.0,F8.4,4A8)
C READ CALIBRATION AND SMOOTHING CONSTANTS
READ (1,3) CON,NSMTH1,NSMTH2,NSMTH3,NSMTH4
3 FORMAT (#10.5,4110)
IF (NR.EQ.1) GO TO 4
NTC=0
GO TO 5
4 NTC=100
GO TO 7
C CONTINUE
IF (K0.EQ.1) GO TO 6
ITC(1)=IPILOTS(1)
ITC(2)=IPILOTS(2)
GO TO 7
6 \text{ITC(1)=IPLOT(1)} \\
\text{ITC(2)=IPLOT(2)} \\
\text{GO TO 7} \\
\text{7 CONTINUE} \\
K_0=10^{10.**} \\
W_0=H_0*10.** \\
W_1=H_1*10.** \\
W_{PLT}=H_{PLT}*10.** \\
\text{C DISTINGUISH BETWEEN A CONTROL CARD & AN EXTRA PLOT CARD} \\
\text{IF \{(NA-NC).EQ.0 \AND \{(EPS+H_0+H_1).EQ.0.0\) GO TO 52 \\
\text{C C} \\
\text{WRITE TABLE OF INPUT DATA} \\
\text{WRITE (2,8) UD, NA, NC, NTC, EPS, H_0, H_1, ITC, H_{PLT}, ATT, CONC, CON} \\
\text{FORMAT (1X,15H6) PERMEATION PROGRAM, 20X, 4A8, 19X, 6HPAGE 1///} \\
114X, 32HNUMBER OF CALIBRATION DATA CARDS, 13X, 1H=, 15X, 15///, 14X, 34HNUM} \\
2MBER OF CONCENTRATION DATA CARDS, 11X, 1H=, 15X, 15///, 14X, 43HBASLINE U} \\
3RED WHEN MEASURING CONCENTRATIONS, 2X, 1H=, 16X, 14///, 14X, 21HMARK-HOWE} \\
4NK EXPONENT, 24X, 1H=, 10X, F10.3 ///, 14X, 39HLLOW MOLECULAR WEIGHT INTEGRAT} \\
5TION LIMIT, 7X, 1H=, 12X, F0.0 ///, 14X, 39HHIGH MOLECULAR WEIGHT INTEGRATI} \\
6ON LIMIT, 6X, 1H=, 10X, F10.0 ///, 14X, 19HTYPE OF PLOT CHOSEN, 26X, 1H=, 15X,} \\
72A4 ///, 14X, 19HLIMIT EXTRA PLOT TO, 26X, 1H=, 10X, F10.0 ///, 14X, 33HATTENUA} \\
TION SETTING OF INSTRUMENT, 12X, 1H=, 14X, F8.0 ///, 14X, 33HSAMPLE CONCENTR} \\
ATION \{(MS.//ITRF), 12X, 1H=, 10X, F10.4 ///, 14X, 20HCALIBRATION CONSTANT,} \\
52X, 1H=, 12X, F8.4 ///} \\
\text{C C} \\
\text{RECALL WHETHER TO READ CALIBRATION DATA, OR USE DATA} \\
\text{FROM A PAST PROBLEM.} \\
\text{IF (NA.EQ.0) GO TO 11} \\
\text{C C} \\
\text{READ CALIBRATION DATA CARDS} \\
\text{READ (1,9) \{AX(1), AZ(1), I=1..NA\)
9 FORMAT (2F10.5)
10 AY(I) = AZ(I) * CN
   CALL DFRNTL (AX, AZ, DAZ, NA, NSMTH1, NSMTH2)
   NASAVE = NA
   CALL DFRNTL (AX, AY, DAY, NA, NSMTH1, NSMTH2)
11 NA = NASAVE
   GO TO 12
12 SIGN = 1,0
   DECIDE WHETHER TO READ CONCENTRATION DATA, OR USE DATA
   FROM A PREVIOUS PROBLEM
   IF (NC.EQ.0) GO TO 15
   DECIDE WHETHER PEAKS ARE MEASURED FROM 0 OR 100 BASELINE
   IF (NR.EQ.0) GO TO 13
   SIGN = SIGN
13 NCSAVE = NC
   READ CONCENTRATION DATA CARDS
   READ (1,9) (CX(I), CY(I), I=1, NC)
   NXV = CY(NC) - CY(1) / (CX(NC) - CX(1))
   NO 14 I = 1, NC
14 CYT(I) = SIGN * (CY(I) - CY(1)) - NXV * (CX(I) - CX(1))
15 NC = NCSAVE
   IF (CX(NC) = AX(NA)) 16, 16, 17
16 IF (CX(1) = AX(1)) 17, 19, 19
17 WRITE (2,18)
18 FORMAT (4H+, 10X, 29HINSUFFICIENT CALIBRATION DATA)
   GO TO 1
19 CALL SUM(CX, CYT, OH, O, 0, NC)
   CALL INTERP(AV, AX, NA, VY, VX, 1)
   IF (HO.LE.O) GO TO 20
   VX(1) = AMAX1(VX(1), ALOG10(HO))
20 CALL INTERP(AV, AX, NA, VY, VZ, XI, 1)
   IF (HI.LE.O) GO TO 21
   XI(1) = AMAX1(XI(1), ALOG10(HI))
21 CONTINUE
   NI = MAX0(51, NC)
   DEL = NI - 1
   DX = (XI(1) - XO(1)) / DEL
   LOG(1) = XO(1)
   NO 22 I = 2, NI
22 XLOG(I) = XLOG(I-1) + DX
   CALL INTERP(AV, AX, NA, XLOG, CX1R, NI)
   CALL INTERP(CX, CYT, NC, CX1R, CY1R, NI)
   CALL INTERP(AV, DAY, NA, CX1R, DCY1R, NI)
   CALL SMOOTH(CY1R, NI, NSMTH3)
   CALL SMOOTH(DCY1R, NI, NSMTH4)
   NO 23 I = 1, NI
23 OX1(1) = 10.**XLOG(I)
   CALL SUM(CX1R, CY1R, OY1, 0, 0, NI)
   NCI = OY1(I)
   N2 = MAX(0, 0)
   NO 24 I = 1, NI
   OY1(I) = OY1(I) / NCI
   NZ1(I) = 0.434295 * CY1R(I) / (NC1 * OX1(I) * DCY1R(I))
\[ \text{NZMAX} = \text{MIN}(\text{NZMAX}, OZ1(i)) \]
\[ \text{OM1}(i) = \frac{OZ1(i)}{OX1(i)} \]
\[ \text{OM2}(i) = OX1(i) * OZ1(i) \]
\[ \text{OM3}(i) = OX1(i) * OM2(i) \]
\[ \text{OM4}(i) = OX1(i) * OM3(i) \]

24 \[ \text{OM5}(i) = OX1(i) * z(i) * \text{EPS} * OZ1(i) \]
\[ \text{CALL SUM} (\text{OX1}, \text{OM1}, \text{OM2}, \text{OM3}, \text{OM4}, \text{OM5}) \]
\[ \text{AVMN} = 1. / \text{OM(N)} \]
\[ \text{CALL SUM} (\text{OX1}, \text{OM2}, \text{OM3}, \text{OM4}, \text{OM5}) \]
\[ \text{AVM} = \text{OM}(\text{N}) \]
\[ \text{CALL SUM} (\text{OX1}, \text{OM3}, \text{OM4}, \text{OM5}) \]
\[ \text{AVHZ} = \text{OM}(\text{N}) / \text{AVMN} \]
\[ \text{CALL SUM} (\text{OX1}, \text{OM4}, \text{OM5}) \]
\[ \text{AVHV} = \text{OM}(\text{N}) * (1./\text{EPS}) \]
\[ \text{PRAT} = \text{AVHM} / \text{AVMN} \]
\[ \text{AVMP} = \sqrt{\text{AVM} * \text{AVMN}} \]

C

WRITE TABLE OF MOLECULAR WEIGHT AVERAGES.
WRITE (2,25) AVMN,AVMP,AVMV,AVMU,AVM2,PRAT,AREA

25 FORMAT (1H0,44X,36H CALCULATED MOLECULAR WEIGHT AVERAGES,//14X,31H 1 NUMBER AVERAGE MOLECULAR WEIGHT,14X,1H=,1PE20.3,//14X,29HPACK AVER 2AGE MOLECULAR WEIGHT,16X,1H=,E20.3,//14X,34HVISCOSITY AVERAGE MOLEC 3ULAR WEIGHT,11X,1H=,E20.3,//14X,31HWIGHT AVERAGE MOLECULAR WEIGHT 4,14X,1H=E20.3,///14X,26HZ AVERAGE MOLECULAR WEIGHT,19X,1H=E20.3,/// 5/14X,28HZ+1 AVERAGE MOLECULAR WEIGHT,17X,1H=E20.3,///14X,20HPOLYDI 6SPERITY RATIO,25X,1H=,E20.3,///14X,12HREDUCED AREA,33X,1H=,E20.3 71=E1N0(NA,NU)
\[ M_1 = M_0 \]
\[ M_2 = M_1 + 1 \]
M3 = MAX0(NA, NC)

WRITE TABLES OF INPUT CALIBRATION & CONCENTRATION DATA
WRITE (2,26) WD
26 FORMAT (1H1/20X,22HGET PERRMATION PROGRAM,20X,4A8,19X,6HPAGE 2/) WRITE (2,27) (AX(I),AZ(I),DAZ(I),CX(I),CY(I),CVT(I);I=1,M1)
27 FORMAT (1H0,18X,26HSTANDARD CALIBRATION CURVE,40X,18HCONEJTURATION
1 DATA,1H0,13X,1HV,13X,5HL0G M,13X,9HDL0G M/DV,19X,1HV,17X,
24HRAD,13X,6HTRANSF,/(1PE20.3,2E18.7,E24.3,2E18.3) IF (NC.GT.M3) GO TO 29 WRITE (2,28) (AX(I),AZ(I),DA7(I),I=M2,M3)
28 FORMAT (1PE20.3,2PE18.7) GO TO 31 WRITE (2,30) (CX(I),CY(I),CV(T(I),I=M2,M3)
30 FORMAT (1H55X,1PE24.3,2E18.3)
31 CONTINUE

DECLARE WHETHER TO GO TO A NEW PAGE
IF (H3.GT.25) GO TO 33 WRITE (2,32) (AX(I),AY(I),DAY(I),I=1;NA)
32 FORMAT (1H0, 21X,24HSAMPLE CALIBRATION CURVE,14X,1HV,13X,5HL0G M
1.13X,9HDL0G M/DV,1PE20.3,2E18.7) GO TO 35 WRITE (2,34) (WD,(AX(I),AY(I),DAY(I),I=1;NA))
34 FORMAT (1H1/20X,22HGET PERRMATION PROGRAM,20X,4A8,17X,8HPAGE 2 A/
1H0,19X,24HSAMPLE CALIBRATION CURVE,14X,1HV,13X,5HL0G M,13X,
20HDL0G M/DV,1PE20.3,2E18.7)
35 CONTINUE

C
WRITE TABLE OF MOLECULAR WEIGHT DISTRIBUTIONS
WRITE (2,36) WD
36 FORMAT (1H1/20X,22H GEL PERMEATION PROGRAM 20X,4A8,19X,6H PAGE 3/1H
10,44X,30H MOLECULAR WEIGHT DISTRIBUTIONS./1H0,36X,6H MOLE WT,14X,7HC
2H AMT,13X,8H AMT/DM/
WRITE (2,37) (OX1(I),0Y1(I),0Z1(I),I=1,N1)
37 FORMAT (1H/27X,1PE17.3,2E20.3)
**X2(I)=0.0
**YY(I)=0.99
CALL INTERP (0Y1,0X1,NI,**YY,**X2(2),I)
**J=1
GO TO 30
30**YY(I)=2MAX
CALL INTERP (**Z1,0X1,NI,**YY,**X2(2),I)
**X2(2)=5.0X2(2)
**J=2
39**CX=100.0/ SIZE(2,0X2;XS,**X2(2)),IF)
**NP=ALOG10(10X**CX-**X0(1))/**DX+1.0
**NP=NT
IF (**NP>NI) 41,40,40
40**NP=NI
IF(KJ.EQ.2) GO TO 45
41 IF(KP.EQ.2) GO TO 43
42 CALL SPLIT (4,WD,**NP,0X1,0Y1,0Z1)
GO TO 44
43 CALL LPLT (4,WD,**NP,0X1,0Y1,0Z1)
44 IF(KJ.EQ.1) GO TO 38
45**YY(I)=0.99
CALL INTERP (0Y1,0X1,NI,**YY,**X2(2),I)
**CX=5.0/ SIZE(2,0X2;XS,**X2(3)),IF)
46 10 47 I=1,21
47 10 X2(I)=0X2(I-1)+SCX
        CALL INTFRP (OX1, OY1, NI, OX2, OY2, 21)
        NO 48 I=1,20
48 10 N2(I)=1000-*(OY2(I+1)-OY2(I))
        KK=2
        NO 49 I=2,20
49 10 IF (O22(I)-O22(I-1)) 49; 49,50
50 CONTINUE
        SCX=SCX/10.
        KK=1
50 10 V Sup=0.
      NO 51 I=1,21
51 10 V Sup=AMAX1(V Sup, OY2(I))
        IPCT=100,*V Sup+0.5
        CALL HSGRAH (4, WD, 20, OX2, OZ2, IPCT)
        IF (KK.EQ.1) GO TO 46
52 IF (HIPLT=10.**X0(1)) 1.1,53
53 NP=(ALOG10(HIPLT)-X0(1))/DDx+1.0
        NP=MINTO(NI,NP)
        IF (KP.EQ.2) GO TO 55
54 CALL SPLOT(4, WD, NP, OX1, OY1, OZ1)
        GO TO 1
55 CALL IPLOT(4, WD, NP, OX1, OY1, OZ1)
        GO TO 1
56 STOP
FND
SUBROUTINE DERNT1 (X,Y,DY,N,N1,N2)
DIMENSION X(50),Y(50),DY(50)
DO 1 I=1,N
1 Y(I)=ALOG10(Y(I))
CALL SMOOTH (Y,N,N1)
NLFS1=N-1
DY(1)=(Y(2)-Y(1))/(X(2)-X(1))
DO 2 I=2,NLFS1
2 DY(I)=(Y(I+1)-Y(I-1))/(X(I+1)-X(I-1))
DY(N)=(Y(N)-Y(N-1))/(X(N)-X(N-1))
CALL SMOOTH (DY,N,N2)
RETURN
END
SUBROUTINE SMOOTH (V, N, K)
DIMENSION V(N), A(5), R(5), C(5), Z(5)
DATA A(1), A(2), A(3), A(4), A(5)
1 0.8571429, 0.25714286, 0.08571429, -0.14285714, 0.08571429/
DATA R(1), R(2), R(3), R(4), B(4)
1 0.25714286, 0.37142857, 0.34285714, 0.17142857, -0.14285714/
DATA C(1), C(2), C(3), C(4), C(5)
1 0.08571429, 0.34285714, 0.48571429, 0.34285714, -0.08571429/
IF (K.LT.1 OR N.LE.4) GO TO 0
NLESS3=N-3
N6=N-6
10 R1=1, K
10 1=1.5
1 R(I)=V(1)
V(1)=0.
V(2)=0.
10 2=1.5
V(1)=V(1)+A(I)*V(I)
2 V(2)=V(2)+B(I)*V(I)
IF (N-5) 6,6,3
3 M=3, NLESS3
V(J)=0.
4 J=J-4
10 4=1.5
J=MOD(I+J4,5)+1
4 V(J)=V(J)+C(I)*V(J)
J=MOD(J-3,5)+1
5 V(J)=V(J)+3
6 V(N-3)=0.
V(N-1)=0.
1305 1310 1312 1315 1317 1320 1322 1325 1330 1335 1340 1345 1350 1355 1360 1365 1370 1375 1380 1385 1390 1395 1400 1405 1410 1415 1420 1425 1430 1435 1440
\[ v(N) = 0. \]
\[ \text{do} \quad I = 1.5 \]
\[ I = \text{MOD}(I + N6, 9) + 1 \]
\[ I = 6 - I \]
\[ v(N-2) = v(N-2) + C(II) * z(JT) \]
\[ v(N-1) = v(N-1) + B(II) * z(JT) \]
\[ v(N) = v(N) + A(II) * z(JT) \]
\[ \text{CONTINUE} \]
\[ \text{RETURN} \]
\[ \text{END} \]
SUBROUTINE INTERP (X1,Y1,N1;X2,Y2,N2)
DIMENSION X1(N1),Y1(N1),X2(N2),Y2(N2)
XMAX=X1(1)
THMAX=1
XMIN=X1(1)
THMIN=1
DO 4 I=1,N1
IF (X1(I)-XMAX) 2,4,1
1 XMAX=X1(I)
THMAX=I
GO TO 4
2 IF (X1(I)-XMIN) 3,4,4
3 XMIN=X1(I)
THMIN=I
4 CONTINUE
DO 5 I=1,N2
5 Y2(I)=0.0
6 IF (Y2(I)-XMAX) 6,6,14
7 IF (Y2(I)-XMIN) 14,7,7
8 Y2(I)=Y2(I)
GO TO 14
9 IF (X1(I)-XUB) 10,13,13
10 XUB=X1(I)
1LUB=11
GO TO 13
11 IF (X1(11)-XGLB) 13,13,12
12 XGLN=X1(11)
1GLH=11
13 CONTINUE
   v2(12)=Y1(IGLB)+(Y1(ILUB)-Y1(IGLB))*(X2(12)-X1(IGLB))/(X1(ILUB)-X1
1(IGLB))
14 CONTINUE
RETURN
END
SUBROUTINE SUM (X,Y,Z,C,N)

DIMENSION X(200), Y(200), Z(200)

I = 1
AA = X(3) - X(1)
BB = X(3) - X(1)
CC = X(2) - X(1)

Y(1) = CC*CC/(AA*BB)*Y(3) + (2.*BB/AA)*Y(2) + (2.*AA/BB)*Y(1)*CC/6 + 2

DO 1 I = 2, NLSS2 - 1

AA = X(I+2) - X(I+1)
BB = X(I+2) - X(I)
CC = X(I+1) - X(I)
DD = X(I+1) - X(I-1)
FE = X(I) - X(I-1)

1 Y(I+1) = (-CC*CC/(AA*BB)*Y(I+2) + (4.*BB/AA*EE/DD)*Y(I+1) + (4.*AA/BB*DD
1/EE)*Y(I) - CC*CC/(DD*EE)*Y(I+1) + CC/12 + Y(I)

CC = X(N) - X(N-1)
DD = X(N) - X(N-2)
FE = X(N-1) - X(N-2)

Y(N) = ((2.*EF/DD)*Y(N) + (2.*DN/EE)*Y(N-1) - CC*CC/(DD*EE)*Y(N-2))/CC/6

RETURN

END
FUNCTION SIZE (N, X, XS, IS, IF)
DIMENSION X(N), IS(11), SC(10)
DATA SC(1), SC(2), SC(3), SC(4), SC(5), SC(6), SC(7), SC(8), SC(9), SC(10)
1 /2.0, 5.0, 5.0, 10.0, 10.0, 10.0, 10.0, 20.0/
  XMIN=0.
  XMAX=X(1)
  N0 2 I=1,N
  2 XMAX=MAX1(XMAX, X(I))
  RANG=0.99*(XMAX-XMIN)
  XMAX=XMAX-0.005*RANGE
  XMIN=XMIN+0.005*RANGE
  RANGF=AMAX1(RANGE, ABS(XMAX+XMIN)/65537.)
  IF (RANGF.LE.0.0) RANGE=1.0E-30
  4 RLOG=ALOG10(RANGE)
  ILOG=RLOG-.5*SIGN(.5, RLOG)
  XBASE=10.0*10**ILOG
  1=RANGE/XBASE
  5 SCL=SC(L)*XRASE/10.
  IA=0
  IF (XMIN.EQ.0.0) GO TO 6
  TA=XMIN/SCL-.5*SIGN(.5, XMIN)
  6 A=IA
  I=I+1
  IF (XMAX-(10.0+A)*SCL.) 7, 7, 5
  7 XS=1.5+10.*A
  SCLG=ALOG10(1.01*SCL)
  IF=SCLOG-.5*SIGN(.5, SCLOG)
  TD=1.01*SCL/10.0*IF
  TS(1)=IA*TD
  N0 8 I=2,11
SUBROUTINE IPLOT (H, WD, N, X, Y1, Y2)

DIMENSION X(N), Y1(N), Y2(N), WD(4), IGRID(101), IS(11), IS1(11), IS2(11)

DATA IPOINT, IBLANK /1H, 1H / 
DATA IID/1HD/, IIC/1HQ/ 
IF (M) 3, 1, 1995
1 WRITE (2, 2) (WD(I), I=1, M)
2 FORMAT (1H1/20X, 22HVEL PERMEATION PROGRAM, 20X, 4A8, 19X, 6HPAGE 4///) 2000
3 XSC=SIZE(N, X, XS, IS, IF)
   V1SC=SIZE(N, Y1, Y1S, IS1, IF1)
   V2SC=SIZE(N, Y2, Y2S, IS2, IF2)
   WRITE (2, 4) IIC, (IS1(I), I=1, 11), IF1; IID, (IS2(I), I=1, 11), IF2
4 FORMAT (1H 4X, A1, 11110.2H F, 13//5X: A1, 11110.2H E, 13///) 2010
   DO 15 K=1, 101
      K1=1+1/(1+MOD(K-1, 10))
      K2=1+(K-1)/10
      K3=1
      IF(K1.EQ.2) GO TO 7
5 K3=10
   DO 6 L=1, 101
6 IGRID(L)=IBLANK
   DO 3 A=1, 101, K3
8 IGRID(L)=IPOINT
   DO 10 L=1, N
      IX=X(L)*XSC+XS 
      IF (IX-K) 10, 9, 10
9 IY1=Y1(L)*Y1SC+Y1S
   IY2=Y2(L)*Y2SC+Y2S
   IGRID(IY1)=IIC
   IGRID(IY2)=IID
10 CONTINUE

1995
2000
2010
2015
2020
2025
2030
2035
2040
2045
2050
2055
2060
2065
2070
2075
2080
2085
2090
2095
2100
2105
2110
2115
2120
2125
2130
2135
2140
IF(K1.EQ.2) GO TO 13
11 WRITE (2,12) (IGRID(L),L=1,101)
12 FORMAT (15X,101A1)
   GO TO 15
13 WRITE (2,14) IS(K2),IF,(IGRID(L),L=1,101)
14 FORMAT (1H8,1HE,13,2X,101A1)
15 CONTINUE
RETURN
END
SUBROUTINE SPLIT (M, WD, N, X, V1, V2)

DIMENSION X(N), V1(N), V2(N), WD(4), IGRID(11), IS(11), IS1(11), IS2(11)

DATA IPOINT, BLANK, H, /1H, /1H/

IF (M, 3, 1)

1 WRITE (2, 2) (WD(I), I=1, M)

2 FORMAT (1H/20X, 22HGBFL PERNMATION PROGRAM, 20X, 4A8, 19X, 6HPAGE 4/)

3 XSC = SIZE(N, X).XS, T1F)

V1SC = SIZE(N, V1, V1S IS1, T1F1)

V2SC = SIZE(N, V2, V2S IS2, T1F2)

V1S = V1S - 0.5

V2S = V2S - 0.5

DO 20 K = 1, 101, 2

KY = 102 - K

K1 = 1 + 1/(1 + I0N(K - 1, 10))

K2 = 11 - (K - 1)/10

K3 = 1

IF (K1 .EQ. 2) GO TO 6

4 K3 = 10

DO 5 L = 1, 101

5 IGRID(L) = IBLANK

6 DO 7 L = 1, 101, K3

7 IGRID(L) = IPOINT

DO 12 L = 1, N

IX = X(L) * XSC + XS

IV1 = V1(L) * V1SC + V1S

IV1 = IV1 / 2 + 1

IF (IV1 = KY) 9, 8, 9

8 IGRID(LX) = IIC

GO TO 12

2285

2280

2275

2270

2265

2260

2255

2250

2245

2240

2235

2230

2225

2220

2215

2210

2205

2200

2195

2190
9 IF (ID.(EQ.IRLANK) GO TO 12
10 \( V_2 = (V_2(L) + V_2(S) + V_2(S)\)
11 \( V_2 = 2 \times (V_2/2) + 1\)
12 IF \( V_2 > V_1 \) GO TO 12
13 IGRD (LX) = I1h
14 CONTINUE
15 IF (K1.EQ.2) GO TO 15
16 WRITE (2,14) IGRID
17 FORMAT (1H, 9X, 101A1)
18 GO TO 20
19 IF (ID.(NE.IRLANK) GO TO 18
20 WRITE (2,17) IC, IS1(K2), IF1, IGRID
21 FORMAT (1H, 1A1, 13, 1HE, 13, 1X, 101A1)
22 GO TO 20
23 WRITE (2,19) IC, IS1(K2), IF1, IGRID, IS2(K2), IF2, I1D
24 FORMAT (1H, 1A1, 13, 1HE, 13, 1X, 101A1, 13, 1HE, 13, 1X, 1A1)
25 CONTINUE
26 WRITE (2,21) IS, IF
27 FORMAT (1H, 1I10, 2H E, 13)
28 RETURN
29 END
SUBROUTINE HSGRAM (M, WD, N, X, Y, IZ)

DIMENSION X(20), Y(21), IS(20), WD(4), IGRINH(101)
DATA ISTAR, IPINT, IRLANK/1H, 1H, 1H /
IF (M) 3, 3, 1
1 URITF (2, 2) (WD(1), I=1, M)
2 FORMAT (4H1/20X, 22HGEF PERIMETOLUTION PROGRAM, 20X, 4A8, 19X, 4HHPAGE 5/)
3 URITF (2, 4) 1Z
4 FORMAT (4X, 4HDIFFERENTIAL HISTOGRAM OF LOWER, 13, 14H P
1CT OF SAMPLE
XSC=SIZE(N, X, XS, IS, IF)
1DEL=5*IS(2)
IF=IF-1
IF (1DEL = 2*IDE1/2) 5, 6, 5
5 IDE1=10*IDE1
IF=IF-1
6 IZAV=IDE1/2
XSC=SIZE(N, V, YS, IS, IF1)
YS=1V=0.5
NO 10 K=1, 1N1, 2
VY=102-K
K1=1+1/(1+MIN(K-1, 10))
K2=11-(K-1)/10
IF(K1, EQ. 2) GO TO 9
7 NO 3 L=1.1N0
8 IGRIN(L)=1B1ANK
GO TO 11
9 NO 10 L=1, 1N0
10 IGRIN(L)=1PINT
11 NO 14 L=1, N
IX=X(L)+XSC+XS
IY=Y(L)*YSC*VS
IY=2*(LY/2)+1
IF ( KY-LY ) 12,12,14
12 IF ( IY=1 ) 14,14,13
13 IGRIN(LX)=IHLANK
IGRIN(LX+1)=STAR
IGRIN(LX+2)=STAR
IGRIN(LX+3)=STAR
IGRIN(LX+4)=IBLANK
14 CONTINUE
IF(K1.EQ.2) GO TO 17
15 WRITE (2,16) ( IGRID(I),I=1,100 )
16 FORMAT (15X,100A1)
GO TO 19
17 WRITE (2,18) IS(K2),IF1,( IGRID(I),I=1,100 )
18 FORMAT (1H,18,1HE,13,2X,10A1)
19 CONTINUE
IS(1)=ISAV
DO 20 I=2,N
20 IS(I)=IS(I-1)+INDL
WRITE (2,21) IS,IF
21 FORMAT (1H0,13X,20I5,2H,F,13)
RETURN
END