Characterisation of long-chain branching in poly (vinyl acetate) and poly (vinyl alcohol)

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:

- Doctoral Thesis. Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University.

Metadata Record: [https://dspace.lboro.ac.uk/2134/7389](https://dspace.lboro.ac.uk/2134/7389)

Publisher: © T.A. Coleman

Please cite the published version.
This item is held in Loughborough University’s Institutional Repository (https://dspace.lboro.ac.uk/) and was harvested from the British Library’s EThOS service (http://www.ethos.bl.uk/). It is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/
Best Copy Available

Variable Print Quality
Characterisation of Long-Chain Branching in Poly(vinyl acetate) and Poly(vinyl alcohol)

by

TREVOR ADRIAN COLEMAN B.Sc.

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University of Technology.

1984

Supervisor Dr. J.V. Dawkins
Department of Chemistry

© by T.A. Coleman 1983
Vinyl acetate monomer has been polymerised in bulk at high and
low temperature to produce polymers of branched and linear structure.
Branches attached via the acetoxy group were removed by a process of
hydrolysis and reacetylation. Thus poly(vinyl acetate) (PVOAc)
polymers were obtained, which would undergo no further structural
changes on hydrolysis.

Fractions of linear and branched polymers were obtained, and
then characterised, along with some commercial whole polymers, by
viscometry (in toluene and tetrahydrofuran), osmometry and gel
permeation chromatography (G.P.C.). Comparison of the results
showed that, in the molecular weight range studied, fractions
behaved similarly whether designated linear or branched, whereas
whole polymers were shown to be definitely branched. A mathematical
method of analysis based on viscometric and G.P.C. data, and assum-
ing that hydrodynamic volume is the universal calibration parameter
in G.P.C., was used to quantitatively assess the branching.

Fractions of poly(vinyl alcohol) (PVOH) were obtained by the
hydrolysis of fractionated PVOAc. These were also characterised by
viscometry and G.P.C. in aqueous solution. Though a similar mathe-
matical analysis was not possible, because G.P.C. calibration
curves could not be correlated in terms of hydrodynamic volume, it
was confirmed that none of the samples studied could be structur-
ally distinguished.

From these observations it was concluded that, under the
conditions employed, and in the molecular weight range studied,
long chain branching of PVOAc occurs mainly through the acetate
group and is therefore removable by hydrolysis; and long chain
branching in PVOH is not particularly significant.
Acknowledgements

I would like to thank my supervisor Dr. J.V. Dawkins for his valued support and advice during my period of research at Loughborough, and for his help and encouragement without which this work may not have been completed. I would also like to thank Professor F.W. Wilkinson, my director of research, and Professor K.W. Bentley, head of the Chemistry Department for the use of the laboratories. My thanks also to the S.S.R.C. from whom I received my grant and to Dr. Salmon and Dr. Ramsey at the U.K.A.E.A., Harwell, who initiated and supported the research. My thanks also go to Dr. R.E. Wetton and Dr. F.P. Warner and the staff of Polymer Laboratories (Church Stretton, Shropshire) for their advice on G.P.C. matters and for carrying out most of the G.P.C. work on poly(vinyl acetate). Also to my colleagues in the department, and to the teaching and technical staff, my appreciation of their help and support over the past four years. Finally to my typist for her speed and accuracy, many thanks.
Originality

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

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><strong>INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td>2.</td>
<td><strong>THEORY</strong></td>
<td>6</td>
</tr>
<tr>
<td>2.1</td>
<td>Vinyl Polymerisation</td>
<td>6</td>
</tr>
<tr>
<td>2.1.1</td>
<td>The Mechanism of Polymerisation</td>
<td>6</td>
</tr>
<tr>
<td>2.1.2</td>
<td>Transfer Reactions and Branching</td>
<td>7</td>
</tr>
<tr>
<td>2.1.3</td>
<td>Polymerisation Kinetics</td>
<td>10</td>
</tr>
<tr>
<td>2.1.4</td>
<td>Kinetic Determination of Branching</td>
<td>11</td>
</tr>
<tr>
<td>2.2</td>
<td>Preparation of Poly(vinyl alcohol) (PVOH)</td>
<td>12</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Hydrolysis of PVOAc</td>
<td>12</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Properties of PVOH</td>
<td>13</td>
</tr>
<tr>
<td>2.3</td>
<td>Theory of Polymer Solutions</td>
<td>13</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Polymer Dimensions</td>
<td>13</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Viscosity Equations</td>
<td>15</td>
</tr>
<tr>
<td>2.3.3</td>
<td>The Flory-Fox Equation</td>
<td>16</td>
</tr>
<tr>
<td>2.3.4</td>
<td>The Mark-Houwink Equation</td>
<td>17</td>
</tr>
<tr>
<td>2.3.5</td>
<td>The Effect of Branching</td>
<td>19</td>
</tr>
<tr>
<td>2.3.6</td>
<td>Mathematical Models for Branching</td>
<td>20</td>
</tr>
<tr>
<td>2.3.6.1</td>
<td>Hydrolysable Branching</td>
<td>20</td>
</tr>
<tr>
<td>2.3.6.2</td>
<td>The Zimm-Stockmayer Equations</td>
<td>22</td>
</tr>
<tr>
<td>2.4</td>
<td>Characterisation</td>
<td>24</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Calibration of G.P.C.</td>
<td>25</td>
</tr>
<tr>
<td>2.4.1.1</td>
<td>Calibration by Narrow Standards</td>
<td>25</td>
</tr>
<tr>
<td>2.4.1.2</td>
<td>Calibration by Broad Standards</td>
<td>26</td>
</tr>
<tr>
<td>2.4.1.3</td>
<td>The Universal Calibration</td>
<td>26</td>
</tr>
<tr>
<td>2.4.2</td>
<td>Characterisation of Branching</td>
<td>28</td>
</tr>
<tr>
<td>2.4.2.1</td>
<td>The Method of Drott and Mendelson</td>
<td>28</td>
</tr>
</tbody>
</table>
2.4.2.2 Similar Methods
2.4.2.3 The Method of Wilh, Kangamch and Ryle
2.4.2.4 The Ram and Hiltz method
2.4.2.5 Comparison of Methods

3. EXPERIMENTAL

3.1 Preparation of Poly(vinyl acetate)
  3.1.1 Polymerisation Techniques for Vinyl Acetate
  3.1.2 Preparation of Monomer
  3.1.3 Preparation of Initiator
  3.1.4 Polymerisation of Vinyl Acetate
    3.1.4.1 Low Temperature Polymerisation
    3.1.4.2 Polymerisation at High Temperature

3.2 Preparation of Poly(vinyl alcohol)
  3.2.1 Hydrolysis of Poly(vinyl acetate)
  3.2.2 Mechanism of Hydrolysis
  3.2.3 Choice of Hydrolysis Method
  3.2.4 Experimental Details

3.3 Acetylation of Poly(vinyl alcohol)

3.4 Test of the Hydrolysis/Reacetylation Reactions
  3.4.1 Method 1: Reacetylation
  3.4.2 Method 2: Hydrolysis

3.5 Details of Other Polymers Used

3.6 Fractionation of Polymers
  3.6.1 Samples for Fractionation
  3.6.2 Fractionation of Poly(vinyl acetate)

3.7 Characterisation
  3.7.1 Viscosity
    3.7.1.1 Poly(vinyl acetate)
3.7.1.2 Poly(vinyl alcohol)

3.7.2 Gel Permeation Chromatography
   3.7.2.1 Poly(vinyl acetate)
   3.7.2.2 Poly(vinyl alcohol)

3.7.3 Osmometry
   3.7.3.1 Poly(vinyl acetate)

4. POLY(VINYL ACETATE) RESULTS

4.1 Polymerisation Kinetics

4.2 Molecular Weight Data of Whole Polymers
   4.2.1 Low Temperature Polymers
   4.2.2 High Temperature Polymers

4.3 Hydrolysis and Reacetylation
   4.3.1 Determination of Degree of Hydrolysis
      4.3.1.1 By Reacetylation
      4.3.1.2 By Hydrolysis
   4.3.2 Comparison of Methods
   4.3.3 Hydrolysis and Reacetylation of Linear Polymers
   4.3.4 Hydrolysis and Reacetylation of Branched Polymers
   4.3.5 Reacetylation in Reaction and Analysis

4.4 Fractionation
   4.4.1 Linear Poly(vinyl acetate)
   4.4.2 Branched Poly(vinyl acetate)

4.5 Characterisation
   4.5.1 Osmometry
   4.5.2 Viscometry
      4.5.2.1 Fractions
      4.5.2.2 Viscosity and Branching
      4.5.2.3 Whole Polymers
   4.5.3 Chromatographic Data
5. LONG BRANCHING IN POLY(VINYL ACETATE)

5.1 Introduction

5.2 Application of the Ram and Miltz Method
   5.2.1 Initial Procedure
   5.2.2 Calibration Data
      5.2.2.1 Elution Volume Plots
      5.2.2.2 The Universal Calibration
      5.2.2.3 Other Methods for Mark-Houwink Constants
   5.2.3 Results from the Ram and Miltz Procedure
   5.2.4 Influence of \( \eta_0 \)
   5.2.5 Conclusions

6. POLY(VINYL ALCOHOL)

6.1 Characterisation Results

6.2 Molecular Weight Data

6.3 The Universal Calibration

6.4 Conclusions

7. CONCLUSIONS AND RECOMMENDATIONS

Appendix I: Relationship Between FVOAc and FVOH

References
1. INTRODUCTION
The commercial applications of poly(vinyl acetate) (PVOAc) and poly(vinyl alcohol) (PVOH) are both numerous and diverse.\textsuperscript{1,2,27} These polymers are used extensively in the coatings and adhesives industries, and PVOH has additional uses, for example in the textile and paper industries and in medicine. PVOAc is manufactured on an industrial scale by either emulsion or solution polymerisation\textsuperscript{99} (for ease of polymerisation control) at elevated temperatures. These processes inevitably lead to polymers having branched structures.\textsuperscript{1}

In contrast, PVOH cannot be formed by a polymerisation reaction, since any attempt to prepare vinyl alcohol monomer results in a rearrangement of the molecule to the more stable acetaldehyde. Thus, the polymer is usually prepared by the hydrolysis of a polymerised vinyl ester\textsuperscript{1,2} (most often PVOAc).

Much work has been carried out on both polymers due to their industrial importance; their chemical and structural properties have been extensively investigated from both scientific and technical viewpoints. The structure of a polymer markedly affects its chemical and physical properties, and ultimately its "usability". Thus, branching in PVOAc and PVOH has been studied for many years. The first report of the structural changes that occurred in PVOAc on hydrolysis and subsequent re-acetylation, was probably that of Blaikie and co-workers\textsuperscript{4} as early as 1936. But it was not until 1952 that Wheeler\textsuperscript{5} proposed the mechanism of random branch formation that has now become generally accepted.

Though the branching of PVOAc may be elucidated from kinetic considerations\textsuperscript{5,7,8,9}, the routine analysis of unknown samples of both PVOAc and PVOH has presented major problems.

Attempts have been made to use a combination of techniques for this purpose, and most have met with some degree of success.\textsuperscript{19,94}
A combination of viscometry and lightscattering (L3) was suggested by Hobbs87, to determine the degree of long chain branching (LCB) in branched polymers, since L3 can give important structural information. Reported measurements on very high molecular weight PVOAc (of the order of $2 \times 10^6$) in benzene, suggested that the non-Newtonian behaviour of solutions, was not an effect of LCB, but was determined by the high molecular weight. Further methods100 were devised based on sedimentation and diffusion effects, again combined with viscometry, in order to determine a factor 'g', whose relationship to LCB had already been derived for several model branched chains, by the theoretical treatments of Zimm and co-workers49. With the advent of gel permeation chromatography (G.P.C.), less emphasis was placed on absolute techniques. The value of G.P.C. is that, although it is not an absolute technique, it can furnish an accurate representation of the molecular size distribution in a polymer sample, with relative ease and speed. It follows that, an analysis of molecular size is crucial to the proper interpretation of characterisation data.

Unfortunately, the need to calibrate G.P.chromatographs has introduced further problems. The most significant advance came from Benoit and co-workers14, who pointed out that, for a large number of polymers, irrespective of type of structure, a plot of $[\eta]M$ (commonly used as the hydrodynamic size parameter of a polymer), where $[\eta]$ is the intrinsic viscosity and $M$ the molecular weight, versus elution volume produces a common curve. Thus having established the curve, knowing the elution volume and $[\eta]$ for a polymer of a different type, enables $M$ to be determined. This method became known as the universal calibration (U.C.), but must be qualified by the statement that, the separation mechanism of the G.P.C. column must be one of size, with the absence of specific
interactions between polymer and porous gel. The usefulness of the U.C. method, and hence its extensive use, has mainly been due to a lack of primary polymer standards (i.e. well characterised in terms of molecular weight and structure) for different types of polymer. Standards for polystyrene (PS) are readily available, covering a molecular weight range from a few hundred to many millions, and having very narrow molecular weight distributions (MWD). (Typically, the polydispersity ratio ($\bar{M}_w/\bar{M}_n$) is less than 1.1). Provder has described a secondary calibration for linear PVAc based on this method. By judicious use of a suitable Mark-Houwink ($\eta$) equation which relates $[\eta]$ directly to $\eta$ for linear polymers, the measurement of $[\eta]$ may be avoided. For branched polymers, the relationship is more complicated. In general, for molecules of the same type and molecular weight, a branched molecule will have a smaller size in solution and hence a lower $[\eta]$. The lowering of $[\eta]$ however, depends not just on the existence, but on the extent and type of branching as well as the distribution of branch lengths. Hence much effort has been directed to deriving suitable methods for the interpretation of characterisation data of branched polymers. Furthermore, the universal validity of $[\eta] M$ as the correct U.C. size parameter has been questioned, and much controversy has arisen in the literature. Other size parameters such as the mean square radius of gyration of the polymer molecule in a good solvent ($<s^2>$), and the unperturbed mean square radius of gyration ($<s_o^2>$) have been proposed, but supporting evidence has so far been inconclusive. For most work the hydrodynamic volume $[\eta] M$ is still the easiest parameter to determine and hence use.

Viscometry, both on and off line, has become the most often used method in combination with G.P.C. This is undoubtedly due to
the relative ease of the method, which requires little or no sophisti-
cated apparatus, and its reproducibility and reliability.
Goedhart and co-workers \(^{102}\) used an on-line technique and reported
reasonable reproducibility of molecular weights (compared with those
derived from osmometry and L.S.) of linear polymers. Their molecular
weight data were derived from a U.C. curve using PS standards. Park
and Graessley \(^{19,91}\), using a similar technique, analysed PS, FVOAc
and poly(butadiene) (FBD). They concluded that calibration at high
molecular weights was aided significantly by on-line viscometry,
since this is the molecular weight region where branching is con-
sidered most prevalent. They stressed the importance of accurate
G.P.C. data, i.e. by correcting chromatograms for band broadening, in
order to interpret correctly the \([\eta]\) data of G.P.C. fractions. Their
analyses nevertheless appeared to underestimate \(\bar{M}_n\) and branching.
They assumed that the branching index \(\lambda\) (equal to the number of
branches per unit molecular weight) was constant, i.e. that branching
increased linearly with molecular weight. This has subsequently been
shown to be incorrect for some polymers \(^{63,78,79,94}\), which may account
for the anomalies in the data of Park and Graessley.

Many methods have been devised for the interpretation of G.P.C./
viscometry data. Those of Ambler \(^{60}\), Kurata \(^{58,59}\), Cote \(^{57}\) and Drott \(^{46}\)
(and respective co-workers) have all relied on some interpretation
of \(\lambda\) as a constant, and have hence met with limited success. Wild
and co-workers \(^{62-64}\) used a preparative G.P.C. technique with visco-
metric characterisation of polyethylene fractions, but concluded that
use of one of the other analytical methods gave sufficiently accurate
data and was far less time consuming. Ram and Hiltz \(^{61}\) proposed a
method that did not rely on an assumption about \(\lambda\), but allowed it
to vary. Few of these methods have been applied to FVOAc. Morishima
and co-workers\textsuperscript{94} reported the analysis of PVOAc via the method of Kurata. They showed that \( \lambda \) increased with conversion, but the data was subject to large degrees of error. \textsuperscript{94} And co-workers reviewed the methods of Drott and Wendelson, and Ram and Hiltz with reference to polyethylene (PE). They concluded that both methods gave essentially the same results, and showed that, for PE, \( \lambda \) was not constant.

The question of hydrolysable and non-hydrolysable branching has always been dealt with by saponification\textsuperscript{5,7,9} studies (where hydrolysable branches are chemically removed) or kinetically.\textsuperscript{5,7-9} Attempts to quantify the amount of non-hydrolysable branching remaining, after hydrolysis and reacetylation of PVOAc, by any of the above methods dependent on molecular size, have not been reported in the literature so far. This work has set out to investigate a routine method for the analysis of LCB in PVOAc, by G.P.C. and viscometry, and in particular with respect to polymers containing only non-hydrolysable branches. Similar analyses for PVOH have not so far been attempted. Though aqueous G.P.C. is a relatively new development, separation studies of water soluble polymers have been made, with silica based column packings.\textsuperscript{104} There are, however, serious problems connected with silica based packings. They tend to show interactive effects, so that separations are not exclusively by size, making interpretation in terms of U.C. quite difficult. Furthermore, silica packings have the reputation of being unstable, undergoing a gradual decrease in efficiency. The problems associated with aqueous G.P.C. have been reviewed.\textsuperscript{103,105,106} With the recent introduction of new, semi-rigid, hydrophilic gels, an attempt has been made here to study some of the aspects of the aqueous G.P.C. of PVOH.
2. THEORY
2.1 VINYL POLYMERISATION

2.1.1 The Mechanism of Polymerisation

The mechanism of vinyl polymerisation, initiated by free radicals has been well established. There are four main reactions to consider:

1) Initiation

An 'initiator' is decomposed under the influence of heat or ultra-violet (u.v.) radiation to produce radicals. These radicals then react with unsaturated double-bonds in the monomer.

\[
\text{Initiator} \xrightarrow{\text{heat or u.v.}} 2 \text{Radicals}
\]

\[
R^* + \overset{\text{monomer}}{\overset{\text{--C=C--}}{\text{}}} \rightarrow R\overset{\text{--C=C--}}{\overset{\text{--C=C--}}{\text{}}} \text{propagating species}
\] (2.1)

2) Propagation

Once a radical has initiated reaction with the monomer, a propagating species is formed which adds more monomer to form a chain.

\[
R\overset{\text{--C-C--}}{\overset{\text{--C=C--}}{\overset{\text{--C-C--}}{\text{}}} \overset{\text{rate constant}}{\xrightarrow{K_p}}} R\overset{\text{--C-C--}}{\overset{\text{--C=C--}}{\overset{\text{--C-C--}}{\text{}}} \text{and so on}}
\] (2.2)

The symbol \( P\overset{\text{--C-C--}}{\overset{\text{--C=C--}}{\overset{\text{--C-C--}}{\text{}}}} \) will be used to represent a propagating chain (i.e. \( \equiv R\overset{\text{--C-C--}}{\overset{\text{--C=C--}}{\overset{\text{--C-C--}}{\text{}}}} \)).

3) Transfer

A transfer reaction occurs when a propagating species abstracts a hydrogen atom from another molecule, leaving itself unreactive. The second molecule may carry on the propagation, thus reactivity
has been transferred. Transfer reactions can take place with almost any species present, e.g. monomer, polymer, solvent or initiator,

\[ \text{transfer species} \]

\[ \text{termination} \]

4) **Termination**

The product of termination is unreactive polymer. Termination can occur either by the combination of two radicals (propagating species) to form one chain or by disproportionation to form two chains,

\[ \begin{align*}
\text{combination} & : \quad \text{P-C-C} \cdot + \text{C-C-P} \rightarrow \text{P-C-C-C-P} \\
\text{disproportionation} & : \quad \text{P-C-C} \cdot + \text{C-C-P} \rightarrow \text{P-C=C} + \text{P-C-C} 
\end{align*} \] (2.4)

(2.5)

In practice, termination by both methods can occur in vinyl acetate polymerisation, though evidence for a predominant disproportionation reaction at elevated temperature may be found.

2.1.2 **Transfer Reactions and Branching**

The transfer reactions with monomer and polymer are those which lead to branching. Depending on the type of transfer reaction, branches may either be of the hydrolysable type (i.e. detachable from the main chain by hydrolysis) or permanent (i.e. not removed by hydrolysis). In the absence of a specific branching agent, the resulting polymer is considered to contain randomly placed, trifunctional branch points only.

The important reactions are illustrated below:
1) **Transfer to Polymer**

a) **Branching at the main chain**, (permanent)

\[
P-\overset{\cdot}{C}-C \overset{\cdot}{+} CH-CH_2 \overset{K_{tr, d}}{\rightarrow} P-\overset{\cdot}{C}-H + CH_2=CH_2
\]

Propagating species, polymer chain (repeating unit) + monomer

b) **Branching at the acetoxy group**, (hydrolysable)

\[
P-\overset{\cdot}{C}-O + CH-CH_2 \overset{K_{tr, dl}}{\rightarrow} P-\overset{\cdot}{C}-H + CH-CH_2
\]

(2.7)

(Repeating unit) + C-HF

(further abstraction of vinylic hydrogens, \(\alpha\) and \(\beta\), is considered unlikely\(^{29}\) (figure 2.1)).

2) **Transfer to monomer**

a) **Through the vinyl group**,

\[
P-\overset{\cdot}{C}-C \overset{\cdot}{+} CH_2=CH \overset{K_{tr, m^2}}{\rightarrow} CH_2=CH_2
\]

Vinyl acetate monomer (VAc)

\[
CH_2=CH_2 \overset{[\cdot]}{\rightarrow} CH_2=CH_2
\]

(2.8)
b) Through the acetoxy group,

\[
P - \text{C-C} + \text{CH}_2=\text{CH} \xrightarrow{\text{Ktr}, \text{M}} \text{CH}_2=\text{CH} + [n] \xrightarrow{} \text{CH}_2=\text{CH}
\]  

(2.9)

3) Terminal Double-Bond Polymerisation

a) Producing permanent branches,

\[
\text{CH}_2=\text{C} \xrightarrow{} \text{RCH}_2 + [n] \xrightarrow{} \text{RCH}_2
\]  

(2.10)

b) Producing hydrolysable branching

\[
\text{CH}_2=\text{C} \xrightarrow{} \text{RCH}_2 + [n] \xrightarrow{} \text{RCH}_2
\]  

(2.11)

It is clear from the reaction schemes that structurally identical polymers are formed, regardless of the route, for the same type of branching.

Thus long, completely random branches can be formed, either by hydrogen abstraction from the polymer (2.6, 2.7) and subsequent growth from the radical sites produced, or by abstraction from a monomer molecule. In the latter case, small radicals are formed (2.8, 2.9), which can initiate polymer chains having terminal double bonds (2.10, 2.11), that may subsequently polymerise. The abstracted hydrogen atom can be one of three belonging to the acetate group or it may be one of the three vinylic (main chain) hydrogens.

Terminally unsaturated polymer molecules can also result from the disproportionation reaction of termination (2.5); these, as well as those produced by transfer at the beta carbon of the vinyl group of
the monomer (Fig. 2.1) and growth of a polymer chain therefrom, will have internal saturation and will therefore polymerise very slowly if at all.\footnote{29}

![Vinyl acetate monomer](image)

Figure 2.1: Vinyl acetate monomer

### 2.1.3 Polymerisation Kinetics

The kinetics of radical polymerisation have been well studied.\footnote{3}

In general, for any radical initiated polymerisation, in the absence of complicating reactions (e.g. transfer), equation 2.12 may be derived,

\[
V = \frac{K_p}{2(f K_d K_t)\frac{[I]}{[I]}^{\frac{1}{2}}} = K' \frac{[M]}{[I]^{\frac{1}{2}}}
\]  

(2.12)

where \(V\) is the kinetic chain length defined as the number of monomer units consumed per active centre

\(K_d, K_p\) and \(K_t\) are rate constants for the decomposition of initiator, for propagation and for termination

\(f\) is the fraction of the radicals formed which successfully initiate chains

\([M]\) is the monomer concentration

and \([I]\) is the initiator concentration.

The degree of polymerisation and hence the final molecular
weight of the polymer are related to $V$ by equation 2.13

$$\overline{M}_n = n_{rp} \overline{x}_n = f (V) \tag{2.13}$$

where $\overline{M}_n$ and $\overline{x}_n$ are the number average molecular weight and degree of polymerisation, and $n_{rp}$ is the molecular weight of the repeating unit. For termination by combination $\overline{x}_n = 2V$ and for disproportionation $\overline{x}_n = V$. In practice, combination and disproportionation may occur together in the same polymerisation reaction and the expression for $\overline{M}_n$ will be further complicated when transfer reactions occur.

2.1.4 Kinetic Determination of Branching

According to Flory, the degree of branching by transfer with polymer increases with conversion. This is because the relative incidence of branching must depend on the ratio of polymer to monomer in the system. If the fraction of monomer molecules which have polymerised out of a total number $N_0$ is denoted by $\Theta$, and the total number of branches is $\gamma$, then the rate of increase in branching is given by equation 2.14,

$$\frac{d\gamma}{dt} = K_{tr,p} [M^*] \Theta N_0 \tag{2.14}$$

and

$$\frac{d\Theta}{dt} = K_p [M^*] (1 - \Theta) \tag{2.15}$$

Dividing 2.14 by 2.15 gives equation 2.16,

$$\frac{d\gamma}{d\Theta} = \frac{K_{tr,p}}{K_p} \frac{\Theta N_0}{(1 - \Theta)} = c_p N_0 \Theta / (1 - \Theta) \tag{2.16}$$

Integrating 2.16 and setting $\gamma / N_0 \Theta = \rho$ gives

$$\rho = - c_p (1 + \frac{1}{\Theta} \ln (1 - \Theta)) \tag{2.17}$$
Equation 2.17, and similar expressions developed for transfer to monomer, have been used, with various embellishments, by most authors to determine the relative incidence of branching, kinetically.\textsuperscript{7,8,10,24}

2.2 PREPARATION OF POLY(VINYL ALCOHOL)

2.2.1 Hydrolysis of Poly(vinyl acetate)

The hydrolysis of poly(vinyl acetate) (PVOAc) is not only a typical high polymer reaction but is also important for the manufacture of poly(vinyl alcohol) (PVOH). Methods are usually grouped into acid or alkaline hydrolysis and anomolysis according to the catalyst used. The general reaction is\textsuperscript{7}

\[ \text{PVOAc} + n\text{ROH} \rightarrow \text{PV-OH} + n\text{ROAc} \] \hspace{1cm} (2.18)

During hydrolysis an important, irreversible, structural change occurs. Long side chains, which are attached to the main chain through the oxygen of the acetoxy group (figure 2.1) are split off, and although the polymer may be reacetylated, the long chains remain as separated molecules.\textsuperscript{4} Since it is generally true that the likelihood of a polymer chain being branched increases as the size of the chain increases, on hydrolysis the longer chains will decrease in length and hence molecular weight, more than shorter ones with a lesser number or even no branches. This leads to a narrowing of the molecular weight distribution of the polymer as well as the expected decrease in molecular weight. Theoretical relationships may be derived to express the change in molecular weight as a function of branching (section 2.3.6.1).
2.2.2 Properties of Poly(vinyl alcohol)

The chemical and physical properties of PVOH can be greatly affected by the amount of residual acetate content (i.e. degree of hydrolysis) of the polymer\(^1,2\), as well as its molecular weight and any branching. It is much easier to ensure consistency from products which have been fully (99-100\%) hydrolysed, than to attempt to hydrolyse different products to the same degree, if this is less than 99\%.

Commercially available grades can vary greatly in their degree of hydrolysis as shown in table 2.1. To illustrate the importance of the degree of hydrolysis on various properties of PVOH, some figures for comparison are reproduced here\(^1\) (figures 2.2-2.4). Clearly, working with fully hydrolysed products is required to achieve good reproducibility of results.

2.3 POLYMER SOLUTION THEORY

2.3.1 Polymer Dimensions

As with low molecular weight compounds, polymer molecules in solution are in constant motion. In dilute solution individual molecules may be considered to be moving independently. Depending on the interaction between solvent and polymer, the latter will tend to curl up or straighten out. The separation of chain ends (in the absence of solvent influence) can be predicted by a number of theoretical models.\(^3\) The most comprehensive leads to equation 2.19.

\[
\langle r_o^2 \rangle = n a^2 \left( \frac{1 - \cos \theta}{1 + \cos \theta} \right) \left( \frac{1 + \cos \phi}{1 - \cos \phi} \right) 
\]  

(2.19)
TABLE 2.1: Various Grades of PVCH Available under the Commercial Name "MOVIOL" (1972)

<table>
<thead>
<tr>
<th>CLASS OF PVCH</th>
<th>HYDROLYSIS DEGREE (x)</th>
<th>VISCOSITY GRADES cP.(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully hydrolysed</td>
<td>100</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>98</td>
<td>4,10,40,56</td>
</tr>
<tr>
<td>Partially hydrolysed</td>
<td>88</td>
<td>4,8,18,40</td>
</tr>
</tbody>
</table>

(a) 4% aqueous solution @ 25°C

TABLE 2.2: Equations for the Manipulation of Viscosity Data.

<table>
<thead>
<tr>
<th>NAME</th>
<th>EQUATION(S)</th>
<th>USE</th>
</tr>
</thead>
<tbody>
<tr>
<td>HUGGINS</td>
<td>( \eta_{sp}/c = [\eta] + k[\eta]^2c )</td>
<td>most generally useful</td>
</tr>
<tr>
<td>KRAEMER</td>
<td>( \ln \eta_{c}/c = [\eta] + k[\eta]^2c )</td>
<td>used with the Huggins equation to check</td>
</tr>
<tr>
<td>MARTIN</td>
<td>( \log(\eta_{sp}/c) = \log([\eta] + k[\eta]c )</td>
<td>useful if Huggins plot shows upward curvature; valid at ( \infty )-dilution not fully established</td>
</tr>
<tr>
<td>SCHULZ-BLASCHKE</td>
<td>( \eta_{sp}/c = [\eta] + \eta_{sp}[\eta] )</td>
<td>not often used but generally linear over a wider range than Huggins</td>
</tr>
<tr>
<td>HELPER</td>
<td>( c/\eta_{sp} = \frac{1}{[\eta]} - \sqrt{c} )</td>
<td>proposed as an alternative to the Huggins-Kraemer double plot</td>
</tr>
<tr>
<td></td>
<td>( c/\ln[\eta] = \frac{1}{[\eta]} - \sqrt{c} )</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 2.2: Equations for the Manipulation of Viscosity Data.
Figure 2.2: Viscosity versus Concentration Plots for PVOH at varying degrees of Hydrolysis.

degree of hydrolysis [%] \{ 98.5, 88, 80 \}

Figure 2.3: Water Solubility versus Solution Temperature of PVOH

Solubility [%] 100

88% hydrolysis

99% hydrolysis

Temperature (°C)
Figure 2.5: Schematic Representation of the Deviation of a Branched Polymer w.r.t. the Mark-Houwink Equation

Figure 2.4: Change of Viscosity with Time of Aqueous Solutions of PVPA (8% solution at 25°C)
where $<r_o^2>^{\frac{1}{2}}$ is the root mean square (rms), unperturbed, end-to-end distance of the chain, $n$ is the number of "links" of length $a$ and $\theta$ is the characteristic bond angle. The value $\cos \theta$ takes into account the restricted rotation of side groups about the chain, and is averaged over the whole chain. This model assumes restricted but symmetrical rotation.

The polymer molecule in solution may be represented by the model of an equivalent impenetrable sphere. The value of $<r_o^2>^{\frac{1}{2}}$ is not however a specific dimension of the sphere but merely the distance between the ends of the polymer chain. The rms distance of any chain segment from the centre of gravity (i.e. the centre of the imaginary sphere) is called the radius of gyration $<s_o^2>^{\frac{1}{2}}$. The two are related by equation 2.20,

$$<s_o^2> = \frac{1}{6} <r_o^2>$$

(2.20)

Long branches in the polymer chain decrease the value of $<s_o^2>^{\frac{1}{2}}$, but since branched chains have a multiplicity of ends, the definition becomes rather meaningless in that context.

In solution, interaction with solvent causes the polymer dimensions to change. An expansion factor $\alpha$ may be defined, where

$$\alpha^2 = \frac{<r^2>}{<r_o^2>^2}$$

(2.21)

$<r^2>$ is the actual rms end-to-end distance of the polymer and $<r_o^2>^{\frac{1}{2}}$ is called the unperturbed dimension, i.e. the value of $<r_o^2>^{\frac{1}{2}}$ when $\alpha$ is unity.

In a sufficiently poor solvent or at a low enough temperature it is possible to achieve the so-called theta-point where interaction with solvent is so small that $\alpha$ becomes unity. $^{31}$
2.3.2 Viscosity Equations

The single, most valuable, property that can be measured easily for most polymers is the intrinsic viscosity $[\eta]$. This may be related to many important parameters of the polymer solution.

Intrinsic viscosity is defined as the ratio of specific viscosity, $\eta_{sp}$, to concentration, $C$, at infinite dilution.

$$[\eta] = \lim_{C \to 0} \frac{\eta - \eta_s}{C} = \lim_{C \to 0} \frac{\eta_{sp}}{C}$$

(2.22)

where $\eta$ and $\eta_s$ are the viscosities of solution and solvent respectively.

There are many equations used for the determination of intrinsic viscosity and these have been reviewed.31-35 The most usual method involves the double plot of the Huggins and Kraemer equations, 2.23 and 2.24 respectively.

$$\frac{\eta_{sp}}{C} = [\eta] + K_H [\eta]^2$$

(2.23)

$$\ln \left( \frac{\eta_{sp} + 1}{C} \right) = \frac{\ln \eta_r}{C} = [\eta] + K_K [\eta]^2$$

(2.24)

This method, however, has been criticised36 since only under limited conditions do the two plots have a common intercept. The difference arises from the nature of the derivation of equation 2.24.

The Taylor expansion of a function $\ln (1 + x)$ for $|x| < 1$ is:

$$\ln (1 + x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \frac{1}{4}x^4 + \ldots$$

(2.25)

substituting $x = \eta_{sp} = \eta_{r} - 1$ gives

$$\ln \eta_r = \eta_{sp} - \frac{1}{2} \eta_{sp}^2 + \frac{1}{3} \eta_{sp}^3 - \frac{1}{4} \eta_{sp}^4 + \ldots$$

(2.26)

and

$$\frac{\ln \eta_r}{C} = \frac{\eta_{sp}}{C} (1 - \frac{1}{4} \eta_{sp} + \frac{1}{3} \eta_{sp}^2 - \ldots)$$

(2.27)
Substituting $\eta_{SP}/C$ from equation 2.23 and ignoring terms in $J$ gives:

\[
\ln \frac{\eta_r}{C} = \left[ \eta \right] + (k_H - 1)\left[ \eta \right]^2_C + \left( \frac{1}{2} - k_K \right)\left[ \eta \right]^2_C c^2 \quad (2.28)
\]

\[
= \left[ \eta \right] + k_K\left[ \eta \right]^2_C + \left( \frac{5}{6} - k_K \right)\left[ \eta \right]^3_C c^2 \quad (2.29)
\]

Clearly, only when $K_H = \frac{1}{3}$ ($K_K = \frac{5}{6}$) is equation 2.24 accurately valid, and furthermore, if $K_H \approx \frac{1}{3}$, $K_K \approx 0$, equation 2.24 becomes dominated by higher order terms, and is no longer linear. Forcing a common intercept under these conditions introduces serious errors into the determination of $\left[ \eta \right]$. Again due to the nature of the Taylor expansion, admissible values of $\eta_r$ must lie in the range $+1 < \eta_r < +2$. Even so, as $\eta_r$ approaches a value 2 (i.e. $x$ approaches 1) the series converges very slowly, and it has been shown\(^{34}\), that for $\eta_r = 1.8$ as determined from equation 2.29, differs from its true value by more than 1% until terms in $\eta_{SP}$ are considered. This too, can lead to large errors in $\left[ \eta \right]$.

There have been numerous further equations proposed to overcome these difficulties.\(^{34,36,37}\) Table 2.2 summarises some of these; yet more are considered by Berger.\(^{32,33}\) In this work, the Huggins equation (equation 2.23) has given good linear fits to the data where applied, and the value of $\left[ \eta \right]$ thus derived has been used throughout.

2.3.3 The Flory-Fox Equation

Intrinsic viscosity may be related to the dimensions of the molecules in solution. For linear polymers the Flory-Fox\(^{41,42}\) equation states that
\[ [\eta] = \Phi \langle \frac{r^2}{N} \rangle^{3/2} \]  

(2.35)

where \( \Phi \) is a universal constant. If the term \( \langle r^2 \rangle \) is substituted for \( \alpha^2 \langle r^2 \rangle \) (equation 2.41) and equation 2.30 rearranged, equation 2.31 is given,

\[ [\eta] = \Phi \left[ \frac{\langle r^2 \rangle}{N^2} \right]^{3/2} \alpha^3 \]  

(2.31)

To a first approximation \( \langle r^2 \rangle / \pi \) is constant and, if \( \alpha \gg 1 \) it is found that \( \alpha^3 \propto N^{0.3} \). Equation 2.31 can then be re-written

\[ [\eta] = K_\alpha^{0.8} \]  

(2.32)

For a theta solvent \( \alpha \) is unity, hence from equation 2.31

\[ [\eta] \] is given by

\[ [\eta] = K_\theta^{0.5} \]  

(2.33)

where \( K_\theta = \Phi \langle \frac{r^2}{N} \rangle^{3/2} \).

2.3.4 The Mark-Houwink Equation

Probably the most useful equation involving the intrinsic viscosity \([\eta]\) of a polymer is the semi-empirical Mark-Houwink \((\eta\alpha)\) equation, relating \([\eta]\) directly to the molecular weight of the polymer,\(^{38,39}\)

\[ [\eta] = K_\eta^a \]  

(2.34)

The \((\eta\alpha)\) equation is based on, and is a good approximation to, the more rigorously derived Flory-Fox equation (equation 2.32) when the exponent 'a' lies in the range 0.5-0.8 as given by equations 2.32 and 2.33.

The values of \( K \) and 'a' are presumed constant for a given polymer/solvent pair. They are best determined by measuring the molecular
weight (by an absolute method) and \([\eta]\) of a series of polymers of narrow molecular weight distribution \(M_w\). A most important point, previously overlooked by some workers, is this; having used narrow fractions to determine \(K\) and \(a\), in order to use the results to determine an average molecular weight of an unknown sample, the unknown must have a similar MWD. Otherwise the molecular weight determined corresponds to what is termed a viscosity average molecular weight \(\bar{M}_v\). This compares to the number and weight average molecular weight \(M_N\) as follows:

\[
\begin{align*}
\text{number average} & \quad \bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \\
\text{weight average} & \quad \bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \\
\text{viscosity average} & \quad \bar{M}_v = \frac{\left[\sum N_i M_i^{1+a}\right]^{\frac{1}{a}}}{\left[\sum N_i M_i\right]} 
\end{align*}
\]

(2.35) \hspace{1cm} (2.36) \hspace{1cm} (2.37)

where \(N_i\) is the number and \(M_i\) the molecular weight of species \(i\) in the sample. As the value of \(a\) approaches unity, \(\bar{M}_v\) is taken as a good approximation to \(\bar{M}_w\).

The value of \(a\) is usually found to lie in the range 0.5-0.8, but over an extended range of molecular weight the log \([\eta]\) vs. log \(M\) plot is both theoretically and experimentally curved.\(^{39}\) The constants \(K\) and \(a\) are also found to vary slightly with temperature.\(^{39}\) Further, for many polymers at low molecular weights there exists a more or less extended linear region where the equation

\[
[\eta] = K_0 M^{0.5}
\]

(2.38)

is obeyed.\(^{40}\) The constant \(K_0\) is found to be very close to \(K_\Theta\), the characteristic value in a \(\Theta\) solvent at the same temperature in the
absence of large, specific, solvent effects, even though conditions are far from being those of a $\Theta$ solvent.

2.3.5 The Effect of Branching

So far the discussion has considered mainly linear molecules, where the preceding equations and derivations hold quite well. When these are applied to branched polymers, in general the theories begin to break down. Above a limiting molecular weight ($M_0$) the logarithmic plot of equation 2.34 begins to show negative deviation from the curve (figure 2.5).

Of two samples of the same molecular weight (and $M_M$), in solution the branched molecule is represented by a smaller hydrodynamic volume, and has therefore a lower intrinsic viscosity. The effect depends on the type as well as the extent of branching.

As a consequence, any results from characterization techniques that rely on the size of a molecule in solution (e.g. viscometry, gel permeation chromatography (GPC), etc.) have to be treated with caution. As an example of this, although a branched polymer might give an apparently normal chromatogram from GPC, the values of molecular weights and distributions cannot be calculated as simply as for a linear polymer. Since a branched molecule in solution is smaller than its linear counterpart having identical molecular weight, it will occur later in the G.P. chromatogram. Therefore in any particular increment in elution volume, molecules having a wide range of molecular weights may exist, but all having the same hydrodynamic size due to different extents of branching. Thus, superimposed on the already distorted molecular weight distribution ($M_M$) curve may be a further distribution due to different sizes and extents of branching. It is a very complicated matter indeed to
attempt to calculate accurate molecular weight data for branched polymers, which is complicated even further when the GPC is calibrated using polymer standards of a different type. Procedures have been outlined and some of these will be discussed (section 2.4).

The occurrence of both long and short branches causes different effects in the polymer. Though short branches occur much more frequently, they do not appear to have any effect on the GPC trace.

2.3.6 Mathematical Models for Branching

2.3.6.1 Hydrolysable Branching

Consider a randomly branched polymer containing tri-functional branch points only, and having branches comparable in length to the back-bone chain. Further, consider only those branches which will detach when the polymer is subjected to hydrolysis and then reacetylation.

If the number of chains of degree of polymerisation $x_1$ is $N_1$, and the number of branch points on a chain is $n_{i,3}$, then, on hydrolysis and reacetylation, the number of chains increases from $N_1$ to $N_1 \left( n_{i,3} + 1 \right)$ (figure 2.6). The number of chains after reacetylation is therefore given by

$$N_{1,a} = N_{1,b} \left( n_{i,3} + 1 \right)$$

(2.39)

where subscripts 'b' and 'a' refer to before and after hydrolysis and reacetylation. The weight of each species $w_i$ is related to $N_1$ and its molecular weight $M_1$ by

$$w_i = \frac{k_i k_i}{N_A}$$

(2.40)

where $N_A$ is Avogadro's number.

Since the total weight of polymer ($= \sum w_i$) remains constant, it
follows from equation 2.40 that \( \sum \delta_i \frac{1}{N_i} \) is constant.

Taking the usual definitions of number average molecular weight, viz

\[
\overline{M}_n(b) = \frac{\sum \delta_i b \frac{N_i b}{N_i}}{\sum N_i b} \quad (2.41)
\]

\[
\overline{M}_n(a) = \frac{\sum \delta_i a \frac{N_i a}{N_i}}{\sum N_i a} \quad (2.42)
\]

and defining the number average number of branch points \( \overline{\eta}_{n,3} \) by,

\[
\overline{\eta}_{n,3} = \frac{\sum \eta_{n,3} \frac{N_i(b)}{N_i(b)}}{\sum N_i(b)} \quad (2.43)
\]

From equations 2.41 and 2.42,

\[
\frac{\overline{M}_n(b)}{\overline{M}_n(a)} = \frac{\sum N_i(a)}{\sum N_i(b)} = \frac{\sum(N_i(b) \frac{\eta_{n,3} + 1}{N_i(b) + 1})}{\sum N_i(b)} \quad (2.44)
\]

which on expansion and rearrangement leads to

\[
\overline{\eta}_{n,3} = \frac{\overline{M}_n(b)}{\overline{M}_n(a)} - 1 \quad (2.45)
\]

A similar expression for \( \overline{\eta}_{w,3} \), the weight average number of tri-functional branch points per molecule is more difficult to derive. An expression equivalent to equation 2.45 with \( \overline{M}_n \) substituted for \( \overline{M}_w \) has little meaning. This is unfortunate as a weighted average is generally more sensitive to branching. The value of \( \overline{\eta}_{n,3} \) may be calculated simply from the absolute values of \( \overline{M}_n(a) \) and \( \overline{M}_n(b) \) (from e.g. osmometry), but this method is destructive and affords no information on non-hydrolysable branching.
2.3.6.2 The Zimm-Stockmayer Equations

A much used concept in the attempt to interpret branching data, is that of the ratio of the radii of gyration of branched and linear molecules, of the same molecular weight.\(^{47}\)

\[
\phi = \frac{\left< s^2 \right>_b}{\left< s^2 \right>_1} \quad (2.46)
\]

where subscripts refer to branched and linear species.

According to the Flory-Fox equation (equation 2.30),

\[
[\eta] \propto \left< r^2 \right>^{3/2} \quad \text{(intrinsic viscosity)}
\]

where \(\left< r^2 \right>^1\) is the root mean square (rms) end-to-end distance of the polymer chain.

For linear molecules \(\left< r^2 \right> \propto \left< s^2 \right>\), therefore \([\eta] \propto \left< s^2 \right>^{3/2}\). If the same holds for branched molecules we may write,

\[
\phi' = \frac{[\eta]_b}{[\eta]_1} = \frac{\left< r^2 \right>_b^{3/2}}{\left< r^2 \right>_1^{3/2}} = \frac{\left< s^2 \right>_b^{3/2}}{\left< s^2 \right>_1^{3/2}} = \phi^{3/2} \quad (2.47)
\]

In general however, this relation has no validity.\(^{47}\) The spatial arrangements of polymer segments is different for branched and linear molecules, and increase in molecular weight affects \(\left< s^2 \right>\) differently for the two species. For a branched polymer the relationship between \(\left< r^2 \right>\) and \(\left< s^2 \right>\) will depend on molecular weight, and the length of branches present, as well as the extent and type of branching, i.e. comb, star, random, etc.\(^{48}\) Furthermore, in a molecule which has a multiplicity of ends, a definition of \(\left< r^2 \right>^1\) as the r.m.s. end-to-end distance of the chain is rather meaningless, although the ratio \(g\) may still be applied.

The value of \(g\) (equation 2.46) can be directly related to the branching of polymers via the Zimm-Stockmayer equations.\(^{49}\)
For a tri-functionally, randomly branched polymer such as PVOAc, the equations for long chain branching (L.C.B.) are

\[
\eta_{3,n} = \left[ (1 + \frac{\eta_{3,n,2}}{7})^3 + \frac{4\eta_{3,n,2}}{9\eta_0} \right]^{-\frac{1}{4}} \tag{2.49}
\]

for monodisperse systems, and

\[
\eta_{3,p} = \frac{6}{\eta_{3,w}} \left[ \frac{1}{2} \left( \frac{2 + \eta_{3,w}}{\eta_{3,w}} \right)^{\frac{1}{4}} \ln \left( \frac{(2 + \eta_{3,w})^{\frac{1}{2}} + \eta_{3,w}}{(2 + \eta_{3,w})^{\frac{1}{2}} - \eta_{3,w}} - 1 \right) \right] \tag{2.49}\]

for polydisperse systems.

\( \eta_{3,n} \) is the number average number of branch points per molecule, and \( \eta_{3,w} \) is the weight average number of branch points per molecule.

A further equation was proposed, to take into account short chain branching (S.C.B.),

\[
\eta_{SCB} = \frac{1}{s+1} \left[ 1 + s(1-2f+2f^2-2f^3) + s^2(-f+4f^2-f^3) \right] \tag{2.50}
\]

where \( s \) is the number of short chains per molecule, and \( f \) is the fractional branch length.

(Long branches are usually considered to be comparable in length to the polymer main chain, whereas short branches are usually pendant groups, only about half a dozen atoms in length).

When considered necessary, the two types of branching may be incorporated in equation 2.51

\[
\eta = \eta_{LCB} \times \eta_{SCB} \tag{2.51}
\]

It is generally found that the effect of an SCB on viscosity is about 1/4 that of an LCB.

Although the value of \( \eta' \) can be easily measured, the relation \( \eta' = f(\eta) \) is largely undefined, and mostly empirical. The majority of workers favour a function of the type \( \eta' = \eta^b \), where the value of
b is found (empirically) to lie between 0.5 and 1.0. Many authors circumvent the issue by adopting a rather unsatisfactory method of choosing whichever exponent gives the best fit of the experimental data to theory.

So far, there has been no method developed for directly measuring $\bar{\eta}_w$ experimentally. In practice $g$ is estimated and compared with tables of $g$ vs. $\bar{\eta}_w$ to obtain the corresponding values of $\bar{\eta}_w$. This is then related to a branching index $\lambda$ (the number of branch points per unit molecular weight) by

$$\bar{\eta}_{w,3} = \lambda \bar{\eta}_w$$

or

$$\lambda = \frac{\bar{\eta}_{w,3}}{\bar{\eta}_w}$$

(2.52)

where $\bar{\eta}_w$ is the molecular weight of the polymer (presumably $\bar{\eta}_w$). The branching index is presumed to remain constant, with $\bar{\eta}_{w,3}$ varying linearly with molecular weight. This assumption, however, is not universally valid. For polystyrene $\lambda$ has been shown to be more or less constant, but for poly(ethylene) and PVAc, $\lambda$ is found to vary considerably, with molecular weight, though much conflicting data exists. If polymers are randomly branched, and the branches are fairly long, then as the relative incidence of branching increases (with molecular weight) so the probability of the branches themselves becoming branched increases. Under such circumstances the linear relationship is unlikely to hold.

2.4 CHARACTERIZATION

Many techniques have been used in combination in an attempt to determine some sort of branching parameter for polymers. The most often used methods include light scattering (LS), viscometry and gel permeation chromatography (GPC), though sedimentation and
diffusion measurements have also been made. All these methods have been the subject of a recent review.\textsuperscript{22}

Light scattering, and sedimentation and diffusion are techniques requiring fairly sophisticated equipment and a good deal of pains-taking care and expertise by the operator. For this reason most work has been done by GPC and viscometric techniques although, as on-line light scattering detectors for GPC are becoming more widely available (and reliable) the current situation will no doubt change. For the present this work has used the viscometry/GPC method since both these are practically, fairly simple techniques, and discussion will be confined to these.

2.4.1 Calibration of GPC

One of the pre-requisites for obtaining accurate molecular weight data from GPC is the existence of a good calibration curve. This is usually a plot in the form of equation 2.53,

\[ \log I' = f(V_e) \] (2.53)

relating molecular weight \((M)\) to elution volume \((V_e)\). Though the form of equation 2.53 may be linear over a small range of molecular weight (maybe 1 or 2 decades) it is more often of the form of figure 2.7.

Calibration procedures fall into two major categories; by narrow \(MWD\) fractions (or standards) and by broad standard polymers.

2.4.1.1 Calibration by Narrow Standards\textsuperscript{45,52}

If polymers having a polydispersity ratio \((D = \bar{M}_w/\bar{M}_n) < 1.1\) of known molecular weight are available for the type of polymer to be analysed, and spanning the expected range in molecular weight, the calibration curve may readily be determined. Chromatograms are
obtained for each of the fractions and the elution volumes corresponding to the peak of the chromatogram (\(V_{\text{peak}}\)) are identified. Since \(D < 1.1\) the molecular weight averages \(\bar{m}_n\), \(\bar{m}_v\) and \(\bar{m}_w\) can be assumed more or less to be equal. A slightly more accurate method is to use the geometric mean given by equation 2.54

\[
\bar{m}_{\text{peak}}^2 = \bar{m}_n \times \bar{m}_w
\]  

Equation 2.54 assumes that the chromatogram can be represented by a symmetrical Gaussian function.

The data enables a plot of log \(\bar{m}_{\text{peak}}\) vs. \(V_{\text{peak}}\) to be constructed for the calibration curve.

2.4.1.2 Calibration by Broad Standards\(^{52}\)

For anything but the most common polymers narrow standards are not usually available. Even when they are, a few are reasonably priced, others extremely expensive to purchase. Broad standards are however more readily available, but identification of \(\bar{m}_{\text{peak}}\) may be more difficult and less accurate. For this reason, several methods have been devised for establishing a calibration curve under such circumstances, and some of these have been discussed.\(^{52,65}\)

2.4.1.3 The Universal Calibration

As already stated, well defined standard polymers for GPC calibration are generally only available for the more common polymers. However, since the introduction by Benoit\(^{14,53}\) of the concept of the universal calibration (U.C.), it is now possible to convert calibration curves from one type of polymer to another.

According to U.C. theory for many polymers, regardless of type or structure, a plot of the product of molecular weight and intrinsic
viscosity ($\eta \eta$ often referred to as the hydrodynamic volume) versus elution volume falls on a single curve. Thus

$$\eta_1 \eta_1 = \eta_2 \eta_2 = \eta_3 \eta_3 = \ldots \text{ at constant } V_e$$

$$\therefore \eta_1 = \frac{\eta_2 \eta_2}{\eta_1 \eta_1}$$ (2.55)

This enables the molecular weight of a polymer to be determined as long as its intrinsic viscosity is known, regardless of the type of polymer used for calibration.

However useful this theory is, there has been much discussion and disagreement in the literature as to the actual form the U.C. should take. Dawkins considers that the separation depends on $\langle s^2 \rangle$, but also showed that, for linear polymers, $[\eta]^M$ gives equally good correlations, so that there were no grounds for choosing between the two. In contrast, Pannell has suggested that $[\eta]^M$ is not the appropriate U.C. size parameter to use for branched molecules, and proposed the use of $\langle s^2 \rangle^{3/2}$.

The view expressed by Casassa and co-workers was that only through a detailed study of the elution behaviour of branched polymers might it be possible to decide which was the appropriate parameter to use. Contrary to previous studies, Pannell showed that some branched polymers eluted later than their linear analogues of the same $[\eta]^M$. Although he criticized the use of $\langle s^2 \rangle^M$ and favoured $\langle s^2 \rangle$ (the mean square radius of gyration in a good solvent) he was unable to provide accurate enough data to support the criticism, citing only unpublished work by Nagawasa. Working with branched and linear polystyrene in toluene, Nagawasa also claimed that his polymers gave a bad U.C. using $[\eta]^M$ but that $\langle s^2 \rangle^{3/2}$, as preferred by Pannell, was the correct parameter. Hamielec and co-workers also examined the
U.C. and concluded that most discrepancies arose out of the incorrect use of $\bar{R}_w$ in the hydrodynamic volume. They showed that the correct value to use was $\bar{R}_n$. Whilst controversy still exists, the use of $[\eta]_i$ still continues as probably the easiest parameter to calculate and no exception is made here.

2.4.2 Characterisation of Branching

There have been numerous attempts by workers to develop systems for the interpretation of chromatographic data from branched polymers. Since GPC alone cannot furnish unambiguous data, use has been made of the intrinsic viscosity of the polymers, and data are usually manipulated via the universal calibration. Some of these systems will be outlined here.

2.4.2.1 The Method of Drott and Hendelson

In this method, a branching density $\lambda$ is defined depending on the type of branching expected. For a polymer in which the ratio of the number of branch points per molecule ($\bar{M}_{w,3}$) to the molecular weight is essentially constant for all molecular weight species in a given sample equation, 2.56 is written,

$$\frac{\bar{M}_{w,3}}{\bar{M}} = \text{constant} = \lambda$$

(2.56)

This is then substituted into the appropriate Zimm-Stockmayer equation \(^{49}\) (section 2.3.6.2) to obtain equation 2.57,

$$\varepsilon_{2, w} = f(\ldots, \lambda)$$

(2.57)

Using the definition of $\varepsilon' = \frac{[\eta]_b}{[\eta]_l}$

(2.58)

(where subscripts 1 and b refer to linear and branched species),
and the Mark-Houwink equation (2.34) gives

\[ [\eta]_b = \zeta [M_\lambda]^a \]  \hspace{1cm} (2.59)

Since it is generally assumed that \( \zeta \) and \( \langle \tilde{M}_\lambda \rangle \) are related by an equation of the form of 2.60

\[ \zeta = \langle \tilde{M}_\lambda \rangle^b \]  \hspace{1cm} (2.60)

where \( b \) is a constant in the range 0.5-1.5, equation 2.59 may be expressed in the more general form

\[ [\eta]_b = [M_\lambda]^a \langle f(\zeta, \lambda) \rangle^b \]  \hspace{1cm} (2.61)

For a polydisperse polymer it is assumed that \( [\eta] \) for the whole polymer may be represented by the weighted sum of the viscosities of the individual species, i.e.

\[ [\eta]_{\text{whole}} = \sum_i [\eta]_i \omega_i = \sum_i [\eta]_i h_i \]  \hspace{1cm} (2.62)

where \( \omega_i \) is the weight fraction of species \( i \). Accepting that the normalized heights \( h_i \) of a GPC trace can be taken to be proportional to the weight fractions \( \omega_i = h_i \) gives

\[ [\eta]_{\text{whole}} = \sum_i [\eta]_i h_i \]  \hspace{1cm} (2.62)

\[ \therefore [\eta]_b = [M_\lambda]^a \sum_i h_i \langle f(h_i, \lambda) \rangle^b \]  \hspace{1cm} (2.63)

A value for \( b \) is chosen and, assuming constant \( \lambda \), an iterative method is employed (usually by computer) to match \([\eta]_b \) (equation 2.64) with the measured \([\eta] \) for the polymer.

In general the value of \( b \) (equation 2.60) is largely empirical (section 2.3.6.2) and based on invalid assumptions, and it is not generally accepted that \( \lambda \) is constant for all types of polymer.\[^{75,76}\]
This method, though useful, is therefore of limited applicability.

2.4.2.2 Similar Methods

There exist other methods by Lote, Kurata, and Ambler for example, but these are more or less based on the Drott method with minor differences or refinements.

2.4.2.3 The Method of Wild, Ranganath and Kyle

The method investigated by Wild and co-workers involves the preparative fractionation of the unknown sample with GRG and viscometric analysis of the resulting fractions. This method however involves considerable experimental equipment, a fairly substantial amount of sample, and is time consuming. Each fraction is analysed to yield branching data and this is then collected to give a picture of branching for the whole polymer.

2.4.2.4 The Ram and Miltz Method

The method employed by Ram and Miltz was intended to circumvent the problem of degree of branching varying with molecular weight. They extended the Mark-Houwink equation into polynomial form:

\[
\ln[\eta] = \ln K + a \ln M + b \ln^2 M + c \ln^3 M \tag{2.65}
\]

for polymers whose molecular weight was sufficiently high enough for branching to be present. Below this minimum molecular weight \(M_o\) the ordinary Mark-Houwink equation was used.

Since for \(M = M_o\)

\[
b \ln^2 M_o + c \ln^3 M_o = 0 \tag{2.66}
\]

the last term coefficient may be written as
\[ c = -\frac{b}{\ln n_0} \]  

(2.67)

A cyclic iteration is then employed to obtain the required data. As a first approximation the universal calibration (assuming equation 2.55) and \( F\) equation are used to convert the chromatographic elution volumes to a molecular weight calibration for the polymer. Then using equation 2.68,

\[ [\eta]_{calc} = \sum [\eta]_1 n_1 = \sum [h_1 K_{M_1} (a + b \ln n_1 + c \ln^2 n_1)] \]  

(2.68)

a value for \( b \) is iterated so that \([\eta]_{calc}\) matches \([\eta]\) measured. This value of \( b \) is then used in the extended \( F\) equation, again with the U.C. to obtain a second estimate of \( M_1 \). A second value for \( b \) is then calculated as before and the whole process continued until successive distributions differ by less than 1\% (or to the accuracy required).

### 2.4.2.5 Comparison of Methods

Wild et al.\(^63\) compared the two methods of Drott and Ram and formed the following conclusions:

1. Although the \( D \) and \( F \) method gives slightly higher \( \bar{M}_w \) values at the high \( M \) end of the chromatogram than the \( R \) and \( h \) method, both lead to essentially the same molecular weight distribution data.

2. Since both methods are virtually equivalent, the \( D \) and \( F \) method is to be preferred on the basis of the reduced computer time required.

3. For more detailed studies of branching the more complex (but more complete) method of Wild, Ranganath and Ryle\(^64\) should be used since the assumption of constancy of \( \lambda \) is not true for
many polymer types.

A problem hitherto unmentioned with the R and M method is the fact that, when dealing with broad chromatograms which may extend over decades of molecular weight, the assumption of linearity of the MH equation may introduce unsuspected errors.
3. EXPERIMENTAL
3.1 PREPARATION OF POLYVINYL(AcETATE)

3.1.1 Polymerisation Techniques for Vinyl Acetate

Vinyl acetate monomer (VAc) may be polymerised by most of the radical processes, e.g. bulk, solution, emulsion and suspension (pearl), according to the general reaction,

\[ R^* + nCH_2=CHOAc \rightarrow R(CH_2=CHOAc)_n\text{H} + 21.3n\text{kcal} \] (3.1)

The characteristics of the four methods mentioned above have been summarized in table 3.1.

Emulsion and suspension polymerisation were not used in this work to avoid contamination of the polymers by emulsifiers or suspending agents. This also avoids the possibility of these agents becoming chemically included in the polymers. Since branched polymers were to be made by bulk polymerisation it was considered more consistent to make linear polymers by this method also. Thus, although solution polymerisation is easiest to perform, bulk polymerisation was chosen as the technique for the purposes of this work.

3.1.2 Preparation of Monomer

Vinyl acetate monomer (VAc, B.D.H., stabilized with 14 p.p.m. quinol) was used for the preparation of poly(vinyl acetate) (PVAc). The stabilizer was removed by distillation of the monomer once through a Vigreux column at 50°C, under reduced pressure (330 mm Hg), with a nitrogen bleed. Before distillation the monomer was saturated with dry nitrogen at room temperature, and on distillation the middle fraction was collected. Purified monomer was used immediately. More rigorous purification was found unnecessary since, at the low temperatures and conversions used for the preparation of linear PVAc, side reactions such as chain transfer are negligible. At high temperatures,
<table>
<thead>
<tr>
<th>METHOD OF POLYMERISATION</th>
<th>CONTROL</th>
<th>CONTROL OF DEGREE OF POLYMERISATION</th>
<th>TREATMENT FOR HYDROLYSIS</th>
<th>METHOD OF HYDROLYSIS</th>
<th>PROPERTIES OF RESULTING PVCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>Difficult</td>
<td>Transfer Addition</td>
<td>Drying then dissolution in methanol</td>
<td>Alcoholysis</td>
<td>Large amount of branching; large terminal carboxyl group content</td>
</tr>
<tr>
<td>Solution</td>
<td>Easy</td>
<td>Solvent Addition</td>
<td>Immediate</td>
<td>Alcoholysis</td>
<td>Very good</td>
</tr>
<tr>
<td>Emulsion</td>
<td>Easy(use of emulsifier)</td>
<td>Transfer Addition</td>
<td>Immediate</td>
<td>Hydrolysis</td>
<td>Large amount of branching; dark colour</td>
</tr>
<tr>
<td>Suspension</td>
<td>Easy(use of suspension agent)</td>
<td>Transfer Addition</td>
<td>Drying then dissolution in methanol</td>
<td>Alcoholysis or Hydrolysis</td>
<td>Large amount of branching; large terminal carboxyl group content</td>
</tr>
</tbody>
</table>

TABLE 3.1: Characteristics of Polymerisation Techniques for Vinyl acetate Monomer.
transfer reactions increase causing the polymer to branch. Drying the monomer was also unnecessary since the monomer was specified to contain less than 3.1% water and it has been reported that up to 5% water has little or no effect on the polymerisation.

3.1.3 Preparation of Initiator

In all cases azobisisobutyronitrile (AZBN, Aldrich) was used as initiator since decomposition to radicals follows well defined kinetics, and in vinyl acetate polymerisation AZBN is not prone to transfer reactions. The initiator was twice recrystallized from absolute ethanol (S. L. R.) by cooling a saturated solution, obtained at 0°C, to -20°C in an acetone/carbon dioxide bath. The white crystalline solid obtained was filtered under suction, washed with small quantities of ice-cold methanol (S. L. R.) and air dried before storage at -20°C.

3.1.4 Polymerisation of Vinyl Acetate

3.1.4.1 Low Temperature Polymerisation

According to Burnett et al. polymerisation of VAc below -20°C, initiated by the photo-decomposition of AZBN, resulted in predominantly linear polymer. Accordingly a low temperature reaction system was devised (figures 3.1 and 3.2). To reach temperatures of -40°C a water/methanol/carbon dioxide bath was used. Ethanol is transparent to ultra-violet (U.V.) radiation at these temperatures and was used as coolant for the lamp.

VAc (170 ml) was introduced into the reaction vessel and cooled to 0°C. A solution of initiator in ice cold VAc (5 ml) was added and the mixture purged overnight with dry nitrogen.
Figure 3.1: Polymerisation Apparatus

- Condenser
- U.V. lamp
- Reaction vessel
- Magnetic stirrer and follower
- Water to flow guard
- Dry nitrogen inlet
- Water inlet
- Coding coil
- Thermostatted heating coil
- Glass tank
Key to Figure 32
1. Pyrex flask
2. Outer quartz jacket
3. Inner quartz jacket
4. Arc tube
5. Cooling water inlet
6. Arc tube support
7. Rubber sleeve
8. Inlet and outlet for gas flush
9. Terminals for power cable
10. Terminal cover
11. Cable clamp
12. Inlet for supply cable
13. Terminal block
14. Retaining screw
15. Sleeve clamps
16. Ceramic insulated leads
17. Cooling water outlet
18. B40 Cone and socket
19. B45 Cone and socket
20. B19 cone and socket
21. Reagent level mark
22. Gas flush space
23. Arc tube support clips
24. Cooling water space
25. Space for magnetic stirrer (see diag.5a).

Figure 3.2: Polymerisation Vessel
(Hanova Lamp, Medium Pressure 254-546 nm)
Before the start of the reaction, the nitrogen purge was replaced by a simple nitrogen blanket and the temperature reduced to \(-40^\circ\text{C}\) using solid \(\text{CaCl}_2\). The U.V. lamp was then switched on. (To guard against the hazard of exposure to U.V. radiation, the apparatus was assembled inside a fume cupboard, whose glass front had been covered with a layer of thick paper and aluminium foil). Reaction was allowed to proceed to \(-5\%\) conversion. To determine conversion, a small amount of reaction mixture (5-10 ml) was removed from the vessel and poured into an excess of carbontetrachloride (S.L.R.). The precipitated polymer was then dried in vacuo and weighed. Final conversion was determined gravimetrically.

In practice, despite cooling, the reaction warmed to \(-5^\circ\text{C}\) after 15 minutes (section 3.1.1). Rather than make use of more complicated cooling equipment, it was decided to run the reaction for 10 minutes, then cool back to \(-40^\circ\text{C}\), continue for another 10 minutes, re-cool and so on, in a stepwise fashion.

When the desired conversion had been reached the polymerisation was stopped. Excess \(\text{VAc}\) was removed by distillation at reduced pressure leaving a syrup of polymer in monomer. Acetone (S.L.R.) was added to form a thin "soup" and the whole added dropwise, with vigorous stirring, to a large excess of isopropanol (S.L.R.) in hexane (S.L.R.) (1:5 by volume, since \(\text{VAc}\) is not miscible with hexane alone).

The recovered polymer was dried and reprecipitated from methanol (S.L.R.) into distilled water twice more before being finally dried in a vacuum desiccator.
3.1.4.2 Polymerisation at High Temperature

To produce a polymer with substantial branching, VAc\textsubscript{N} was polymerised to $>\%$ conversion at high temperature in a sealed ampoule. Initiation was through the thermally induced decomposition of AZBN. At high temperatures transfer reactions which cause a polymer to be branched become increasingly significant.

Destabilized VAc\textsubscript{N} (40 ml) with the required amount of initiator was added to an ampoule. The monomer was degassed four times on a vacuum line by the freeze-thaw method, then the ampoule sealed. The ampoule was protected by an "orange net" sheath (in case of explosion) and suspended in a water bath at 80\degree C for $\sim 90$-100 minutes, when the polymer resembled a gel. Polymer was recovered by smashing the ampoule, adding acetone (C.L.R.) to form a "soup" and continuing with the recovery as described for PVOAc produced at low temperature (section 3.1.4.1).

3.2 PREPARATION OF POLY(VINYL ALCOHOL)

3.2.1 Hydrolysis of Poly(vinyl acetate)

Methods of hydrolysis are usually grouped into acid or alkaline hydrolysis, and ammnonolysis according to the catalyst used. The main reactions are\textsuperscript{1}

a) Alcoholysis:

$$\text{PV-OAc} + n\text{ROH} \xrightarrow{\text{acid or alkali}} \text{PV-OH} + n\text{ROAc} \tag{3.2}$$

b) Hydrolysis:

$$\text{PV-OAc} + n\text{H}_2\text{O} \xrightarrow{\text{acid or alkali}} \text{PV-OH} + n\text{HOAc} \tag{3.3}$$
c) Direct hydrolysis:

\[
P V-OAc + nNaOH \xrightarrow{H_2O} PV-OH + nNaOAc \tag{3.4}
\]

d) Aminolysis:

\[
P V-OAc + nNH_{3} \xrightarrow{H_2O} PV-OH + nNH_{3} \tag{3.5}
\]

e) Ammonolysis:

\[
P V-OAc + nNH_{3} \xrightarrow{NH_{4}Cl \text{ or } NH_{4}OAc} PV-OH + nNH_{2} \tag{3.6}
\]

Simultaneously, side reactions may occur:

\[
ROAc + NaOH \xrightarrow{H_2O} ROH + NaOAc \tag{3.7}
\]

\[
HOAc + NaOH \xrightarrow{} H_2O + NaOAc \tag{3.8}
\]

and residual amounts of monomer may be converted to acetaldehyde:

\[
V-OAc + ROH \xrightarrow{H^+ \text{ or } OH^-} CH_3CHO + ROAc \tag{3.9}
\]

\[
V-OAc + H_2O \xrightarrow{H^+} CH_3CHO + HOAc \tag{3.10}
\]

\((V \equiv CH_2CH_2-).\)

The characteristics of each method are summarized in table 3.2.

3.2.2 Mechanism of Hydrolysis

The hydrolysis of PV0Ac to PV0H follows an analogous mechanism to that of the alcoholysis of organic esters of low molecular weight.  

a) Alkaline hydrolysis

\[
\begin{align*}
PV-O-\text{C}=O \overset{\text{OH}}{\rightleftharpoons} PV-O-\text{O}^- \overset{\text{OH}}{\rightleftharpoons} PV-O-\text{C}=O^- \\
\overset{\text{Me}}{\text{Me}} \quad \overset{\text{Me}}{\text{Me}} \quad \overset{\text{Me}}{\text{Me}}
\end{align*}
\]
<table>
<thead>
<tr>
<th>CATALYST</th>
<th>MEDIUM</th>
<th>MAIN REACTION EQUATION</th>
<th>CATALYST CONSUMPTION</th>
<th>BY-PRODUCTS</th>
<th>RATE CONTROL</th>
<th>RESIDUAL ACETATE DISTRIBUTION (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALKALINE</td>
<td>MeOH</td>
<td>3.2</td>
<td>Very small</td>
<td>MeOAc</td>
<td>Very difficult</td>
<td>Blocky</td>
</tr>
<tr>
<td></td>
<td>H₂O/MeOH</td>
<td>3.2 (small 3.4)</td>
<td>Small</td>
<td>MeOAc NaOAc</td>
<td>Difficult</td>
<td>Blocky</td>
</tr>
<tr>
<td></td>
<td>H₂O or H₂O/acetone</td>
<td>3.4</td>
<td>Equivalent to PVOAc unit</td>
<td>Equivalent NaOAc</td>
<td>Easy</td>
<td>Very Blocky</td>
</tr>
<tr>
<td>ACID</td>
<td>MeOH</td>
<td>3.2</td>
<td>None</td>
<td>MeOAc</td>
<td>Easy (rate too slow)</td>
<td>Random</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>3.3</td>
<td>None</td>
<td>HOAc</td>
<td>Easy (rate too slow)</td>
<td>Completely Random</td>
</tr>
</tbody>
</table>

(a) Type of intramolecular distribution of residual acetate groups of partly hydrolyzed PVOH

TABLE 3.2: Characteristics of the Hydrolysis of PVOAc to PVOH. (1)
b) **Acid hydrolysis**

\[
\text{PV-O-C=O} + \text{H}_2\text{O} \rightleftharpoons \text{PV-O-C=OH} + \text{H}^+ + \text{OH}^-
\]

\[
\text{PV-O-C=OH} + \text{HA} \rightleftharpoons \text{PV-O-C=CH} + \text{A}^-
\]

3.2.3 **Choice of Hydrolysis Method**

In considering which type of hydrolysis reaction is suitable for converting FVOAc to FVOH the following points have been borne in mind:

a) **Alcoholysis**

Hydrolysis in the presence of alcohol (transesterification) and catalysed by acid or base, is an *equilibrium* reaction requiring removal of one component during reaction to drive the conversion to completion.

b) **Acid hydrolysis**

Hydrolysis catalysed by acid in the presence of water only, is also an equilibrium reaction, and again requires certain measures to
allow the reaction to go to completion.

c) **Alkaline hydrolysis**

The products of alkaline hydrolysis are a resonance stabilized carboxylate anion and an alcohol:

\[
\begin{align*}
R-O & \xrightarrow{\text{OH}} R-C & O^- + R'OH \\
\text{salt} & \text{alcohol}
\end{align*}
\] (3.11)

Since these show little tendency to react together, the reaction is essentially irreversible and readily goes to completion.

Clearly, alkaline hydrolysis is the best method.

### 3.2.4 Experimental Details

Hydrolysis of PVOAc to PVCH was carried out in methanol solution using sodium hydroxide. It has been reported that saponification of poly(vinyl ester)s by alkali produces a product containing \(-0.3\%\) infusible ash, owing to absorption and actual salt formation between PVCH and alkali metal ions. Procedures have been devised for reducing the ash content, but this was not felt to be necessary in the present work.

Two methods were readily available for the conversion, one using a high and one a low amount of alkali. Table 3.3 summarizes the conditions employed in each case.

In method 1, PVOAc is dissolved in methanol at 50°C with stirring, in a flask fitted with condenser and dropping funnel. Methanolic sodium hydroxide (NaOH) solution is added dropwise over the course of about 30 minutes. Thereafter the mixture is kept at 50°C with vigorous stirring for a further hour. During the reaction PVCH precipitates as a white granular solid, which is recovered by filtration.
<table>
<thead>
<tr>
<th>CONDITION</th>
<th>METHOD 1</th>
<th>METHOD 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Volume (ml)</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>Required NaOH (g)</td>
<td>0.03</td>
<td>0.20</td>
</tr>
<tr>
<td>Conc. NaOH (g/ml) x 10^3</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Conc. Polymer (g/ml)</td>
<td>0.1</td>
<td>0.02</td>
</tr>
<tr>
<td>Reaction Time (mins)</td>
<td>90</td>
<td>30</td>
</tr>
<tr>
<td>Conditions</td>
<td>(a)</td>
<td>(b)</td>
</tr>
</tbody>
</table>

(a) Vigorous Stirring  
(b) Standing

**TABLE 3.3:** Comparison of Methods for the Hydrolysis of PVOAc. (Based on 1g Polymer)

---

<table>
<thead>
<tr>
<th>PVOAc SOURCE</th>
<th>NOMINAL MOL.WT.</th>
<th>VISCOSITY</th>
<th>DEGREE OF HYDROLYSIS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.D.H.</td>
<td>45,000</td>
<td>6-8 (a)</td>
<td></td>
</tr>
<tr>
<td>B.D.H.</td>
<td>160,000</td>
<td>89-90 (a)</td>
<td></td>
</tr>
<tr>
<td>B.D.H.</td>
<td>500,000</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PVOH SOURCE</th>
<th>NOMINAL MOL.WT.</th>
<th>VISCOSITY</th>
<th>DEGREE OF HYDROLYSIS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.D.H.</td>
<td>14,000</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>B.D.H.</td>
<td>125,000</td>
<td>35-45 (b)</td>
<td>87-89</td>
</tr>
<tr>
<td>BAKER</td>
<td>---</td>
<td>28-32 (b)</td>
<td>99-100</td>
</tr>
</tbody>
</table>

(a) 8.6% solution (w/v) in benzene @ 20°C  
(b) 4% solution (w/v) in water @ 20°C

**TABLE 3.4:** Details of Commercial Polymers Used.
The solid is then washed extensively with methanol in a soxhlet extractor (to remove residual catalyst) and dried under vacuum.

In method 1, a solution of PVOAc in methanol in a suitable vessel, is held at 40°C in a water bath. Sodium hydroxide (aqueous) solution is added, the mixture stirred once and then allowed to stand for 30 minutes. During this time PVOH precipitates and the polymer is recovered, washed and dried as in method 1.

Method 2 has been reported to produce a product with degree of hydrolysis $\geq 99.5\%$. This method has the advantages over method 1 that it requires less time, a lower temperature and no special apparatus. Method 1 however requires a smaller amount of catalyst and the ratio of alkali to polymer is about six times lower than in method 2. Method 1 however does not produce a consistent product in terms of percent hydrolysis, probably due to the small amount of alkali used. Method 2 was therefore chosen.

The catalyst solution was prepared by grinding NaOH (East Anglian Chemicals) to a powder and adding the required amount of methanol (S.L.R.) in a conical flask. Some sediment was left after the alkali had dissolved, and this was removed by filtration.

Washing of PVOH was continued until the washings gave no indication of alkali when tested with phenolphthalein and with methanolic phenol red indicators. (The latter was prepared by adding methanol (S.L.R.) dropwise to one or two drops of aqueous phenol red until a golden yellow solution was obtained. In the presence of alkali, the solution turns magenta in colour).
3.3 ACETYLATION OF POLY(VINYL ALCOHOL)

Acetylation of PVOH to PVOAc was carried out according to the method of Braun.\(^6^7\)

An acetylating mixture of pyridine (S.L.R., distilled and dried over NaOH pellets), glacial acetic acid (Fisons, 99.5\(^\text{c}\)) and acetic anhydride (Fisons, 97%) (1:10:10 by volume) was prepared. In a boiling tube fitted with an air condenser, PVOH (5 g) and acetylating reagent (75 ml) were heated together at 100\(^\circ\)C over a steam bath for 24 hours. After this time excess reagent was removed using a rotary evaporator and the product dissolved in methanol. The PVOAc was precipitated in water, redissolved in methanol and precipitated once more in water before being dried in a vacuum desiccator. A slightly pink product was obtained.

3.4 TESTS OF THE HYDROLYSIS/REACETYLATION REACTIONS

PVOH has a different structure to the branched PVOAc from which it is made, due to hydrolysable branches (section 2.2). Before any comparison is made between the two polymers, this must be taken into account. The way chosen here was to hydrolyse PVOAc to PVOH, then reacetylate to PVOAc. The resulting PVOAc then undergoes no further structural changes on hydrolysis.\(^4^,^5\)

It was necessary to test that the reactions involved were capable of fully hydrolysing and reacetylating the polymers. Both methods discussed are capable of doing this same job.

There are several methods available for the detection of hydroxyl groups in polymers. Most of these however refer to the determination of end groups, and are not generally suitable for
polymers containing large numbers of hydroxyl functions. Infra-red spectroscopy may be used, but it is a technique which requires a highly accurate instrument, which must be calibrated against polymers whose hydroxyl content is reliably known.

Two methods were examined in this work. The first, reacetylation by acetic anhydride, the second, hydrolysis of remaining acetate groups by strong alkali.

3.4.1 Method 1: Reacetylation

This method involves the conversion of hydroxyl groups to acetate groups, followed by the titrimetric determination of the remaining acetylating reagent.

An acetylating mixture of pyridine (5 ml, S.L.R., distilled and dried over NaOH pellets) and acetic anhydride (0.7 ml, Fisons 97%) was prepared. A sample of this mixture (1 ml) was pipetted into a boiling tube containing PVNOH (0.1 g). An air condenser was fitted and the mixture heated over a steam bath for 8 hours. Toluene (1.5 ml S.L.R., distilled) was added and the boiling tube stoppered and shaken vigorously to affect solution of the acetylated polymer. Water (5 ml, distilled) was added and three drops of phenolphthalein indicator, and the whole titrated, with shaking, with 0.2 N aqueous sodium hydroxide (A.R.) solution, to a permanent pink end-point. A blank solution containing no polymer was treated likewise.

3.4.2 Method 2: Hydrolysis

In this method, acetate groups present in PVNOH are hydrolysed by NaOH to hydroxy groups. The amount of alkali required is determined by titration.
To a solution of polymer (1 g) in methanol (50 ml, distilled, S.L.R.) in a 150 ml conical flask was added NaOH (A.R.) (25 ml aqueous solution) by pipette. (0.5 N NaOH was used when a polymer was suspected of having a degree of hydrolysis < 97 mol%, otherwise 0.1 N NaOH was used.) The flask was stoppered, shaken well, and allowed to stand for 2 hours at room temperature. Hydrochloric acid (25 ml of 0.6 N or 0.11 N depending on the amount of alkali used) was pipetted into the flask to ensure remaining alkali was neutralized and the contents of the flask slightly acidic. Excess acid ensures a positive titration. Phenolphthalein indicator (3 drops) was added and the contents of the flask titrated with 0.1 N NaOH (A.R.) solution to a permanent pink end-point. A blank solution was treated similarly.

3.5 DETAILS OF OTHER POLYMERS USED

Some commercial polymers were used for the purpose of comparing laboratory and industrial products. Details of these are given in table 3.4.

3.6 FRACTIONATION OF POLYMERS

Fractional precipitation, or fractionation, of polymers is the process whereby a polymer having a broad molecular weight distribution (MWD) may be separated into a number of samples each having a much narrower MWD than the parent. Although it is possible to carry out the process for PVOH this is a complicated and often unsatisfactory procedure, and is seldom performed, though some work has been reported.
In contrast PVOAc may be separated into relatively narrow, well defined fractions by this method\textsuperscript{73}, with comparatively little experimental difficulty. No special equipment is required beyond that of a large vessel, a method of agitation and a means of controlling temperature. Experimental and theoretical considerations are dealt with fully by Cantow.\textsuperscript{73}

3.6.1 Samples for Fractionation

Three samples of PVOAc prepared at low temperature (designated A, B and C) were combined in approximately equal proportions by dissolution in methanol (S.L.R.) and reprecipitation in water. The large batch (designated L) (\textasciitilde27 g) was then dried in vacuo to be used for fractionation. Fractions from this batch were designated "Lf". Polymer obtained from high temperature polymerisation was sufficient in quantity to obtain fractions without combining batches. Fractions were obtained from polymer designated B4, whilst another, B3, was used whole.

3.6.2 Fractionation of PVOAc

Fractionation of PVOAc was performed in the vessel shown in figure 3.3, held in a water bath at 25\textdegree C. A solution of PVOAc in methanol (S.L.R., 1500 ml) was added to the vessel and distilled water was added in 50 ml aliquots with vigorous stirring until the solution became cloudy. Just enough methanol was then added to give a clear solution. The temperature was raised to 30\textdegree C and the solution slowly stirred for approximately one hour. The vessel was then stoppered and allowed to cool back to 25\textdegree C when a clear solution remained.
Figure 3.3 FRACTIONATING VESSEL

modified 5L conical flask

ground glass joint
Water was then added carefully with vigorous stirring to give a slightly turbid solution. The temperature of the solution was raised once more and held at 30°C with stirring until the solution was clear. The vessel was then stoppered, the temperature lowered to 25°C and the vessel left to stand overnight, when precipitating polymer collected at the bottom. The central stem was put in place, isolating the precipitated polymer from the supernatant solution. Methanol was added to re-dissolve the precipitated polymer and the resulting solution removed through the central glass tube. The polymer fraction was recovered by precipitation in water and dried. Further fractions were collected by repeating the procedure.

3.7 CHARACTERISATION

3.7.1 Viscosity

3.7.1.1 Poly(vinyl acetate)

The viscosity of PVOAc in toluene (S.L.R., distilled) and THF (BDH A.R., stabilized with 0.1% quinol) at 25°C was measured with a modified Ubbelohde viscometer (figure 3.4). The viscometer was cleaned with hot, filtered chromic acid, rinsed thoroughly with filtered, distilled water and oven dried at 30°C. Flow times for toluene and THF were −188 and −157's respectively. Maximum and minimum volumes were 22 and 12 ml, allowing up to 5 successive dilutions of 2 ml each.

Solutions were made up in volumetric flasks (10 ml) and held at 35°C in a water bath prior to use. Each solution was carefully filtered before being introduced into the viscometer. The initial concentration was adjusted to give an η_r value < 2 (η_r (relative
Figure 3.4: Suspended Level Viscometer (modified)
viscosity) = \frac{t_{\text{solution}}}{t_{\text{solvent}}}. Solution was timed until successive readings agreed within ± 0.1 s. A further aliquot of solvent (2 ml) was added with shaking to ensure mixing, and flow timed again. Further dilutions and timings were made ensuring η_r > 1.2. Within the range 2 > η_r > 1.2 the Huggins equation (2.23) was found to give a good fit to the experimental data.

Adjustments for end effects and kinetic energy were considered unnecessary. Huggins plots were constructed manually to check behaviour, and a linear least squares analysis of the data performed to obtain the intrinsic viscosity [γ], dg⁻¹.

3.7.1.2 Poly(vinyl alcohol)

A PSL 1627/03 Ubbelohde viscometer was used for the determination of the intrinsic viscosity of PVOH in distilled water at 25°C. The viscometer was not modified since glass sinters proved too much of a restriction to aqueous flow. Solutions of PVOH were prepared as follows; the polymer was allowed to swell overnight in distilled water and the whole boiled to effect solution. The solution was then filtered and a small sample (0.5 - 1.0 ml) evaporated first at 30°C and then at 50°C in a vacuum oven to determine accurately the concentration of the solution. The flow time for water was ~130 s. Maximum and minimum solution volumes were 17 and 10 ml, allowing up to four dilutions of 1.5 ml. The method and evaluation of results were as stated in section 3.7.1.1.
3.7.2 Gel Permeation Chromatography (GPC)

3.7.2.1 Poly(vinyl acetate)

Some GPC work was carried out by the author using a modified Waters 502 ALC/GPC with THF (BDH, A.R., stabilized with 0.1\% quinol) as solvent. A 60 cm mixed bed PL gel column (Polymer Laboratories, Church Stretton, Shropshire) was used and calibrated with polystyrene standards of molecular weights from 200 to 2 x 10^6. Refractive index was used as concentration detector. Column efficiency as determined by toluene was > 40,000 p.p.m.

Most work on PVOAc however was carried out at the premises of Polymer Laboratories by their staff using a 60 cm mixed bed column with THF as solvent and refractive index detection. Sample injection volumes were 200 \( \mu \)l at 0.02 - 0.05 % concentrations and a flow rate of 1 ml/min. The column was calibrated with polystyrene standards and computational analysis of the results was performed by a "Tri-vector systems" microprocessor. Corrections for skew and broadening effects were found unnecessary except for work carried out by the author; thus samples A, B, C and L (figures 4.2 and 4.3) have been corrected, according to the procedure on page 323 of reference 45.

3.7.2.2 Poly(vinyl alcohol)

Aqueous GPC was carried out in distilled, degassed, filtered water. The column set comprised a 60 cm TSK 5000 pw and a 30 cm TSK 3000 pw type column in series, from the Toyo Soda Company of Japan. Refractive index was used as a means of detection. An Altex model 110A metering pump was used to deliver a constant flow rate of 1 ml/min. The column set efficiency as determined at regular intervals, using ethyleneglycol, (injection of 50 \( \mu \)l at 0.5\%) was > 21000 p.p.m. and the set was calibrated (as recommended by Toyo Soda) with
standard poly(ethylene oxide) (PEO) and poly(ethylene glycol) (PEG) polymers. The exclusion limit for PEO was $\sim 600,000$. A sample concentration of $\frac{1}{60}$ with a 50 μl injection volume was used, each solution containing a small amount of ethanol as internal marker and antidegradant (since high molar mass PEOs are not particularly stable in solution).

3.7.3 Osmometry

Osmometry was performed on samples of unfractionated poly(vinyl acetate) to determine number average molecular weight.

3.7.3.1 Poly(vinyl acetate)

Measurements of the osmotic pressure of solutions of PVOAc were performed on a Hewlett Packard High Speed Membrane Osmometer Model 502, thermostatted at 33°C. Toluene (S.L.R., distilled, degassed and filtered) was used as solvent with 0-8 type non-aqueous membranes (pore size 5-10 nanometers). A stock solution was made up to the highest concentration ($\sim 2\%$) and then diluted in volumetric flasks to obtain four samples. Each sample was filtered and kept at 35°C before being introduced into the osmometer. Manual plots of $\Pi/c$ and $(\Pi/c)^{\frac{1}{2}}$ were performed to check behaviour before $(\Pi/c)_0$ was determined by linear least squares analysis (see Chapter 3, reference 40).
4. POLY(VINYL ACETATE)

RESULTS
4.1 POLYMERISATION KINETICS

Batch polymerisations were performed with varying concentrations of initiator, in order to control the molecular weight of the final product. Five polymers were produced using initiator concentrations of 0.15 to 0.30 mmol/mol monomer.

From equation 2.12, equation 4.1 can be derived

$$\frac{1}{\bar{X}_n} = \frac{1}{K'} \left[ \frac{[I]^\frac{1}{2}}{[H]} \right]$$

Equation 4.1 is appropriate for simple polymerisations only, where interfering reactions are negligible. Under conditions of constant monomer concentration, and in the absence of solvent (therefore no transfer to solvent) equation 4.1 may be modified to

$$\frac{1}{\bar{X}_n} = K'' [I]^{\frac{1}{2}} + C_m$$

where $K'' = 1/K'[H]$ and $C_m$ is the constant for transfer to monomer. Since the initial monomer concentration has been constant, and conversion kept to below 5%, $C_m$ can be assumed to be constant for the five polymers. Furthermore, transfer to initiator may be neglected for AZ3N in vinyl acetate polymerisation, thus a plot of $[I]^{\frac{1}{2}}$ versus $1/\bar{X}_n$ should be linear. This plot is shown in figure 4.1. Values for $\bar{X}_n$ were calculated from $\bar{M}_n$ given by GPC. The GPC was calibrated using polystyrene (PS) standards (section 3.7.2) and no attempt has been made to convert the data to PVOAc molecular weights. (However, since the MM constants K and a are similar for both linear polymers, the molecular weights do not differ greatly.) The reasonable linearity of the plot in figure 4.1 indicates that the kinetics of the system are behaving as predicted.
Figure 41:
Plot of Reciprocal Degree of Polymerisation versus Initiator Concentration
4.2 MOLECULAR WEIGHT DATA OF WHOLE POLYMERS

4.2.1 Low Temperature Polymers

The GP chromatograms for batch "L" and its constituent polymers (PVOAc's A, B and C) are shown in figures 4.2 and 4.3. Table 4.1 gives molecular weight data for the polymers. The data are not converted to PVOAc molecular weights, but are corrected for band broadening. The polydispersity ratio ($D = \frac{\bar{M}_w}{\bar{M}_n}$) is much larger than the theoretical value of 1.5 for radical chain polymerisation in the absence of transfer. This is most likely to be due to an increase in temperature during the polymerisation reaction (section 3.1.4.1). It has been shown that, below 100°C, in the photopolymerisation of vinyl acetate, molecular weight increases with temperature. A rise in temperature during reaction could therefore lead to a broadening of the molecular weight distribution (MWD) and hence an increase in D.

Expressions for the values of $\bar{M}_n$ and $\bar{M}_w$ of a mixture of polymers have been derived (equations 4.3 and 4.4).

\[
\frac{1}{\bar{M}_n^{(\text{mix})}} = \frac{w_{i,1}}{\bar{M}_n^{(1)}} + \frac{w_{i,2}}{\bar{M}_n^{(2)}} + \frac{w_{i,3}}{\bar{M}_n^{(3)}} \tag{4.3}
\]

\[
\bar{M}_w^{(\text{mix})} = w_{i,1} \bar{M}_w^{(1)} + w_{i,2} \bar{M}_w^{(2)} + w_{i,3} \bar{M}_w^{(3)} \tag{4.4}
\]
TABLE 4.1: Molecular Weight Data for Polymers Prepared at Low Temperature.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>SOURCE</th>
<th>NOMINAL mol. wt. (PVAc)</th>
<th>DEGREE OF HYDROLYSIS(%)</th>
<th>COMMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B.D.H.</td>
<td>125,000</td>
<td>87-89</td>
<td>manufacturers specification</td>
</tr>
<tr>
<td>B</td>
<td>BAKER</td>
<td>---</td>
<td>99-100</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>B.D.H.</td>
<td>250,000</td>
<td>100</td>
<td>PVOAc, 100% hydrolysed by method 2, sec. 3.2.4.</td>
</tr>
<tr>
<td>D</td>
<td>B.D.H.</td>
<td>80,000</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 4.2: Polymers Used in Tests on Hydrolysis and Re-acetylation.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>WEIGHT OF POLYMER (g)</th>
<th>TITRE (ml)</th>
<th>Wt%OH (a)</th>
<th>MEAN OH</th>
<th>HYDROLYSIS DEGREE(%) (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1</td>
<td>1.0069</td>
<td>16.90</td>
<td>14.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.0001</td>
<td>16.80</td>
<td>14.53</td>
<td>14.40</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>0.9911</td>
<td>15.80</td>
<td>16.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.0203</td>
<td>15.70</td>
<td>16.35</td>
<td>16.20</td>
</tr>
<tr>
<td>BLANK</td>
<td>0.0</td>
<td>25.50</td>
<td></td>
<td></td>
<td>(a)equation 4.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(b)equation 4.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 4.3: Results of Tests on Hydrolysis Reaction by Re-acetylation Method.
where \( w_i \) is the weight fraction of polymer \( i \) in the mixture. Table 4.1 shows measured and calculated values of \( \tilde{M}_n \) and \( \tilde{M}_w \) for polymer mix "L". The \( \tilde{M}_w \) values are in good agreement but a higher \( \tilde{M}_n \) value is predicted than found.

The highest molecular weights for any one polymer reported here are \( \tilde{M}_n \sim 10^5 \) and \( \tilde{M}_w \sim 5 \times 10^5 \). Using more complicated cooling systems, Burnett claimed to be able to produce linear polymers of \( \tilde{M}_n \) up to 500,000, though in some cases the value of \( D \) as derived from osmometry and light scattering was \( <1 \). Atkinson and Dietz prepared high molecular weight linear PVOAc at \(-24^\circ C\) under essentially similar conditions to this work. They obtained polymers of different molecular weight by the addition of chain transfer agent. Fractionation of the polymers by preparative GPC enabled samples of \( D<1.3 \) to be produced.

4.2.2 High Temperature Polymers

The GPC chromatograms of whole branched polymers obtained at high temperature (designated B3 and B4) are shown in figures 4.4 and 4.5. As predicted by theory the molecular weight distributions of these polymers are much broader than for vinyl polymers of low to medium conversions. The abnormal breadth of the distribution can be attributed to chain transfer reactions causing the polymer molecules to branch. The probability of branching is approximately proportional to \( \tilde{M}_w \), hence branched molecules tend to become more highly branched and still larger. This results in the long high molecular weight tail seen in the chromatograms.

The high molecular weight of B4 (figure 4.5) caused some problem when analysed by GPC. The high molecular weight tail appears to have been excluded from the packing gel. This appears as a shoulder at
Figure 4.4: GPC Chromatograms of PVOAc B2 (whole)

M - as made
R - reacetylated

Figure 4.5: GPC Chromatograms of PVOAc B4 (whole)

M - as made
R - reacetylated
molecular weights greater than $10^7$ (figure 4.5). This makes interpretation in terms of molecular weight unreliable.

4.3 HYDROLYSIS AND REACETYLATION

4.3.1 Determination of Degree of Hydrolysis

4.3.1.1 By Reacetylation

This method involves the conversion of hydroxyl groups to acetate groups followed by the titrimetric determination of remaining acetylating reagent (section 3.4.1).

Assuming a polymer chain consisting of the repeat unit

$$-[\text{CH}_2\text{-CH(OH)}]-$$

1 mole of PVOH (100% hydrolysed PVOAc) $\equiv \frac{M_r}{M_w}$ moles hydroxyl (OH) groups

where $M_r$ is the molecular weight of the polymer and the molecular weight of the repeat unit is 44

$$1 \text{ g polymer} \equiv \frac{M_r}{M_w} \times \frac{1}{\text{mol/PVOAc}} = 22.73 \times 10^{-3} \text{ moles of OH groups.}$$

Acetic anhydride provides 2 moles of acetic acid per mole of anhydride. 1 mole of acetic acid attaches to the polymer chain, the other being complexed with pyridine. For every mole of -OH groups in the polymer, one mole of AA is used, a mole of acetic acid is produced and a mole of NaOH is required in the titration.

The blank solution will require 2 moles of NaOH per mole of AA. Let $x = \text{moles of AA in the blank}$ and $y = \text{moles of AA required for acetylation}$ then $x-y = \text{moles of AA remaining}$ this requires $2(x-y)$ moles of NaOH in the titration.

Since $y$ moles AA also give $y$ moles of acetic acid during
acetylation, the total amount of acetic acid produced is \(2(x-y) + y = 2x-y\) moles which required \(2x-y\) moles of NaOH.

The amount of OH groups present due to polymer = \(y = 2x - (2x-y)\)
or (Blank titre - Sample titre), i.e. the amount of OH groups is

\[\text{(Blank titre - Sample titre)} \times \frac{N}{g} \times 10^{-3}\text{ per gram of polymer (4.5)}\]

where \(N\) is the normality of the NaOH and \(g\) the weight of polymer taken. Thus the equivalent weight \% of hydroxyl groups in the polymer is given by

\[\text{wt} \% \text{OH} = \frac{w_{\text{POH}}}{\text{M}_{\text{pol}}} = \frac{17 \times V \times \frac{N}{g} \times 10^{-3} \times 100}{1.7 \frac{WN}{g}} = 1.7 \frac{WN}{g} \]  (4.6)

where \(V = \text{(Blank titre - Sample titre)}\) and 17 is the molecular weight of the hydroxyl function. Since the molecular weights of the acetate and hydroxyl group are different, equation 4.6 must be rewritten in terms of mole \% in order to determine the degree of hydrolysis (i.e. the number of OH groups present as a percentage of the total number of groups).

Let \(K_{\text{OH}} = \text{Number of moles of OH groups}\)

and \(T = \text{Total number of groups (i.e. OH and OAc)}\)

Taking 44 and 86 as the molecular weights of the alcohol and acetate repeat units respectively, equation 4.7 may be derived.

\[w_{\text{POH}} = \frac{17 \times K_{\text{OH}}}{(44 \times K_{\text{OH}}) + (T - K_{\text{OH}}) \times 86} \times \frac{100}{1} = \frac{1700}{44 + 86(T - K_{\text{OH}})} \]  (4.7)

The mole \% OH, \(w_{\text{POH}} = \frac{\text{No. of moles of OH}}{\text{Total moles of all groups}} \times \frac{100}{1} = \frac{100K_{\text{OH}}}{T} \)  (4.8)

\[\therefore \frac{T}{K_{\text{OH}}} = \frac{100}{w_{\text{POH}}} \]  (4.9)

and \(w_{\text{POH}} = \frac{1700}{44 + (\frac{100}{w_{\text{POH}}} - 1) \times 86} = \frac{17w_{\text{POH}}}{86 - 0.42w_{\text{POH}}} \)  (4.10)
which gives on rearrangement

\[
\text{Mol} \% \text{ OH} \equiv \text{Degree of Hydrolysis} = \frac{86\hat{w}_{\text{POH}}}{17 + 0.42\hat{w}_{\text{POH}}} \quad (4.11)
\]

Table 4.2 gives a list of the polymers used in the tests on hydrolysis and reacetylation, and table 4.3 shows the results of tests by the reacetylation method on 2 polymers.

4.3.1.2 By Hydrolysis at Room Temperature

The degree of hydrolysis is simply the degree of acetylation subtracted from 100. In this method, acetate groups remaining in PVOH are detected.

Using the same notation as in 4.3.1.1, and taking the molecular weight of the acetate group as 59

\[
\hat{M}_{\text{POAc}} = \frac{\hat{M}_{\text{OAc}}}{T} \times 100
\]

(mole \% OAc)

\[
\therefore \frac{T}{\hat{M}_{\text{OAc}}} = \frac{100}{\hat{M}_{\text{POAc}}} \quad (4.12)
\]

analogously to the derivation of equation 4.7

\[
\hat{w}_{\text{POAc}} = \frac{59\hat{M}_{\text{OAc}} \times 100}{44(T - \hat{M}_{\text{OAc}}) + 86\hat{M}_{\text{OAc}}} = \frac{5900\hat{M}_{\text{OAc}}}{44T + 42\hat{M}_{\text{OAc}}} \quad (4.13)
\]

Substituting 4.12 into 4.13 gives

\[
\hat{w}_{\text{POAc}} = \frac{\hat{M}_{\text{POAc}}}{\frac{44\hat{M}_{\text{POAc}}}{59} + 0.42\hat{M}_{\text{POAc}}} \quad (4.14)
\]

\[
\therefore \hat{M}_{\text{POAc}} = \frac{44\hat{M}_{\text{POAc}}}{59 - 0.42\hat{M}_{\text{POAc}}} \quad (4.15)
\]

and since \(\hat{M}_{\text{POH}}\) (degree of hydrolysis) = 100 - \(\hat{M}_{\text{POAc}}\)

\[
\hat{M}_{\text{POH}} = \frac{5900 - 86\hat{w}_{\text{POAc}}}{59 - 0.42\hat{w}_{\text{POAc}}} \quad (4.16)
\]
In the reaction, one mole of acetate groups produces one mole of acetic acid which requires one mole of NaOH to neutralize it. To ensure a positive titration, enough acid (HCl) is added to neutralize the original NaOH put in, and ensure acid is in excess. The excess acid is determined by titrating a blank solution (containing no polymer) treated in the same manner. The blank titre is subtracted from the sample titre to give the amount of alkali required to neutralize the acetic acid, and hence the original acetate content.

Let \( V \) be the volume of NaOH of normality \( N \) required, then

\[
\text{moles of NaOH used} = \frac{V \times N}{1000} \quad \text{moles of OAc groups} \quad (4.18)
\]

\[
\text{weight of OAc} = \frac{V \times N}{1000} \times 59 \quad (4.19)
\]

\[
\therefore \text{weight of OAc per gram of polymer} = \frac{59VN}{1000 \ g} \quad (4.20)
\]

\[
\therefore \text{weight percent OAc (}\omega_{\text{FOAc}}\text{)} = \frac{5.9VN}{g} \quad (4.21)
\]

Table 4.4 gives the results of tests by this method on the polymers of table 4.2.

4.3.2 Comparison of Test Methods

Table 4.5 shows a comparison of the results of the two test methods. The method of acetylation is clearly unsatisfactory, giving results far below those expected. This is probably due to incomplete reaction of the hydroxyl groups despite the fairly rigorous conditions. In contrast the method of hydrolysis is easily performed, requires comparatively innocuous reagents and, more importantly, gives correct results. This also serves to show that the chosen method of converting PVOAc to PVOH does indeed give a product of \( >99\% \) hydrolysis.
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>WEIGHT OF POLYMER (g)</th>
<th>TITRES (ml)</th>
<th>Wt% OAc (a)</th>
<th>HYDROLYSIS DEGREE (%) (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SAMPLE</td>
<td>BLANK</td>
<td>SAMPLE</td>
<td>MEAN</td>
</tr>
<tr>
<td>A 1</td>
<td>1.0320</td>
<td>11.16</td>
<td>11.00</td>
<td>6.16</td>
</tr>
<tr>
<td>2</td>
<td>0.9914</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B 1</td>
<td>1.0040</td>
<td>7.12</td>
<td>7.13</td>
<td>4.94</td>
</tr>
<tr>
<td>2</td>
<td>0.9910</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C 1</td>
<td>1.0271</td>
<td>6.35</td>
<td>6.18</td>
<td>5.78</td>
</tr>
<tr>
<td>2</td>
<td>0.9974</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D 1</td>
<td>1.0015</td>
<td>6.13</td>
<td>6.18</td>
<td>5.78</td>
</tr>
<tr>
<td>2</td>
<td>1.0135</td>
<td>5.97</td>
<td>5.78</td>
<td></td>
</tr>
</tbody>
</table>

Normality of NaOH in A: 0.4914 (a) equation 4.21
B: 0.0987 (b) equation 4.17
C, D: 0.0948

TABLE 4.4: Results of Tests on Hydrolysis Reaction by Hydrolysis Method.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>METHOD</th>
<th>HYDROLYSIS DEGREE (%)</th>
<th>SPECIFIED % HYDROLYSIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>HYDROLYSIS</td>
<td>88.3</td>
<td>87- 89</td>
</tr>
<tr>
<td>B</td>
<td>HYDROLYSIS</td>
<td>99.0</td>
<td>99-100</td>
</tr>
<tr>
<td></td>
<td>ACETYLATION</td>
<td>53.7</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>HYDROLYSIS</td>
<td>99.8</td>
<td>99.5</td>
</tr>
<tr>
<td></td>
<td>ACETYLATION</td>
<td>58.5</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>HYDROLYSIS</td>
<td>99.9</td>
<td>99.5</td>
</tr>
</tbody>
</table>

TABLE 4.5: Comparison of Results of Test Methods for Degree of Hydrolysis.
4.3.3 Hydrolysis and Reacetylation of Linear Polymers

The procedure was carried out on three linear polymers of high, medium, and low molecular weight. The experiments served firstly to confirm the linearity of the polymers (by comparing GP chromatograms before and after reaction) and secondly to demonstrate that the method chosen was capable of fully reacetylating the polymers. Degree of acetylation was determined as described in section 4.3.1.2.

Data before and after hydrolysis and reacetylation are presented in table 4.6 and figure 4.6. Clearly, no significant change has occurred in the shape of the chromatograms or in the derived molecular weight data, suggesting that the polymers contain no hydrolysable branches. The procedure does not give any information on non-hydrolysable branches; however, previous work suggests that the occurrence of hydrolysable branching is usually greater than non-hydrolysable. In the absence of the former the absence of the latter may be implied.

4.3.4 Hydrolysis and Reacetylation of Branched Polymers

Before fractionation, the branched PVOAc polymers were hydrolysed and reacetylated to remove hydrolysable branches. This ensured that, when fractions were subsequently hydrolysed to PVOH, no further structural changes occurred.

The narrowing of the MWD and the lowering of the molecular weight of branched PVOAc on hydrolysis and reacetylation is well known. This is obviously so, since it is the molecules of higher molecular weight that will be branched and will change on hydrolysis, whereas the lower molecular weight chains may have a sufficiently small number (or even no) branches, that comparatively
### TABLE 4.6: Molecular Weight Data for Linear Samples of FVQAc Subjected to Hydrolysis and Re-acetylation.

<table>
<thead>
<tr>
<th>SAMPLE (a)</th>
<th>$\bar{M}_n$ (PS)</th>
<th>$\bar{M}_w$ (PS)</th>
<th>POLYDISPERSITY RATIO D</th>
<th>% ACETYLATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. B</td>
<td>104,400</td>
<td>1.21</td>
<td>99.88</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>105,000</td>
<td>1.24</td>
<td>99.91</td>
<td></td>
</tr>
<tr>
<td>2. B</td>
<td>309,000</td>
<td>1.49</td>
<td>99.93</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>302,500</td>
<td>1.46</td>
<td>99.90</td>
<td></td>
</tr>
<tr>
<td>3. B</td>
<td>537,000</td>
<td>1.53</td>
<td>99.94</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>540,000</td>
<td>1.61</td>
<td>99.95</td>
<td></td>
</tr>
</tbody>
</table>

(a) B = Before hydrolysis, A = After re-acetylation

### TABLE 4.7: Molecular Weight Data for Branched Samples of FVQAc Subjected to Hydrolysis and Re-acetylation.

<table>
<thead>
<tr>
<th>SAMPLE (a)</th>
<th>$\bar{M}_n$ (PS)</th>
<th>$\bar{M}_w$ (PS)</th>
<th>POLYDISPERSITY RATIO D</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3. B</td>
<td>186,700</td>
<td>1,014,000</td>
<td>5.43</td>
</tr>
<tr>
<td>A</td>
<td>96,970</td>
<td>219,230</td>
<td>2.26</td>
</tr>
<tr>
<td>B4 B</td>
<td>304,800</td>
<td>2,017,000</td>
<td>6.62</td>
</tr>
<tr>
<td>A</td>
<td>103,700</td>
<td>238,150</td>
<td>2.30</td>
</tr>
</tbody>
</table>

(a) B = Before hydrolysis, A = After re-acetylation

TABLE 4.6: Molecular Weight Data for Linear Samples of FVQAc Subjected to Hydrolysis and Re-acetylation.

TABLE 4.7: Molecular Weight Data for Branched Samples of FVQAc Subjected to Hydrolysis and Re-acetylation.
little effect is seen. Figures 4.4 and 4.5 demonstrate the changes seen in the GP chromatograms. Not only is the molecular weight lowered but the whole chromatogram is compressed from the higher end of the molecular weight scale. The changes in molecular weight and in D are shown in table 4.7.

4.3.5 Reacetylation in Reaction and Analysis

The methods of determination of degree of hydrolysis by reacetylation and the reacetylation of whole polymers are virtually identical techniques, yet the former failed. Unlike whole polymer reacetylation, no solvent for the polymer was included during the analysis reaction, and reaction times were shorter. Furthermore, the titration required the addition of non solvent (water) which could cause partial precipitation of the polymer and adsorption or occlusion effects. In essence, trying to improve the already difficult technique by, for example, increased reaction time or addition of solvent may indeed have an adverse effect and is not considered a worthwhile exercise when hydrolysis techniques have been shown to be much easier and more accurate.

4.4 FRACTIONATION

4.4.1 Linear Poly(vinyl acetate)

Fifteen fractions in the molecular weight range 60,000 to 600,000 were obtained from the fractionation of the whole polymer "L". Further fractions were not collected, since branching was not considered significant for polymers of molecular weights below 50,000. The cumulative weight distribution of the parent polymer has been
plotted in figure 4.7. Also in the figure is shown the same data for the fractions. The first of the collected fractions were discoloured and of very broad MD and so were discarded. No investigation was made into the cause of the discolouration; however, it may be that degradation of very high molecular weight chains occurred due to the nature of the acetylating media (section 3.3). The discarded fractions have been taken into account in figure 4.7. The remaining fractions were all of a good white colour. Six fractions (chosen for the quantity of polymer) were characterised by GPC. Molecular weight data (based on a PS calibration) are shown in table 4.9 and GP chromatograms presented in figures 4.8 and 4.9.

4.4.2 Branched Poly(vinyl acetate)

Fractions were obtained from whole reacetylated PVOAc B4. Six of these were characterised by GPC. Molecular weight data (based on PS) are shown in table 4.9. GP chromatograms are presented in figure 4.10 with cumulative molecular weight data in figure 4.11.

4.5 CHARACTERISATION

4.5.1 Osmometry

Number average molecular weights ($\bar{M}_n$) were determined for whole polymers by osmometry in toluene. The results are presented graphically in figure 4.12 and in table 4.10. Figure 4.13 shows a comparison of $\bar{M}_n$ values from osmometry and unconverted GPC. Since GPC (based on a linear calibration) underestimates the molecular weight of branched species (section 2.3.5) a linear correlation with weight absolute molecular $\overline{\chi}$ as in figure 4.13, would not be expected.
Figure 4.7: Cumulative Weight Distribution of Linear PVOCk - whole polymer and fractions

<table>
<thead>
<tr>
<th>LOG Mw1 (PSI)</th>
<th>Cumulative weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>70</td>
<td>40</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>90</td>
<td>60</td>
</tr>
<tr>
<td>100</td>
<td>70</td>
</tr>
</tbody>
</table>

whole polymer ———
fractions o
<table>
<thead>
<tr>
<th>FRACTION</th>
<th>$\bar{M}_n$ (PS)</th>
<th>$\bar{M}_w$ (PS)</th>
<th>POLYDISPERSITY RATIO D</th>
</tr>
</thead>
<tbody>
<tr>
<td>L6</td>
<td>247,400</td>
<td>395,000</td>
<td>1.60</td>
</tr>
<tr>
<td>L7</td>
<td>248,700</td>
<td>374,800</td>
<td>1.51</td>
</tr>
<tr>
<td>L8</td>
<td>251,800</td>
<td>337,300</td>
<td>1.34</td>
</tr>
<tr>
<td>L9</td>
<td>177,100</td>
<td>148,600</td>
<td>1.27</td>
</tr>
<tr>
<td>L14</td>
<td>68,900</td>
<td>83,500</td>
<td>1.21</td>
</tr>
<tr>
<td>L15</td>
<td>63,100</td>
<td>75,600</td>
<td>1.20</td>
</tr>
</tbody>
</table>

**Table 4.8: Molecular Weight Data for Fractions of Linear PVQAc.**

<table>
<thead>
<tr>
<th>FRACTION</th>
<th>$\bar{M}_n$ (PS)</th>
<th>$\bar{M}_w$ (PS)</th>
<th>POLYDISPERSITY RATIO D</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF2</td>
<td>192,000</td>
<td>251,900</td>
<td>1.31</td>
</tr>
<tr>
<td>BF3</td>
<td>340,400</td>
<td>536,900</td>
<td>1.53</td>
</tr>
<tr>
<td>BF4</td>
<td>207,400</td>
<td>309,000</td>
<td>1.49</td>
</tr>
<tr>
<td>BF5</td>
<td>258,800</td>
<td>369,700</td>
<td>1.43</td>
</tr>
<tr>
<td>BF7</td>
<td>165,000</td>
<td>206,900</td>
<td>1.25</td>
</tr>
<tr>
<td>BF9</td>
<td>86,600</td>
<td>104,400</td>
<td>1.21</td>
</tr>
</tbody>
</table>

**Table 4.9: Molecular Weight Data for Fractions of Branched PVQAc.**
Figure 4.8: GPC Chromatograms for Fractions of Linear PVOAc

Figure 4.9: GPC Chromatograms for Fractions of Linear PVOAc
Figure 4.10
GC Chromatograms for Fractions of Branched PVOAc
### Table 4.10: Values of $\bar{M}_n$ Determined Osmotically for Whole Branched Polymers.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$\bar{M}_n$</th>
<th>$A_2 \times 10^3$</th>
<th>$\bar{M}_n$ (PS, GPC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3.M</td>
<td>192,000</td>
<td>0.93</td>
<td>186,700</td>
</tr>
<tr>
<td>B3.R</td>
<td>101,500</td>
<td>0.60</td>
<td>96,970</td>
</tr>
<tr>
<td>B4.M</td>
<td>396,770</td>
<td>0.68</td>
<td>304,820</td>
</tr>
<tr>
<td>B4.R</td>
<td>103,070</td>
<td>0.74</td>
<td>103,700</td>
</tr>
<tr>
<td>BDH 160T.M</td>
<td>136,800</td>
<td>1.05</td>
<td>143,250</td>
</tr>
<tr>
<td>BDH 160T.R</td>
<td>92,600</td>
<td>1.58</td>
<td></td>
</tr>
</tbody>
</table>

(a) Before and after hydrolysis and reacetylation

### Table 4.11: Values of the Number Average Degree of Hyrolysable Branching ($\eta_n$) from Osmometry.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$\bar{M}_n$ (OS)</th>
<th>$\eta_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDH 160T</td>
<td>136,800</td>
<td>92,600</td>
</tr>
<tr>
<td>B3</td>
<td>192,800</td>
<td>101,500</td>
</tr>
<tr>
<td>B4</td>
<td>396,770</td>
<td>103,070</td>
</tr>
</tbody>
</table>

### Table 4.12: Intrinsic Viscosity of Linear and Branched PVQAc Fractions in toluene at 25°C.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LF4</td>
<td>1.026</td>
<td>0.384</td>
<td>BF3</td>
<td>1.066</td>
<td>0.310</td>
</tr>
<tr>
<td>LF9</td>
<td>0.700</td>
<td>0.520</td>
<td>BF5</td>
<td>0.821</td>
<td>0.439</td>
</tr>
<tr>
<td>LF12</td>
<td>0.593</td>
<td>0.466</td>
<td>BF6</td>
<td>0.656</td>
<td>0.463</td>
</tr>
<tr>
<td>LF14</td>
<td>0.526</td>
<td>0.514</td>
<td>BF7</td>
<td>0.571</td>
<td>0.516</td>
</tr>
</tbody>
</table>

TABLE 4.12: Intrinsic Viscosity of Linear and Branched PVQAc Fractions in toluene at 25°C.
Figure 4.13: Comparison of $M_n$ by Osmometry and GPC (whole branched polymer).

Figure 4.14: Number Average Degree of Branching of PVOAc versus Molecular Weight.
However, $\bar{M}_w$ is more sensitive than $\bar{M}_n$ to higher molecular weight and thus branched molecules. Hence in plots based on $\bar{M}_n$, deviation is only noticed, as in figure 4.13, at higher molecular weights.

An estimate of hydrolysable branching content is furnished by equation 2.45. Table 4.11 gives values of $\bar{n}_n$ (number average degree of branches), and the data is plotted in figure 4.14.

4.5.2 Viscometry

4.5.2.1 Fractions

The intrinsic viscosity $[\eta]$ of linear and branched PVOAc fractions was obtained in both toluene and tetrahydrofuran (THF), via the Huggins equation (equation 2.23). Tables 4.12 and 4.13 give the relevant data. This is plotted in figure 4.15 where the molecular weights are weight average based on polystyrene (PS). In both plots little difference appears between branched and linear fractions, though the points for the branched fractions appear a little more scattered than the linear. It can be concluded from this that, in the range of molecular weight studied, long chain branching of the non-hydrolysable type (if present) is not significant enough to cause deviation in intrinsic viscosity behaviour.

The relative slopes of the plots are 0.77 for THF and 0.61 for toluene. For the same molecular weight, PVOAc has a lower viscosity in toluene than in THF, indicating a tighter "coil" in toluene. This is expected since toluene is almost a theta-solvent for PVOAc under these conditions, whereas THF is a good solvent. The values of the slopes are higher than typical literature values of 0.53 for toluene and 0.71 for THF, but this is not unreasonable since the values used in figure 4.15 are not true PVOAc molecular weights.
Table 4.13: Intrinsic Viscosity of linear and Branched PVOAc Fractions in tetrahydrofuran at 25°C.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LF6</td>
<td>1.241</td>
<td>0.378</td>
<td>BF3</td>
<td>1.460</td>
<td>0.489</td>
</tr>
<tr>
<td>LF7</td>
<td>1.220</td>
<td>0.324</td>
<td>BF5</td>
<td>1.256</td>
<td>0.342</td>
</tr>
<tr>
<td>LF8</td>
<td>1.185</td>
<td>0.353</td>
<td>BF4</td>
<td>1.105</td>
<td>0.369</td>
</tr>
<tr>
<td>LF9</td>
<td>0.640</td>
<td>0.286</td>
<td>BF2</td>
<td>0.913</td>
<td>0.486</td>
</tr>
<tr>
<td>LF14</td>
<td>0.408</td>
<td>0.408</td>
<td>BF7</td>
<td>0.862</td>
<td>0.440</td>
</tr>
<tr>
<td>LF15</td>
<td>0.378</td>
<td>0.387</td>
<td>BF9</td>
<td>0.468</td>
<td>0.605</td>
</tr>
</tbody>
</table>

Table 4.14: Intrinsic Viscosities of Whole Polymers in tetrahydrofuran at 25°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[η]</th>
<th>K'</th>
<th>Sample</th>
<th>[η]</th>
<th>K'</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3 M</td>
<td>1.744</td>
<td>0.317</td>
<td>BDH 45T</td>
<td>0.351</td>
<td>0.490</td>
</tr>
<tr>
<td>B3 R</td>
<td>0.852</td>
<td>0.321</td>
<td>BDH 160T</td>
<td>1.204</td>
<td>0.354</td>
</tr>
<tr>
<td>B4 M</td>
<td>2.722</td>
<td>0.532</td>
<td>BDH 500T</td>
<td>1.403</td>
<td>0.337</td>
</tr>
<tr>
<td>B4 R</td>
<td>0.927</td>
<td>0.242</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.15: Intrinsic Viscosity of PVAc versus Molecular Weight
4.5.2.2 Viscosity and Branching

Berger\textsuperscript{77,32,33} has investigated the influence of molecular weight, polydispersity, and branching on the constants of various viscosity equations. Data were collected from the literature on 16 different polymers and were found to be highly conflicting. It was therefore impossible to express a general view. For PVOAc \( K \) (Huggins) was thought, in general, to be constant or to show a slight increase with branching. This result was also found by Hobbs\textsuperscript{80,81} who claimed values of \( K \) between 0.32 and 0.35 for fractions of linear PVOAc, and 0.34 to 0.42 for branched. In this work, the average value of \( K \) for linear and branched fractions in THF was found to be 0.36 and 0.43 respectively, while in toluene this was 0.47 and 0.43. Little difference has been found in the value of \( [\eta] \) for branched and linear species with respect to molecular weight, and this small difference in \( K \) values is therefore considered insignificant. Further work\textsuperscript{96} suggests that \( K \) is not dependent on branching, but on shear rate for higher molecular weight polymers.

4.5.2.3 Whole Polymers

Viscosity data for whole polymers are given in table 4.14. The average value for \( K \) is 0.37, re-inforcing the view that the variation in \( K \) is not particularly significant, with respect to branching.

4.5.3 Chromatographic Data

Chromatograms of linear and branched fractions and whole polymers are shown in figures 4.4, 4.5 and 4.8-4.10. The computed molecular weights (based on a PS calibration) and average elution
volumes are given in tables 4.15-4.17. The figures $V(\tilde{n}_n)$, $V(\tilde{m}_p)$ and $V(\tilde{m}_w)$ are values of elution volume (viz time) corresponding to the number, peak and weight average molecular weights. The use of similar $v_e$ parameters has been reported. Figure 4.16 shows a typical GPC chromatogram with $\tilde{n}_n$, $\tilde{m}_w$ and $\tilde{m}_p$ identified (though $\tilde{m}_p$ need not necessarily lie between $\tilde{n}_n$ and $\tilde{m}_w$). Having obtained values for the molecular weight averages, the corresponding elution volume parameters may be obtained directly from the calibration curve of molecular weight versus elution volume.
### Table 4.15: Molecular Weight Data of Linear PVAc Fractions (based on polystyrene calibration)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$\overline{M}_n$</th>
<th>$\overline{M}_w$</th>
<th>$\overline{M}_p$</th>
<th>D</th>
<th>$V(\overline{M}_n)$</th>
<th>$V(\overline{M}_w)$</th>
<th>$V(\overline{M}_p)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LF6</td>
<td>247,400</td>
<td>395,000</td>
<td>396,500</td>
<td>1.60</td>
<td>688</td>
<td>667</td>
<td>667</td>
</tr>
<tr>
<td>LF7</td>
<td>248,700</td>
<td>374,800</td>
<td>373,300</td>
<td>1.51</td>
<td>688</td>
<td>670</td>
<td>670</td>
</tr>
<tr>
<td>LF8</td>
<td>251,800</td>
<td>430,400</td>
<td>333,400</td>
<td>1.34</td>
<td>686</td>
<td>674</td>
<td>674</td>
</tr>
<tr>
<td>LF9</td>
<td>117,100</td>
<td>148,600</td>
<td>151,300</td>
<td>1.27</td>
<td>724</td>
<td>712</td>
<td>711</td>
</tr>
<tr>
<td>LF14</td>
<td>68,930</td>
<td>83,510</td>
<td>93,060</td>
<td>1.21</td>
<td>753</td>
<td>742</td>
<td>736</td>
</tr>
<tr>
<td>LF15</td>
<td>63,090</td>
<td>75,630</td>
<td>82,400</td>
<td>1.20</td>
<td>758</td>
<td>748</td>
<td>743</td>
</tr>
</tbody>
</table>

### Table 4.16: Molecular Weight Data of Branched PVAc Fractions (based on polystyrene calibration)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$\overline{M}_n$</th>
<th>$\overline{M}_w$</th>
<th>$\overline{M}_p$</th>
<th>D</th>
<th>$V(\overline{M}_n)$</th>
<th>$V(\overline{M}_w)$</th>
<th>$V(\overline{M}_p)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF3</td>
<td>340,400</td>
<td>536,900</td>
<td>516,500</td>
<td>1.58</td>
<td>674</td>
<td>655</td>
<td>656</td>
</tr>
<tr>
<td>BF5</td>
<td>258,800</td>
<td>369,700</td>
<td>333,400</td>
<td>1.43</td>
<td>685</td>
<td>670</td>
<td>674</td>
</tr>
<tr>
<td>BF4</td>
<td>207,400</td>
<td>309,000</td>
<td>246,800</td>
<td>1.49</td>
<td>696</td>
<td>678</td>
<td>688</td>
</tr>
<tr>
<td>BF2</td>
<td>192,000</td>
<td>251,900</td>
<td>213,600</td>
<td>1.31</td>
<td>700</td>
<td>687</td>
<td>694</td>
</tr>
<tr>
<td>BF7</td>
<td>165,000</td>
<td>206,900</td>
<td>201,700</td>
<td>1.25</td>
<td>707</td>
<td>696</td>
<td>697</td>
</tr>
<tr>
<td>BF9</td>
<td>86,580</td>
<td>104,400</td>
<td>108,600</td>
<td>1.21</td>
<td>740</td>
<td>730</td>
<td>728</td>
</tr>
<tr>
<td>SAMPLE</td>
<td>$\bar{M}_n$</td>
<td>$\bar{M}_w$</td>
<td>$\bar{M}_p$</td>
<td>D</td>
<td>$V(\bar{M}_n)$</td>
<td>$V(\bar{M}_w)$</td>
<td>$V(\bar{M}_p)$</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td>---</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>B3.M</td>
<td>186,700</td>
<td>1,014,100</td>
<td>449,600</td>
<td>5.43</td>
<td>701</td>
<td>630</td>
<td>662</td>
</tr>
<tr>
<td>B3.R</td>
<td>97,000</td>
<td>219,200</td>
<td>129,700</td>
<td>2.26</td>
<td>734</td>
<td>693</td>
<td>719</td>
</tr>
<tr>
<td>B4.M</td>
<td>304,800</td>
<td>2,016,600</td>
<td>834,700</td>
<td>6.62</td>
<td>679</td>
<td>606</td>
<td>637</td>
</tr>
<tr>
<td>B4.R</td>
<td>103,700</td>
<td>238,100</td>
<td>150,400</td>
<td>2.30</td>
<td>731</td>
<td>690</td>
<td>711</td>
</tr>
<tr>
<td>BDH 45T</td>
<td>34,700</td>
<td>82,400</td>
<td>86,370</td>
<td>2.37</td>
<td>795</td>
<td>743</td>
<td>740</td>
</tr>
<tr>
<td>BDH 160T</td>
<td>143,200</td>
<td>511,300</td>
<td>371,300</td>
<td>3.57</td>
<td>714</td>
<td>657</td>
<td>670</td>
</tr>
<tr>
<td>BDH 500T</td>
<td>164,500</td>
<td>713,100</td>
<td>583,100</td>
<td>4.34</td>
<td>707</td>
<td>643</td>
<td>651</td>
</tr>
</tbody>
</table>

**TABLE 4.17: Molecular Weight Data of Whole Polymers**

*(based on polystyrene calibration)*
Figure 416: Relationship between Average Molecular Weights and Elution Volumes
5. LONG BRANCHING IN POLY-
(VINYL ACETATE)
5.1 INTRODUCTION

Much emphasis has been placed on methods of determining the true molecular weight distributions of branched polymers from GPC chromatograms. Gel permeation chromatography cannot alone furnish unambiguous data. As normally practised, GPC separates by size and cannot distinguish structural differences in polymers. Molecules having the same size, and thus appearing in the same elution volume increment, may have different molecular weights due to differences in the distributions of branch length and density. Calibrating a GPC with branched polymers presupposes the same type and degree of branching in both calibrants and samples under test, and a completely general calibration (as with conventional GPC) is not possible. Some work has been done along these lines but the method requires a fairly substantial amount of sample and time.

For this reason further information on the polymer under test is required and many methods have been used. Mostly GPC has been a base, since this method alone can give, in the first instance, a complete molecular size distribution. This has been combined with lightscattering (LS), viscometry, diffusion and sedimentation methods. Work has been reported on the combination of any of the above techniques, details of which may be found in Scholte's review. All these methods are considered valid, since the physical quantities involved are assumed to depend only on molecular weight and hydrodynamic radius (R). Certainly for measurements at constant conditions (i.e. same solvent at the same temperature) R is constant regardless of the technique. However to actually define R accurately is almost as difficult a problem as branching itself, and plotting data to extract information has to be done with more care.
than is sometimes realized if hopefully accurate data are to be obtained.

The combination of GPC with either on\textsuperscript{19,32,33} or off-line additional detection has proved to be a popular technique with many workers. As an off-line technique viscometry, requiring little sophisticated apparatus, other than a constant temperature bath, is an obvious choice. Indeed automatic viscometers make this combination of methods almost routine.

The ease of gathering intrinsic viscosity and GPC data however, is in contrast to the painstaking analysis required to transform the initial data into an accurate molecular weight analysis of the polymer. For the purposes of this work, the Ham and Miltz\textsuperscript{61} method has been chosen since this requires no initial estimate of any branching parameters.

5.2 Application of the Ram and Miltz Method for Long Branching

5.2.1 Initial Procedure

Until now the Ram and Miltz (R/H) method has not been applied to either PVOAc or PVOH. The procedure applied in this work was as follows:—

a) In the first instance, to avoid having to assume a calibration curve, plots of $[\eta]$ versus various elution volume parameters were drawn up using linear and branched (reacetylated) fractions, and whole polymers. From the plots, the elution volume parameter most compatible with the R/H method was decided.

b) A universal calibration plot was then set up in order to be consistent with observed results. Hence values for the Mark-Houwink (MH)
constants $K$ and $a$ could be deduced.

c) The $R/\eta$ method was applied to all fractions and whole polymers, and an investigation into the dependence of $\eta_0$ on the generated data was made.

5.2.2 Calibration Data

5.2.2.1 Elution Volume Plots

From computer analysis of GP chromatograms and the $R_3$ calibration, values for various elution volume parameters were evolved according to figure 4.16. These are plotted against $[\eta]$ from tables 4.13-4.17 and are presented in figures 5.1-5.3.

Clearly the data are best correlated using $V(\bar{\eta}_w)$ as the elution volume parameter. This plot shows the data as theory predicts it to be, viz. branched polymers having lower $[\eta]$'s than linear ones (see figure 2.5). The scattering of the points in the other two plots is probably an effect of the different polydispersities of the polymers (ranging from 1.2-6.6). The dependence on average molecular weight of calibration curves derived from polydisperse polymers is well known. 52

Some very important inferences may be drawn from these initial plots. All the fractions, within acceptable experimental limits, fall on the same line (figure 5.3) regardless of whether designated linear or branched. It has been demonstrated that the linear fractions are truly linear (section 4.3.3). The branched fractions have had hydrolysable branching removed and appear to behave as linear polymers. It may be deduced from this that, either branching of the non-hydrolysable type is insignificant in these polymers at the molecular weight levels studied, or that the method is insensi-
Figure 51: Intrinsic Viscosity of PVOAc versus Elution Volume

Figure 52: Intrinsic Viscosity of PVOAc versus Elution Volume
Figure 5.3: Intrinsic Viscosity of PVOAc versus Elution Volume

Log[η] vs. Elution Volume V(Mw)

- Linear fractions
- Branched fractions
- Whole, re-acetylated
- Whole, as mode
tive to small amounts of branching.

The whole polymers shown in figure 5.3 clearly demonstrate branching, having lower $[\eta]$'s for the same $V_e$. The reacetylated whole polymers however fall on the same curve as the fractions. This may be further evidence that hydrolysable branches are more significant i.e. prevalent than main chain branches. Previous work has indeed indicated that branching through the acetoxy group (i.e. hydrolysable) in either monomer or polymer occurs more frequently than at the main chain, and this frequency increases with temperature. The different polydispersities of the polymers do not appear in this instance to be of great importance, though this may be responsible for a certain amount of scatter in the data.

5.2.2.2 The Universal Calibration

In order for the $R/\bar{M}$ procedure to work properly, the correct values for the Mark Houwink ($k$-$\bar{M}$) constants $K$ and $a$ are required. Though these may be obtained from the literature, agreement between various authors is poor, and this warrants the re-determination of the constants applicable to the systems studied.

Since the $k$-$\bar{M}$ constants for polystyrene (PS - with which the GPC was calibrated) are known (and agreed), and since $[\eta]$ has been measured for several linear fractions, the universal calibration may be used to determine PVOAc molecular weights. Equation 2.55 (section 2.4.1.3) states that

$$\bar{M}_{PVOAc} = \frac{[\eta]_{PS}}{[\eta]_{PVOAc}} \frac{M_{PS}}{M_{PVOAc}} \text{ at constant } V_e.$$  \hspace{1cm} (5.1)

The question arises as to which is the best $M_{PS}$ to take, and what value of $\bar{M}_{PVOAc}$ does this give. Since it has already been shown in figure 5.3 that $V(\bar{M}_n)$ gives the best interpretation of the
data, this value was chosen. The values of \( r_{1-VOC} \) were thus derived and plotted against \([\eta]\). Values for \( k \) and \( a \) were obtained by linear least squares analysis. The derived molecular weights are given in table 5.1. The \( H \) constants gave equation 5.1

\[
[\eta] = 0.942 \times 10^{-5} n^{0.737}
\]

This data based on \( \bar{f} \) compares reasonably with that of other authors (see table 5.2) based on \( \bar{f} \).

5.2.2.3 Other methods for MH constants

Two further methods of obtaining \( K \) and \( a \) values have been derived by Weiss and Cohn-Ginsberg (J CG).86 The quantities \( \bar{f}_n \), \( \bar{f}_w \) and \([\eta]\) can be expressed by equations 5.2-5.4.

\[
\bar{f}_n = \frac{\frac{K^{1/a+1}}{a+1}}{\sum \left( \frac{w_i}{j_i^{1/a+1}} \right)}
\]

(5.2)

\[
\bar{f}_w = K^{1/a+1} \sum w_i j_i^{1/a+1}
\]

(5.3)

\[
[\eta] = K^{1/a+1} \sum w_i j_i^{a/a+1}
\]

(5.4)

where \( w_i \) is the weight fraction of species \( i \)

\( j_i = [\eta]_i n_i \), the hydrodynamic volume of species \( i \)

and \( K \) and \( a \) are the relevant MH constants.

Method 1: From \([\eta]\) and GPC

If the intrinsic viscosities \([\eta]\) and GPC chromatograms of two polymers of the same type (in the same solvent) are obtained, then \( K \) and \( a \) can be determined as follows; from equation 5.4, for two
TABLE 5.1: Conversion of Polystyrene Molecular Weights to Poly(vinyl acetate) via the Universal Calibration.

<table>
<thead>
<tr>
<th>PVOAc SAMPLE</th>
<th>$\overline{M}_w$(PS) (GPC)</th>
<th>$\overline{M}$(PVOAc) (u.c.)</th>
<th>$[\eta]$(PVOAc) (T.H.F. 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lf 6</td>
<td>395,000</td>
<td>416,100</td>
<td>1.241</td>
</tr>
<tr>
<td>Lf 7</td>
<td>374,800</td>
<td>386,700</td>
<td>1.220</td>
</tr>
<tr>
<td>Lf 8</td>
<td>337,400</td>
<td>332,000</td>
<td>1.185</td>
</tr>
<tr>
<td>Lf 9</td>
<td>148,600</td>
<td>149,500</td>
<td>0.640</td>
</tr>
<tr>
<td>Lf 14</td>
<td>83,510</td>
<td>86,870</td>
<td>0.408</td>
</tr>
<tr>
<td>Lf 15</td>
<td>75,630</td>
<td>79,040</td>
<td>0.378</td>
</tr>
</tbody>
</table>

TABLE 5.2: Mark-Houwink Constants for PVOAc in T.H.F. from various Authors.

<table>
<thead>
<tr>
<th>Mol.Wt. PARAMETER</th>
<th>Kx10^4</th>
<th>a</th>
<th>TEMPERATURE (°C)</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\overline{M}_n$</td>
<td>2.63</td>
<td>0.65</td>
<td>25</td>
<td>84</td>
</tr>
<tr>
<td>$\overline{M}_n$</td>
<td>0.682</td>
<td>0.766</td>
<td>23</td>
<td>85</td>
</tr>
<tr>
<td>$\overline{M}_w$</td>
<td>0.51</td>
<td>0.791</td>
<td>25</td>
<td>19</td>
</tr>
<tr>
<td>$\overline{M}_p$</td>
<td>1.56</td>
<td>0.708</td>
<td>30</td>
<td>21</td>
</tr>
<tr>
<td>$\overline{M}_w$</td>
<td>0.942</td>
<td>0.737</td>
<td>25</td>
<td>This Work</td>
</tr>
</tbody>
</table>
samples (subscripted 1 and 2) equation 5.5 may be derived

\[
\frac{[\eta]_1}{[\eta]_2} = \frac{(\sum w_i j_i^{a/a+1})_1}{(\sum w_i j_i^{a/a+1})_2}
\] (5.5)

Values of \(a\) are iterated by computer program until both sides of equation 5.5 agree, to within the required accuracy. A value of \(K\) can then be calculated from equation 5.4 from either polymer.

**Method 2: From \([\eta]\), \(\overline{M}_n\) and GPC**

Values for \(K\) and \(a\) may also be derived from a single sample, if an independent value for \(\overline{M}_n\) is known (e.g. from osmometry). From equations 5.2 and 5.4

\[
\overline{M}_n = \frac{\sum w_i j_i^{a/a+1}}{\sum j_i^{1/a+1}}
\] (5.6)

As before, a value for \(a\) is found by iteration, \(K\) is calculated from equation 5.4 and \(\overline{M}_n\) from 5.3.

Both these methods have been tried and the results are presented in table 5.3. Clearly the linear fractions give a better estimate of \(K\) and \(a\) values than any other species. Furthermore they are in reasonable agreement with the values determined directly. The branched fractions give similar \(a\) values though less than 50\% of these gave consistent answers. In both the double \([\eta]\) and \([\eta]\) \(\overline{M}_n\) methods the whole polymers performed badly. This failure is most likely due to their broad molecular weight distributions. Inherent in the assumptions of the method is the linearity of the MH equation. It has long been accepted, however, that this assumption is not valid over extended ranges of molecular weight.39 The whole polymers have polydispersities between 2 and 7 (table 4.17) and their chromatograms
(figures 4.4 and 4.5) span between 3 and 4 decades of molecular weight. It is therefore not unexpected that unreliable results should occur.

Other workers\textsuperscript{97-99}, using these methods, have found similar results; the methods work with reasonable accuracy for narrow MWD (low D) polymers but tend to give poor results when polymers of broad MWD are used. It has been suggested\textsuperscript{93} that the classical method is better than the GPC method. The accuracy of the latter depends on whether or not corrections have been applied for band broadening, and how accurate the corrections are. The constants as derived in equation 5.1 have thus been used throughout.

5.2.3 Results from R/H Procedure

The values chosen for $K$ and $a$ for PVOAc have been established (equation 5.1). Values for polystyrene (PS) were taken from the literature\textsuperscript{21} as $a = 3.724$ and $K = 1.16 \times 10^{-4}$.

A computer program was used to obtain data with a series of $n_0$ values (equation 2.67, section 2.4.2.4). The results are presented in table 5.4 as linear equivalent and branched molecular weights. As expected the molecular weights increase when converted to branched from linear. Since, for two molecules of the same molecular weight a branched molecule will have a smaller molecular size, it follows that, of two molecules of the same size the branched one should have a higher molecular weight. The GPC separates by size so that a branched molecule is predicted to have a molecular weight less than the true value. Also as expected, $\bar{M}_W$ increases (over the linear equivalent) much more than $\bar{M}_n$. This is because $\bar{M}_W$ is more sensitive to larger (and hence more highly branched) molecules. Consequently the molecular weight distribution broadens.
<table>
<thead>
<tr>
<th>Mo</th>
<th><strong>BDH160T</strong></th>
<th></th>
<th><strong>BDH500T</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\overline{M}_n$</td>
<td>$\overline{M}_w$</td>
<td>$\overline{M}_n$</td>
<td>$\overline{M}_w$</td>
</tr>
<tr>
<td>0 (lin.)</td>
<td>149,300</td>
<td>520,250</td>
<td>171,200</td>
<td>727,250</td>
</tr>
<tr>
<td>20,000</td>
<td>155,550</td>
<td>600,250</td>
<td>178,400</td>
<td>845,600</td>
</tr>
<tr>
<td>50,000</td>
<td>153,700</td>
<td>601,500</td>
<td>176,300</td>
<td>847,500</td>
</tr>
<tr>
<td>100,000</td>
<td>152,300</td>
<td>602,900</td>
<td>175,000</td>
<td>848,700</td>
</tr>
<tr>
<td>200,000</td>
<td>(151,100)</td>
<td>(605,700)</td>
<td>(173,200)</td>
<td>(850,300)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th><strong>B3M</strong></th>
<th></th>
<th><strong>B4M</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\overline{M}_n$</td>
<td>$\overline{M}_w$</td>
<td>$\overline{M}_n$</td>
<td>$\overline{M}_w$</td>
</tr>
<tr>
<td>0 (lin.)</td>
<td>192,700</td>
<td>1,026,900</td>
<td>313,600</td>
<td>2,026,900</td>
</tr>
<tr>
<td>20,000</td>
<td>200,740</td>
<td>1,217,600</td>
<td>330,470</td>
<td>2,436,300</td>
</tr>
<tr>
<td>50,000</td>
<td>198,300</td>
<td>1,219,800</td>
<td>326,100</td>
<td>2,438,000</td>
</tr>
<tr>
<td>100,000</td>
<td>(196,200)</td>
<td>(1,210,100)</td>
<td>322,450</td>
<td>2,439,050</td>
</tr>
<tr>
<td>200,000</td>
<td>194,700</td>
<td>1,149,200</td>
<td>(319,100)</td>
<td>(2,439,300)</td>
</tr>
</tbody>
</table>

(Brackets indicate a value derived from an incomplete execution of the computer programme, see sec. 5.2.4.)

**TABLE 5.4:** Results from the Ram and Miltz Method on PVQAc.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$[\eta]_b$</th>
<th>$[\eta]_1$</th>
<th>$\overline{\eta}_w$</th>
<th>$\overline{\eta}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$b = 0.5$</td>
<td>$b = 0.8$</td>
</tr>
<tr>
<td>BDH160T</td>
<td>0.869</td>
<td></td>
<td>1.833</td>
<td>1.038</td>
</tr>
<tr>
<td>BDH500T</td>
<td>0.809</td>
<td></td>
<td>3.146</td>
<td>1.696</td>
</tr>
<tr>
<td>B3M</td>
<td>0.827</td>
<td></td>
<td>2.701</td>
<td>1.478</td>
</tr>
<tr>
<td>B4M</td>
<td>0.785</td>
<td></td>
<td>3.793</td>
<td>2.001</td>
</tr>
</tbody>
</table>

**TABLE 5.5:** Dependence of $\overline{\eta}_w$ (weight average number of branches) on $b$ for Branched PVQAc. ($\overline{\eta}_n$ values from table 4.11)
5.2.4 Influence of $n_0$

Choosing the correct value for $n_0$ (the molecular weight at which branching becomes significant) is an important consideration in the analysis. In general as the value of $n_0$ increases, the value of $M_n$ decreases, but the value of $M_w$ increases. From the calibration curves generated by the computer (figures 5.4-5.7) it can be seen that the calibrations for the branched species do not deviate from the linear calibration until a molecular weight of approximately 100,000, almost irrespective of the value of $n_0$. The higher molecular weight end of the calibration curves are shown enlarged in figures 5.8 to 5.11. These show more clearly not just how branching affects the calibrations, but also the influence of the value of $n_0$. As $n_0$ is increased the calibrations for branched species become more separated. This is therefore another reason for using the correct value for $n_0$, for the production of accurate calibration curves.

Little data is available in the literature on the onset of branching in PVOAc, but since this also depends on conversion the problem is not a simple one. Graessley and co-workers estimated the value to be about 300,000 for conversions of 41 and 71\%\textsuperscript{1}. Agarwal\textsuperscript{2} studied the effect of shear on the distribution of long chains in PVOAc and concluded that branching may be detected at a molecular weight of at least 70,000. Melville and Sewell\textsuperscript{3} gave a value of 200,000.

A further point to notice from table 5.4 is bracketed values. These refer to figures derived by the computer in cases where, though the molecular weights are no longer changing, the calculated $\eta$ does not match the measured one. The possible cause of this is too high a value for $n_0$. As $n_0$ is increased, the amount of polymer of a given sample above this value, decreases. Thus the values for molecular weights greater than $n_0$ have to be increasingly modified.
Figure 55: Calibration Curves generated by Ram and Miltz Procedure.

- Fractions and re-acetylated whole polymers
- Whole polymers (as made)

M₀ = 50,000
Figure 5.7: Calibration Curves generated by Ram and Miltz Procedure.

- Fractions and re-acetylated whole polymer
- Whole polymer (as made)

$M_0 = 200,000$
Figure 58: Calibration Curves generated by Rom and Miltz
Procedure for Mo = 20,000

- B3M, B4M, BDH160T
- BDH 500T

Linear calibration

All fractions and re-acetylated whole polymer
Figure 5.9 Calibration Curves generated by Ram and Miltz Procedure for Mw=50,000
Figure 510 Calibration Curves generated by Ram and Miltz Procedure for M₀=100,000

- B3M, B4M
- BDH500T, BDH160T

linear calibration

all fractions and re-acetylated whole polymer
Figure S11: Calibration Curves generated by Ram and Milz
Procedure for M₀ = 200,000.

- B3M/B4M
- BDH 160T
- BDH 500T

Linear calibration

All fractions and re-acetylated whole polymer

Elution volume
in order to fit \([\eta]_{\text{calculated}}\) to \([\eta]_{\text{measured}}\). If \(k_0\) is too high, no amount of modification suffices and the routine fails. There is therefore a check on \(k_0\) by considering the behaviour of the computer program.

5.2.5 Conclusions on \(R/\eta\)

The values of \(\bar{\eta}_w\) and corresponding \(V(\bar{\eta}_w)\) obtained from the \(R/\eta\) method have been plotted in figures 5.12 and 5.13. Figure 5.12 shows the \(\log \bar{\eta}_w\) vs. \(\log [\eta]\) plot with the derived Mark-Houwink equation, and figure 5.13 the shift in values, caused by the \(R/\eta\) procedure. Clearly, while the whole branched polymers have changed their positions, the reacetylated whole polymers have stayed relatively constant. This can be taken to be more evidence in favour of a lack of branching in these polymers.

Though this method has been used favourably both in this work and others, a criticism which has not been previously highlighted is the (invalid) assumption of the linearity of the \(K-H\) equation. For narrow MWD polymers this is of little consequence providing that the \(K-H\) constants have been obtained over the desired molecular weight range. For broad distribution polymers however this is inevitably going to lead to poor estimations of the molecular weights of the polymers.

5.3 Branching Parameters

Using molecular weight data for branched polymers, branching parameters (e.g. weight average number of branches \(N_{w}\)) can be calculated via equations 2.47 and 2.49. Table 5.5 gives values of
Figure 5.12: Plot of $\eta$ versus $\bar{M}_w$ for Whole Polymers and linear fractions.

- Limit of equation
- Linear
- Whole polymer
Figure 5.13: Comparison of Data for Whole Polymers from GPC and Ram and Mitz

- o data based on poly(styrene) (GPC)
- • data based on PVOAc (Ram and Mitz)
Values for the number average degree of branching \( n_n \) are also shown. Comparing \( n_n \) with \( n_w \), since it is likely that \( n_w > n_n \), the value for \( b = 0.5 \) would seem to be correct. There is evidence\(^{22,29}\) which also supports this view.

An estimate of the relative amounts of each type of branching is usually possible only if kinetic studies are undertaken\(^7,8,11\); changes in \( n_n \) on hydrolysis and reacetylation give a value for \( n_n \) of hydrolysable branches. Values of \( n_w \) are less easy to obtain by this method (section 2.3.6.1). Conversely, \( n_w \) for total branching may be obtained via the Zimm-Stockmayer equations (2.3.6.2), but values for \( n_n \) by this method apply to monodisperse species. In contrast to much previous work (Small's review\(^{29}\)), it is suggested here that branching through the acetate group (for polymers prepared at 80\(^\circ\)C) resulting in hydrolysable branching is far more important than branching at the main chain. It is accepted that hydrolysable branching is usually predominant\(^3,8,11,24\), and since the amount of branching in the polymers studied here is quite small (cf. polyethylene for example\(^{62}\)), that no permanent long branches have been detected is not necessarily anomalous. Kinetic studies put the amount of hydrolysable branching at about 70% of the total (depending on conditions). The interpretation of the data here would suggest that, though this may be the case, detection of such low degrees of non-hydrolysable branching is not possible by GPC and viscometric analysis. Considering the highest molecular weight polymer studied here; \( n_w \) for \( B^4 \) was found to be \(-4\), i.e. 4 branches per molecule. Assuming that more than 70% of these are hydrolysable leaves about 1 branch per molecule. It is hardly surprising that this remains undetected.
6. **POLY(VINYL ALCOHOL)**
6.1 CHARACTERISATION RESULTS

The intrinsic viscosity ([\eta]) of whole and fractionated polyvinyl alcohol (PVOH) was determined in aqueous solution. The results are shown in table 6.1. G.P. chromatograms are shown in figures 6.1 to 6.3 with the relevant elution volume parameters \(V(\tilde{M}_n), V(\tilde{M}_w)\) and \(V(\tilde{M}_p)\) in table 6.2. The data from tables 6.1 and 6.2 are plotted in figures 6.4 to 6.6. As in the case of PVOAc (section 5.2.2.1), the plot of \(\log[\eta]\) versus \(V(\tilde{M}_n)\) (figure 6.5) for PVOH shows best correlation of the data. All the points fall on a single line indicating that, either the method is insensitive to branching or branching is absent in these polymers.

6.2 MOLECULAR WEIGHT DATA

In order to obtain molecular weight data, the G.P.C. was calibrated with poly(ethylene oxide) (PEO) and poly(ethylene glycol) (PEG) standards as recommended. To convert data based on this calibration to true PVOH molecular weights via the universal calibration (U.C.) equation 2.55 was used. This required knowledge of the Mark-Houwink (M-H) constants for both polymers. Equation 6.1 was obtained for PEO/PEG from the literature.

\[
[\eta] = 12.5 \times 10^{-5} n^{0.73}
\]  

(6.1)

An exercise similar to that of section 5.2.2.2 was performed to obtain M-H constants for the PVOH samples under study. From the U.C. based on PEO/PEG, using the elution volume \(V(\tilde{M}_n)\), a value for \([\eta]_{M(PVOH)}\) was obtained. A value for \(M(PVOH)\) was then calculated since the value of\([\eta]\) for the samples was known (table 6.3). The
<table>
<thead>
<tr>
<th>LINEAR FRACTIONS</th>
<th>BRANCHED FRACTIONS</th>
<th>WHOLE POLYMERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLE</td>
<td>$[\eta]$</td>
<td>SAMPLE</td>
</tr>
<tr>
<td>Lf 4</td>
<td>1.076</td>
<td>Bf 3</td>
</tr>
<tr>
<td>Lf 10</td>
<td>0.798</td>
<td>Bf 5</td>
</tr>
<tr>
<td>Lf 12</td>
<td>0.585</td>
<td>Bf 6</td>
</tr>
<tr>
<td>Lf 13</td>
<td>0.592</td>
<td>Bf 7</td>
</tr>
<tr>
<td>Lf 14</td>
<td>0.435</td>
<td>Bf 8</td>
</tr>
<tr>
<td>Lf 15</td>
<td>0.392</td>
<td>Bf 9</td>
</tr>
</tbody>
</table>

**TABLE 6.1**: Intrinsic Viscosity of PVOH in Water at 25°C.
Figure 61: Chromatograms of Linear PVOH Fractions

50 elution volume  60  70
Figure 62: Chromatograms of Fractions of Branched PVOH
Figure 63: GP Chromatograms of Whole PYDH

normalised height

elution volume

BAKER

B4

B3

BDHT
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>LINEAR FRACTIONS</th>
<th>BRANCHED FRACTIONS</th>
<th>WHOLE POLYMERS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V(M_n)$</td>
<td>$V(M_w)$</td>
<td>$V(M_p)$</td>
</tr>
<tr>
<td>Lf 4</td>
<td>59.1</td>
<td>55.0</td>
<td>56.8</td>
</tr>
<tr>
<td>Lf 10</td>
<td>61.3</td>
<td>58.0</td>
<td>59.7</td>
</tr>
<tr>
<td>Lf 12</td>
<td>63.7</td>
<td>60.7</td>
<td>62.3</td>
</tr>
<tr>
<td>Lf 13</td>
<td>63.8</td>
<td>60.5</td>
<td>62.3</td>
</tr>
<tr>
<td>Lf 14</td>
<td>65.5</td>
<td>63.5</td>
<td>64.6</td>
</tr>
<tr>
<td>Lf 15</td>
<td>66.2</td>
<td>64.4</td>
<td>65.4</td>
</tr>
</tbody>
</table>

TABLE 6.2: Elution Volume Parameters of PV0H Polymers from G.P.C.
Figure 66: Elution Volume versus Intrinsic Viscosity of PVOH
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$\overline{M}_n$(PFO) (GPC)</th>
<th>$[\eta]$</th>
<th>$\overline{M}_n$(PVCH) (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lf 4</td>
<td>220,346</td>
<td>1.776</td>
<td>376,600</td>
</tr>
<tr>
<td>Lf 10</td>
<td>140,600</td>
<td>0.798</td>
<td>228,200</td>
</tr>
<tr>
<td>Lf 12</td>
<td>93,600</td>
<td>0.585</td>
<td>150,800</td>
</tr>
<tr>
<td>Lf 13</td>
<td>97,100</td>
<td>0.592</td>
<td>159,100</td>
</tr>
<tr>
<td>Lf 14</td>
<td>62,400</td>
<td>0.435</td>
<td>98,600</td>
</tr>
<tr>
<td>Lf 15</td>
<td>54,700</td>
<td>0.392</td>
<td>86,500</td>
</tr>
</tbody>
</table>

**TABLE 6.3:** Molecular Weight Data of Linear PVCH from Universal Calibration.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$\overline{M}_n$(PFOAc)</th>
<th>$\overline{M}_n$(PVCH) predicted</th>
<th>$\overline{M}_n$(PVCH) calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bf 3</td>
<td>360,000</td>
<td>184,200</td>
<td>263,100</td>
</tr>
<tr>
<td>Bf 5</td>
<td>267,700</td>
<td>136,900</td>
<td>305,100</td>
</tr>
<tr>
<td>Bf 7</td>
<td>170,700</td>
<td>87,300</td>
<td>141,900</td>
</tr>
<tr>
<td>Bf 9</td>
<td>90,700</td>
<td>46,400</td>
<td>100,600</td>
</tr>
<tr>
<td>BfM</td>
<td>100,700</td>
<td>51,500</td>
<td>101,150</td>
</tr>
<tr>
<td>BfM</td>
<td>107,400</td>
<td>54,970</td>
<td>116,700</td>
</tr>
</tbody>
</table>

**TABLE 6.4:** Comparison of Calculated and Predicted Molecular Weights of PVCH.
molecular weight of PVOH of known degree of hydrolysis may be predicted from a knowledge of the molecular weight and structure of the PVOAc from which it was made (Appendix 1). A comparison of predicted and calculated data is given in table 6.4 for some fractions. The values for \( \bar{M}_n \) (PVOAc) were obtained from chromatograms and a polystyrene calibration, via the universal calibration. Clearly, the PVOH molecular weights derived from the PEO/PEG calibration are too high. Since it has been shown that the fractions and whole reacetylated polymers are virtually free of branches, changes in structure cannot be responsible for the anomalies. Estimated polydispersity ratios for the polymers are given in table 6.5. It is considered that, regardless of the true values for \( \bar{M}_w \) and \( \bar{M}_n \), the ratio of these will be approximately constant. A re-appraisal of the method of determining molecular weights of PVOH by aqueous G.P.C. was therefore considered necessary.

6.3 THE UNIVERSAL CALIBRATION

One possibility for the cause of anomalies in molecular weight could have been incorrect \( KN \) coefficients. As previously discussed (section 5.2.2.3), the method of Weiss and Cohn-Ginsburg could be used to determine \( K \) and \( a \) since the relevant data were available. The method also requires knowledge of the constants for PEO/PEG, so, as well as equation 6.1, a second equation \( [\eta] = 39.7 \times 10^{-5} n^{0.686} \) was examined, to ensure that it was not these equations that were producing the poor results.
<table>
<thead>
<tr>
<th>LINEAR FRACTIONS</th>
<th>BRANCHED FRACTIONS</th>
<th>WHOLE POLYMERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLE</td>
<td>D</td>
<td>SAMPLE</td>
</tr>
<tr>
<td>Lf 4</td>
<td>1.91</td>
<td>Bf 3</td>
</tr>
<tr>
<td>Lf 10</td>
<td>1.67</td>
<td>Bf 5</td>
</tr>
<tr>
<td>Lf 12</td>
<td>1.59</td>
<td>Bf 6</td>
</tr>
<tr>
<td>Lf 13</td>
<td>1.67</td>
<td>Bf 7</td>
</tr>
<tr>
<td>Lf 14</td>
<td>1.37</td>
<td>Bf 8</td>
</tr>
<tr>
<td>Lf 15</td>
<td>1.32</td>
<td>Bf 9</td>
</tr>
</tbody>
</table>

**TABLE 6.5: GPC Polydispersity Ratios** *(D = \( \overline{M}_w / \overline{M}_n \)) of FVOH.*

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>MARK-HOUWINK CONSTANTS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kx10^5</td>
</tr>
<tr>
<td>PE0  (a)</td>
<td>39.7</td>
</tr>
<tr>
<td>FVOH  (b)</td>
<td>3.96</td>
</tr>
</tbody>
</table>

(a)literature values; (1)reference 109  
(2)reference 108  
(b)from Weiss/John-Ginsberg method

**TABLE 6.6: Mark-Houwink Constants for Poly(ethylene oxide) and Poly(vinyl alcohol).**
Table 6.6 shows the values of $K$ and $a$ for PVOH as determined by the Weiss-Cohn-Ginsburg method using the two different equations for PEO/PEG. These values clearly cannot be correct. Water is generally a poor solvent for PVOH and most reported values for $a$ lie in the region 0.55-0.65 depending on temperature. \(^2\)

Figure 6.7 shows a plot of universal calibration curves for PEO/PEG and PVOH based on literature values for the MH constants. \(^{110-112}\)

The hydrodynamic volume ($\eta[^1 H]$) for PEO was calculated from

$$\eta[^1 H] = 12.5 \times 10^{-5} \, \mu^{-1.78}$$ \hspace{1cm} (6.3)

using values of $\mu$ supplied with the standard polymers. Since, for PVOH, the value of $\eta$ had been measured, $\eta[^1 H]$ was obtained from

$$\eta[^1 H] = \frac{\eta^{a+1/a}}{K^{1/a}}$$ \hspace{1cm} (6.4)

The elution volume parameter used was $V(\mu)$. From figure 6.7 it can be seen that the U.C. curves are not coincidental, which offers an obvious explanation for the discrepancy in the results; the U.C. does not hold for either one or both polymers on the column used.

It has not been possible to make a thorough investigation of this phenomenon, though similar anomalies have been noted in the literature. Belenkii \(^{104}\), using sephadex gels (which have certain similarities to TSKPW gels, though the structure of the latter has not been fully revealed) found that PVOH and PEO fell below the U.C. plot for dextrans and polyvinylpyrolidone (PVP), though they were not coincident. An explanation based on the compatibility of the polymers with the column gel, was proposed. Dubin \(^{105}\), using TSKPW gel also noticed a displaced U.C. plot for PEO compared with dextrans and proteins. Various types of secondary interactive mechanisms
Figure 67: Universal Calibration Plots for PEO and PV0H

PEO: $K \times 10^5 = 12.5$, $a$ (MM constants)
PV0H: $K \times 10^5 = 94$, $a = 0.56$ (open line)
- $300$: $K \times 10^5 = 0.50$, full line
- $666$: $K \times 10^5 = 0.64$, full line

log[M]/M vs. elution volume

50 60 70 80
which may perturb the size exclusion mechanism in aqueous G.P.C. have been reviewed.\textsuperscript{103,106} It is therefore not possible in this instance to quote accurate molecular weight data for PVOH from G.P.C. analysis.

6.4 CONCLUSIONS

This work has shown that under the conditions employed, branching in PVOH is not detected by intrinsic viscosity/G.P.C. methods. Most authors\textsuperscript{5,10,24,94} have considered that, since FVOAc contains a small amount of non-hydrolysable branching, FVOH must also be branched. Little or no evidence has been put forward to substantiate these statements. The polymers used here have, however, estimated molecular weights of less than 200,000. Higher molecular weight polymers may indeed have branching densities significant enough to be measured. It has been suggested\textsuperscript{2} that a study under theta conditions should reveal most about the structure of the polymer; a true theta solvent for PVOH has yet to be identified.

It is well known\textsuperscript{117} that commercial samples of PVOH, though specified to have similar aqueous viscosities, can differ greatly in other physical properties (table 2.1). This has most often been thought to be due to branching. However, it is more likely, in the light of this work, to be due to the molecular weight, molecular weight distribution and degree of hydrolysis of the polymers. If PVOH still retains a certain amount of acetate groups (i.e. not fully hydrolysed), the possibility exists of some hydrolysable long chain branches remaining on the polymer. It has also been suggested\textsuperscript{113} that, though long chain branches may be absent in PVOH, short chain branches formed by intramolecular chain transfer may be present, and these would not necessarily be detected by viscometry (section 2.3.6.2).
Clearly, the practice of stating an aqueous solution viscosity and degree of hydrolysis as sole specifications for a commercial PVK, is neither satisfactory nor useful in predicting solution behaviour.
7. CONCLUSIONS AND RECOMMENDATIONS
Although poly(vinyl acetate) (PVOAc) and poly(vinyl alcohol) (PVOH) are by no means novel polymers, the interpretation of characterisation data of unknown or commercial samples has been largely ignored. This work has attempted to identify some of the problems involved in the characterisation of PVOAc and PVOH by gel permeation chromatography and viscometry.

The hydrolysis and reacetylation techniques commonly used with PVOAc have been shown to be mostly reliable. It is important when studying PVOH to know the extent of hydrolysis of the polymer as this greatly influences the properties of the polymer. Reliable methods of determination of the degree of hydrolysis are therefore necessary. The method of detecting hydroxyl groups by acetylation has been shown to be a difficult, time consuming technique requiring fairly noxious chemicals. A better method has been proposed, based on the hydrolysis of PVOAc, which is a simple, reliable high polymer reaction, requiring fairly innocuous chemicals and a fraction of the time to complete. The similarity between acetylation of PVOH and the determination of hydrolysis by a virtually identical reaction has been noted, and the failure of the latter explained.

As expected the decrease in $[\eta]$ of branched compared with linear polymer of the same molecular weight has been demonstrated, but it has also been revealed that demonstration of such behaviour, particularly for polydisperse samples, is strongly dependent on the molecular weight parameters used; and this in turn has highlighted the importance of correct G.P.C. calibration methods. Combined results have re-iterated the dangers of attempting to use the already empirical Mark-Houwink equation to cover extended molecular weight ranges, when it is known that the equation is not linear under such circumstances. Thus the Weiss-Cohn-Ginsberg methods of determination
of K and a are not suitable for use with polymers of broad molecular weight distribution.

The main effort of this work has been to study long chain branching in PVOAc and PVOH. Though kinetic studies have shown the existence of two types of branching\(^3,5,7,8,9\) (i.e. hydrolysable and non-hydrolysable) and have estimated the relative amounts of each, this knowledge has necessarily come from the preparation of polymers under carefully controlled conditions. Furthermore, the effects of polymerisation conditions on the various degrees of branching and branch type have also been studied, making it possible to predict the expected results of such polymerisation. Notwithstanding this, the information derived from kinetic measurements is largely of no avail to the analytical polymer scientist, when faced with the problem of analysing a polymer, the preparative history of which is probably unknown.

Previous work on PVOAc, and indeed on many polymers using combined techniques of characterisation, has mostly involved an almost arbitrary estimate of the way in which branching changes with molecular weight. It has become obvious that there is no universal parameter which holds for all samples of the same polymer type. As outlined above, polymeric structure largely depends on preparation. In this work the methods of characterisation chosen have been used many times before\(^6\) for, for example, polystyrene (PS) and polyethylene (PE). However, knowing the behaviour of model branched polymers, e.g. PS does not necessarily indicate that when this behaviour is noted, a particular structure is unambiguously involved. Fortunately, common commercial polymers, PVOAc included, are most often and easily manufactured by the free radical techniques\(^3\), leading almost exclusively to random long chain branching in the final polymer. Characterisation
techniques in this work have shown that it is better to use a method of data analysis that makes no initial assumption as to the extent of branching in the polymer, and the Ram and Hilz method has been successful in this respect.

Perhaps one of the reasons why little work has been carried out on PVOAc is the fact that, compared with for example PE, the amount of branching in PVOAc is considerably smaller. Typical values of the branching index $\lambda$, for PE (depending on molecular weight) are of the order of $10^{-4}$ and $10^{-5}$. For PVOAc this can be as low as $10^{-6}$, and with PVOH having even less branching, $\lambda$ values of $10^{-7}$ or $10^{-8}$ are not impossible, though they may be just that to detect. It has been shown here that long chain branching in PVOAc is predominantly of the hydrolysable type and that, for medium molecular weight polymers, any non-hydrolysable branching remains undetected by G.P.C./viscometry techniques.

The problems associated with the G.P.C. of PVOH have been identified as not necessarily those of the polymer alone. Problems have also been encountered in the calibration of TSKPW type G.P.C. columns using poly(ethylene oxide) (P20) standards. It has been noted that the universal calibration (U.C.) plots for these polymers are not coincident. Sufficient data has not been produced here to be able to tell whether only one or both of the polymers behave anomalously. However, similar anomalies have been reported in the literature, and since the full structure of the gel has not been revealed, it may be difficult to elucidate the actual separation mechanism. In literature reported by TSK, it has been shown that PVOH of only 86% hydrolysis elutes without distortion from PW type columns. However no molecular weight data was reported. Notwithstanding this, it must be made clear that a calibration curve can
only be applied to PVOH of a single degree of hydrolysis. It was for this reason that 100% hydrolysed PVOH was used in this work. Regardless of the problems it has been shown that PVOH of medium molecular weight has no long chain branching detectable by G.P.C./viscometric methods.

Further work in this field should include the preparation of higher molecular weight (and hence more highly branched) polymers. Though preparation of such polymers presents few practical problems, separating them into narrow fractions requires more skill. Solubility techniques become less efficient for high molecular weight polymers, but these may be overcome by use of preparative G.P.C. Very high molecular weight polymer was not used in this work for these reasons.

Characterisation of such very high molecular weight polymers presents its own problems as illustrated by PVOAcB4 (section 4.2.2). Furthermore, the higher the molecular weight, the higher is the degree of branching, this can lead to increasing ambiguity in the results, due to differences in the extent of branching. The use of more sensitive, on-line detection techniques with G.P.C. could resolve a lot of these difficulties. Low angle laser light scattering (LALLS) is a relatively new technique but has the power of measuring $R_w$ (which is more sensitive to higher molecular weights and hence branching than $R_h$), directly and absolutely. Light scattering also provides structural information which could resolve the problems of the relationship $g' = f(g)$ (equation 2.47, section 2.3.6.2). Furthermore, on-line light scattering has fewer of the problems of static LALLS since solutions are efficiently filtered by the G.P.C. before entering the detector.
A further investigation into the aqueous G.F.C. of PVOH (and PEOs) is required. Alternative G.F.C. packings could be used with on-line absolute detection in order to elucidate the separation mechanisms of the polymers. Use of PVOH of different degrees of hydrolysis could provide some useful data here.
Appendix I

Relationship Between PVAc and PVAc

A simple theoretical relationship should exist between the molecular weights of PVAc and derived PVAc providing no structural changes occur on hydrolysis (i.e. the polymer is linear or branches through the acetoxy group have been separated).

If the average degree of polymerisation of PVAc is $n$, and the hydrolysis has converted a fraction $x$ of the OAc groups to OH groups then,

$$\bar{\eta}_{pol} = nx\bar{\eta}_{OAc} + n(1-x)\bar{\eta}_{OH}$$

hydrolysed

where $\bar{\eta}_{OAc}$ and $\bar{\eta}_{OH}$ are the molar masses of the acetate and alcohol repeat units.

acetate $\bar{\eta}_r = 86$

alcohol $\bar{\eta}_r = 44$

$$\therefore \bar{\eta}_{pol} = n(x(\bar{\eta}_{OAc} - \bar{\eta}_{OH}) + \bar{\eta}_{OH})$$

$$= n(42x + 44) \quad (A.2)$$

But since $\bar{\eta}_{PVAc} = 86n$  \quad $n = \frac{\bar{\eta}_{PVAc}}{86}$

then $\bar{\eta}_{pol} = \frac{\bar{\eta}_{PVAc}}{86} (42x + 44) \quad (A.3)$

Defining the degree of hydrolysis as the percentage of functional groups which are hydroxyl groups (i.e. $100(1-x)$) gives

$$\frac{86 \bar{\eta}_{pol}}{\bar{\eta}_{PVAc}} = 42x + 44 \quad (A.5)$$
\[ x = \frac{\bar{M}_{\text{pol}}}{42} \frac{P}{P_{\text{VOC}}} - \frac{44}{42} \]  \hspace{1cm} (A.6)

\[ 1 - x = \frac{86}{42} - \frac{44}{42} \frac{M_{\text{pol}}}{P_{\text{VOC}}} \]  \hspace{1cm} (A.7)

\[ \therefore \text{degree of hydrolysis} = 100(1-x) = \frac{8600}{42} (1 - \frac{\bar{M}_{\text{pol}}}{\bar{M}_{\text{PVOAc}}}) \% \]  \hspace{1cm} (A.8)

For PVOAc completely hydrolysed to PVCH degree of hydrolysis = 100\% and equation (A.8) reduces to,

\[ \bar{M}_{\text{PVCH}} = \frac{44}{86} \bar{M}_{\text{PVOAc}} \]
REFERENCES

10. Ibid, 2781-2792.
11. Ibid, 2853-2866.
12. Ibid, 2867-2873.
   York (1953).
27. Textbook of Polymer Science, F. W. Billmeyer, 2nd Ed., Wiley,
   and Bacon, Boston (1974).
32. R. Berger, Plaste und Kautschuk, 14, 1, 11 (1967).
35. Techniques of Polymer Characterisation, P. F. Onyon, Ed. P. W.
36. F. Ibrahim and H. G. Elias, Die Makromolekulare Chemie, 26, 1
   (1964).
40. Molar Mass Measurements in Polymer Science, N. C. Billinghan,
45. Modern Size-Exclusion Liquid Chromatography, J. W. Yau et al.,

70. No. 1 in series of ref. 68.

71. Private Communication with B.D.H. Ltd.


84. J. Pannell, Polymer, 12, 543 (1971).


