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CHARACTERISATION OF VINYL CHLORIDE OLIGOMERS

by

MARTIN JOHN FORREST, Grad.P.R.I., M.Sc.

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award DOCTOR OF PHILOSOPHY of Loughborough University of Technology

1988

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I would like to acknowledge the help given to me by the technical staff of the Chemistry Department, in particular Mr. D. Wilson (Polymer Science Technician) and Mr. J. Greenfield (GC-MS operator).

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ABSTRACT

Characterisation of Vinyl Chloride Oligomers

Martin J. Forrest

A low molecular weight fraction was obtained from a mass polymerised PVC resin by using diethyl ether Soxhlet extraction followed by either preparative gel filtration or solvent fractionation. A gas chromatography - mass spectroscopy (GC-MS) analysis of this fraction revealed that, in addition to vinyl chloride (VC) oligomers, it contained a large number of other compounds, in particular a large concentration of phthalates. By using adsorption liquid chromatography it was possible to remove the phthalates, along with other contaminants having a similar or greater polarity, from the low molecular weight PVC fraction. A recycle high performance steric exclusion chromatography (HPSEC) system based on two 60 cm columns containing PL gel 5μm, 50Å packing was employed to separate the low molecular weight PVC fraction into its constituent oligomers. VC oligomers ranging from trimer to decamer were isolated in this way, there being no evidence of a dimer species. Analysis by GC-MS of both the low molecular weight PVC fraction and the isolated oligomers showed that each oligomer existed as a number of structural isomers, the quantity increasing with chain length. A high performance liquid chromatography (HPLC) system comprised of a column containing S5W silica packing and a mobile phase consisting of hexane modified with methyl tert-butyl ether (MTBE) was found to be capable of separating the VC oligomer species tetramer to heptamer into their isomeric forms. All the isolated oligomer isomers were analysed by GC-MS, and those that could be collected in a sufficient mass by 1H nuclear magnetic resonance (NMR) spectroscopy. The MS results did not yield
much information on the structure of the oligomer isomers but partial and, in some cases, complete characterisations were possible by NMR.

The analytical techniques that had been developed to characterise the oligomers present in the mass polymerised PVC resin were applied to two other materials: a suspension polymerised PVC resin and PVC bottles produced from a commercial formulation based on suspension PVC. It was not possible in the time available to accumulate enough mass of each oligomer obtained from these two matrices for a structural characterisation to be attempted by NMR. However, the oligomer separations obtained by HPSEC did show that, with the exception of the trimer species which was not found in either material, the same oligomers were present in these two materials as had been located in the mass PVC. In addition, a comparison of the HPLC isomer chromatograms obtained for the oligomers isolated from the three PVC materials demonstrated that, on the whole, for a given oligomer, the same number and relative quantities of isomers exist. The comparative study therefore showed that the structure of the oligomers present in suspension and mass polymerised PVC resins is similar, if not identical, and that the processing stages used to produce a PVC bottle do not alter the structure of the oligomers to any great extent.
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CHAPTER ONE

Introduction

1.1 Polymerisation of vinyl chloride

1.1.1 Polymerisation kinetics (1,2)

The kinetics that apply to mass and suspension polymerisations are the same and it is these that are described here, the kinetics of emulsion polymerisation are far more complicated and will not be discussed as no emulsion polymerised poly (vinyl chloride) (PVC) was used in this work.

PVC is an addition polymer obtained from vinyl chloride monomer (VCM) by a free radical mechanism usually initiated by a labile peroxide or azo compound. The general kinetics are influenced by a significant chain transfer to monomer reaction which increases more rapidly with temperature than the chain propagation reaction. As a consequence the molecular weight of the resultant PVC is determined by the polymerisation temperature and is little affected by the initiator concentration. The polymerisation is thought to proceed by the following scheme, where I represents the initiator, R· a free radical, M a monomer molecule, M· a monomer radical, RM· a chain radical and P a polymer molecule.

Initiation

\[
\begin{align*}
I \xrightarrow{K_d} & 2R^* \\
R^* + M \xrightarrow{K_j} & RM^*
\end{align*}
\]
Rate expression:
\[ R_i = \frac{d[R_i]}{dt} = 2fKd[I] \]  \hspace{1cm} (1.1)

where \( f \) is the initiator efficiency, i.e., the proportion of initiator radicals that initiate a chain.

Propagation

\[ RM^\cdot + xM \xrightarrow{K_p} R(M)_xM^\cdot \]

Rate expression:
\[ R = -\frac{d[M]}{dt} = K_p[M][RM^\cdot] \]  \hspace{1cm} (1.2)

Termination

i) By combination

\[ RM^\cdot_x + RM^\cdot_y \xrightarrow{K_{tc}} P_{x+y} \]

Rate expression:
\[ R_t = -\frac{d[RM^\cdot]}{dt} = 2K_{tc}[RM^\cdot]^2 \]  \hspace{1cm} (1.3)

ii) By disproportionation

\[ RM^\cdot_x + RM^\cdot_y \xrightarrow{K_{td}} P_x + P_y \]

Rate expression:
\[ R_t = -\frac{d[RM^\cdot]}{dt} = 2K_{td}[RM^\cdot]^2 \]  \hspace{1cm} (1.4)
Chain transfer to monomer

\[ \text{RM} \cdot + \text{M} \xrightarrow{K_{tr}} \text{P} + \text{M} \cdot \]

Rate expression:

\[ R_{tr} = K_{tr}[\text{RM} \cdot ][\text{M}] \]  \quad (1.5)

Degree of polymerisation

An indication of the molecular weight of a polymer can be obtained by calculating the degree of polymerisation (DP). This can be defined as:

\[ \text{DP} = \frac{K_{p}[\text{M}](K_{d}[\text{I}]/K_{t})^{1/2} + 2K_{d}[\text{I}]}{K_{tr}[\text{M}](K_{d}[\text{I}]/K_{t})^{1/2}} \]  \quad (1.6)

where \( K_{t} \) is the combined termination constant, ie. \( K_{tc} + K_{td} \)

In viscous VCM/PVC solutions polymer molecule production by chain transfer to monomer will be far more frequent than production by the two termination reactions where bulky molecules are involved. This situation results in \( K_{tr} \gg K_{t} \) and so Eq. 1.6 simplifies to:

\[ \text{DP} = \frac{K_{p}}{K_{tr}} \]  \quad (1.7)

Kuchanov and Bort have obtained a value of \( 9.2 \times 10^{-3} \exp \frac{7400}{RT} \) for \( K_{p}/K_{tr} \) implying a DP of 950 (\( \bar{M}_n = 59,000 \)) at 50°C, 670 (\( \bar{M}_n = 42,000 \)) at 60°C and 482 (\( \bar{M}_n = 30,000 \)) at 70°C. Freeman and Manning have produced experimental data which corroborate these values and so confirmed that Eq. 1.7 is an accurate measure of the molecular weight achieved.
1.1.2 Polymerisation methods (6)

Commercially VCM is polymerised by a free radical mechanism using the following methods:

a) Suspension polymerisation
b) Mass, or bulk polymerisation
c) Emulsion polymerisation

Suspension polymerisation

This is the dominant technique for the production of PVC, accounting for approximately 85% of the world's name plate capacity. A typical suspension polymerisation recipe for a 10 m³ autoclave is given below.

<table>
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<th>Weight (kg)</th>
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<tr>
<td>Water</td>
</tr>
<tr>
<td>Dispersing Agent</td>
</tr>
<tr>
<td>Buffer</td>
</tr>
<tr>
<td>Initiator</td>
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<td>VCM</td>
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Polymerise at 60°C for up to 6 hours

Suspension polymerisation is a heterogeneous process consisting of a dispersed phase (VCM) and dispersion medium (water). The identity of the dispersed phase particles is maintained by vigorous stirring and the action of dispersing agents. Partially hydrolysed poly (vinyl acetate) is used extensively as a protective colloid. Because it is in a bead form the polymer is easy to isolate at the end of a polymerisation and is relatively pure. Other advantages of the process are:

1. The reaction is easily controlled. Although the process may be regarded as a myriad of mini bulk polymerisations taking place at the same time in the dispersed droplets,
the heat build-up associated with bulk polymerisations does not occur since the heat of polymerisation is dissipated by the aqueous dispersion medium.

2. The process is economical. This is due to two factors: the dispersion medium, water, is both cheap and non-hazardous; and the polymerisation can be carried to almost complete exhaustion of monomer before being stopped, whereas with bulk polymerisations the polymerisation has to be ended at ~80% conversion to avoid excessive heat build-up.

In general, suspension PVC resin particles are irregular in shape, have a mean size of 100-150 μm and have a porous structure. The resin particles possess a skin which hinders the absorption of diffusants such as plasticisers.

**Mass or bulk polymerisation**

A number of attempts have been made to produce PVC by mass polymerisation, but the only process to reach commercial status is that developed by Pechiney St Gobain (PSG), now Rhone-Poulenc Industries Limited. A large tonnage of PVC is now made by this process, the majority by a number of PVC manufacturers who are licencees of the PSG process.

Mass polymerisation has the advantage over other techniques in that the process is simple and no elaborate isolation or purification step is needed. The polymerisation is carried out in two stages. In the first, or prepolymerisation stage, only half the monomer required for the polymerisation is used and conversion is only taken to between 8 and 12%. This seed polymer is then transferred to the second stage reactor, along with additional monomer and an initiator in solution in a plasticiser, and the conversion taken to ~80%.

The polymer particles produced by mass polymerisation are the same size as for suspension polymerisation, are regular
in shape and porous. Unlike the suspension PVC resin particles they have no skin around them and so the sorption of diffusants is considerably quicker.

**Emulsion polymerisation**

In the emulsion polymerisation process the liquefied monomer is emulsified in water containing a water soluble initiator. It is, therefore, like the suspension process, a heterogeneous system. The emulsifying agent is usually present in a concentration greater than the critical micelle concentration and the polymer particles produced are less than 10 μm in diameter.

1.1.3 **Molecular weight**

It is an inherent feature of addition and condensation polymerisations that a distribution of molecular weights exists in the final polymer product. This distribution can vary very greatly depending upon the polymerisation mechanism used: ionic mechanisms giving polymers with very narrow distributions, free radical mechanisms resulting in a very broad distribution of molecular sizes? As has been mentioned, commercial PVC is produced using a free radical mechanism and so consequently, although resins are produced which differ in average molecular weight, they all possess a wide range of molecular sizes.

The molecular weight distribution (MWD) of a polymer may be characterised by utilising its average molecular weights. There are a number of average molecular weights that can be determined for any given polymer, but the two most commonly used are the number average molecular weight ($\bar{M}_n$) and weight average molecular weight ($\bar{M}_w$).

The number average molecular weight is found by dividing the total mass of polymer (M) by the total number of moles
If \( W_1 \) is the weight of the species with molecular weight \( M_1 \) then:

\[
W = \sum_{i=1}^{\infty} N_i M_i
\]  

(1.8)

and \( \bar{M}_n \) is defined by

\[
\bar{M}_n = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i}
\]  

(1.9)

A value for \( \bar{M}_n \) can be determined experimentally by using vapour pressure or osometry techniques.

The weight average molecular weight can be computed by summing up the weight contributions of each molecular species \( i \) and its molecular weight \( M_i \).

\[
\bar{M}_w = \frac{\sum_{i=1}^{\infty} W_i M_i}{\sum_{i=1}^{\infty} W_i} = \frac{\sum_{i=1}^{\infty} W_i M_i}{\sum_{i=1}^{\infty} W_i}
\]  

(1.10)

\( \bar{M}_w \) is determined in the laboratory by using light scattering or ultracentrifugation techniques.

By using the two expressions for the number and weight molecular weight averages the width of the MWD is characterised by the polydispersity \( (\bar{M}_w/\bar{M}_n) \).

\[
\frac{\bar{M}_w}{\bar{M}_n} = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i} \bigg/ \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i}
\]  

(1.11)
The value of the polydispersity gives an insight into the molecular weight range existing in the polymer, being unity for a completely homogeneous polymer and 2 for a most probable distribution. Figure 1.1 shows a typical molecular weight distribution for a free radical polymerised PVC resin. It can be seen that, although they are not in great abundance, oligomers are present.

The molecular weights for most commercial PVC polymers are in the range $M_w = 100,000 - 200,000$; $M_n = 45,000 - 64,000$. The polydispersity is usually about 2, although it may be larger for the higher molecular weight grades. For commercial purposes the molecular weight is usually characterised from measurements of the viscosity of dilute solutions. For dilute solutions, the relationship between the viscosity and the molecular weight (in this case the viscosity average molecular weight ($M_v$)) is given by:

$$[\eta] = K^1 M^\alpha$$  \hspace{1cm} (1.12)

where $K^1$ and $\alpha$ are constants
- $M$ is the molecular weight ($M_v$)
- $[\eta]$ is the intrinsic viscosity

The intrinsic viscosity is found by plotting $(\eta - \eta_0)/\eta_0 c$ against $c$, where $\eta$ is the viscosity of the polymer solution, $\eta_0$ is the viscosity of pure solvent and $c$ is the polymer concentration, and noting the extrapolated value at zero concentration.

It is common practice to characterise the molecular weight of a PVC resin by its Fikentscher $K$-value rather than quote an actual figure for molecular weight. The $K$-value is found by using the following equation:
\( \bar{M}_n = 34,400 \)
\( \bar{M}_w = 68,800 \)

**Figure 1.1**

*Typical Molecular Weight Distribution of a Free Radical Polymerised PVC Resin*

Molecular Weight Data obtained by HPSEC
\[
\log_{10} \eta_{\text{rel}} = \left[ \frac{75K^2 \times 10^{-6}}{1+1.5Kc \times 10^{-3}} \right] + (K \times 10^{-3}) \quad (1.13)
\]

where \( \eta_{\text{rel}} = \text{relative viscosity} = \frac{\eta}{\eta_0} \)
\( K = \text{K-value} \)
\( c = \text{polymer concentration in g/100 ml} \)

The K-value is a measure of the molecular weight, the lower the K-value the lower the molecular weight. A disadvantage in using the K-value is that it varies depending on the solvent and concentration used. This has led people to use the ISO viscosity number in preference to the K-value. Table 1.1 gives K-values and ISO numbers for a range of molecular weights.

1.1.4 Removal of VCM from PVC Resins (9)
The kinetics of the polymerisation of VCM are such that it is impossible to polymerise all the VCM to PVC because the rate of polymerisation falls rapidly at high conversion. As a consequence, the PVC resin that results from each of the polymerisation processes contains substantial quantities of unreacted VCM. Because of the toxicity of VCM (Section 1.8.), the residual level present in the resin must be reduced dramatically. The way in which this is done is dependent on the polymerisation process concerned.

**Stripping VCM from suspension PVC**
The unreacted VCM is removed in two stages:

i) After polymerisation to the normal 80-90% conversion the remaining VCM is vented from the autoclave either to a gas holder at atmospheric pressure or to the inlet of a gas compressor when the effective pressure is
### Table 1.1  Molecular weight characterisation of PVC

<table>
<thead>
<tr>
<th>Average Molecular Weight</th>
<th>ISO/R174 - 1961 (E)</th>
<th>K - Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight Number</td>
<td>Viscosity Number</td>
</tr>
<tr>
<td>54,000</td>
<td>26,000</td>
<td>57</td>
</tr>
<tr>
<td>70,000</td>
<td>36,000</td>
<td>70</td>
</tr>
<tr>
<td>100,000</td>
<td>45,500</td>
<td>87</td>
</tr>
<tr>
<td>140,000</td>
<td>55,000</td>
<td>105</td>
</tr>
<tr>
<td>200,000</td>
<td>64,000</td>
<td>125</td>
</tr>
<tr>
<td>260,000</td>
<td>73,000</td>
<td>145</td>
</tr>
<tr>
<td>340,000</td>
<td>82,000</td>
<td>165</td>
</tr>
</tbody>
</table>
higher. Both of these techniques result in PVC resins containing approximately 3% of unreacted VCM.

ii) The residual level of VCM is reduced to the permissible limit (Section 1.8) by purging the aqueous PVC slurry with steam. The steam heats the slurry up to temperatures between 80 and 120°C and then the resulting steam/VCM mixture is drawn off and separated using a condenser. It is possible to reduce the level of VCM in PVC resins to less than 1 ppm using this technique.

**Stripping VCM from mass PVC**

The elimination of the aqueous phase removes one of the rate controlling steps, namely, the transfer of VCM from the PVC particles to the water and from there to the gas space. The absence of any water and, hence, steam to act as a carrier gas, means that removal of the VCM is dependent on the quality of the vacuum achieved. Because it is not easy to obtain a very good vacuum economically on a large scale, higher, although still acceptable, residual levels of VCM are present in mass resins compared to suspension resins.

**Stripping VCM from emulsion PVC**

The same basic stripping techniques that are used for suspension PVC apply to emulsion PVC. The small size of the particles means that the loss of VCM from the particles by diffusion is rapid. However, this advantage is far outweighed by the difficulties arising from the tendency of the latex to foam, due to its low surface tension, and to coagulate under the influence of shear forces. Emulsion PVC normally has a VCM level of less than 150ppm w/v after stripping, but drying and milling operations reduce this to 10 ppm.
In each case the procedures used to strip VCM from the PVC resin will also reduce the concentration of VC oligomers, particularly the lower species such as dimer and trimer, ie. a VC dimer analogue, 1,3 dichlorobutane, has a boiling point of 136°C.

1.2 Fractionation of polymers by solubility

1.2.1 Introduction
Almost invariably the composition of a polymeric substance is not homogeneous. The macromolecules that constitute a particular polymer can vary from one another in four respects: molecular weight, chemical composition, molecular configuration and molecular structure. The fact that all polymers possess, to a greater or lesser degree, a molecular weight distribution has already been discussed in Section 1.1.3. It is one of their fundamental properties and exerts a powerful influence on all other properties of the polymer, both in solution and in the solid state. The existence of chemical composition heterogeneity results from the synthesis of such materials as random, block and graft copolymers, and the various transformation reactions which can be carried out on a polymer. Molecular configuration, or tacticity, heterogeneity manifests itself in the varying amount of crystalline and amorphous material present in a polymer. The last category, molecular structure, refers to the differing degrees of branching possessed by the molecules of a given polymer.

1.2.2 Polymer solubility
Applying thermodynamics to polymer-solvent systems allows predictions to be made as to whether a given liquid will be a solvent or a non-solvent for a stated polymer. For a polymer to dissolve in a liquid at a fixed temperature the free energy change in Eq.1.14 must be negative.
\[ \Delta G = \Delta H - T \Delta S \]  

(1.14)

where \( \Delta G \) is the free energy change; \( \Delta H \) is the enthalpy change; \( T \) is the temperature; and \( \Delta S \) is the entropy change on mixing. Assuming that there is no volume change on mixing, \( \Delta S \) will be positive and so therefore favour mixing, although it will be lower than the ideal entropy of mixing for two liquids. As a consequence, dissolution depends upon the sign and magnitude of \( \Delta H \). If specific interactions take place between the molecules of the polymer and liquid, e.g. hydrogen bonding, then \( \Delta H \) may be negative. For less polar liquids \( \Delta H \) will be nearly always positive and so its value must be less than \( T \Delta S \) for dissolution of the polymer.

It has been shown by Hildebrand and Scott\(^{10}\) that in the absence of specific interactions

\[ \Delta H = V_m \left[ \left( \frac{\Delta X_1}{V_1} \right)^{\frac{1}{2}} - \left( \frac{\Delta X_2}{V_2} \right)^{\frac{1}{2}} \right]^2 a_1 a_2 \]  

(1.15)

where \( V_m \) is the total volume of the mixture; \( \Delta X \) is the energy of vaporisation; \( V \) is the molar volume; \( a \) is the volume fraction; and the subscripts 1 and 2 represent the liquid and polymer respectively. The expression \((\Delta X/V)^{\frac{1}{2}}\) is regarded as the solubility parameter and is usually given the symbol \( \delta \). Substituting \( \delta \) into Eq. 1.15 gives

\[ \Delta H = V_m (\delta_1 - \delta_2) a_1 a_2 \]  

(1.16)

It can be seen from Eq. 1.16 that when \( \delta_1 \) is equal or very similar to \( \delta_2 \) \( \Delta H \) will be zero or almost zero and it follows from Eq. 1.14 that the liquid will be a solvent for the polymer. It is therefore possible to be guided as to which
liquids will be solvents for a given polymer by consulting solubility parameter data." The solubility parameter defines only the heat of mixing of liquids or amorphous polymers. A noncrystalline polymer will, therefore, dissolve in a solvent of similar \( \delta \) without the need of solvation, chemical similarity, association or any specific interaction. The high entropy change that results from the dissolution of polymers is sufficient reason for it to occur.

To date only amorphous polymers have been considered. If the polymer is of the nonpolar crystalline type then even a liquid having exactly the same solubility parameter will not be a solvent for it at room temperature. However, as the temperature is raised and approaches the crystalline melting point \( (T_m) \) then the solvent becomes effective.

Most polar crystalline polymers also have no solvents at room temperature, but there are some exceptions. It has been possible to find solvents for the nylons, PVC and the polycarbonates due to specific interactions, for example hydrogen bonding that occurs between the polymer and the solvent.

Another parameter which is important in theoretical studies of polymer-solvent systems is the polymer-solvent interaction parameter. The polymer-solvent interaction parameter is a semiempirical constant which gives a measure of the solvating power of a given liquid for a polymer. It is given the symbol \( \chi \) and was originally introduced in the independent studies of the statistical thermodynamics of polymer solutions carried out by Huggins and Flory. A number of equations have been employed to define this parameter. An example is:

\[
\chi = \frac{ZAW}{KT} \tag{1.17}
\]
where $Z$ is the lattice coordination number (normally in the range 6-12); $\Delta W$ is the interaction energy between the polymer and a solvent molecule; $K$ is Boltzmann's constant; and $T$ is the absolute temperature.

1.2.3 **Methods of fractionating polymers by solubility** (12,13)

There are a number of ways in which polymers can be fractionated by solubility. The techniques used in this work were variations of the fractional precipitation and fractional solution methods.

**Fractional precipitation**

There are three ways in which this method can be carried out:

a) **Addition of nonsolvent** The successive precipitation of polymer species from a solution by the addition of a miscible non-solvent. The larger molecules precipitate first.

b) **Lowering the temperature** The successive precipitation of polymer species from a solution by controlled cooling. The larger molecules precipitate first.

c) **Solvent volatilisation** The successive precipitation of polymer species from a solution of the polymer in a solvent/nonsolvent mixture by controlled evaporation of the more volatile solvent. The larger molecules precipitate first.

**Fractional solution**

This method can be carried out in the following ways:

a) **Direct extraction** Direct and successive extraction of a polymer with a liquid of increasing solvent power. The small molecules are extracted first.

b) **Film extraction** A metal foil is given a thin coating of polymer and then cut into strips. The strips are extracted
successively with solvent/nonsolvent mixtures of increasing solvent power. The small molecules are extracted first.

c) Extraction of a coacervate The successive extraction of polymer species from a coacervate. The small molecules are extracted first.

1.2.4 Fractionation of PVC by solubility

Commercial PVC is about 55% syndiotactic and as a consequence has been shown by X-ray diffraction methods to be about 5% crystalline\textsuperscript{14}. The solubility parameter of PVC is 9.5 (cal/cm\(^3\))\(^{1/2}\). As has been mentioned in Section 1.2.2, PVC does have very limited solubility and the only solvents that are effective are those which are capable of interacting with the polymer. It is believed that PVC behaves as a weak proton donor and therefore effective solvents are weak proton acceptors, for example THF and methyl ethyl ketone. A comprehensive list of solvents and nonsolvents for PVC at ambient temperatures is available\textsuperscript{11}. PVC has been fractionated to enable the following studies to be carried out.

Characterisation of VC oligomers

The only published structural characterisation work carried out on VC oligomers obtained from commercial base resins is that produced by Gilbert et al\textsuperscript{15-19} of the MAFF Food Laboratories in Norwich, UK. Diethyl ether Soxhlet extraction was used to obtain a low molecular weight PVC fraction from which VC oligomers were isolated using various chromatographic techniques. Partial characterisation of some of the oligomers was achieved using GC-MS and \(^1\)H NMR.

Characterisation of defect structures in PVC and their relation to stability

It is known that PVC starts to degrade at much lower temperatures than model compounds representing an 'ideal'
PVC chain structure. It is generally accepted that defect structures in the PVC act as initiation sites for dehydrochlorination. The concentration of these defect structures is greatest in low molecular weight fractions of PVC and so such fractions are used to facilitate spectroscopic characterisation of such anomalies. Most of the structural defect studies discussed in Section 1.5 have as an initial step a fractionation procedure based on solvent fractionation techniques. Low molecular weight PVC fractions are also used to obtain information on the thermal stability of PVC and the relative importance of the structural defects as sites of initiation of dehydrochlorination.

**Polymerisation studies**

It has helped in the study of the polymerisation kinetics of PVC to know the molecular weight distribution obtained at different degrees of conversion. Pezzin et al. fractionated, using THF-water mixtures, PVC samples produced by suspension polymerisation that varied in conversion from 4 to 94%. From these fractions it was possible to determine the molecular weight distribution of each polymer. This type of study has also been carried out on emulsion polymerised PVC samples.

1.3 **Steric exclusion chromatography**

1.3.1 **Introduction**

Porath and Flodin were the first to effectively demonstrate that macromolecules could be separated according to their molecular size by their degree of penetration into the pores of a stationary packing. They used highly swollen soft dextran gels (Xerogels) which had poor mechanical properties and so could not be used at high pressures and fast flow rates. This disadvantage was overcome by Moore who introduced rigid, porous semi-crosslinked polystyrene gels (Xerogel-Aerogels) which could be used at high pressures and fast flow rates. It was Moore who introduced the term gel permeation chromatography.
(GPC) for separations carried out on such gels. Rigid packings (Aerogels) were also developed to fractionate polymers; they included glass particles having uniform pore sizes which were introduced by Haller\textsuperscript{24} and porous silica\textsuperscript{25}. Recently, the term steric (or size) exclusion chromatography (SEC) has been gaining acceptance at the expense of GPC, due to its more accurate description of the separation mechanism. Today, there are two distinct forms of SEC: high performance SEC (HPSEC) and gel filtration. In HPSEC columns containing microparticulate (10 or 5 \( \mu \)m diameter) Aerogel-Xerogels are used in conjunction with high performance solvent delivery pumps. Separations are carried out at eluent flow rates of \( 1 \text{ cm}^3 \text{min}^{-1} \) at pressures in excess of 1000 p.s.i. With such systems high separation efficiencies are achieved in a short (<40mins) time. With columns containing 5 \( \mu \)m diameter packing, efficiencies as high as 70,000 theoretical plates per metre (Section 1.3.2) can be achieved. Because Aerogel-Xerogels are semi-rigid there is a limit to the amount of back pressure that they can withstand and so there is a finite limit to the length of gel bed that can be utilised for a separation carried out on a standard system. If a sample contains a large number of components the limited peak capacity (Section 1.3.2) of SEC columns can be overcome by using a recycle technique. This modification to the standard HPSEC system involves the use of a switching valve which diverts the analyte away from the outlet and recycles it through the column(s). The two main types of techniques used are the alternate pumping recycle technique\textsuperscript{26} which has been used in this work, and the closed loop technique\textsuperscript{27}. For preparative work HPSEC columns are available that can handle in excess of ten times the maximum loading time of analytical columns. These columns have much larger internal diameters, eg. 25mm, and are very expensive.
Gel filtration, in comparison to HPSEC, is a low performance technique in that the separations take longer and the columns are less efficient. Gel filtration columns are usually packed under gravity using slurry packing techniques and are often operated under gravity. The packings are polydisperse with respect to particle diameter, eg. 200-400 mesh, unlike HPSEC packings and are of a much larger diameter. The advantages of gel filtration are that the columns are cheap and can withstand high (>200mg) loadings. They are therefore ideal for accurately fractionating polymers and low molecular weight polymer extracts. The packings for both gel filtration and HPSEC are available in a range of pore sizes. The pore size of the packing dictates the molecular weight range over which the packing will perform satisfactorily. The detector employed most commonly in SEC is the refractive index, or differential refractometer, detector.

1.3.2 Theory of SEC

Separation mechanism

The separation of a solute of given size in solution is determined by a distribution coefficient $K_D$ which relates to the volume of solvent that is accessible within the porous gel particles to this solute. The retention volume $V_R$ of this solute, calculated from the point that the sample is applied to the column to the volume that corresponds to the maximum peak height, is given by:

$$V_R = V_0 + K_D V_1$$

where $V_0$ is the volume of the mobile phase which is accessible to all molecules (the interstitial or void volume); and $V_1$ is the volume of the solvent in the porous gel particles. At slow flow rates an equilibrium distribution of solute between the two phases takes place enabling the
dependence of $K_D$ on $V_R$ as a function of solute size and the size distribution of the pores within the swollen gel particles to be calculated using statistical thermodynamics. The following expression has been derived for both rigid and flexible coil molecules using a simple model.

\[ K_D \propto \exp \left(-\bar{L}/2\right) \] (1.19)

where $\bar{L}$ is defined as the mean external length of the solute. Very large molecules have a coil volume greater than the gel pores and so are excluded, ie. $K_D=0$. Very small molecules have free access to both the stationary phase solvent in the pores and the mobile phase, ie. $K_D=1$. When solvent is pumped down the column the large molecules are eluted first followed by molecules of decreasing size which have penetrated deeper into the pores of the particles and so have occupied an increasing fraction of the stationary phase solvent present in the gel particles. This is demonstrated in Figure 1.2 which shows an example of a size exclusion calibration curve.

**Column efficiency**

The efficiency of a column can be determined by the degree of peak broadening that it produces. The efficiency can be expressed in plate numbers and is found using the equation:

\[ N = \left[ \frac{4V_R}{W} \right]^2 \] (1.20)

where $N$ is the plate number; $V_R$ is the retention volume of the solute; and $W$ is the peak width, expressed as a volume, at its base. A low molecular weight standard is normally used to evaluate the efficiency of a column. The efficiency of a column depends upon a number of variables, examples are: gel type, eluent flow rate, particle size and shape, and column packing.
Figure 1.2

Calibration Curve for a Size Exclusion Separation

TE = Total Exclusion
PP = Partial Penetration
TP = Total Penetration
Resolution

If a separation is carried out on a sample containing two constituents, the resolution, R, of the two components is given by:

\[
R = \frac{(V_2 - V_1)}{W_1 + W_2}
\]  

(1.21)

where \(V_1\) and \(V_2\) are the peak elution volumes of compound 1 and 2 respectively; and \(W_1\) and \(W_2\) are the base line volumes of the two peaks. The separating power of a column is dependent upon the packing and its pore size distribution, gel capacity or solvent regain \((V_1/V_0)\) and on the column length. In SEC, resolution is restricted by a limited peak capacity due to the fact that the analyte must elute within the total exclusion and total permeation volumes, ie. \(K_D\) is always between 0 and 1. The number of components, \(n\), that can be resolved in one separation is given by:

\[
n = (1 + 0.2N^{1/2})
\]  

(1.22)

where \(N\) is the column efficiency in terms of number of plates.

Dispersion mechanisms

The degree of dispersion of the solute in the mobile and stationary phases affects the efficiency of a chromatographic column. The dependence of the column efficiency, \(H\), on the linear flow rate, \(\mu\), has been investigated and the following relationship proposed for monodisperse polymers.

\[
H = 2\lambda dp + [R(1-R)\mu dp^2/3OD_s]
\]  

(1.23)

where \(\lambda\) is a constant which is dependent on the packing and numerically close to unity; \(dp\) is the particle diameter; \(R\) is the ratio of solute zone velocity to mobile phase velocity;
and $D_s$ is the diffusion coefficient of the solute in the stationary phase. The two terms that make up the equation relate to two different dispersion mechanisms. The first term represents an eddy diffusion mechanism in the mobile phase, in which some solute molecules are present in mobile phase currents that move directly between the gel particles and others in currents that are obstructed by particles and have to circumnavigate them. The second term represents solute dispersion due to incomplete mass transfer in and out of the stationary phase, i.e. some solute molecules are left behind in the stationary phase. Equation 1.23 dictates that column efficiency will increase as gel particle size, eluent flow rate and solute size decrease.

The efficiency of a column, $H$, is related to the number of plates, $N$, as follows:

$$ H = \frac{L}{N} \quad (1.24) $$

where $L$ is the length of the column.

1.3.3 Separation of oligomers by SEC

In recent years there has been a rapid increase in the use of HPSEC for separating small molecules and oligomers. The technique has been used to make qualitative comparisons between samples, to isolate fractions for subsequent characterisation by spectroscopic techniques, and to perform quantitative analyses. The uncertainty in quantitative analysis and repeatability of retention volumes for small molecule analysis by SEC have been studied and were found to be 1% and 0.3% respectively. To achieve the best separations, columns should be used that contain small (5-10 μm) diameter particles having the smallest (50 Å or 100 Å) pore sizes. It is possible to use both microparticulate organic and rigid silica microparticle packings.
Gel filtration columns do not have the efficiency to isolate individual oligomer species from one another but they have been used very successfully by Gilbert et al to separate a VC oligomer fraction from a commercial PVC base resin (Section 1.8). In the same work programme a VC tetramer was isolated from a VC oligomer fraction by HPSEC and partially characterised by GC-MS and $^1$H NMR.

Polystyrene standards have been used extensively to characterise and evaluate liquid chromatography systems and there has been a lot of work published on them. There are three reasons for their popularity: they are readily available; they are relatively stable; and the molecule contains a strong chromophore, making detection easy. If the correct system is chosen it is possible to separate the lower molecular weight standards into their constituent oligomers. Mori$^{28}$ separated a polystyrene 600 standard and then, by a number of different methods, calculated its actual average molecular weight. In one method a recycle technique was employed and the 600 standard separated into 13 peaks, corresponding to the oligomer species dimer to tetradecamer. Fujishige et al$^{29}$ used recycle HPSEC to isolate the oligomer species dimer to pentamer from a polystyrene 600 standard (Figure 1.3) and then, after determining the purity of each collected fraction by reinjecting it into the same system, characterised the oligomers using 60MHz $^1$H NMR. Nakamura et al$^{30}$ used polystyrene standards to investigate the resolving power of Shodex KF800 series SEC columns. The columns were packed with resilient, porous styrene-divinyl benzene copolymers of particle size 4-8μm, which are considered to be capable of withstanding higher pressures than chemically similar gels. HPSEC columns from the same series were used by Ishiguro et al$^{31}$ to separate the oligomers present in a polystyrene 474 standard and Epikote 1001, an epoxy resin. Good resolution of
Figure 1.3

Separation of a Polystyrene 600 Standard by Recycle HPSEC according to Fujishige and Ohguri (29)

Chromatographic conditions: Chromatograph: J.A.I. Model LC-08; Column: 20 mm x 2.4 m JAI-Gel-2; Eluent: Chloroform; Flow Rate: 3 ml min⁻¹; Detector: Refractive Index; Sample Size: 810 mg.
oligostyrenes up to a degree of polymerisation of 12 was obtained in under two hours with a column system consisting of two sets of four 30 cm long columns connected in series having exclusion limits of $5 \times 10^3$ and $2 \times 10^4 \text{ g mol}^{-1}$, respectively. A similar column system was used to fractionate the epoxy oligomeric compound into fourteen oligomer species. The effect that the eluent flow rate had on the separation of the styrene oligomers was also evaluated; an increase in resolution being observed as the flow rate decreased.

The use of poly(ethylene terephthalate) (PET) in refrigeration compressors results in PET oligomers being present in the refrigeration oil. Shiono studied the PET oligomers that were present in both used refrigeration oils and PET film on a HPSEC system consisting of four columns containing 40, 250, 1500 and 10,000 Å pore size packings. The following types of oligomer were identified: cyclic dimer, trimer, tetramer and pentamer; and a cyclic dimer containing one diethylene glycol unit and bis(2-hydroxyethyl) terephthalate. A preparative SEC system was also used to isolate a cyclic trimer from PET film extracts.

Birley has employed HPSEC with infrared detection to characterise phenol-formaldehyde prepolymer (Novolaks). The separations were studied by monitoring the phenolic hydroxyl group at 3400 cm$^{-1}$. Preparation gel filtration has been used by Birley et al. to fractionate poly(propylene terephthalate) prepolymer. The fractions were collected and analysed by $^1$H NMR. The infrared detector response was interpreted quantitatively to deduce the concentration of each oligomer present in the prepolymer.

HPSEC with infrared detection has also been utilised by Mori to study the oligomers present in oligoethylene glycol.
sebacate (OEGS). Infrared sensitive functional groups were attached to the ends of the oligomers in order to characterise the end groups of the OEGS as a function of molecular size.

Two recent studies have been carried out on polyurethane and its intermediates. The identification of oligomers in the reaction of polyols with isocyanates has been carried out by Sebenik et al.\textsuperscript{36} using HPSEC in conjunction with \textsuperscript{13}C NMR. The results enabled kinetic and mechanism schemes to be derived for the reaction.

Noel and Van Gheluwe\textsuperscript{37} analysed an industrial polyether-polyol mixture used for the manufacture of polyurethane foams by HPSEC and were able to quantitatively analyse the oligomers present.

A sensitive detection technique has been developed by Warner et al.\textsuperscript{39} for the SEC (both gel filtration and HPSEC) analysis of poly(oxy 1,2 ethanediyl) oligomers (POE's). The technique involves attaching a solid-phase complexation column, containing ammonium cobaltothiocyanate (ACTC) adsorbed on a solid support, to the outlet of the SEC column. Upon analysis a POE-ACTC complex is produced which can be sensitively detected by a UV/visible photometer set at 320 or 620 nm.

Mori\textsuperscript{39} has addressed the problem of universal calibration for the analysis of small molecules by SEC. The geometrical shapes of molecules in solution were assumed to obtain universal calibration graphs. The approach was applied to varied small molecules and the oligomers of styrene and ethylene, good correlations being observed.

A technique that has been extensively used to study oligomers is micro-SEC. The columns used in this work are packed with
conventional SEC gels but have very small internal
diameters (e.g. 0.35mm). With a number of these columns
connected in series very high efficiencies can be achieved
and a 2m x 0.35mm combination column has been shown to give
better resolution of oligomers than a conventional
1m x 8mm SEC column. Mori\textsuperscript{14-16} has used this technique to
study the oligomers of styrene, epoxy resin, phenol-
formaldehyde resin and methylated melamine-formaldehyde
resin.

1.4 The separation of oligomers

1.4.1 Introduction

The application of HPSEC to the task of separating oligomer
species in low molecular weight polymer fractions and
standards has already been discussed in Section 1.3.3. A
number of other chromatographic techniques have also been
used to achieve the same result. A widely used technique
for the separation of oligomers is high performance liquid
chromatography (HPLC). Both reversed phase and normal
phase HPLC have been employed, with good separations being
achieved in both cases under either isocratic or gradient
elution conditions. If the oligomers of interest have
sufficient thermal stability and are volatile enough then
gas chromatography (GC) can be employed. Although not ex-
tensively used for oligomer analysis, thin layer chroma-
tography (TLC) has been evaluated for the separation of
oligomer standards. One technique which is increasingly
used to separate oligomers is supercritical fluid chromato-
graphy (SFC). SFC is a powerful separating technique which
can be used to analyse substances that are not amenable to
GC analysis.

Although most of the published work has been concerned with
the separation of oligostyrenes, a variety of other
oligomer species have also received attention.
1.4.2 HPLC

The theoretical relationships used to determine the performance of a liquid chromatographic system are independent of the separation mode being used. Hence, the equations and discussion presented in Section 1.3.2, except those specifically pertaining to SEC, i.e. Eq. 1.23, also apply to HPLC.

HPLC has undergone rapid development over the past 15 years, so that today rapid, efficient separations can be achieved. Such improvements have been brought about by reducing the packing particle size (3-5μm particles are most commonly used today) and particle size range, together with improvements in column packing technology. In order to increase the versatility of the technique, procedures have been developed to bond a variety of phases/groups onto the surface of the silica packing. This has enabled the chromatographer to vary selectivity by choosing different bonded phase packings in addition to changing the mobile phase composition. In general, the four types of HPLC column currently available contain the following packings: a hydrocarbon bonded phase (reverse phase HPLC), an ion exchange material, a polar bonded phase or silica. Other bonded phases which encourage specific interactions have been developed for specialised areas such as the resolution of optical enantiomers (chiral bonded phase).

Over the past few years interest has been shown in microbore HPLC columns, that is columns having an internal diameter of 1mm or less. There are three basic advantages to microbore columns: economic use of solvents; high mass sensitivity; and good temperature stability due to low heat generation coupled with good heat loss characteristics. The low consumption of solvent makes microbore HPLC systems attractive components for coupled analysis techniques in which
the solvent has to be ultimately volatilised off, for example LC-MS and LC-GC. For the same reason, microbore columns are an advantage if the incorporation of an electron capture detector into an HPLC system is desired.

The separation of oligostyrenes has been carried out by a number of workers using both reverse phase and normal phase (adsorption) HPLC. Attempts have also been made to resolve the isomers of the polystyrene trimer.

Schou et al.\textsuperscript{43} accumulated relatively high masses of individual styrene oligomers for pore size distribution determinations by separating low molecular weight polystyrene standards on a preparative non-aqueous reversed phase HPLC system. Oligomers of degree of polymerisation 1 to 9 were isolated (Figure 1.4). The purity of the preparative oligomer fractions was determined using analytical columns containing the same packing (ODS(Me\textsubscript{2})-silica).

Parris\textsuperscript{44} used a highly retentive reversed phase packing (Zorbax ODS), in conjunction with a mobile phase consisting of methanol with tetrahydrofuran as modifier, to fractionate a polystyrene 800 standard. Very good oligomer separations were achieved with a gradient elution programme of 1.4%/min. Larmann et al.\textsuperscript{45} separated a polystyrene standard of molecular weight 800 into its constituent oligomers by isocratic and gradient elution reverse phase chromatography with tetrahydrofuran - water mobile phases. The HPLC columns were packed with C\textsubscript{18} - silica having 6nm diameter pores.

Sackett et al.\textsuperscript{46} fractionated low molecular weight polystyrene standards using normal phase HPLC with hexane-methylene chloride gradients. It was demonstrated that the detail in the chromatograms could be used for 'fingerprint' indentification.
Separation of a Polystyrene 500 Standard by Preparative Reversed Phase HPLC according to Schou et al. (43)

Chromatographic conditions: Column: Jobin Yvon (4 cm I.D.) containing 135 g of ODS(Me₂)-silica; Mobile Phase: Methanol-Dichloromethane (97:3); Flow Rate: 20 ml min⁻¹; Detection: UV at 260 nm; Sample Size: 1 g.
In a theoretical paper Jandera and Rozkosna\textsuperscript{47} compared the separation of styrene oligomers on silica gel using 1,4 dioxane — n-heptane and tetrahydrofuran — n-heptane mobile phases. Both isocratic and gradient elution liquid chromatography was carried out. An expression was presented which described the dependence of the capacity factors for oligomers in normal phase chromatography both on the degree of polymerisation and on the mobile phase composition. With a convex gradient of dioxane in n-heptane at least a partial separation of individual oligostyrenes having up to 25-30 monomer units was obtained.

Mourey\textsuperscript{48} investigated the adsorption chromatography of anionically and cationically prepared polystyrene oligomers using 5 \( \mu \)m silica with n-hexane — dichloromethane mobile phases. It was found that end-group differences between the two samples produced significant differences in the retention of oligomers of equivalent size.

In another paper Mourey et al\textsuperscript{49} analysed narrow molecular weight polystyrene standards on 6 and 50 nm pore diameter silica with n-hexane — tetrahydrofuran, n-hexane — ethyl acetate and n-hexane — dichloromethane gradients. The tetrahydrofuran and ethyl acetate eluents gave separations according to the number of oligomer units and dichloromethane eluents further separated the stereoisomers of individual oligomers.

Lai and Locke\textsuperscript{50} have used normal nitrile bonded phase HPLC to separate the oligomers present in oligostyrenes of molecular weight 600 and 730 (Figure 1.5). A 0.77 ml/min gradient of iso-octane — dichloromethane was found to give better results than isocratic ratios of 12:1 and 13:1.

A team led by Rogers at the University of Georgia, U.S.A. have investigated the ability of HPLC to separate isomers
Separation of Polystyrene 600 and 730 Standards by Normal Phase HPLC (From Lai and Locke (50))

Chromatographic conditions: Chromatograph: Varian 8500 LC; Column: CN-Micropak 25 cm x 2 mm; Mobile Phase: PS 600 Isooctane–Dichloromethane (13:1), PS 730 Isooctane–Dichloromethane (12:1); Detector: Fluorescence–Excit. 270 nm, Monit. 320 nm; Flow Rate: 20 ml hr⁻¹.
of polystyrene oligomers\textsuperscript{51-56}. The following bonded phase packings were evaluated: cyanopropyl, aminopropyl, nitropropyl, alkyl, phenyl and fluorinated. In addition, the effect various mobile phases had on the separation achieved with a reversed phase (C\textsubscript{18}) HPLC column was also studied. Structural elucidation of the resolved isomer peaks was carried out by GC-MS and \textsuperscript{13}C NMR.

Van der Wal and Snyder\textsuperscript{55} have used the separation of PEG oligomers by reversed phase HPLC with acetonitrile – water mobile phases to demonstrate that UV detection at wavelengths as low as 185nm is possible in both isocratic and gradient elution modes.

Lai\textsuperscript{55} analysed a PEG 400 standard using open-tubing liquid chromatography - mass spectroscopy. A reversed phase column and methanol-water (80:20) mobile phase was used to separate the oligomers which were then characterised by the mass spectrometer. The relative abundances of the molecular ions were used to calculate the average molecular weight and the polydispersity.

Alexander et al\textsuperscript{57} demonstrated that underivatised silica and silica lightly derivatised with octadecyl groups produced better separations of oligomers of nonylphenol-oligo(ethylene glycol) than a more extensively derivatised silica packing.

Guryanova and Pavlov\textsuperscript{58} investigated the concept of polymer chromatography under 'critical conditions' which allows the separation of oligomers by virtue of their functionality. Several types of polycondensation oligomers were studied and their molecular weight distribution and functional type distribution determined.

LC-MS has been used by Lattimer et al\textsuperscript{59} to separate and characterise oligomers of styrene and 2,2,4 trimethyl 1,2-
dihydro quinoline (TMDQ). A reversed phase C$_{18}$ column was used with methanol-THF (polystyrene) or water-THF (poly-TMDQ) gradients. Oligomers containing up to 18 styrene monomer units and up to eight TMDQ Units were identified.

Van der Maeden et al$^{69}$ gave examples of oligomer separations with epoxy resins, novolak resins, poly(2,6 diphenyl-p-phenylene oxide), poly(ethylene terephthalate) and poly (ethylene oxide) derivatives. Gradient elution with various mobile phases was used in all cases in conjunction with C$_{18}$ and NH$_{2}$ bonded phase columns. The resolution obtained with gradient elution HPLC was found to be adversely affected by size exclusion effects and sample solubility.

Chromatograms obtained in the critical region (the boundary of the exclusion and adsorption separation modes) give information only on the type of functionality of the oligomers under study since separation by molar masses has disappeared. Gorshkov et al$^{64}$ separated linear oligocarbonates according to their type of functionality by using critical region HPLC. The critical point for the oligocarbonates was found for silica columns with the binary mobile phase carbon tetrachloride-chloroform. The effect of pore size on the retention volume of oligomers of different functionality under critical conditions was then investigated.

Ballistreri et al$^{62}$ analysed oligomers that had been extracted from Nylon 6 and poly(butylene isophthalate). Isocratic reverse phase HPLC was used to separate the oligomers in both cases, with the resolved chromatogram peaks identified by mass spectrometry and by comparison with known oligomer standards.
1.4.3 SFC

SFC was first reported in 1962 by Klesper et al\textsuperscript{63}, who used supercritical Freons to separate metal porphyrins.

Above its critical point a substance has a density and solvating power approaching that of a liquid but its viscosity is similar to that of a gas. Its diffusivity is intermediate between those of a gas and a liquid. These properties make supercritical fluids very useful as chromatographic mobile phases because they give the following advantages:

a) extraction and solvation effects allow the migration of materials of high molecular weight.

b) the high diffusivity confers very useful mass-transfer properties, so that higher efficiencies in shorter analysis times are possible than are achieved with HPLC.

c) the low viscosity means that the pressure drop across the column is greatly reduced for given flow rates.

d) the density of the supercritical fluid and hence the solubility and retention of different compounds can be easily varied by changing the applied pressure.

In addition to these advantages, SFC has an advantage over GC in that it can be used to analyse compounds that are thermally labile or non-volatile, and is preferable to HPLC for some work because it can be used with a sensitive universal detector (flame ionization detector (FID))\textsuperscript{64}.

The main limitation of SFC is the limited solubility of analytes containing polar groups with mobile phases such as carbon dioxide. Other limitations include the slow progress in the commercial availability of certain instrument parts and the need to inject relatively concentrated sample.
solutions on to capillary columns in order to get a signal from the detector without overloading the column by injecting large (>30 nl) volumes.  

The instrumentation for SFC may be obtained by modifying a conventional HPLC system. The mobile phase is pumped as a liquid and the pressurised fluid is preheated above the critical temperature before passing into the column via a sample injection device. The sample introduction devices for SFC are either high pressure injection valves with which the sample is introduced as a solution in an appropriate solvent, or extraction cells in which the analyte of interest is extracted from a matrix, concentrated and introduced immediately into the SFC system. The pumping system is controlled by a micro-processor to ensure precise and accurate pressure (ie. density) control and enable pressure programming (the analogy of temperature programming in GC and gradient elution in HPLC) when desired. Carbon dioxide is the most convenient mobile phase although many other fluids have been studied. The addition of small quantities of polar modifiers can drastically alter the elution behaviour of analytes. Standard HPLC columns can be used for SFC, as well as capillary columns which give greater efficiency and sensitivity. The column is placed in a chromatographic oven which is controlled isothermally or programmed above the critical temperature of the mobile phase. A number of detectors can be used with SFC, the most common being the flame ionization and UV detectors. A pressure restrictor is located after the detector to ensure supercritical conditions. It is also possible to interface an SFC system to a mass spectrometer or a Fourier transform infrared spectrometer.
Klesper and Hartmann\textsuperscript{66} designed an apparatus that was capable of being used for SFC and then used oligostyrenes to analyse its performance. The separations were carried out with n-pentane–methanol as the mobile phase and porous silica as the stationary phase. The resolved peaks were characterised by mass spectroscopy, which revealed that oligomers with a degree of polymerisation up to 45–49 were separated from a polystyrene 2200 standard. Slow upward pressure and temperature programming were found to be beneficial for the separation.

Conaway et al\textsuperscript{67} studied the effect of pressure, temperature, adsorbent surface and mobile phase composition on the SFC fractionation of oligostyrenes. With n-pentane as the mobile phase, no significant difference in the separation behaviour of the oligostyrenes was observed between phenyl or n-octadecyl bonded stationary phases. Concentrations of isopropanol modifier above 5\% v/v resulted in reduced capacity ratios of higher molecular weight oligomers. Non-linear pressure programming was found to produce a more regular elution of an oligomeric series while linear downward temperature programming was found to produce irregular elution behaviour near the critical temperature.

One of the earliest reported uses of gradient elution in SFC for the separation of oligomeric species was presented by Schmitz and Klesper\textsuperscript{68}. Three oligostyrene standards of molecular weight 800, 2200 and 4000 were fractionated on a silica column with pentane–1,4 dioxane gradients. Good separations were achieved, with oligomers up to a degree of polymerisation of 54 being resolved from the higher molecular weight standards (Figure 1.6).

Schmitz et al\textsuperscript{69} have investigated the effect that a number of mobile phase compositions have in the separation of
Figure 1.6

Separation of Polystyrene 2200 and 4000 Standards
by SFC according to Klesper and Schmitz (68)

Chromatographic conditions: Column: 25 cm × 4.6 mm LiChrosorb Si 100; Detection: UV at 262 nm; Flow Rate: 1 ml min⁻¹; Oven Temperature: 227 °C; Mobile Phase: Pentane-1,4 dioxane mixture.

--- Content of 1,4 dioxane in Mobile Phase
----- Column end Pressure
Numbers represent Degree of Polymerisation
oligostyrenes by gradient elution SFC. Alkanes and diethyl ether were used as the primary eluents, with alcohols, cyclohexane and dioxane as the secondary component. With a silica stationary phase it was found that a combination of an alkane with dioxane produced the best separations.

Work with gradient elution SFC was extended to the separation of oligomers of vinyl arene compounds by Schmitz et al. A silica stationary phase was used with n-pentane -1,4 dioxane gradients. Separations were found to occur not only with respect to degree of polymerisation, but also between sub-series of oligomeric species. SFC chromatograms showed superior separations compared with HPLC chromatograms obtained at ambient temperature using the same elution gradient.

Hirata studied the retention behaviour of samples having different polarities with silica and ODS columns and n-hexane as the eluent. Separations were also carried out with n-hexane -ethanol (90:10) as the mobile phase. The samples investigated, in order of increasing polarity, were: styrene oligomers, OV-17(poly siloxane, 50% phenyl) and Triton x-100(poly ethylene glycol-p-isoctyl phenyl ether). For a given oligomer series, the separation achieved varied markedly depending upon the column and mobile phase used.

Schmitz et al. have recently published a paper concerned with the possibilities for optimising oligomer separations with SFC. The oligomers used for the investigation were an oligostyrene 800 standard and an oligo(2-vinylnaphthalate) sample prepared by anionic polymerisation. Temperature programming was shown to be applicable if the appropriate temperature region is chosen. Optimisation strategies were also given for both pressure programmed separations and for

- 34 -
separations using gradient elution. In particular, multiple gradient techniques were demonstrated to be capable of enhancing the efficiency of oligomer separations.

Fujimoto et al\textsuperscript{73} used the buffer-memory technique for SFC-IR. The effluent from a microtubular SFC column was deposited onto a crystal of potassium bromide as a continuous band with instant mobile phase elimination. The deposited compounds were then detected and analysed by IR. This technique was used in the separation of medium polarity oligomers by a reversed phase column with hexane — ethanol (90:10) as the mobile phase. Chromatograph resolution was maintained, even for closely separated peaks, and identifiable spectra of the deposited peaks obtained.

1.4.4 GC

Of the chromatographic techniques available today GC is the most powerful separating tool. The number of plates for a given column can be calculated using the method that applies to LC columns (Section 1.3.2). GC is restricted by two factors: the sample to be analysed must be sufficiently volatile to be eluted from the chromatograph; and the analyte must possess a minimum degree of thermal stability. There are basically two types of GC column: open tubular and packed. The open tubular columns are generally longer and smaller in diameter than packed columns, the smallest diameter types being referred to as capillary columns. The conventional packed columns contain stationary phases supported on diatomaceous earths. Open tubular columns are divided into two types: wall coated open tubular (WCOT) and porous layer open tubular (PLOT). In such columns the walls of the column, made from stainless steel or fused silica, act as support. The stationary phases used in GLC (the most popular form of GC) are involatile liquids. The mobile
phase, for example helium, transports the volatilised analyte along the heated column where it interacts with the stationary phase. The separation obtained depends upon the relative solubilities and adsorption potential of the compounds with regard to the stationary phase. In GSC the stationary phase is either a surface active material or a molecular sieve. GSC offers little, if any, advantage over GLC and is of minor importance.

The temperature of the column in GC, for a given mobile phase flow rate, determines the time which a compound will take to elute from the chromatograph. For a given column held at a given temperature (isothermal GC) the retention time of a homologous series increases exponentially, as does peak width. In practice this means that if a sample consisting of a homologous series is analysed isothermally the lower members will not be completely resolved and the higher members will take a very long time to elute from the column, appearing as increasingly broader peaks. These problems can be overcome by column temperature programming, and this is the method used to analyse oligomer mixtures. Programmes are chosen so that the lower oligomers are well separated and higher oligomers appear as sharp peaks in practical analysis times.

One development that has greatly increased the usefulness of GC is the coupling of gas chromatographs to mass spectrometers. With this arrangement, use can be made of the high resolving power of GC to separate compounds in a mixture and then the compounds identified from their mass spectrum.

The standard detector used in GC is the flame ionization detector (FID), although an electron capture detector can be used for the selective detection of halogen containing compounds etc.
It is discussed in Section 1.8 how GC has been applied to the analysis of VC oligomers. In addition, Schwenk et al.\textsuperscript{74} has studied a PVC fraction of molecular weight 800, obtained by extracting a mass polymer with methanol. This fraction was then hydrogenated with Raney nickel and distilled. The initial distillate which represented 7.5% of the starting material was collected at 200°C and analysed by GC-MS. The results showed that low molecular weight paraffins in the sample consisted of a sequence of even-numbered homologs. Compounds up to C\textsubscript{24} were separated from one another.

Rama Rao et al.\textsuperscript{75} carried out a photo-initiated oligomerisation of bromotrifluoroethylene and then analysed the products using a number of spectroscopic techniques. The presence of oligomers up to pentamer was observed and the structures of these species elucidated by GC-MS.

Aldissi et al.\textsuperscript{76} employed GC-MS to investigate living oligo (ethylene) species. The ethylene oligomers were obtained using sec-butyl-lithium complexed with tetramethylethylenediamine. The reaction was deactivated by oxygen prior to GC-MS analysis. The GC-MS results enabled the structure of three types of oligomer species to be determined. The GC was capable of resolving oligomers up to C\textsubscript{28}.

A widely used application of GC-MS, and GC in isolation, is the separation and characterisation of oligomer mixtures obtained by pyrolysing high polymers. Lai and Locke\textsuperscript{77} used GC to analyse the collected pyrolysates from the stepwise pyrolysis of polystyrene. Only the monomer, dimer and trimer were found to be sufficiently volatile to be eluted from the gas chromatograph; the higher oligomers being lost.
Lewis et al. used capillary GC to separate the oligomers of a polystyrene 666 standard. With a DB-1 column and a temperature programme, oligomers up to a degree of polymerisation of 9 were separated.

1.4.5 TLC

In TLC a stationary phase of uniform thickness is supported by a solid surface. The stationary phase can be of the normal (silica or aluminium oxide) or reverse (non-polar) phase type. The flow of the mobile phase is based on capillary forces (ascending and horizontal development), a combination of capillary forces and gravity (descending development), or controlled solvent delivery provided by a pump (over pressurised TLC). In comparison with LC, TLC is less accurate, sensitive and reproducible. However, it does approach LC for selectivity and the apparatus is simpler and less complicated to use.

To get the best performance possible from a system the analyte should be spotted onto the plate with the least amount of spreading that is practically possible, i.e. the spot should be as small as possible. TLC results are presented in the form of $R_f$ values. The $R_f$ value for a given compound is numerically equal to the distance ($a$) that it has travelled up the plate from its origin of spotting divided by an arbitrary distance ($b$) set near the top of the plate which the plate is developed to.

$$R_f = \frac{a}{b}$$

(1.25)

An $R_f$ value for a given compound depends, therefore, on the activity of the plate, spot size and developing conditions and is not a definite analytical value. For this reason, calibration tests etc should be conducted at the same time and on the same plate as the analysis itself. With TLC
the selection of the mobile phase is much less limited than in LC. The only criteria is that it must be possible to remove all the solvent by drying.

TLC is one of the lesser used techniques for the analysis of oligomers, and this is reflected in the amount of work published. A number of workers have used TLC to separate oligomers of poly(ethylene terephthalate) (PET). Recently, Hudgins et al reported a number of new TLC systems used to separate individual species of three separate series of PET oligomers, namely \( (GT)_n \), \( G(TG)_n \) and \( T(GT)_n \), where \( G \) is an ethylene glycol unit and \( T \) is a terephthalate unit. Adsorption TLC was used with single and multiple direction development. Separations were achieved between oligomers of differing molar mass and also between cyclic and linear oligomers of equal molar mass. The separations were regarded as being superior to those previously reported.

Bui and Armstrong used reverse phase TLC to separate low molecular weight standards of polyisoprene, polystyrene and poly(ethylene oxide). The performance of reverse phase TLC was compared to gradient elution HPLC and SEC. It was found that TLC had from two to five times the resolving power of SEC for the molecular weight range investigated. As expected the HPLC system exhibited the greatest resolving power of the three. In an earlier paper the same workers used reverse phase TLC to separate polystyrene standards. The mobile phases evaluated consisted of mixtures of methylene chloride and methanol. By varying the composition of the developing solvent different molecular weight ranges could be focused on.
1.5 The structure of PVC

1.5.1 Introduction

Commercial, free radical polymerised PVC does not have a regular head-to-tail structure based on the repeat unit \( \rightarrow \text{CH}_2-\text{CHCl} \rightarrow \). There are a number of structural anomalies present in the polymer which have the undesirable effect of reducing its thermal stability. For this reason extensive characterisation studies have been carried out on PVC in a number of locations around the world in the past 20 years. In an effort to co-ordinate this work the International Union of Pure and Applied Chemistry (IUPAC) set up a working party in 1977 to investigate the molecular structure of PVC. This ensured that the different teams were analysing similar base resins and so enhanced the efficiency of the work. A report summarising the results of the working party has recently been published\(^8\). It has already been mentioned in Section 1.2.4 that there is a higher concentration of defects in the low molecular weight fractions than in the PVC resin as a whole. Consequently, the first step of any characterisation programme is usually the isolation of a low molecular weight fraction from a base resin by solvent extraction. Another approach to the characterisation problem has been to synthesise, and then analyse, model compounds containing those structures that are believed to be present in PVC in order to aid the interpretation of results obtained from PVC itself. The tool most frequently employed for the elucidation of the structure of PVC is NMR. The following structural defects have been located in PVC:

1. Unsaturation
2. Branching
3. Initiator end groups
4. Head-to-head structures
5. Oxygen containing structures
6. Tacticity
1.5.2 Unsaturation

There are a number of mechanisms whereby a double bond in a PVC molecule arises.

1. **Termination by disproportionation**

   \[ -\text{CH}_2-\cdot\text{CH} \rightarrow -\text{CH}_2-\cdot\text{CH}_2 + -\cdot\text{CH}=\text{CH} \]
   \[ \text{Cl} \quad \text{Cl} \quad \text{Cl} \]

2. **Chain transfer to monomer**

   \[ -\text{CH}_2-\cdot\text{CH} + \text{CH}_2=\cdot\text{CH}_2 \rightarrow -\text{CH}_2-\cdot\text{CH}_2 + -\cdot\text{CH}=\text{CH} \]
   \[ \text{Cl} \quad \text{Cl} \quad \text{Cl} \]

   \[ \text{CH}_2=\cdot\text{C} + \text{VCM} \rightarrow \text{CH}_2=\cdot\text{C}-\text{CH}_2-\cdot\text{CH}_2 \]
   \[ \text{Cl} \quad \text{Cl} \quad \text{Cl} \]

3. **Mechanism proposed by Bezadea et al.** (83)

   \[ -\text{CH}_2-\cdot\text{CH} + \text{CH}_2=\cdot\text{CH}_2 \]
   \[ \text{Cl} \quad \text{Cl} \]

   \[ \downarrow \text{head-to-head addition} \]

   \[ -\text{CH}_2-\cdot\text{CH}-\cdot\text{CH}_2 \]
   \[ \text{Cl} \quad \text{Cl} \]

   \[ \downarrow 1,2 \text{ Cl migration} \]

   \[ -\text{CH}_2-\cdot\text{CH}-\cdot\text{CH}_2 \]
   \[ \text{Cl} \quad \text{Cl} \]

   \[ \downarrow -\cdot\text{Cl} \]

   \[ -\cdot\text{Cl} \]
The concentration of double bonds in PVC has been determined by Boissel using liquid phase bromination. An incidence of $2 \times 10^{-3}$ double bonds per monomer unit was observed.

A number of workers have used NMR with spectrum accumulation to analyse the double bond content of PVC. Pethiaud and Pham studied low molecular weight ether extracts obtained from mass PVC by $^1$H NMR and unambiguously demonstrated 1,5 dichloro-3-pentyl to be the main unsaturated structure present. This type of structure was present at a concentration of 2-3 per 1000 monomer units. Another study on this type of structure has put its population at between 13 and 0.6 per 1000 monomer units, depending on the molecular weight of the sample.

Schwenk et al obtained a low molecular weight fraction ($M_n = 1500$) by extracting mass PVC with methanol and analysed it by using $^1$H and $^{13}$C NMR. In addition to 1,5 dichloro-3-pentyl, 2,5 dichloro-3-pentyl and 1,2 dichloro-ethyl structures were also found, their ratios per molecule being 2:1:5, respectively.
The presence of these three structures has been confirmed by Maddams. Hjertberg and Sorvik investigated suspension PVC samples with $^1$H and $^{13}$C NMR and found 1,5 dichloro-3-pentyl to be the main unsaturated chain end structure and 1,2 dichloroethyl the main saturated chain end structure. Other unsaturated structures were found in small quantities.

Barboiu et al. determined unsaturated end groups in low molecular weight PVC by $^1$H NMR spectroscopy of the hydroxyphenol substituted product. It was possible to distinguish between 1,5 dichloro-3-pentyl and 2,5 dichloro-3-pentyl structures, and even between their cis and trans forms.

Simak has developed an infra-red spectroscopy method to characterise the double bond content of PVC. Good agreement was found between the double bond content found this way and by the chemical method described by Hildebrand et al.

Several other chemical methods have been developed to determine the double bond content of PVC. The internal double bond concentration has been evaluated by measuring the changes in molecular weight resulting from oxidative double bond scission caused by reacting PVC with N-dimethyl acetamide. Using this method Braun and Quarge calculated 0.3 to 2.5 x $10^{-3}$ double bonds per monomer unit from the change in intrinsic viscosity. Hjertberg and Sorvik calculated that there were 0.2 double bonds per 1000 monomer units in a suspension PVC sample by measuring the molecular weight change after ozonolysis.
1.5.3 Branching

Branches can occur in PVC due to transfer reactions to the polymer during the polymerisation. A number of other mechanisms have also been proposed to account for different branch types. The principle mechanisms are:

1. **Transfer to polymer**

   \[
   -
   \begin{array}{c}
   \text{CH}_2\text{CH}_2\text{CH}_2 \\
   \text{Cl} & \text{Cl} & \text{Cl} \\
   \\
   \text{CH}_2\text{CH}_2\text{CH}_2 \\
   \text{Cl} & \text{Cl} & \text{Cl} \\
   \end{array}
   \]

   Long Chain Branch \(-\text{CH}_2\text{C-CH}_2\)

2. **Head-to-head addition followed by a 1,2 chlorine atom shift** (94)

   \[
   -
   \begin{array}{c}
   \text{CH}_2\text{CH}_2 \\
   \text{Cl} & \text{Cl} \\
   \\
   \text{CH}_2\text{CH}_2 \\
   \text{Cl} & \text{Cl} & \text{Cl} \\
   \end{array} 
   \xrightarrow{\text{VCM}}
   \]

   Chloromethyl Branch
3. Backbiting

The branching present in PVC has been the subject of much research. One method used to study branching has been to reduce the polymer and then determine the methyl content by using IR spectroscopy. This enables an estimation of the amount of branching to be made. Baker et al.\textsuperscript{55} found levels of branching in the range 1.8 to 16 per 1000 monomer units. By using high field NMR techniques Darricades-Llauro et al.\textsuperscript{86} reported 4 to 5 branches per chain of high molecular weight PVC.

Petiaud and Pham\textsuperscript{85} studied low molecular weight fractions obtained from mass PVC using high resolution $^1$H NMR and reported that the amount of branch increased with increasing molecular weight.

The mechanism for the production of chloromethyl branches in PVC was originally proposed by Rigo et al.\textsuperscript{96} (mechanism No. 2).
Starnes et al. have investigated the formation of these branches by applying $^{13}$C NMR to LiAlH$_4$ reduced PVC and have found evidence to support Rigo's mechanism.

In an attempt to investigate the possibility of butyl branches existing in commercial PVC, Hjertberg and Sorvik prepared PVC samples at subsaturation conditions (the conditions that prevail at the end of a standard polymerisation) and analysed them using $^{13}$C NMR after reduction with tributyl tin hydride. Butyl branches were found in the concentration 3.4 per 1000 monomer units.

Schwenk et al. isolated two fractions of molecular weight 1500 and 800 g mol$^{-1}$ from a mass PVC polymer, hydrogenated them with Raney nickel and then analysed them using $^{13}$C NMR. Almost 2 out of 1000 carbon atoms were found to be linked to a side chain consisting of more than five carbon atoms and 5 out of 1000 carbon atoms were methyl branched.

A paper has been published by Liebman et al. comparing the use of pyrolysis hydrogenation gas chromatography with $^{13}$C NMR for the determination of short chain branching in reduced PVC. Satisfactory agreement was found in the results obtained using both techniques.

In a recent paper Starnes presents PVC branch information obtained from the $^{13}$C NMR analysis of chemically reduced PVC. Tertiary chlorines were found to be present at all of the branch points except chloromethyl.

Recently, two reviews of branching in PVC have been published. In the first by Abbas the different techniques used to determine the branched structures in PVC were discussed and their respective efficiencies compared. Common PVC grades were found to contain 2-3 pendant chloromethyl groups and approximately 0.5 long chain branches per
1000 carbon atoms. A comprehensive examination by $^{13}$C NMR of the branch structures present in a number of PVC samples has been carried out by Starnes et al.$^{102}$ The following branches were found in varying concentrations depending on the polymer: long chain, butyl, ethyl and methyl.

1.5.4 **Initiator endgroups**

In polymerisation reactions initiator moieties are incorporated into the polymer molecules. If there are no transfer reactions during the polymerisation, at least half the polymer chain ends will carry initiator fragments. In the free radical polymerisation of VCM transfer reactions dominate the formation of dead polymer chains and less than 30% of the chain ends contain initiator residues.$^{103}$ It is obvious that the chemical nature of the endgroup containing an initiator fragment will entirely depend upon the initiator used in the polymerisation. For example, if benzoyl peroxide is used as the initiator, some of the polymer molecules will have terminal phenyl groups.

1.5.5 **Head-to-head structures**

Head-to-head units in PVC can either be formed through termination by combination or by head-to-head addition during propagation.

Mitani et al.$^{104}$ found 2.5 to 7.0 head-to-head structures per 1000 monomer units, the number increasing with the polymerisation temperature. Hjertberg et al.$^{105}$ studied various PVC samples using the chemical method followed by Mitani et al and concluded that it mainly gave a measure of the content of saturated 1,2 dichloroethyl chain endgroups. They proposed the much lower concentration of 0 to 0.2 head-to-head structures per 1000 monomer units.
It is not possible to detect internal head-to-head structures by $^{13}$C NMR spectroscopy because of its detection limit of 2 per 1000 monomer units.

1.5.6 Oxygen containing defects
Oxygen containing structures can arise in the PVC molecules either by a reaction with traces of oxygen present during polymerisation or by oxidation during storage or treatment of the polymer in air. Another prime source of oxygen is initiator residues present at the chain ends. Virgin PVC has been found by Landler and Lebel$^{106}$ to contain up to 500ppm of peroxide. In a recent study van der Heuvel and Weber$^{107}$ discovered the presence of an ethoxycarbonyloxy structure in a low molecular weight fraction of a commercial suspension PVC resin.

\[
\begin{align*}
\text{ethoxycarbonyloxy structure} \\
\| \\
\text{O-C-O-C}_2\text{H}_5
\end{align*}
\]

This structure was identified by both IR and $^1$H NMR techniques; its occurrence, calculated from $^1$H NMR data, was considered to be about 0.8 per 1000 monomer units.

1.5.7 Tacticity
Commercial PVC produced at temperatures between 50-60°C is an atactic polymer with a content of syndiotactic diads of about 50-55%. The effect that the polymerisation temperature has on the tacticity of PVC has been a subject of mild controversy. From the NMR and IR studies that have been conducted over the years, it has been concluded that PVC prepared at 100°C is virtually atactic and that decreasing the polymerisation temperature even to -78°C does not increase the syntiotactic content very significantly.$^{108}$
Simak\textsuperscript{91} used IR spectroscopy to determine the amount of crystallisable syndiotactic sequences in PVC. It was assumed that only long syndiotactic sequences of at least four monomer units are able to form crystals. This crystallisable content was found to be slightly greater than the X-ray crystallinity due to not all sequences which have a potential to crystallise actually doing so. Pham et al\textsuperscript{109} examined the tacticities of radically polymerised PVC by \textsuperscript{13}C NMR (in terms of triads and tetrads) and IR spectroscopy (in terms of diads). Sorvik\textsuperscript{110} extensively compared the quantitative evaluation of PVC tacticity by different techniques and concluded that NMR spectroscopy is a more precise method that either IR or Raman spectroscopy.

Mirau and Bovey\textsuperscript{111} have examined one and two dimensional heteronuclear \textsuperscript{1}H and \textsuperscript{13}C NMR and homonuclear \textsuperscript{1}H NMR for their usefulness in establishing stereochemical sequence assignments in PVC. Their studies showed that many of the techniques developed for small molecules are applicable to polymer systems and that complete stereochemical resonance assignments may be obtained by using a number of two dimensional experiments.

Robinson et al\textsuperscript{112} used the C-Cl stretching vibration region from the Raman spectra of PVC to determine its tacticity. The results obtained were similar to those determined by NMR. The advantage of the Raman method is that no special sample preparation technique is required; hence there is no possibility of the polymer being altered in any way.

1.6 PVC Processing

1.6.1 Introduction

PVC is one of the four most important plastics materials today; it is used in the manufacture of records, cables, furniture, windows, clothing and flooring, and has many
applications as a packaging material for the food industry where it is used in one of three forms:

a) **Bottles**
These are produced by blow moulding and blow forming and are mainly used as containers for cooking oil and squash.

b) **Rigid film**
The film is either calendered or extruded and then vacuum formed into trays and nestings for cakes, biscuits and chocolates. It is also used to provide 'windows' in box packaging to enable the food to be viewed.

c) **Plasticised film**
This is produced by blowing or calendering and is used to package fresh and cooked meats, sandwiches, fruit, vegetables and cheese.

PVC is also made use of for bottle closure liners, lacquered food cans and heat-seal aluminium foil. It is encountered in the food manufacturing processes where pipes and conveyor belts are made of PVC.

Because of the fact that 'pure' PVC is a colourless, rigid material which starts to degrade above 70°C and has a tendency to stick to metallic surfaces when heated, a wide range of additives have to be incorporated into the polymer for it to become a useful material with all the applications just described.

1.6.2 **Compounding of PVC** (113, 114)
The following additives may be present in a PVC compound:
Stabilisers

These are essential and must be present if the fabricated product is to be of any use. As previously mentioned, PVC begins to degrade at temperatures above 70°C and since it is subjected to processing temperatures between 150-200°C extensive thermal degradation will occur without stabilisers. The stabilisers that are used commercially can be grouped into the following categories:

a) Inorganic metal salts. eg. tribasic lead sulphate
b) Metal soaps of organic acids. eg. zinc octanoate
c) Metal complexes of barium, cadmium and zinc.
d) Organotin compounds.
e) Epoxy compounds.
f) Organic phosphites.

Some of these stabilisers also protect PVC products from photodegradation. Organic phosphites such as tris nonyl phenyl phosphite and butylated hydroxy toluene are used as stabilisers for the polymerisation stage.

Plasticisers

The electronegative nature of the chlorine atoms in the PVC molecules create permanent dipoles along the chains which produce high secondary valence forces. These in turn greatly reduce the flexibility of the chains and so render the unplasticised material rigid at room temperature - the glass transition temperature (Tg) of unplasticised PVC is 80°C. The incorporation of a plasticiser into a PVC polymer matrix reduces the interchain forces and results in a flexible product which has a greatly reduced Tg. In addition to this change virtually every other property of PVC is altered by the introduction of plasticisers. For example, as the plasticiser level increases there are reductions in modulus, tensile strength, hardness, density and
volume resistivity, while at the same time increases in elongation at break, toughness, dielectric constant, softness and power factor. The plasticisers themselves are essentially non-volatile solvents for PVC, having similar solubility parameters as PVC. A number of materials have the potential to be used as plasticisers for PVC, but for economic reasons phthalate and adipate esters, especially di-2-ethylhexyl phthalate (DOP) and dioctyl adipate (DOA), are mainly used commercially.

**Extenders**

Extenders are materials which are not themselves plasticisers for PVC due to their very limited compatibility with the polymer, but when incorporated along with a true plasticiser an acceptable degree of compatibility results. They are cheaper than plasticisers and can be used to replace up to a third of the plasticiser without serious deleterious effects on the properties of the compound. There are three common types of extender:

a) chlorinated paraffin waxes
b) chlorinated liquid paraffinic fractions
c) oil extracts

**Lubricants**

In plasticised PVC the main function of the lubricant is to prevent sticking of the compound to processing equipment. This is achieved by utilising a material of very limited compatibility which will 'bloom' and form a film between the PVC and the metal surfaces of the processing equipment. These materials are known as external lubricants and examples are calcium stearate for opaque products and stearic acid for transparent compounds.
With unplasticised PVC it is common to incorporate at least one other lubricant. These materials are used to improve the flow of the melt by lowering the apparent melt viscosity, hence they are reasonably compatible with the PVC. They are described as internal lubricants and examples of the type are wax derivatives, glyceryl esters, and long chain esters such as cetyl palmitate.

**Fillers**

There are a number of reasons why a filler might be added to a PVC compound. Cheap fillers, such as the various forms of calcium carbonate (whiting, ground limestone etc), are employed in opaque PVC compounds to reduce cost. If an improvement in electrical insulation is required, then china clay is used. Other uses for fillers include increasing the hardness of a compound, reducing the tackiness of highly plasticised compounds and improving the hot deformation resistance of cables.

**Pigments**

For a material to be a useful pigment it must exhibit the following properties:

a) It must not decompose, fade or plate-out under the prevailing processing conditions.

b) It should not adversely affect the functioning of the stabiliser and lubricant.

c) It must be able to withstand the conditions of service without fading or leaching out.

d) It should not adversely affect any of the important end-use properties of the compound.

**Polymeric impact modifiers and processing aids**

For some applications such as bottle and film, unplasticised PVC is too brittle and its impact resistance has to be increased by the incorporation of an impact modifier. These
materials are semicompatible rubbery polymers that normally have solubility parameters about 0.4 - 0.8 MPa$^{1/2}$ different from PVC (19.4 MPa$^{1/2}$). Polymeric impact modifiers that are used commercially today include butadiene-acrylonitrile copolymers, acrylonitrile-butadiene-styrene (ABS) graft terpolymers, methacrylate-butadiene-styrene (MBS) terpolymers; chlorinated polyethylene, ethylene-vinyl acetate - PVC graft polymers and some polyacrylates. The particular impact modifier chosen depends upon the application and the compound properties desired. For example, for bottles where high clarity is required the MBS type of impact modifier is used because it has a very similar refractive index to the PVC and so light scattering at the MBS-PVC interface is at a minimum.

Another problem encountered with unplasticised PVC is that of high melt viscosity which leads to some difficulties in processing. Polymeric additives, referred to as processing aids, are used to overcome this problem. They have a similar chemical constitution to the impact modifiers and include ABS, MBS, chlorinated polyethylene, methacrylate-acrylate copolymers and EVA-PVC grafts. They are produced in such a way to be more compatible with PVC and so ensure quicker gelation and more uniform flow.

**Miscellaneous additives**

Other ingredients can be used in PVC formulations from time to time. For example, blowing agents such as azodicarbonamide and azodi-iso butyronitrile are used to produce cellular PVC. If improved fire resistance is required then Antimony oxide is used and for the reduction of static in such products as gramophone records quaternary ammonium compounds.

In this work bottles that have been blow moulded have been used as a source for VC oligomers. An example of a bottle formulation is given overleaf.
Suspension or mass homopolymer of 150 viscosity No. 70-90
Octyltin stabiliser 2
Epoxy compound 2
Glyceryl monostearate 1
Acrylic impact modifier 5

1.6.3 Production of PVC bottles (115)

In common with other general purpose plastics materials PVC is made into many useful articles by a wide range of fabrication processes. As the only fabricated article to be used in this work was a bottle, only the production of bottles from compounded PVC will be discussed.

Unplasticised PVC offers the following advantages for the production of bottles:

a) Excellent chemical resistance and resistance to stress cracking
b) Low permeability to air, flavours and essential oils
c) High rigidity, permitting the use of thin walls
d) High clarity

The main limiting factor in the use of unplasticised PVC for bottles is that the material cannot contain high CO₂ pressures.

Four fabrication processes are used for the production of PVC bottles:

a) Extrusion blow moulding
b) Injection blow moulding
c) Stretch blow moulding
d) Blow forming from PVC foil

Parts

|Suspension or mass homopolymer of 150 viscosity No. 70-90 | 100 |
|Octyltin stabiliser | 2 |
|Epoxy compound | 2 |
|Glyceryl monostearate | 1 |
|Acrylic impact modifier | 5 |
Blow moulding is a particularly useful technique for the production of bottles because it is rapid and uses the plastics material economically. The basic principle of blow moulding is that a tube, or parison, of molten polymer is sealed at both ends and then enclosed by two halves of a hollow mould. Air is then injected into the parison, which inflates and makes contact with the cold wall of the mould. The temperature of the mould is rapidly reduced below the \( T_g \) or \( T_m \) of the polymer, which gives the formed bottle dimensional stability. The bottle is then ejected and the process repeated. The method in which the parison is produced gives the process its name, ie. if by extrusion, extrusion blow moulding; injection, injection blow moulding. In stretch blow moulding, biaxial orientation in the bottle is increased by longitudinal stretching. The parison is initially produced by extruding or injecting, it is then clamped in a mould and blow moulded into a tube shaped preform. This preform is trimmed and transferred to the bottle mould where it is simultaneously blown and stretched by an internal rod into the desired shape.

The less important process by which bottles are made from PVC, blow forming from foil, is a simple one. The two halves of the bottle are blow formed from the PVC foil and then stuck together.

1.7 Stability of PVC

1.7.1 Introduction

Because this work has been concerned with the characterisation of VC oligomers in PVC base resins and bottles, it is inappropriate to give a lengthy treatment to the stability of the polymer. However, it is pertinent to introduce the subject because of the possible structural changes that the VC oligomers could undergo during processing and service.
life due to the polymers inherent instability. The subject of PVC stability, in particular the mechanism by which it undergoes dehydrochlorination and the relative effect that anomalous structures in the polymer molecules have in promoting degradation, has received a great deal of attention over the years and still remains a controversial and interesting area. Two good reviews which cover this topic have been published recently.\textsuperscript{116,117}

Ideally, free radical polymerisation of vinyl chloride should result in a regular head-to-tail polymer. However, studies made on low molecular weight model compounds such as 1,3,5 trichlorohexane, which correspond to the idealised structure of PVC, show them to be considerably more stable than the polymer. This relative instability of the polymer is attributed to structural defects in the polymer chain which act as initiation sites for degradation. In practice this tendency to thermally decompose at temperatures over 70°C is not a great problem due to the development of effective stabiliser systems (Section 1.6.2). Decomposition of PVC by ultra-violet light is very dependent on the additives present in the polymer and to the extent that it has been decomposed during processing; the rate of decomposition by ultra-violet light increasing with increased prior degradation. In general, PVC is one of the more stable plastics materials to the deleterious effects of ultra-violet light.

In the initial stages of the thermal degradation of PVC, hydrogen chloride "zips off" from the polymer backbone, resulting in the formation of polyene sequences which, as they lengthen, cause the polymer to undergo a colour change from white to black via various shades of brown. This stage of the degradation has been studied by Martinez et al\textsuperscript{118} using a fluidised bed reactor and a
conductivity cell to monitor the evolved hydrogen chloride. They carried out a study of the degradation kinetics at low temperatures (80°C) and small (1%) amounts of decomposition. Their work confirmed the catalytic effect that hydrogen chloride has on the thermal degradation of PVC and they postulated an activation energy of 29 K cal mol⁻¹. Further heating of the polymer causes chain scission, which manifests itself in a deterioration of mechanical properties and chemical resistance. Also, cross-linking reactions begin to take place which predominate over chain scission in the later stages of the degradation.

Hirschler has used simultaneous thermal analysis (thermogravimetric, differential thermogravimetric and differential thermal analysis) and differential scanning calorimetric techniques to study the thermal decomposition of a range of PVC compounds (base resins and formulated compounds) under a variety of atmospheres (N₂, O₂, and air) and heating rates (5-100 deg min⁻¹). For all conditions each compound was found to decompose in three main breakdown stages, the first accounting for over 60% of the weight loss of the base resins and over 50% for the compounded resins. In this first stage two processes were considered to take place: the dehydrochlorination of the polymer backbone by the unzipping mechanism, and chain scission. The latter being something not usually considered to take place in the first stage. The mass polymerised base resin could be distinguished from the suspension polymerised base resin by virtue of the fact that the mass polymerised base resin underwent a greater exothermic reaction in the third breakdown stage.
1.7.2 Mechanism of dehydrochlorination

Although a great many studies have been carried out on this subject over the years, the mechanism by which PVC undergoes dehydrochlorination is still the subject of much controversy. Three main mechanisms have been proposed and still receive support: radical, ionic, and unimolecular.

Free Radical Mechanism

This particular mechanism has received most support over the years. The kinetics observed in the decomposition of PVC at a temperature of 235°C and above agree with the following free radical scheme:

**Initiation**

\[ -\text{CH}_2-\text{CH}-\text{CH}_2\text{CH} - \rightarrow -\text{CH}_2-\text{CH}-\text{CH} - \text{CH}^\cdot + \text{Cl}^\cdot \]

\[
\begin{array}{ccc}
\text{Cl} & \text{Cl} \\
\end{array}
\]

**Propagation**

\[ -\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH} - + \text{Cl}^\cdot \rightarrow -\text{CH}_2-\text{CH}^\cdot \text{CH}-\text{CH} - + \text{HCl} \]

\[
\begin{array}{ccc}
\text{Cl} & \text{Cl} & \text{Cl} \\
\end{array}
\]

\[ -\text{CH}_2-\text{CH}^\cdot \text{CH}-\text{CH} - \rightarrow -\text{CH}_2-\text{CH}=\text{CH}-\text{CH} - + \text{Cl}^\cdot \]

\[
\begin{array}{ccc}
\text{Cl} & \text{Cl} & \text{Cl} \\
\end{array}
\]

**Termination**

\[ \text{Cl}^\cdot + \text{Cl}^\cdot \rightarrow \text{Cl}_2 \]

\[ \text{R}^\cdot + \text{R}^\cdot \rightarrow \text{R} - \text{R} \]

\[ \text{R}^\cdot + \text{Cl}^\cdot \rightarrow \text{RCI} \]
Other evidence which has been put forward to support this mechanism includes: an increase in the rate of dehydrochlorination has been observed on addition of free radical sources and by subjecting the polymer to gamma and UV radiation; isotropic tracer and electron spin resonance techniques have given direct evidence for the formation of polymeric radicals; and a number of workers have claimed to have found direct or indirect evidence for the presence of chlorine atoms.

**Ionic mechanism**

PVC is dehydrochlorinated by a number of bases and, if the substitution reactions which normally occur simultaneously are inhibited, long polyene chains imparting colour to the polymer result. The elimination of hydrogen chloride is thought to proceed via an ionic mechanism, an example of which is:

\[
\begin{align*}
\text{Cl} & \\
-\text{CH-CH-} & + \text{B:} \\
\text{H} & \rightarrow -\text{CH=CH-} + \text{BH}^+ + \text{Cl}^- \\
\end{align*}
\]

Other ionic mechanisms have also been proposed, for example a protonation scheme. The existence of an ionic mechanism is supported by the autocatalytic effect that HCl has on the thermal degradation of PVC. It has also been found that thermal degradation in inert solvents is not influenced by inhibitors for radical reactions and that polar solvents which favour β-elimination of the E₁-type enhance thermal degradation. Furthermore, an ionic mechanism is in accord with the thermal decomposition mechanism of model PVC compounds.
Unimolecular expulsion theory

The proposal that the degradation of PVC occurs as a result of unimolecular elimination of HCl followed earlier work on the decomposition of poly(vinyl acetate). The 'zipping off' of HCl being due to allylic activation of the chlorine atoms attached to carbon atoms adjacent to double bonds resulting from an initial loss of HCl. Although there is some kinetic evidence to support this theory, it is mainly given credence by evidence that opposes other mechanisms.

Because evidence exists to support and oppose each of the three theoretical mechanisms, it has been postulated that all three may be operative simultaneously in the degradation of PVC, and it is the conditions under which the dehydrochlorination is studied that determine the relative contributions of each. Such an approach has led to the proposal of unified mechanisms in which two or more of the individual mechanisms are involved.

1.7.3 Effect of structural defects on the stability of PVC

The structural characterisation of PVC has already been extensively discussed in Section 1.5. Very often the object behind an investigation into the structure of commercial PVC is to characterise and quantify the defects and then evaluate the relative effect that each has on its stability. A number of publications have therefore combined both these areas.

The structural anomalies that can influence the thermal stability of PVC are listed below, along with recent papers reporting studies carried out on their effectiveness in promoting degradation.

1. Branching
2. Chloroallyl groups
3. End groups
4. Oxygen containing groups
5. Head-to-head structures
6. Tacticity

A study of the correlation between structural defects and thermal stability in PVC has been carried out by Guyot et al. They investigated the effect that increasing the concentration of the various defect structures had on the initial dehydrochlorination rate; bad correlations were observed. The defects were found to be concentrated in low molecular weight fractions in which a new type of labile chlorine atom (homoallylic) was discovered by high resolution NMR.

1.8 Vinyl chloride oligomers
VC oligomers are the homologues of VCM. VC oligomers having a molecular weight of less than 500 are of interest because of the possibility of their contamination of food as a result of migration from PVC packaging; higher oligomers are considered too large to have a potential for migration.

VCM was regarded as being non-toxic until Viola reported in 1970 that inhalation of very high concentrations (30,000 ppm) of VCM in air produced tumors in test animals. Since Maltoni and Leferime observed in 1974 the occurrence of angiosarcoma of the liver in animals exposed to much lower concentrations, investigations have been made into the quantities of VCM present in PVC and PVC packaged food. In 1974 PVC packaging contained more than 10 mg kg\(^{-1}\) of VCM but, due to modifications in the manufacturing process, this level had been reduced to less than 1 mg kg\(^{-1}\) by 1977. As a consequence, the VCM level in food dropped from up to 0.2 mg kg\(^{-1}\) in 1974 to 0.01 mg kg\(^{-1}\) in 1977. These levels were not considered to present a health hazard and safety limits were set at 1 mg kg\(^{-1}\) of VCM in food packaging materials and 0.01 mg kg\(^{-1}\)
in foodstuffs. The USA imposed stricter controls with rigid PVC being banned as a food packaging material; the use of flexible PVC film was, however, still allowed. If VC oligomers were found to have a structure similar to VCM, then they could also be carcinogenic and represent a further food contamination problem.

Although extensive characterisation studies have been carried out on oligomers of other plastics, particularly oligostyrenes (Section 1.3.3 and 1.4). Gilbert et al. reported in 1980 that no work had been published on the structural characterisation of VC oligomers obtained from PVC. In view of this dearth of information, and the possible health hazards constituted by VC oligomers migrating into food, the Ministry of Agriculture, Fisheries and Food (Food Laboratories, Norwich) initiated a research programme, the aim of which was to characterise VC oligomers obtained from commercial food grade PVC resins. Initially, a low molecular weight fraction was isolated from food grade PVC resins using Soxhlet extraction followed by steric exclusion chromatography, and estimations of oligomer levels were made on the basis of gravimetric measurements and microchlorine determinations. These results assumed that all the oligomers had the same empirical formula as VCM and that all the available chlorine was present as oligomers rather than as alternative chlorinated organic compounds. The resins used covered the range of molecular weights (K values) commercially available and it was found that the highest yield of oligomers resulted from the polymer with the lowest nominal molecular weight. The quantity of oligomers found of molecular weight less than approximately 600 ranged from 100 to 350 mg kg⁻¹ depending upon the base resin. Further analysis of the low molecular weight fractions using GC-MS resulted in the separation of the individual oligomer
species trimer to hexamer, with some evidence of heptamer and octamer. A number of other compounds were also identified in the resin extracts, namely, mixed phthalates, alkanes, nonylphenyl and undecyl dodecanoate, the latter being derived from the polymerisation initiator lauryl peroxide. From mass spectrometry data obtained from hydrogenation studies, each oligomer species was postulated as existing in both cyclic and straight chain forms, with each form itself occurring as a number of structural isomers. The total population of isomers was found to increase with chain length. For any given oligomer the mass spectra of its isomers were very similar and so, apart from a molar mass characterisation, no detailed information on the structure of each isomer could be elucidated. The most striking features of the oligomer spectra were the clusters of ions due to $^{35}\text{Cl}-^{37}\text{Cl}$ combinations and fragment ions due to the sequential loss of hydrogen chloride from the molecular ion.

The sensitive detection of VC oligomers in HPLC is a problem due to their lack of UV absorption and fluorescence. In an attempt to overcome this problem, MAFF modified a commercial Hall electrolytic conductivity gas chromatographic detector to enable it to be used for HPLC halogen selective monitoring. Work with this detector on a low molecular weight PVC fraction analysed by reverse phase HPLC resulted in the selective detection of a homologous series of VC oligomer species, even in the presence of other non-chlorinated contaminants, and allowed the trapping of the separated species for structural characterisation by spectroscopic techniques.

It was apparent with the failure of mass spectrometry to elucidate the structure of VC oligomers that other characterisation techniques such as NMR would have to be employed. The drawback of NMR is that a few milligrams of relatively pure compound are needed to facilitate an easy analysis. To enable a sufficient quantity of one
particular VC oligomer, a straight chain tetramer, to be prepared for proton NMR analysis, Gilbert et al. developed a multi-stage chromatographic procedure whereby a low molecular weight fraction obtained by Soxhlet extraction of a food grade PVC resin was fractionated, first by gel filtration to yield a mixture of VC oligomers, and then by HPSEC to give the single species. This fractionation procedure was repeated until 0.5 mg of the VC tetramer had been isolated. The accumulated VC tetramer was analysed using 200 MHz proton NMR in an attempt to elucidate its structure. Only a partial characterisation was possible due to complex overlapping signals thought to be due to impurities which hindered interpretation of the spectrum. However, there was evidence for the existence of the following end group:

\[-CH_2-CH=CH-CH_3Cl\]

Epoxidation and hydrogenation of the tetramer, followed by GC-MS analysis, gave supportive evidence for the existence of the above end group and also revealed that the isolated material consisted of two isomeric components. The presence of two isomers would have contributed to the complexity of the NMR spectrum and impeded interpretation.

The research programme carried out by MAFF on VC oligomers has been the subject of a MSc thesis produced by Wallwork.

1.9 **Aims of the work**

Because VC oligomers of molecular weight 500 and below have a potential for migration into food, and due to the fact that they could be carcinogens, it is important that they should be structurally characterised so that toxicity tests can be carried out using synthesised analogues. The main aim of this work was therefore to characterise, as
fully as possible, VC oligomer species which had been isolated from food grade PVC base resins. To achieve this a wide range of chromatographic and spectroscopic techniques were employed. Because of their greater importance with regard to migration into food compared to the higher oligomers, work was concentrated on the lower oligomers, i.e. up to and including the pentamer species. A base resin obtained immediately after the polymerisation process was used as a source for the oligomers because it represented an easier matrix to analyse than a compounded and processed PVC product. However, it was always appreciated that this did not represent a 'real life' situation and that the oligomers present in a fabricated article, after having been subjected to high processing temperatures in the presence of stabilisers and other additives, might be substantially different from those obtained from base resins. In view of this, investigations were carried out, using the techniques developed for the analysis of base resin oligomers, on PVC bottles produced from a commercial formulation. Unfortunately, time did not permit a detailed structural characterisation of the oligomers obtained from the bottles.
CHAPTER TWO

Experimental

2.1 Materials and equipment

2.1.1 PVC base resins and bottles
Corvic S57/116 homopolymer (K value 57) produced by suspension polymerisation and a mass polymerised homopolymer (no further information given) were supplied by ICI Petrochemicals and Plastics Division, Runcorn, Cheshire.

Lucovyl RB 8010 homopolymer (K value 56) produced by mass polymerisation was provided by Atochem UK, Thatcham, Berkshire. Norvinyl VY 80/30 homopolymer (K value 57) produced by suspension polymerisation and a batch of bottles blow moulded from a commercial bottle formulation based on Norvinyl VY 80/30 resin were supplied by Norsk Hydro, Aycliffe, Durham.

2.1.2 Solvents
Diethyl ether, dichloromethane, methyl ethanoate, acetone, propanol, 2-chloropropane, methanol (all SLR grade), tetrahydrofuran (AR grade), toluene, dichloromethane, hexane (95% n-hexane) and pentane (95% n-pentane) (all HPLC grade) were supplied by Fisons, Loughborough, Leicestershire. Methyl tert-butyl ether (MTBE) (HPLC grade) was supplied by Fluka, Glossop, Derbyshire. Acetonitrile (HPLC grade 5) was supplied by Rathburn Chemicals, Walkerburn.

2.1.3 Chromatographic columns and packing materials
Polymer Laboratories, Church Stretton, Shropshire provided HPSEC columns (60cm x 7mm) containing the following packings: PL gel 10μm, mixed gel, PL gel 10μm, 50Å and PL gel 5μm, 50Å.
Gel filtration SR 100/25 glass columns (100cm x 25mm) were obtained from Pharmacia, Uppsala, Sweden, and Bio-Beads S-XB (38-75μm) packing gel from BioRad Labs., Richmond, U.S.A. A preparative adsorption liquid chromatography column (31cm x 25mm) containing LiChrorep Si60 (40-63μm) packing was procured from Merck, Germany.

Microbore HPLC columns (25cm x 1mm) containing Spherisorb S5 ODS2 and Spherisorb S5W, and standard size (25cm x 4.6mm) HPLC columns containing Spherisorb S5W were supplied by Phase Separations, Clwyd, U.K.

2.1.4 Solvent delivery pumps
Three types of HPLC pump were used in this investigation, namely, a Knauer 64, an Altex 410 and a Waters 6000 A.

2.1.5 HPLC detectors
The types of HPLC detectors used in this work were as follows: A Knauer differential refractometer; a Pye Unicam PU 4025 UV detector; and a Pye Unicam liquid chromatography - electron capture (LC-EC) detector.

2.1.6 TLC plates
Two types of TLC plate, both obtained from Merck, Germany were used; these were an aluminium oxide 60 F254 (type E) pre-coated plate having a layer thickness of 0.25mm and a silica gel 60 F254 pre-coated plate having a layer thickness of 0.25mm. Both types of plate were glass backed and had dimensions 20cm x 20cm.

2.1.7 Chromatographic valves and tubing
The HPLC valves used in the investigation were supplied by Rheodyne (7125 and 7520 injection valves, 7000 switching valve) and Altex (210 injection valve).
A four port low pressure injection valve was provided by Pharmacia, Uppsala, Sweden for use with the gel filtration system.

For the HPLC systems zero dead volume connectors and narrow bore (0.15mm) stainless steel tubing were used to make all the essential connections. This ensured that dead volume, and hence peak broadening, was kept to a minimum. The gel filtration and preparative LC systems were less critical and so medium bore (0.5mm) PTFE tubing was used to keep back pressure down; both types of column could not withstand high (greater than 100 psi) back pressures.

2.1.8 Chromatographic and Spectroscopic Instrumentation
A Waters 501 chromatograph having a refractive index detector was used with a Polymer Laboratories PL gel, 10μm, 60cm x 7mm mixed gel column.

The gas chromatograph was a Analytical Instruments model 92 equipped with a Chrompak CP Sil5 CB (0.11μm thick film) 25cm x 0.22mm capillary column.

Two GC-MS instruments were used. A Carlo Erba 4200 gas chromatograph fitted with a 25m x 0.22mm capillary column coated with BPl which was connected to a Kratos MS80 mass spectrometer via an all glass direct coupling interface. Also, a Carlo Erba 4160 gas chromatograph fitted with a 25m x 0.22mm capillary column coated with a 0.12μm thick layer of CP Sil CB which was directly coupled to a VG Mass Labs Quadrupole 15-250 mass spectrometer.

$^1$H NMR studies were carried out using a Nicolet NTC FT-NMR at 200 MHz.
2.1.9 Standards
Polystyrene 580 and a set of polystyrene standards ($\bar{M}_n = 1850 - 2100000$) were supplied by Polymer Laboratories, Church Stretton, Shropshire. The following were supplied by Dr. M.J. Shepherd, MAFF, Food Laboratories, Norwich:

- Dimethyl phthalate
- n-dibutyl phthalate
- Iso dioctyl phthalate
- 1,3 dichlorobutane
- 1,4 dichlorobutane
- 2,3 dichlorobutane
- 1,6 dichlorobutane
- Trans 1,2 dichlorocyclohexane
- Trans 1,4 dichloro-2-butene
- 2,3 dichloro-1-propene
- 1,9 dichlorononane
- 1-phenyl hexane

Vinyl chloride oligomers (decamer to pentamer), which were prepared by the author (Figure 3.22), were used to calibrate the SEC and LC systems later on in the work.

Samples of partially hydrolysed poly(vinyl acetate) dispersing agent, used in the suspension polymerisation of VCM, were provided by ICI Petrochemicals and Plastics Division, Runcorn, Cheshire. No technical information was supplied by ICI, but it was apparent that one of the samples was of a much higher molecular weight than the other (Section 3.2.1).

2.2 Soxhlet extractions
2.2.1 Initial PVC base resin extractions
Initial work was carried out on Corvic S57/116 and a range of solvents were evaluated as extracting agents. The
following solvents were used: dichloromethane, methyl ethanoate, acetone, propanol, 2-chloropropane, diethyl ether and methanol. The extractions were performed with a small Soxhlet extractor (chamber volume 90 cm$^3$) having a thimble which had been pre-extracted for 2 hours. Typical Soxhlet conditions were: PVC (20g), solvent (150 cm$^3$), extraction time (20 hours), cycle time (5 mins.), with isomantle heating.

2.2.2 Large-scale PVC base resin extractions

In order to maximise the yield of oligomers, a large-scale Soxhlet extractor (chamber volume 700 cm$^3$) was constructed. Initially, the Soxhlet was used with a thimble that had been pre-extracted for 20 hours. However, this procedure proved to be unsatisfactory and the Soxhlet was modified as described in Section 2.2.3. All of the PVC base resins that were available were extracted in this Soxhlet, methanol and diethyl ether being the solvents used. With methanol a heating tape was placed around the Soxhlet chamber to keep it warm because the cycle time was so long that the methanol had time to cool to room temperature which was not the case in the small scale experiments. The heating tape was not used with diethyl ether which is more volatile and has greater solvating power. Typical extraction conditions were: PVC (250g), solvent (500 cm$^3$), extraction time (20 hours), cycle time (30 mins.), with water bath heating.

2.2.3 Modification of large-scale Soxhlet

It was found that the extract was contaminated with the material constituting the Soxhlet thimble, even though the thimble had been extensively pre-extracted. In order to be used successfully without an extraction thimble, the Soxhlet was prepared for use as follows. A layer of glass wool was placed in the bottom of the Soxhlet chamber to a
sufficient depth to cover the syphon outlet, the outlet being partially blocked to retain the polymer particles in the chamber but allowing the solvent to drain out in the usual way. A glass tube was then gently pushed through the glass wool to a position 2 cm from the syphon outlet; this tube allows air to reach the outlet and break the syphon, once the solvent has drained away, when the chamber is full of PVC. If the tube is placed too near the outlet, the syphon will be broken prior to complete solvent drainage; too far away and the syphon will never be broken. A second layer of glass wool is then placed in the bottom of the chamber to ensure that the insertion of the glass rod in the first layer has not opened up a route of escape for the PVC particles, a final layer of glass wool being placed on the surface to prevent 'splashing' of the particles.

2.2.4 Extraction of suspension polymerisation dispersing agents
Partially hydrolysed poly(vinyl acetate) is used as a dispersing agent in suspension polymerisation (see Section 1.1). Samples of dispersing agent, having low and high molecular weight, were subjected to small-scale Soxhlet extraction under the following conditions: diethyl ether (250 cm³), dispersing agent (20g), extraction time (20 hours), cycle time (5 mins.), with isomantle heating. As with the large-scale PVC extractions, the Soxhlet was modified to eliminate the need for a thimble. The high molecular weight dispersing agent was also Soxhlet extracted with methanol using identical conditions to the diethyl ether extractions. The low molecular weight dispersing agent was found to be soluble in methanol and so a Soxhlet extraction with this solvent was not attempted.

2.2.5 Extraction of PVC bottles
Because a prerequisite of extraction work is that as large a surface area as possible should be subjected to the
extracting medium the first task was to finely comminute the PVC bottles. This was achieved by cutting them up with a pair of scissors; 'chips' having the approximate dimensions 5mm x 2mm x bottle thickness (which varied greatly over the bottle profile) being produced. The PVC bottles in this form were extracted in the modified large-scale Soxhlet under the following conditions: PVC bottles (250g), diethyl ether (500 cm$^3$), extraction time (20 hours), cycle time (30 mins.), with water bath heating.

2.2.6 Isolation of dry Soxhlet extracts

When an extraction had been completed, the extract was filtered (to remove any PVC particles) and then most of the solvent was removed with a rotary evaporator. The extract was then dried in a vacuum oven at room temperature. For the oligomers, the percentage yield in the dried extract was calculated from the mass of material which dissolved readily in tetrahydrofuran at room temperature. Consequently, the percentage yield did not include components, such as dispersing agents which were not completely soluble in tetrahydrofuran. The yield of the other extracts was taken as the whole extract weight. The components in a dried extract were characterised by HPSEC (Section 2.3).

2.3 Molecular weight characterisation of the PVC base resins and Soxhlet extracts by HPSEC

Molecular weight data (g mol$^{-1}$) were obtained from chromatograms for separations of samples in tetrahydrofuran with a Polymer Laboratories mixed gel column (60cm, 10μm, PL gel) in a Waters 501 chromatograph having a refractive index detector. The chromatograph was fitted with a Rheodyne 7125 injection valve having a 100μl loop. The amount of sample loaded onto the column for each analysis was 0.2 mg. Molar mass calibration of the column was performed with polystyrene standards. Values of number average, weight average and peak
molecular weight, $\bar{M}_n$, $\bar{M}_w$ and $M_p$ respectively, were computed from a chromatogram.

2.4 Isolation of low molecular weight PVC fractions from the Soxhlet extracts by preparative gel filtration

2.4.1 Packing the column

The packing used in this work was Bio-beads S-XB, which is a material produced by the suspension polymerisation of styrene and divinyl benzene. The concentration of divinyl benzene in the polymerisation determines the degree of crosslinking and hence the chromatographic working range of the packing. Bio-Beads S-XB, which is in the form of beads with a diameter of 38-75μm, is crosslinked to the degree of 8% and has a molecular weight exclusion limit of 1000 g mol$^{-1}$ (polystyrene calibration). The packing of the column in gel filtration is very critical for optimum column efficiencies so great care was taken over this stage. Bio-Beads S-XB (200g) were weighed into a beaker and then 800 cm$^3$ of filtered, stabilised THF added. A magnetic stirrer was added and the mixture stirred for 70 hours to allow equilibrium to take place. Once the stirrer had been switched off the whole mixture was degassed for 30 minutes. When the gel had settled, the supernatent liquor was taken off with a pipette until it constituted half the volume of the settled gel. This gave the slurry a consistency such that it could be poured into the column in one operation, this technique being known as slurry packing. The bottom end piece was fitted into the Pharmacia SR 100/25 column and filtered, stabilised THF added to a depth of 10cm. The slurry was then slowly poured into the column, the packing being carried out under a flow rate. The slurry was added until a full bed had been achieved and then the column was run (with the top end piece in place) until the bed had settled: a 86cm x 25mm gel bed was achieved. The top end piece was then gently lowered onto the top of the bed and the securing mechanism expanded until the PTFE seal gripped the inside wall.
of the column. This packing procedure was repeated when it became desirable to first change the eluent to unstabilised THF and finally to toluene. The column was run under gravity with flow rates, directly after packing, of between 2 and 3 ml min$^{-1}$ being achieved with the different eluents used.

### 2.4.2 Calibration of the column

The gel filtration column was calibrated with a polystyrene 580 standard. The column was not capable of completely resolving the oligomers that constitute this standard, but it was efficient enough to reveal the position of the oligomer (pentamer $+ \text{C}_4\text{H}_9$ (butyl) end group) that corresponded to a molar mass of 578. The peak elution volume of the other oligomers was also discernable and so it was possible to construct a calibration curve for the column. The oligomers in the standard had been assigned by injecting the monomer $+ \text{butyl end group analogue, 1-phenyl hexane, and comparing peak elution volumes. In this way the elution volume range that contained oligomers with molecular weights up to 578 g mol$^{-1}$ was found for each gel filtration experiment. It was assumed that the VC oligomers would exhibit the same size exclusion behaviour as the oligostyrenes. Each calibration run was performed by injecting 2 ml of a 1% w/v solution of the standard, a Knauer differential refractometer being used as the detector.

### 2.4.3 Fractionation of the Soxhlet extracts

A separation of an extract (Section 3.3.1) was performed by injecting 2 ml of a 10% w/v solution. The extract was dissolved in a sample of the mobile phase to avoid refractive index detection problems. The fraction eluting from the gel filtration column within the elution volume range assumed to contain VC oligomers with molecular weights up to 578 g mol$^{-1}$ (polystyrene calibration) was collected and the dried fraction obtained by distilling off the bulk of the toluene on a
vacuum frame at room temperature, final dryness being achieved in a vacuum oven at room temperature. The oligomer fraction collected was analysed by analytical gel permeation chromatography to ensure that no oligomers of interest had been missed. Once this fact had been established the gel filtration system was used routinely to accumulate a sizeable mass of VC oligomers.

2.5 Isolation of low molecular weight PVC fractions from the Soxhlet extracts by fractional precipitation in Pentane

The diethyl ether Soxhlet extract was reduced to approximately 20 cm$^3$ in volume on a rotary evaporator and then added to 350 cm$^3$ of pentane at room temperature. The mixture was left for approximately 20 minutes to ensure that the precipitation of the long chain PVC was complete and then the mixture was filtered to leave a clear filtrate containing low molecular weight PVC in solution. The dry low molecular weight fraction was obtained by employing the standard technique for solvent removal i.e. rotary evaporator followed by a vacuum oven at room temperature.

2.6 Purification of the low molecular weight PVC fraction by adsorption liquid chromatography

The low molecular weight PVC fraction had been shown by GC-MS analysis (Section 3.8) to contain other compounds, such as initiator residues, as well as VC oligomers. Some of these compounds, particularly phthalates, were present in high enough concentrations to register prominently in HPSEC chromatograms of the fractions and obscured some oligomer peaks. As the initial HPSEC
chromatograms were used to develop recycle programmes for the routine preparation of the oligomers, it was vital that such impurities should be removed from the low molecular weight PVC fractions prior to HPSEC analysis. The technique chosen to effect this purification was adsorption liquid chromatography since it had been observed that with a relatively non-polar mobile phase, compounds more polar than VC oligomers, such as phthalates, were retained on the column much longer, thus giving a complete separation.

2.6.1 Chromatographic system

The system was based on a Merck Lobar Size B (31cm x 25mm) column containing LiChroprep Si 60 (40-63μm) packing. A Knauer 64 pump was used in conjunction with a Pye Unicam PU 4025 UV detector with a 2.4μl flow cell and a Rheodyne 7125 injection valve fitted with a 200μl loop. The mobile phase was hexane containing 5% v/v of MTBE modifier.

2.6.2 Calibration of the chromatographic system

To calibrate the system the following two standards were used: dibutyl phthalate and the VC decamer fraction that had been prepared by HPSEC (Figure 3.22). The VC decamer fraction was chosen as retention volumes increase with oligomer molar mass, and so using this oligomer ensured that none of the isomers of the oligomers of interest, octamer and below, would be lost. As has been previously mentioned, dibutyl phthalate is retained on the column longer than low molecular weight VC oligomers and so initial work involved modifying the
mobile phase, by varying the amount of MTBE in the hexane, to investigate the effect that this had on the separation of the two standards and the analysis time. Owing to the large internal volume of the column, it was found that a modifier content below 5% v/v gave separation times in excess of four hours, which was considered too long. At a concentration of 5% v/v, however, a good separation of the two standards was obtained and so this mobile phase composition was chosen for routine work. To ensure that none of the isomers of the lower oligomers would be lost upon routine fractionation of the low molecular weight PVC fraction, it was decided to start collecting the desired oligomer fraction from the injection point (ie. elution volume = 0 ml) as the complicated solvent front, which results due to low wavelength UV detection, makes the early part of the chromatogram hard to interpret. The other fraction partitioning point was set at the elution volume of the longest retained decamer isomers (420 mls).

The dibutyl phthalate standard was analysed at a detection wavelength of 254 nm, 20 mg being loaded onto the column. Approximately 10 mg of the VC decamer fraction was loaded onto the column with a chromatograph being obtained at a wavelength of 203 nm. Both analyses were carried out with a mobile phase flow rate of 3 ml min⁻¹.
2.6.3  **Purification of the low molecular weight PVC fraction**

With the flow rate set at 3 ml min⁻¹, the low molecular weight PVC fraction was purified by injecting aliquots (150 mg) and collecting the fraction within the elution volume range 0-420 mls, assumed to contain all the isomers of VC oligomers decamer and below (Section 2.6.2) and some isomers of higher oligomers. The UV detector was set at 203 nm for the purification runs. The bulk of the solvent was removed using a rotary evaporator, final dryness being achieved in a vacuum oven at room temperature. The dried fraction was weighed and then analysed by HPSEC (Section 2.7).

2.6.4  **Attempted purification of the low molecular weight PVC bottle fraction**

The bottle formulation had been kindly supplied by Norsk Hydro (Section 4.1) and so the type of compound present in the bottles was known. Because most of the additives were of a low molecular weight they were coextracted with the VC oligomers by the diethyl ether in the Soxhlet extraction procedure. It was hoped that the VC oligomers could be separated from the additives by using adsorption chromatography. It was observed that the additives were either of a higher or lower polarity than the VC oligomers and so it was thought possible to find a chromatographic 'window' in which the oligomers could be isolated. Unfortunately, when a sample (200 mg) of the bottle fraction was analysed using the chromatographic system described in Section 2.6.1 the elution profile obtained at 203 nm was greatly altered due to the presence of additives eluting at a volume corresponding to the oligomers. However, a further analysis was performed and the fraction within the elution volume range 140-380 mls (chosen to reduce VC oligomer contamination as much as possible) collected. The solvent was removed from the fraction by using first a rotary evaporator and then
a vacuum oven at room temperature. The fraction was then analysed by HPSEC (Section 2.7.4).

2.7 Analysis of the low molecular weight PVC fractions by HPSEC

2.7.1 Chromatographic system
Two 60 cm HPSEC columns containing 5μm, 50Å, PL gel packings were obtained from Polymer Laboratories for the purpose of isolating individual oligomer species from the low molecular weight PVC fraction obtained by gel filtration or fractional precipitation. The columns were used in conjunction with a Knauer 64 pump and Knauer differential refractometer. In order to achieve the length of gel bed required to effectively resolve the individual oligomer species from the low molecular weight PVC fraction an alternative pumping recycle system was set up using a Rheodyne 7000 switching valve. The injection valve used was a Rheodyne 7125. In the course of this project the following solvents were used as the mobile phase: stabilised THF, unstabilised THF, dichloromethane and toluene. A flow rate of 1 ml min⁻¹ was used at all times.

2.7.2 Calibration of the chromatographic system
The efficiency of the system was such that it was able to resolve individual oligomer species present in the polystyrene 580 standard. It was therefore possible, once the oligostyrene peaks had been assigned by the use of the monomer + butyl end group analogue (1-Phenyl hexane), to construct a calibration curve. As with the calibration of the gel filtration system, it was assumed that this calibration curve could be used for assigning VC oligomer peaks. In the HPSEC system the VC oligomer peaks that had been designated as being due to the species trimer to octamer using the oligostyrene calibration curve were shown by GC-MS to be the species pentamer to decamer.
(Section 4.4.1). In view of this, before any further preparative work was attempted the system was recalibrated using the VC oligomers that had been prepared in the previous work i.e. the species pentamer to decamer. This enabled a far more accurate characterisation of the technique to be carried out and eliminated any ambiguity.

2.7.3 Separation of the VC oligomers
Initially, a chromatogram was produced of the low molecular weight PVC fraction, using 120 cm of gel bed, for the purpose of assigning the oligomer peaks using the calibration curve. When this had been accomplished, chromatograms were produced utilising 240, 360 and 480 cm of gel bed to investigate the effect that this had on the separation of the oligomers. A visual evaluation of the chromatograms revealed that 480 cm of gel bed was required to effectively resolve the oligomer species. Aliquots (10 mg) of the low molecular weight PVC fraction were routinely fractionated using 480 cm of gel bed and the peaks that corresponded to VC oligomers collected. The oligomer fractions were dried in a vacuum oven at room temperature. In order to unambiguously identify the collected VC oligomer species they were submitted for GC-MS analysis (Section 2.11.1).

2.7.4 Analysis of the low molecular weight PVC bottle fraction
A sample of the bottle fraction that had been subjected to adsorption liquid chromatography was analysed using, initially, 120 cm of gel bed. The chromatogram obtained was more complex than usual due to the additives which were still present in the extract. This meant that the VC oligomers were obscured and a recycle programme could not be devised by a visual examination as had been possible with the base resin fractions. In view of this, the same recycle programme
that had been employed with the Norvinyl 80/30 base resin fraction was used and a chromatogram obtained utilising 480 cm of gel bed. From this chromatogram it was still not clear which peaks were due to additives and which to VC oligomers, and so for the purpose of dividing up the chromatogram for preparative collections, the fractions were assigned by using the volume range that each VC oligomer was known to elute within from previous experiments. It had to be assumed that the high concentration of additives did not effect the elution volume of the oligomers. Aliquots (30 mg) of the bottle fraction were injected onto the column and the designated fractions collected. The fractions were dried in a vacuum oven at room temperature and then analysed by HPLC (Section 2.10.2).

2.8 Analysis of the VC oligomer fractions by TLC
TLC was evaluated as a means of separating the isomers present in each VC oligomer fraction obtained by HPSEC (Section 2.7).

2.8.1 Calibration
It was known from the GC-MS analysis of the VC oligomer fractions that the oligomers existed in a number of isomeric forms and that other compounds, such as phthalates, were present. One oligomer fraction in particular (the hexamer) contained a considerable mass of a phthalate which could not be unambiguously identified using the mass spectrometer data base (Section 3.8). A number of phthalate and chlorinated standards were therefore obtained (Section 2.1.9) and analysed at the same time as the oligomer fractions in an attempt to identify the phthalate present and elicit information of the chemical structure of the oligomer isomers.
2.8.2 Identification of the chlorinated compounds

The inherent fluorescent indicator in the chromatographic layer on the TLC plates cannot be utilised to indicate the presence of aliphatic compounds containing only carbon, hydrogen and chlorine, e.g. VC oligomers, and so a different technique has to be employed. The method used in this work originated from a paper by Hollies et al. A Merck aluminium oxide 60 F_{254} (type E) pre-coated TLC plate having a layer thickness of 0.25mm was taken and marked in an identical way to the developed silica TLC plate. The two plates were then clamped together face to face and placed in an oven at 250°C for 15 minutes. The plates were then removed from the oven and allowed to cool to ambient temperature before being unclamped. To develop the 'printed' spots the aluminium oxide TLC plate was sprayed evenly with a silver nitrate reagent [45 ml ethanol, 2.5 ml aqueous silver nitrate (10% w/v) and 2.5 ml aqueous ammonia (0.8)] and placed under a UV lamp for 10 minutes. Any spots which had contained chlorinated compounds were grey in appearance. The R_f values of the grey spots were recorded quickly, as the whole plate gradually darkened. This technique utilises the best properties of both types of TLC plate, namely the resolving power of silica plates and the sensitivity of aluminium oxide plates.

2.8.3 Analysis of the VC oligomer fractions

The VC oligomer fractions were analysed using Merck silica gel 60 F_{254} pre-coated plates having a layer thickness of 0.25mm. The amount of sample spotted each time varied from 0.2μl to 2μl depending upon concentration. Great care was taken to ensure that the diameter of the spot was kept to a minimum, thus ensuring that the performance of the system was impaired as little as possible. The following developing solvents were investigated to ascertain their ability...
to selectively separate the isomers of the oligomer fractions: toluene, and hexane containing varying amounts of methyl tert-butyl ether or ethyl acetate. The plates were developed in standard TLC developing tanks that had been equilibrated by placing filter papers that had been soaked in the developing solvent around the sides. After development the plates were dried at room temperature and then examined under a UV source (wavelength: 254 nm) to elucidate the position of any phthalates present; with the inherent fluorescent indicator, the phthalates appeared as black spots against a green background. To detect and obtain $R_f$ values for any chlorinated components present, the developed plate was then subjected to the test procedure described in Section 2.8.2.

2.9 Analysis of the VC heptamer by microbore HPLC

2.9.1 General chromatographic system

Development work was carried out on a microbore HPLC system which consisted of a Waters 6000 A pump controlled with a Waters microflow module to enable eluent flow rates of less than 100 µl/min to be achieved, a Pye Unicam PU 4025 UV detector fitted with a 1.0 µl flow cell, a Pye Unicam LC-EC detector and a Rheodyne 7520 injection valve having an internal 0.5 µl loop. Two spherisorb 25 cm x 1 mm columns containing 55W silica and 55 ODS2 were used. For normal phase HPLC hexane or hexane containing concentrations of MTBE were used as the mobile phase. Acetonitrile HPLC grade S was used for reverse phase HPLC. The eluents were continuously degassed using a helium purge to avoid the formation of bubbles in the UV detector flow cell and quenching of the standing current in the electron capture detector.
2.9.2 Chromatographic system optimisation

When assembling a microbore HPLC system it is crucial to keep the amount of dead volume to an absolute minimum as this property, due to the small internal volume of the columns used, has an enhanced deleterious effect on efficiency compared with HPLC systems. This is why a special injection valve was used in this system, a small volume flow cell in the UV detector, and all the connecting tubing kept as short as possible. The performance of the system was gauged by injecting standards such as toluene (0.02% w/v) and n-dibutyl phthalate (0.03% w/v) and calculating the number of theoretical plates per metre of column from the resulting chromatograms by the peak width at half peak height method. It was also very important to find the eluent flow rate that resulted in optimum system performance. Using standards once again, the flow rate was varied from 10 μl min⁻¹ to 100 μl min⁻¹ and a Van Deemter curve plotted to ascertain the flow rate that yielded the highest number of theoretical plates per metre of column. This turned out to be 20 μl min⁻¹.

One of the problems encountered when working with VC oligomers is that of detection, since they possess no strong UV chromophore. In an attempt to overcome this problem, a Pye Unicam LC-EC detector was obtained and used in series with the UV detector which was set at 200 nm (the peak absorbance for carbon-chlorine bonds is at 170 nm but solvent cut-off renders this wavelength unattainable). Because the electron capture detector was in the system the normal phase HPLC microbore column, containing S5W packing, was used for experiments on the VC heptamer fraction, prepared by HPSEC (Figure 3.22), as the mobile phase (hexane) was less electron capturing than the reverse phase HPLC eluents. Unfortunately, the electron capture detector would not function properly, but work with the chlorinated...
standards and the VC heptamer fraction revealed that low wavelength (200 nm) UV detection could be used to detect adequately the presence of VC oligomer isomers. It was found that a modifier (MTBE) had to be added to the hexane at a level of 5% v/v in order to produce an acceptable VC heptamer chromatogram.

2.9.3 Analysis of the VC heptamer fraction
The VC heptamer fraction was analysed using a normal phase microbore HPLC system which was comprised of a Waters 6000A pump controlled with a Waters micro-flow module, a Pye Unicam PU 4025 UV detector fitted with a 1.0 μl flow cell and set at 200 nm and a Rheodyne 7520 injection valve having an internal 0.5 μl loop. A Spherisorb 25cm x 1mm column containing S5W silica was used with hexane containing 5% v/v MTBE as the mobile phase. Aliquots of the VC heptamer fraction (0.12% w/v in hexane) were analysed at a flow rate of 20 μl min⁻¹. The results obtained were sufficiently good enough for the procedure to be scaled up and a standard size HPLC column containing S5W to be used.

2.10 Analysis of the VC oligomer fractions by normal phase HPLC
The results obtained with the microbore HPLC suggested that a silica column with a mixture of hexane and MTBE as the mobile phase was capable of separating the isomers of each VC oligomer prepared by HPSEC (Figures 3.22 and 3.24).

2.10.1 Chromatographic system
A Waters 6000 A pump was used in conjunction with a Pye Unicam PU 4025 detector with a 2.4 μl flow cell and an Altex 210 injection valve fitted with a 50 μl loop. To enable semi-preparative work to be carried out a Highcrom 25cm x 4.6mm column containing S5W silica packing was used. Low wavelength (200 nm) UV detection was used throughout.
2.10.2 Separation of the VC oligomer isomers
Initially, the composition of the mobile phase was varied from pure hexane to hexane containing 10% v/v MTBE modifier in order to locate the optimum separating conditions, these being found to occur with a modifier concentration of 1% v/v. These conditions proved satisfactory for the VC oligomers heptamer to pentamer, but the concentration of modifier had to be reduced to 0.25% v/v to separate the VC tetramer due to the speed with which the smaller sized isomers were coming off the column; the reduction in modifier content resulted in the tetramer isomers being retained on the column longer and an improvement in resolution. The other two VC oligomer fractions prepared by HPSEC for characterisation in this work, the octamer and trimer, could not be separated into their constituent isomers by this technique (Section 4.5). The mobile phase flow rate was maintained at 1 ml min⁻¹ for all the separations. Once the optimum conditions had been established, routine fractionation of the VC oligomers was carried out by injecting 2 mg aliquots. The chromatogram peaks were trapped and the solvent removed by blowing down with nitrogen at room temperature.

2.10.3 Identification of the chromatogram peaks
Because low wavelength UV detection had been used, the HPLC chromatograms of the VC oligomers contained peaks that were not due to VC oligomer isomers. A number of tests were therefore carried out on each trapped peak in order to identify those peaks that were due to VC oligomer isomers. The fractions were tested for the presence of chlorine by using a modified version of the TLC spot detection technique (Section 2.8.2). Each fraction was spotted onto a silica TLC Plate and the spot 'printed' onto an aluminium oxide TLC plate by clamping the plates together.
and heating in an oven at 230°C for 15 minutes. The fractions (peaks) containing chlorine were then identified by testing with the silver nitrate reagent and exposing to UV light. The fractions were also analysed using gas chromatography which revealed the presence of VC oligomer isomers by virtue of them possessing a common retention time range for isomers of a given VC oligomer; this technique also indicated the purity of each HPLC fraction. Work was carried out using an Analytical Instruments Model 92 gas chromatograph equipped with a Chrompak 25m x 0.22 mm column coated with a chemically bonded 0.11μm thick layer of CP Sil 5CB. The carrier gas, hydrogen, was set at a flow rate of 2 ml min⁻¹. A 1 μl sample of each fraction was injected onto the column with the injector at 300°C and split ratio of 30:1. Each fraction was analysed isothermally at 240°C for 13 mins. The FID detector was kept at 310°C with attenuation and range settings 2 and 11, respectively. To verify the results obtained by TLC plate spotting and GC, each fraction was subjected to GC-MS which unambiguously identified VC oligomers isomers (their characteristic mass spectra were already known) and also revealed the presence of any 'rogue' isomers in the oligomer fractions (eg. a pentamer isomer in a hexamer fraction) due to the incomplete HPSEC separation (see Section 3.5). The experimental details for the GC-MS work are given in Section 2.11.2).

2.10.4 Gradient elution HPLC

Because it took a long time for all the isomers of the higher oligomers to elute from the HPLC silica column, and due to the fact that the later isomers had a peak width volume of up to four millilitres, which meant that a lot of solvent had to be removed increasing the concentration of impurities, gradient elution HPLC was attempted. With the
initial conditions being set at pure hexane, a further
benefit would be greater separation of the early isomers.
Unfortunately, because low wavelength UV detection had to
be used to detect the isomers, the back-off changed as the
concentration of MTBE modifier in the mobile phase increased
and so it was not possible to obtain a chromatogram.

2.11 Analysis of the <578 molecular weight PVC fraction, VC oligomer
fractions and VC oligomer HPLC fractions by GC-MS

2.11.1 <578 molecular weight PVC fraction and VC oligomer fractions
Capillary column GC-MS analysis of the <578 molecular weight
fraction (Figure 3.12) and the VC oligomer fractions
decamer to pentamer (Figure 3.22) (all obtained from
Lucovyl RB 8010 PVC base resin) was carried out with a
Carlo Erba 4200 gas chromatograph connected to a Kratos
MS80 mass spectrometer via an all glass direct coupling
interface. The gas chromatogram was fitted with a
25mm x 0.2mm column coated with BP1. The velocity of the
carrier gas, helium, was 30 cm sec⁻¹. Analysis of the
<578 molecular weight PVC and the VC oligomers was performed
by injecting 0.2 µl of a 10% w/v solution with the
injector at 250°C. Temperature programming in each case
was as follows: 60°C for 5 minutes, then at 4°C min⁻¹ to
130°C and at 8°C min⁻¹ to 300°C, finally 20 minutes iso-
thermally. Electron impact spectra were obtained with a
source temperature of 200°C, electron energy 70 eV and a
trap current of 100 µA. All spectra were processed using a
Data General Nova 3 computer equipped with Kratos DS55
software. Perfluorokerosene was used to calibrate the mass
spectrometer.

Capillary column GC-MS analysis of a VC trimer fraction
obtained from Lucovyl RB 8010 PVC base resin (Figure 3.24)
was carried out with a Carlo Erba 4200 gas chromatograph connected to a VG Mass Labs 7070EQ mass spectrometer. The gas chromatograph was fitted with a 25m x 0.2mm column coated with BP1. The velocity of the carrier gas, helium, was 1 ml min⁻¹. The injector was set at 280°C with a split ratio of 20:1. The transfer line between the gas chromatograph and the mass spectrometer was set at 250°C. The column was programmed from 120°C to 270°C at 10°C min⁻¹. The source conditions were: temperature 200°C; electron energy 70 eV; and trap current 200μA. Spectra were produced by scanning the range 40-600 daltons over 1.0 second.

2.1.1.2 VC oligomer HPLC fractions

HPLC fractions of the VC oligomers heptamer to pentamer (Section 2.10.2) were analysed by capillary column GC-MS using a Carlo Erba 4160 gas chromatograph directly coupled to a VG Mass Labs Quadrupole 15-250 mass spectrometer. The gas chromatograph was fitted with a Chrompak 25m x 0.22mm column coated with a chemically bonded 0.12μm thick layer of CP Sil 5 CB. The carrier gas, helium, was set at 0.8 bar to give a flow rate of 1 ml min⁻¹. The injector was set at 280°C with a split ratio of 20:1. The transfer line between the gas chromatograph and the mass spectrometer was set at 250°C. All work was carried out isothermally, the following GC oven temperatures being used: VC pentamer HPLC fractions, 190°C; VC hexamer HPLC fractions, 230°C; VC heptamer HPLC fractions, 240°C. The source conditions were: pressure 1 x 10⁻⁶ torr; temperature 200°C; electron energy 70 eV; and trap current 200 μA. Spectra were produced by scanning the range 35 to 600 daltons over 1.9 seconds with a 0.1 second interscan delay. All the data was processed on a VG 11-250 data system.

The HPLC fractions of the VC tetramer (Section 2.10.2) were analysed by capillary column GC-MS using a Carlo Erba 4160.
gas chromatograph connected to a VG Mass Labs 7070 EQ mass spectrometer. The gas chromatograph was fitted with a 25m x 0.2mm column coated with BP1. The velocity of the carrier gas, helium, was 1 ml min\(^{-1}\). Spitless injections were made with the injector set at 280°C. The transfer line between the gas chromatograph and the mass spectrometer was set at 250°C. The column was programmed from 60°C to 270°C at 14°C min\(^{-1}\). The source conditions were: temperature 200°C; electron energy 70 eV; and trap current 200 μA. Spectra were produced by scanning the range 40-600 daltons over 1.0 second.

2.12 Analysis of the VC oligomer HPLC fractions and a VC trimer fraction by \(^1\)H NMR

HPLC fractions of the VC oligomers heptamer, pentamer and tetramer (Section 2.10.2), and a VC trimer fraction prepared by HPSEC (Section 2.7.3) were analysed by \(^1\)H NMR. The spectra were obtained with a Nicolet NTC FT-NMR instrument at 200 MHz. The samples were dissolved in deuterated chloroform and analysed at room temperature. The spectra were reported in ppm relative to tetramethyl silane.
CHAPTER THREE

Results

3.1 HPSEC analysis of the PVC base resins and suspension polymerisation dispersing agents

The PVC base resins and suspension polymerisation dispersing agents were characterised using the method described in Section 2.3. Table 3.1 gives the molecular weight data obtained for the PVC base resins. The HPSEC chromatograms of the dispersing agents are given in Figure 3.1.
<table>
<thead>
<tr>
<th>PVC base resin</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>$M_p$</th>
<th>$\bar{M}_w/\bar{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corvic S57/116</td>
<td>47,000</td>
<td>104,400</td>
<td>70,000</td>
<td>2.22</td>
</tr>
<tr>
<td>ICI Mass PVC</td>
<td>69,800</td>
<td>115,500</td>
<td>89,800</td>
<td>1.65</td>
</tr>
<tr>
<td>Lucovyl RB 8010</td>
<td>34,400</td>
<td>68,800</td>
<td>48,600</td>
<td>2.00</td>
</tr>
<tr>
<td>Norvinyl VY 80/30</td>
<td>57,500</td>
<td>104,200</td>
<td>77,400</td>
<td>1.81</td>
</tr>
</tbody>
</table>

*Analysis procedure given in Section 2.3*
Figure 3.1
HPSEC Chromatograms of Suspension Polymerisation Dispersing Agents
Chromatographic System given in Section 2.3
Mobile Phase: Stabilised THF
Flow Rate: 1 ml min⁻¹
Molecular Weights shown in g mol⁻¹
3.2 Soxhlet extractions
Each Soxhlet extract was characterised by HPSEC as described in Section 2.3.

3.2.1 Small scale Soxhlet extractions
Small scale Soxhlet extractions were carried out on a suspension PVC base resin, Corvic S57/116, and suspension polymerisation dispersing agents, using the techniques described in Sections 2.2.1 and 2.2.4, respectively. The extraction results for Corvic S57/116 with a range of solvents are shown in Table 3.2. The dispersing agents were extracted with methanol and diethyl ether only to ascertain as to whether they would be extracted under Soxhlet conditions. For this reason the extract yield was not calculated in every case. The high molecular weight dispersing agent was almost completely extracted by methanol and the low molecular weight type was found to be completely soluble in this solvent. Diethyl ether extracted 0.60% of the low molecular weight dispersing agent but only trace quantities of the high molecular weight agent, which could only be detected by HPSEC.

3.2.2 Large scale Soxhlet extractions
All the PVC base resin extractions were carried out under the conditions described in Section 2.2.2. Corvic S57/116 suspension PVC was extracted in a standard Soxhlet with methanol and diethyl ether. The HPSEC chromatograms of the extracts are given in Figures 3.2 and 3.3. A blank extraction was performed on an extraction thimble under identical conditions and the fraction of the extract that was soluble in the THF characterised by HPSEC, as shown in Figure 3.4. Extractions with methanol and diethyl ether were carried out using the modified Soxhlet (Section 2.2.3) on Corvic S57/116 and an ICI mass polymerised PVC.
The HPSEC chromatograms are shown in Figures 3.5 to 3.8. Lucovyl RB 8010 mass PVC and Norvinyl VY 80/30 suspension PVC were extracted in the modified Soxhlet with diethyl ether. Figures 3.9 and 3.10 give the HPSEC chromatograms of each extract. The quantitative data for each extract obtained with the modified Soxhlet are given in Tables 3.3 and 3.4.

The PVC bottles were extracted in the modified Soxhlet, as described in Section 2.2.5. A viscous, grey coloured oil was obtained which weighed 2.49g (0.99%). The HPSEC chromatogram of this extract is given in Figure 3.11.
Table 3.2  Small scale Soxhlet extractions of Corvic S57/116 suspension PVC

<table>
<thead>
<tr>
<th>Solvent</th>
<th>B.Pt. (°C)</th>
<th>Solubility Parameter*</th>
<th>Oligomer Yield(%)</th>
<th>Extract Colour</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>$\bar{M}_p$</th>
<th>$\bar{M}_w/\bar{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethane</td>
<td>40</td>
<td>9.7</td>
<td>31.2</td>
<td>Brown</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Methyl Ethanoate</td>
<td>77</td>
<td>9.6</td>
<td>24.1</td>
<td>Brown</td>
<td>27500</td>
<td>48100</td>
<td>36400</td>
<td>1.74</td>
</tr>
<tr>
<td>Acetone</td>
<td>56</td>
<td>9.9</td>
<td>23.6</td>
<td>Clear</td>
<td>38700</td>
<td>79600</td>
<td>55500</td>
<td>2.05</td>
</tr>
<tr>
<td>Propanol</td>
<td>49</td>
<td>9.8</td>
<td>22.1</td>
<td>Brown</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-Chloropropane</td>
<td>34</td>
<td>8.6</td>
<td>5.3</td>
<td>Brown</td>
<td>12600</td>
<td>20900</td>
<td>16300</td>
<td>1.65</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>34</td>
<td>7.4</td>
<td>1.3</td>
<td>Clear</td>
<td>4700</td>
<td>6200</td>
<td>5400</td>
<td>1.33</td>
</tr>
<tr>
<td>Methanol</td>
<td>64</td>
<td>14.5</td>
<td>0.15</td>
<td>Brown</td>
<td>-</td>
<td>-</td>
<td>800</td>
<td>1500</td>
</tr>
</tbody>
</table>

* Values in (cal cm$^{-3}$)$^{0.5}$ from Polymer Handbook

+ Extracts characterised by HPSEC as described in Section 2.3
### Table 3.3  Methanol and diethyl ether large scale extraction results using suspension polymerised PVC base resins

<table>
<thead>
<tr>
<th>Colour of extract</th>
<th>Methanol Corvic S57/116</th>
<th>Diethyl Ether Corvic S57/116</th>
<th>Norvinyl VY 80/30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligomer Yield (%)</td>
<td>0.10</td>
<td>0.50</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>6500</td>
<td>2600</td>
</tr>
<tr>
<td>$M_\text{p}$</td>
<td>1500</td>
<td>6500</td>
<td>2600</td>
</tr>
<tr>
<td>Maximum Molecular Weight of Chromatogram*</td>
<td>6500</td>
<td>20000</td>
<td>8500</td>
</tr>
</tbody>
</table>

*Extracts characterised by HPSEC as described in Section 2.3*
Table 3.4 Methanol and diethyl ether large scale extraction results using mass polymerised PVC base resins

<table>
<thead>
<tr>
<th>Colour of Extract</th>
<th>Methanol</th>
<th>Diethyl Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ICI</td>
<td>Lucovyl RB 8010</td>
</tr>
<tr>
<td></td>
<td>Dark Brown</td>
<td>Light Brown</td>
</tr>
<tr>
<td>Oligomer Yield (%)</td>
<td>0.19</td>
<td>0.80</td>
</tr>
<tr>
<td>( M_p^* )</td>
<td>1900</td>
<td>3300</td>
</tr>
<tr>
<td>Maximum Molecular Weight of Chromatogram*</td>
<td>6500</td>
<td>12000</td>
</tr>
</tbody>
</table>

*Extracts characterised by HPSEC as described in Section 2.3*
Figure 3.2

HPSEC Chromatogram of a Methanol Soxhlet* Extract of Corvic S57/116

Chromatographic System given in Section 2.3
Mobile Phase: Stabilised THF
Flow Rate: 1ml min⁻¹
Molecular Weights shown in g mol⁻¹

*Unmodified Soxhlet
Figure 3.3

HPSEC Chromatogram of a Diethyl Ether Soxhlet\textsuperscript{x} Extract of Corvic S57/116

Chromatographic System given in Section 2.3

Mobile Phase: Stabilised THF

Flow Rate: 1 ml min\textsuperscript{-1}

Molecular Weights shown in g mol\textsuperscript{-1}

\textsuperscript{x} Unmodified Soxhlet
Figure 3.4

HPSEC Chromatogram of a Methanol Extract of a Soxhlet Thimble

Chromatographic System given in Section 2.3
Mobile Phase: Stabilised THF
Flow Rate: 1 ml min⁻¹
Molecular Weights shown in g mol⁻¹
**Figure 3.5**

HPSEC Chromatogram of a Methanol Soxhlet Extract of Corvic S57/116

Chromatographic System given in Section 2.3
Mobile Phase: Stabilised THF
Flow Rate: 1 ml min$^{-1}$
Molecular Weights shown in g mol$^{-1}$
Figure 3.6

HPSEC Chromatogram of a Methanol Soxhlet Extract of ICI Mass PVC

Chromatographic System given in Section 2.3
Mobile Phase: Stabilised THF
Flow Rate: 1 ml min⁻¹
Molecular Weights shown in g mol⁻¹
Figure 3.7

HPSEC Chromatogram of a Diethyl Ether Soxhlet Extract of ICI Mass PVC

Chromatographic System given in Section 2.3
Mobile Phase: Stabilised THF
Flow Rate: 1 ml min$^{-1}$
Molecular Weights shown in g mol$^{-1}$
Figure 3.8

HPSEC Chromatogram of a Diethyl Ether Soxhlet Extract of Corvic S57/116

Chromatographic System given in Section 2.3
Mobile Phase: Stabilised THF
Flow Rate: 1 ml min⁻¹
Molecular Weights shown in g mol⁻¹
HPSEC Chromatogram of a Diethyl Ether Soxhlet Extract of Lucovyl RB 8010

Chromatographic System given in Section 2.3
Mobile Phase: Stabilised THF
Flow Rate: 1 ml min$^{-1}$
Molecular Weights shown in g mol$^{-1}$

Figure 3.9
Figure 3.10

HPSEC Chromatogram of a Diethyl Ether Soxhlet Extract of Norvynl VY 80/30

Chromatographic System given in Section 2.3
Mobile Phase: Stabilised THF
Flow Rate: 1 ml min⁻¹
Molecular Weights shown in g mol⁻¹
Figure 3.11
HPSEC Chromatogram of a Diethyl Ether Soxhlet Extract of the PVC Bottles
Chromatographic System given in Section 2.3
Molecular Weights shown in g mol$^{-1}$
3.3 Isolation of low molecular weight PVC fractions from the Diethyl Ether Soxhlet extracts

3.3.1 Isolation by preparative gel filtration
Diethyl ether Soxhlet extracts obtained from Lucovyl RB 8010, Corvic 557/116 and the ICI mass PVC were all fractionated by gel filtration using the method described in Section 2.4. The chromatograms obtained from each extract with stabilised THF as the eluent are shown in Figure 3.12. The elution volume range which corresponds to the collected fraction of VC oligomers with molecular weights up to 578 g mol$^{-1}$ (polystyrene calibration) is designated. It was not possible to accurately determine the mass of the dry <578 molecular weight fractions with stabilised or unstabilised THF as the eluent due to the concentration (0.1%) of quinol stabiliser in the former case and residual breakdown products in the latter. The majority of the gel filtration work for this thesis was carried out on diethyl ether Soxhlet extracts obtained from Lucovyl RB 8010, with toluene as the eluent. In this case the dry <578 molecular weight fraction constituted approximately 40% of the mass of Soxhlet extract (200mg) loaded onto the gel filtration column. The mass of this fraction increased as the column aged.

3.3.2 Isolation by fractional precipitation
The method described in Section 2.5 was used to isolate a low molecular weight fraction from diethyl ether Soxhlet extracts of Lucovyl RB 8010, Norvinyl VY 80/30 and PVC bottles. Examples of the solvent free low molecular weight fraction mass obtained in each case are 0.50g (25%), 0.10g (10%) and 2.29g (92%), respectively. The masses obtained were very dependent on the volume of diethyl ether that the extract was dissolved in when it was added to the pentane. A higher concentration of diethyl ether in the
resulting precipitating mixture gave a higher fraction mass due to an increase in the quantity of long chain PVC remaining in solution and not precipitating.
Figure 3.12  Gel Filtration Chromatograms of Diethyl Ether Soxhlet Extracts of Corvic S57/116, ICI Mass PVC and Lucovyl RB 8010

Chromatographic System given in Section 2.4
Mobile Phase: Stabilised THF    Molecular Weights shown in g mol⁻¹
3.4 Purification of the low molecular weight PVC fractions isolated by fractional precipitation from the Diethyl Ether Soxhlet extracts

An adsorption liquid chromatography technique, which is described in Section 2.6, was used to separate the VC oligomers in the low molecular weight fractions that had been isolated from the diethyl ether Soxhlet extracts by fractional precipitation (Sections 2.5 and 3.3.2) from the other compounds that were known to be present in low molecular weight PVC fractions (c.f. the GC-MS analysis of the Lucovyl RB 8010 <578 molecular weight fraction (Section 3.8)). The chromatograms obtained for the low molecular weight fractions derived from Lucovyl RB 8010 and Norvinyl VY 80/30 are shown in Figures 3.13 and 3.14; the purified fraction was collected over the elution volume range indicated. The dry, purified low molecular weight fraction masses obtained from the low molecular weight fractions of Lucovyl RB 8010 and Norvinyl VY 80/30 were 45 mg (22.5%) and 40 mg (20%), respectively. An attempt was also made to separate the VC oligomers from the additives in the low molecular weight fraction derived from PVC bottles. The resulting chromatogram, with the elution volume range collected marked, is shown in Figure 3.15. With the solvent removed the 'purified' low molecular weight fraction weighed 35 mg (17.5%).
Adsorption LC Chromatogram of a Lucovyl RB 8010 Low Molecular Weight Fraction

Chromatographic System given in Section 2.6.1
Mobile Phase: Hexane-MTBE (95:5)
Flow Rate: 3 ml min⁻¹
Figure 3.14

Adsorption LC Chromatogram of a NorvinyL VY 80/30 Low Molecular Weight Fraction

Chromatographic System given in Section 2.6.1
Mobile Phase: Hexane-MTBE (95:5)
Flow Rate: 4 ml min⁻¹
SoLvent
Front

VC Oligomers and Bottle Additives

UV Absorbance

|– Fraction Collected –|

0  40  80  120  160  200
Time (min)

Figure 3.15

Adsorption LC Chromatogram of a PVC Bottle
Low Molecular Weight Fraction

Chromatographic System given in Section 2.6.1
Mobile Phase : Hexane - MTBE (95:5)
Flow Rate : 4 mL min⁻¹
3.5 HPSEC analysis of the low molecular weight fractions obtained from PVC base resins and PVC bottles

Low molecular weight (<578 g mol⁻¹) fractions isolated from Lucovyl RB 8010 by diethyl ether Soxhlet extraction (Sections 2.2.2 and 3.2.2) followed by preparative gel filtration (Sections 2.4 and 3.3.1) (Figure 3.12) were analysed by HPSEC as described in Section 2.7. Where possible the oligomer peaks on the chromatograms contained in this Section have been assigned, the numbers corresponding to the degree of polymerisation of each VC oligomer. Also, where it is relevant, the portion of the chromatogram selected for recycling is designated, as are the fractions collected. Figures 3.16 to 3.18 show HPSEC chromatograms obtained using 120 cm of gel bed with stabilised THF as the eluent for low molecular weight fractions from the following: ICI mass PVC, Corvic 557/116 and Lucovyl RB 8010.

Figures 3.19 to 3.22 show HPSEC chromatograms of <578 molecular weight fractions obtained from Lucovyl RB 8010 utilising 120, 240, 360 and 480 cm of gel bed with toluene as the eluent. Table 3.5 gives typical dry fraction masses obtained for six Lucovyl RB 8010 <578 molecular weight fractionation using 480 cm of gel bed with toluene as the eluent (Section 2.7.3).

Low molecular weight fractions isolated from PVC base resins and bottles by diethyl ether Soxhlet extraction (Sections 2.2.2 and 3.2.2) followed by fractional precipitation (Sections 2.5 and 3.3.2) were, after they had been purified by adsorption liquid chromatography (Sections 2.6 and 3.4), also analysed by HPSEC (Section 2.7), with dichloromethane as the eluent. HPSEC chromatograms of low molecular weight fractions obtained from Lucovyl RB 8010, Norvinyl VY 80/30 and PVC bottles using 120 cm and 480 cm of gel bed in each case are shown in Figures 3.23 and 3.28. Table 3.5A gives typical dry fraction masses obtained for
six Lucovyl RB 8010 low molecular weight fraction fractionations using 480 cm of gel bed with dichloromethane as the eluent (Section 2.7.3).
Table 3.5  Typical HPSEC dry VC oligomer fraction masses for six Lucovyl RB 8010 <578 molecular weight fraction fractionations with toluene as the eluent

<table>
<thead>
<tr>
<th>Fraction Designation</th>
<th>Elution Volume Range* (ml)</th>
<th>Dry Mass (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC Decamer</td>
<td>101.5 - 103.5</td>
<td>2.4</td>
</tr>
<tr>
<td>VC Nonamer</td>
<td>103.5 - 105.5</td>
<td>2.3</td>
</tr>
<tr>
<td>VC Octamer</td>
<td>105.5 - 108.0</td>
<td>3.9</td>
</tr>
<tr>
<td>VC Heptamer</td>
<td>108.0 - 111.0</td>
<td>3.1</td>
</tr>
<tr>
<td>VC Hexamer</td>
<td>111.0 - 114.0</td>
<td>36.4</td>
</tr>
<tr>
<td>VC Pentamer</td>
<td>114.0 - 117.0</td>
<td>4.7</td>
</tr>
</tbody>
</table>

* See Figure 3.22 for HPSEC chromatogram
Table 3.5A  Typical HPSEC dry VC oligomer fraction masses for six Lucovyl RB 8010 purified low molecular weight fraction fractionations with Dichloromethane as the Eluent

<table>
<thead>
<tr>
<th>Fraction Designation</th>
<th>Elution Volume Range* (ml)</th>
<th>Dry Mass (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC Pentamer</td>
<td>111.5 - 114.5</td>
<td>18.0</td>
</tr>
<tr>
<td>VC Tetramer</td>
<td>114.5 - 118.5</td>
<td>14.6</td>
</tr>
<tr>
<td>BHT</td>
<td>118.5 - 121.0</td>
<td>29.6</td>
</tr>
<tr>
<td>VC Trimer</td>
<td>121.0 - 123.0</td>
<td>5.9</td>
</tr>
</tbody>
</table>

* See Figure 3.24 for HPSEC chromatogram
Figure 3.16

HPSEC Chromatogram of a ICI Mass PVC

<578 Molecular Weight Fraction

Chromatographic System given in Section 2.7.1
Mobile Phase: Stabilised THF
Flow Rate: 1 ml min⁻¹
120 cm PL gel 5 μm, 50 Å
Figure 3.17

HPSEC Chromatogram of a Corvic S57/116 <578 Molecular Weight Fraction

Chromatographic System given in Section 2.7.1
Mobile Phase: Stabilised THF
Flow Rate: 1 ml min⁻¹
120 cm PL gel 5μm, 50Å
Impurity Peaks

Low Molec. Wt. PVC

20 22 24 26 28 30 32
Time (min)

3 = Trimer etc

Figure 3.18

HPSEC Chromatogram of a Lucovyl RB 8010 < 578 Molecular Weight Fraction

Chromatographic System given in Section 2.7.1
Mobile Phase: Stabilised THF
Flow Rate: 1 ml min⁻¹
120 cm PL gel 5 μm, 50 Å
120 cm PL gel 5μm, 50Å

Low Molec. Wt. PVC

5=Pentamer etc

Figure 3.19
HPSEC Chromatogram of a Lucovyl RB 8010 < 578

Molecular Weight Fraction

Chromatographic System given in Section 2.7.1
Mobile Phase: Toluene at 1ml min⁻¹
Figure 3.20
HPSEC Chromatogram of a Lucovyl RB 8010 < 578

Molecular Weight Fraction

Chromatographic System given in Section 2.7.1
Mobile Phase: Toluene at 1 ml min⁻¹
360 cm PL gel 5μm, 50Å

5=Pentamer etc

Figure 3.21
HPSEC Chromatogram of a Lucovyl RB 8010 <578
Molecular Weight Fraction
Chromatographic System given in Section 2.7.1
Mobile Phase: Toluene at 1 ml min⁻¹
Figure 3.22

HPSEC Chromatogram of a Lucovyl RB 8010 <578 Molecular Weight Fraction

Chromatographic System given in Section 2.7.1
Mobile Phase: Toluene at 1 mL min⁻¹
Figure 3.23
HPSEC Chromatogram of a Lucovyl RB 8010 Purified Low Molecular Weight Fraction
Chromatographic System given in Section 2.7.1
Mobile Phase: Dichloromethane
Flow Rate: 1 mL min⁻¹
HPSEC Chromatogram of a Lucovyl RB 8010 Purified Low Molecular Weight Fraction

Chromatographic System given in Section 2.7.1
Mobile Phase: Dichloromethane
Flow Rate: 1 ml min⁻¹
HPSEC Chromatogram of a Norvynl VY 80/30 Purified Low Molecular Weight Fraction

Chromatographic System given in Section 2.7.1
Mobile Phase: Dichloromethane
Flow Rate: 1 ml min⁻¹
Figure 3.26

HPSEC Chromatogram of a Norvinyl VY 80/30 Purified Low Molecular Weight Fraction

Chromatographic System given in Section 2.7.1

Mobile Phase: Dichloromethane

Flow Rate: 1 ml min⁻¹
HPSEC Chromatogram of a PVC Bottle
 'Purified' Low Molecular Weight Fraction

Chromatographic System given in Section 2.7.1
Mobile Phase: Dichloromethane
Flow Rate: 1 ml min⁻¹
480 cm PL gel 5 μm, 50 Å

Bottle Additive Peaks

Collected Fractions

108 112 116 120 124
Time (min)

4 = Tetramer etc

Figure 3.28

HPSEC Chromatogram of a PVC Bottle "Purified" Low Molecular Weight Fraction

Chromatographic System given in Section 2.7.1
Mobile Phase: Dichloromethane
Flow Rate: 1 mL min⁻¹
3.6 Chromatographic analysis of the VC oligomer fractions obtained from PVC base resins and PVC bottles

A number of chromatographic techniques were evaluated in an attempt to separate the VC oligomer fractions that had been prepared by HPSEC from various sources (Sections 2.7 and 3.5) (Figures 3.22, 3.24, 3.26 and 3.28) into their constituent isomers.

3.6.1 TLC

The VC hexamer and pentamer fractions that had been isolated from Lucovyl RB 8010 (Figure 3.22), together with a number of phthalate and chlorinated standards, were analysed by TLC using the method described in Section 2.8. The TLC data obtained with toluene as the developing solvent for the VC hexamer fraction and the standards is given in Table 3.6, and for the VC pentamer fraction in Table 3.7. The VC hexamer fraction (Figure 3.22) was also analysed using mixtures of hexane and MTBE and hexane and ethyl acetate as the developing solvents. The results obtained are given in Tables 3.8 and 3.9.

3.6.2 Microbore HPLC

Microbore HPLC was used to analyse the Lucovyl RB 8010 VC heptamer fraction (Figure 3.22) as described in Section 2.9. The chromatograms obtained with mobile phases of hexane and hexane-MTBE (95:5) are shown in Figures 3.29 and 3.30, respectively.

3.6.3 HPLC

The VC oligomer fractions octamer to trimer (Figures 3.22 and 3.24), which had been isolated from Lucovyl RB 8010, were analysed using the technique described in Section 2.10. Where it is relevant, the fractions that were collected for further analysis are designated on the HPLC chromatograms.
The chromatograms obtained with the VC heptamer fraction using mobile phases of hexane-MTBE (95:5) and hexane-MTBE (99:1) are shown in Figures 3.31 and 3.32. The VC oligomer fractions octamer, hexamer and pentamer were all analysed using the mobile phase hexane-MTBE (99:1) and the chromatograms are shown in Figures 3.33 to 3.35.

The VC tetramer and trimer fractions were analysed using a mobile phase which consisted of hexane-MTBE (99.75:0.25) and the resulting chromatograms are shown in Figures 3.36 and 3.37.

The same HPLC technique was used to analyse the VC oligomer fractions hexamer to tetramer (Figure 3.26) which had been isolated from Norvinyl VY 80/30. A mobile phase of hexane-MTBE (99:1) was used in each case and the chromatograms obtained are shown in Figures 3.38 to 3.40. The VC oligomer fractions hexamer to tetramer (Figure 3.28), which had been obtained from the PVC bottles, were also investigated using this technique. A hexane-MTBE (99:1) mobile phase was utilised in each case and the resulting chromatograms are shown in Figures 3.41 to 3.43.
Table 3.6  TLC analysis of the Lucovyl RB 8010 VC hexamer fraction, chlorinated and phthalate standards, using toluene as the developing solvent

<table>
<thead>
<tr>
<th>Analyte</th>
<th>RF Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibutyl phthalate</td>
<td>0.129</td>
</tr>
<tr>
<td>Di (2-ethyl hexyl) phthalate</td>
<td>0.250</td>
</tr>
<tr>
<td>1,3 dichlorobutane</td>
<td>0.032</td>
</tr>
<tr>
<td>Trans 1,4 dichloro-2-butene</td>
<td>No development</td>
</tr>
<tr>
<td>Trans 1,2 dichlorocyclohexane</td>
<td>0.056 and 0.301</td>
</tr>
<tr>
<td>1,6 dichlorohexane</td>
<td>0.673</td>
</tr>
<tr>
<td>VC hexamer fraction</td>
<td></td>
</tr>
<tr>
<td>Phthalate impurity</td>
<td>0.118</td>
</tr>
<tr>
<td></td>
<td>0.086</td>
</tr>
<tr>
<td>VC Hexamer Isomers</td>
<td>0.301</td>
</tr>
<tr>
<td></td>
<td>0.643*</td>
</tr>
</tbody>
</table>

* The most intense spot
Table 3.7  TLC analysis of the Lucovyl RB 8010 VC pentamer fraction using toluene as the developing solvent

<table>
<thead>
<tr>
<th>Analyte</th>
<th>R_f Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC Pentamer fraction</td>
<td>0.072</td>
</tr>
<tr>
<td>Phthalate impurity</td>
<td>0.058</td>
</tr>
<tr>
<td>VC Pentamer Isomers</td>
<td>0.646*</td>
</tr>
</tbody>
</table>

* This spot was far more intense than the other
## Table 3.8 TLC analysis of the Lucovyl RB 8010 VC Hexamer fraction using combinations of hexane and MTBE as the developing solvent

<table>
<thead>
<tr>
<th>Developing solvent</th>
<th>Phthalate impurity</th>
<th>VC Hexamer Isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spot</td>
<td>band</td>
</tr>
<tr>
<td>Hexane 95</td>
<td>0.056</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.500 - 0.158</td>
</tr>
<tr>
<td>MTBE 5</td>
<td></td>
<td>0.182 - 0.238</td>
</tr>
<tr>
<td>Hexane 90</td>
<td>0.247</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.165 - 0.294</td>
</tr>
<tr>
<td>MTBE 10</td>
<td>0.088</td>
<td>0.329 - 0.400</td>
</tr>
<tr>
<td></td>
<td>0.124</td>
<td></td>
</tr>
<tr>
<td>Hexane 85</td>
<td>0.320</td>
<td>0.074</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.206 - 0.349</td>
</tr>
<tr>
<td>MTBE 15</td>
<td>0.137</td>
<td>0.369 - 0.434</td>
</tr>
<tr>
<td></td>
<td>0.177</td>
<td></td>
</tr>
<tr>
<td>Hexane 80</td>
<td>0.440</td>
<td>0.109</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.309 - 0.469</td>
</tr>
<tr>
<td>MTBE 20</td>
<td>0.229</td>
<td>0.489 - 0.554</td>
</tr>
<tr>
<td></td>
<td>0.289</td>
<td></td>
</tr>
<tr>
<td>Hexane 75</td>
<td>0.661</td>
<td>0.175</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.479 - 0.702</td>
</tr>
<tr>
<td>MTBE 25</td>
<td>0.363</td>
<td>0.731 - 0.795</td>
</tr>
<tr>
<td></td>
<td>0.439</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.9  TLC analysis of the Lucovyl RB 8010 VC hexamer fraction using combinations of hexane and ethyl acetate as the developing solvent

<table>
<thead>
<tr>
<th>Developing solvent</th>
<th>Phthalate impurity</th>
<th>VC Hexamer Isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane 95</td>
<td>0.183</td>
<td>0.030, 0.065</td>
</tr>
<tr>
<td>Ethyl acetate 5</td>
<td>0.444</td>
<td>0.083 - 0.290</td>
</tr>
<tr>
<td>Hexane 85</td>
<td>0.444</td>
<td>0.190, 0.237 - 0.308</td>
</tr>
<tr>
<td>Ethyl acetate 15</td>
<td>0.331 - 0.568</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.29 Microbore HPLC Chromatogram of the Lucovyl RB 8010 VC Heptamer Fraction
Chromatographic System given in Section 2.9.3
Mobile Phase: Hexane at 20 µL min⁻¹
Figure 3.30  Microbore HPLC Chromatogram of the Lucovyl RB 8010 VC Heptamer Fraction
Chromatographic System given in Section 2.9.3
Mobile Phase: Hexane-MTBE (95:5) at 20 μL min⁻¹
Figure 3.31  HPLC Chromatogram of the Lucovyl RB 8010 VC Heptamer Fraction

Chromatographic System given in Section 2.10.1
Mobile Phase: Hexane-MTBE (95:5)
Flow Rate: 1 ml min⁻¹
Figure 3.32 HPLC Chromatogram of the LucovyL RB 8010 VC Heptamer Fraction

Chromatographic System given in Section 2.10.1
Mobile Phase: Hexane-MTBE (99:1)
Flow Rate: 1 mL min⁻¹
Figure 3.33  HPLC Chromatogram of the Lucovyl RB 8010 VC Octamer Fraction

Chromatographic System given in Section 2.10.1
Mobile Phase: Hexane-MTBE (99:1)
Flow Rate: 1 ml min⁻¹
SoLvent Front VC Hexamer Isomers

Figure 3.34 HPLC Chromatogram of the Lucovyl RB 8010 VC Hexamer Fraction
Chromatographic System given in Section 2.10.1
Mobile Phase: Hexane - MTBE (99:1) at 1 ml min⁻¹
Figure 3.35

HPLC Chromatogram of the Lucovyl RB 8010 VC Pentamer Fraction

Chromatographic System given in Section 2.10.1
Mobile Phase: Hexane-MTBE (99:1)
Flow Rate: 1 ml min⁻¹
Figure 3.36

HPLC Chromatogram of the Lucovyl RB 8010 VC Tetramer Fraction

Chromatographic System given in Section 2.10.1
Mobile Phase: Hexane-MTBE (99.75:0.25)
Flow Rate: 1 mL min⁻¹
Figure 3.37

HPLC Chromatogram of the Lucovyl RB 8010 VC Trimer Fraction

Chromatographic System given in Section 2.10.1
Mobile Phase: Hexane - MTBE (99.75 : 0.25)
Flow Rate: 1 mL min⁻¹
Figure 3.38

HPLC Chromatogram of the Norvinyl VY 80/30 VC Hexamer Fraction

Chromatographic System given in Section 2.10.1

Mobile Phase: Hexane-MTBE (99:1) at 1 ml min⁻¹
Figure 3.39

HPLC Chromatogram of the Norvinyl VY 80/30 VC Pentamer Fraction
Chromatographic System given in Section 2.10.1
Mobile Phase: Hexane-MTBE (99:1)
Flow Rate: 1 ml min⁻¹
Figure 3.40

HPLC Chromatogram of the Norvinyl VY 80/30 VC Tetramer Fraction

Chromatographic System given in Section 2.10.1
Mobile Phase: Hexane-MTBE (99:1)
Flow Rate: 1 ml min⁻¹
Figure 3.41 HPLC Chromatogram of the PVC Bottle VC Hexamer Fraction
Chromatographic System given in Section 2.10.1
Mobile Phase: Hexane-MTBE (99:1)
Flow Rate: 1 ml min⁻¹
Figure 3.42

HPLC Chromatogram of the PVC Bottle VC Pentamer Fraction

Chromatographic System given in Section 2.10.1
Mobile Phase: Hexane-MTBE (99:1)
Flow Rate: 1 ml min⁻¹
Figure 3.43

HPLC Chromatogram of the PVC Bottle VC Tetramer Fraction

Chromatographic System given in Section 2.10.1
Mobile Phase: Hexane-MTBE (99:1)
Flow Rate: 1 mL min⁻¹
3.7 Summary of the fractionation schemes used to characterise VC oligomers in PVC base resins and PVC bottles.

There were basically two fractionation schemes used in this work. The first scheme to be developed (Section 3.7.1) enabled the VC oligomers octamer to pentamer in the PVC base resin Lucovyl RB 0010 to be characterised. However, due to its inherent properties it was not possible to characterise VC oligomers having a lower molecular weight than a pentamer and, in addition, was somewhat inefficient (Section 4.4.2). A second fractionation scheme was therefore developed (Section 3.7.2) which was more efficient and enabled VC oligomers to the dimer, if present in the analyte, to be analysed. It was this second scheme that was used to characterise the Lucovyl RB 0010 VC oligomers not characterised by the first scheme, i.e. tetramer and below, and the VC oligomers in the PVC base resin Norvinyl VY 80/30 and the PVC bottles.
3.7.1 Fractionation scheme used to characterise the Lucovyl RB 8010 VC oligomers octamer to pentamer

Lucovyl RB 8010 PVC Base Resin

\[\downarrow\]

Diethyl Ether Soxhlet Extraction

\[\downarrow\]

Diethyl Ether Soxhlet Extract

\[\downarrow\]

Preparative Gel Filtration

(Bio-Beads S-X8 Gel)

\[\downarrow\]

<578 Molecular Weight PVC Fraction

\[\downarrow\]

HPSEC - Eluent : Toluene

(PL gel, 5µm, 50Å)

\[\downarrow\]

Isolated VC oligomers
HPLC - Mobile Phase: Hexane - MTBE (99:1)
(S5W, 5μm Packing)

Isolated VC oligomer isomers

3.7.2 Fractionation scheme used to characterise VC oligomers in Lucovyl RB 8010, Norvinyl VY 80/30 and PVC bottles

PVC Base Resin or Bottles

Diethyl Ether Soxhlet Extraction

Diethyl Ether Soxhlet Extract

Fractional Precipitation in Pentane

Low Molecular Weight PVC Fraction
Adsorption Liquid Chromatography

(Si60, 40-63μm Packing)

Purified Low Molecular Weight PVC Fraction

HPSEC - Eluent: Dichloromethane

(PL gel, 5μm, 50Å)

Isolated VC oligomers

HPLC - Mobile Phase: Hexane - MTBE*

(SSW, 5μm Packing)

Isolated VC Oligomer Isomers

*Relative proportions for each VC oligomer species given in Section 3.6.3.
A <578 molecular weight fraction which had been isolated from Lucovyl RB 8010 by Soxhlet extraction (Sections 2.2.2 and 3.2.2) followed by preparative gel filtration (Sections 2.4 and 3.3.1) (Figure 3.12), and VC oligomer fractions prepared by HPSEC (Sections 2.7 and 3.5) (Figures 3.22 and 3.24) from low molecular weight fractions of the same PVC base resin, were analysed by GC-MS under the conditions described in Section 2.11.1. Figure 3.44 shows the 94-635 ion current chromatogram of the Lucovyl RB 8010 <578 molecular weight fraction. The peaks due to VC oligomers are labelled according to their degree of polymerisation and the major impurity peaks are labelled alphabetically. The impurities which could be identified by the mass spectroscopy data base are listed in Table 3.10.

Only three Lucovyl RB 8010 VC oligomer fractions prepared by the HPSEC system with toluene as the eluent (Figure 3.22) eluted from the gas chromatograph. These were identified by consulting VC oligomer mass spectra data\textsuperscript{16,18,129} and were found to range from the pentamer to the heptamer. The total ion current values for the main constituents found in these three Lucovyl RB 8010 VC oligomer fractions by GC-MS analysis are given in Tables 3.11 to 3.13 and, where possible, the compounds have been identified. It can be seen that the large concentration of phthalate that was discovered in the Lucovyl RB 8010 <578 molecular weight fraction (Figure 3.44 and Table 3.10) was found to be mainly present in the Lucovyl VC hexamer fraction (Table 3.12), although some phthalate impurity was found in each of the three VC oligomer fractions. The higher VC oligomer fractions did not elute from the gas chromatograph due to thermal decomposition.
The Lucovyl RB 8010 VC trimer fraction prepared by the HPSEC system with dichloromethane as the eluent (Figure 3.24) could not be resolved into its structural isomers by the HPLC technique (Section 2.10) developed for the other VC oligomers and so was analysed by GC-MS to obtain a mass spectrum of each isomer. The total ion current chromatogram of the Lucovyl RB 8010 VC trimer fraction is shown in Figure 3.45 and the mass spectra of the two VC trimer isomers are given in Figure 3.46. No other mass spectra of the Lucovyl RB 8010 VC oligomers are given in this Section because the spectra obtained from the GC-MS analysis of the individual oligomer isomers which had been isolated by HPLC (Section 3.6.3) are more accurate and these are presented in Section 3.9.
Table 3.10  Impurity compounds detected in the Lucovyl RB 8010 <578 molecular weight fraction by GC-MS

<table>
<thead>
<tr>
<th>Impurity⁺</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>mono(o-methyl benzyl)phthalate</td>
</tr>
<tr>
<td>E</td>
<td>dodecanoic acid</td>
</tr>
<tr>
<td>F</td>
<td>A phthalate*</td>
</tr>
<tr>
<td>G</td>
<td>A phthalate*</td>
</tr>
<tr>
<td>H</td>
<td>A phthalate*</td>
</tr>
<tr>
<td>I</td>
<td>Undecyl dodecanoate</td>
</tr>
</tbody>
</table>

* Either dibutyl, butyl 2-methyl propyl or dipropyl phthalate

⁺ See Figure 3.44 for GC-MS chromatogram
Table 3.11 Data obtained from the GC-MS analysis of the Lucovyl RB 8010 VC Pentamer fraction

<table>
<thead>
<tr>
<th>Mass Spectrometer Scan Number*</th>
<th>Total Ion Current</th>
<th>Compound°</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>96,148</td>
<td>The Same</td>
</tr>
<tr>
<td>31</td>
<td>145,220</td>
<td>Unknown</td>
</tr>
<tr>
<td>34</td>
<td>116,932</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>126,772</td>
<td></td>
</tr>
<tr>
<td>461</td>
<td>156,928</td>
<td>θ</td>
</tr>
<tr>
<td>516</td>
<td>52,004</td>
<td></td>
</tr>
<tr>
<td>534</td>
<td>1,698,560</td>
<td></td>
</tr>
<tr>
<td>541</td>
<td>39,238</td>
<td>An Unknown</td>
</tr>
<tr>
<td>573</td>
<td>28,753</td>
<td>An Unknown</td>
</tr>
<tr>
<td>609</td>
<td>143,144</td>
<td>An Unknown</td>
</tr>
<tr>
<td>624</td>
<td>429,808</td>
<td></td>
</tr>
<tr>
<td>627</td>
<td>77,316</td>
<td>The Same</td>
</tr>
<tr>
<td>653</td>
<td>18,373</td>
<td>Unknown</td>
</tr>
<tr>
<td>668</td>
<td>42,280</td>
<td>The Same</td>
</tr>
<tr>
<td>676</td>
<td>67,567</td>
<td></td>
</tr>
<tr>
<td>691</td>
<td>5,312,256</td>
<td>A Phthalate+</td>
</tr>
<tr>
<td>695</td>
<td>71,924</td>
<td>A Phthalate+</td>
</tr>
<tr>
<td>699</td>
<td>91,184</td>
<td>VC Pentamer Isomer</td>
</tr>
<tr>
<td>707</td>
<td>1,516,800</td>
<td>VC Pentamer Isomer</td>
</tr>
<tr>
<td>710</td>
<td>1,478,016</td>
<td>VC Pentamer Isomer</td>
</tr>
<tr>
<td>733</td>
<td>35,461</td>
<td>An Unknown</td>
</tr>
<tr>
<td>747</td>
<td>100,812</td>
<td>VC Pentamer Isomer</td>
</tr>
<tr>
<td>751</td>
<td>122,916</td>
<td>VC Pentamer Isomer</td>
</tr>
<tr>
<td>756</td>
<td>96,872</td>
<td>VC Pentamer Isomer</td>
</tr>
</tbody>
</table>

*Instrument conditions given in Section 2.11.1
°Compounds other than VC Pentamer isomers identified using an expert system data base
+Either dibutyl, butyl 2-methyl propyl or dipropyl phthalate
Δ Unidentified impurity B in Figure 3.44
Ψ Unidentified impurity C in Figure 3.44
Φ Unidentified impurity D in Figure 3.44
Table 3.12  Data obtained from the GC-MS analysis of the Lucovyl RB 8010 VC Hexamer fraction

<table>
<thead>
<tr>
<th>Scan Number*</th>
<th>Total Ion Current</th>
<th>Compound(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>14,811</td>
<td>An Unknown</td>
</tr>
<tr>
<td>13</td>
<td>244,016</td>
<td>The Same</td>
</tr>
<tr>
<td>18</td>
<td>312,384</td>
<td>Unknown</td>
</tr>
<tr>
<td>628</td>
<td>140,420</td>
<td>The Same</td>
</tr>
<tr>
<td>631</td>
<td>426,880</td>
<td>Unknown</td>
</tr>
<tr>
<td>666</td>
<td>254,420</td>
<td>A Phthalate(^+)</td>
</tr>
<tr>
<td>680</td>
<td>558,784</td>
<td>A Phthalate(^+)</td>
</tr>
<tr>
<td>701</td>
<td>3,120,064</td>
<td>A Phthalate(^+)</td>
</tr>
<tr>
<td>813</td>
<td>339,776</td>
<td>VC Hexamer Isomer</td>
</tr>
<tr>
<td>815</td>
<td>566,976</td>
<td>VC Hexamer Isomer</td>
</tr>
<tr>
<td>817</td>
<td>273,520</td>
<td>VC Hexamer Isomer</td>
</tr>
<tr>
<td>821</td>
<td>523,536</td>
<td>VC Hexamer Isomer</td>
</tr>
</tbody>
</table>

*Instrument conditions are given in Section 2.11.1

\(^a\) Compounds other than VC Hexamer isomers identified using an expert system data base

\(^+\) Either dibutyl, butyl 2-methyl propyl or dipropyl phthalate
Table 3.13  Data obtained from the GC-MS analysis of the Lucovyl RB 8010 VC Heptamer fraction

<table>
<thead>
<tr>
<th>Mass Spectrometer Scan Number*</th>
<th>Total Ion Current</th>
<th>Compound*</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>296,256</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>88,680</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>92,460</td>
<td>The Same</td>
</tr>
<tr>
<td>32</td>
<td>66,656</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>58,644</td>
<td>Unknown</td>
</tr>
<tr>
<td>48</td>
<td>32,050</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>27,403</td>
<td></td>
</tr>
<tr>
<td>679</td>
<td>44,049</td>
<td>An Unknown</td>
</tr>
<tr>
<td>685</td>
<td>10,640</td>
<td>An unknown</td>
</tr>
<tr>
<td>692</td>
<td>179,584</td>
<td>A Phthalate*</td>
</tr>
<tr>
<td>729</td>
<td>28,681</td>
<td></td>
</tr>
<tr>
<td>734</td>
<td>46,927</td>
<td>The Same</td>
</tr>
<tr>
<td>774</td>
<td>84,108</td>
<td>Unknown</td>
</tr>
<tr>
<td>783</td>
<td>68,952</td>
<td></td>
</tr>
<tr>
<td>787</td>
<td>102,320</td>
<td></td>
</tr>
<tr>
<td>904</td>
<td>144,856</td>
<td>VC Heptamer Isomer</td>
</tr>
<tr>
<td>908</td>
<td>344,384</td>
<td>VC Heptamer Isomer</td>
</tr>
<tr>
<td>911</td>
<td>348,384</td>
<td>VC Heptamer Isomer</td>
</tr>
<tr>
<td>914</td>
<td>184,260</td>
<td>VC Heptamer Isomer</td>
</tr>
<tr>
<td>917</td>
<td>257,368</td>
<td>VC Heptamer Isomer</td>
</tr>
</tbody>
</table>

*Instrument conditions are given in Section 2.11.1

*Compounds other than VC Heptamer isomers identified using an expert system data base

+Either dibutyl, butyl 2-methyl propyl or dipropyl phthalate
Figure 3.44

GC-MS 94-635 Ion Current Chromatogram of the Lucovyl RB 8010 <578 Molecular Weight Fraction

GC-MS conditions given in Section 2.11.1
Peaks due to Vinyl Chloride Oligomers are labelled according to degree of polymerisation
Major Impurity Peaks are labelled alphabetically
Figure 3.45

GC-MS Total Ion Current Chromatogram of the LucovyL RB 8010 VC Trimer Fraction

GC-MS conditions given in Section 2.11.1
Figure 3.46  Mass Spectra of VC Trimer Isomers

GC-MS conditions given in Section 2.11.1
3.9 Characterisation of the Lucovyl RB 8010 VC oligomer isomers by GC-MS

Isomers of the Lucovyl RB 8010 VC oligomers heptamer to tetramer, which had been isolated by HPLC (Sections 2.10 and 3.6) (Figures 3.32 and 3.34 to 3.36), were analysed by GC-MS as described in Section 2.11.2 in an attempt to structurally characterise them. The VC oligomer isomers were submitted in the form of HPLC fractions and this investigation yielded information on fraction purity, composition and isomer concentration. The total ion current chromatograms for the HPLC fractions of the VC tetramer (Figure 3.36), pentamer (Figure 3.35), hexamer (Figure 3.34) and heptamer (Figure 3.32) are given in Figures 3.47 and 3.48, 3.49 to 3.51, 3.52 to 3.56 and 3.57 to 3.61, respectively.

For the species tetramer and pentamer, the mass spectra of the major VC oligomer isomer present in each of the HPLC fractions that contain VC oligomers, are given in Figures 3.62 and 3.63 to 3.65. Due to the large number of isomers existing for the VC hexamer and heptamer species, along with the marked similarity of their mass spectra, only representative isomer mass spectra are included for these two oligomers. They are given in Figures 3.66 to 3.70. The mass spectra of the three VC heptamer isomers (HPLC fractions 11, 18 and 29 - Figure 3.32) that were analysed by \(^1\)H NMR (Sections 2.12 and 3.10) are given in Figure 3.71.
Figures 3.47 and 3.48

GC-MS Total Ion Current Chromatograms of the VC Tetramer HPLC Fractions

GC-MS conditions given in Section 2.11.2

Peaks due to VC Tetramer Isomers are Assigned

*Figure 3.36
Figure 3.47

VC Tetramer Fraction 1

VC Tetramer Fraction 2

VC Tetramer Fraction 3
VC Tetramer Fraction 4

VC Tetramer Fraction 5

VC Tetramer Fraction 6

Figure 3.48
Figures 3.49 to 3.51

GC-MS Total Ion Current Chromatograms of the VC Pentamer HPLC Fractions

GC-MS conditions given in Section 2.11.2
Peaks due to VC Pentamer Isomers are Assigned

*Figure 3.35
VC Pentamer Fraction 1

VC Pentamer Fraction 2

VC Pentamer Fraction 3

VC Pentamer Fraction 4

Figure 3.49
Figure 3.50
Figure 3.51
Figures 3.52 to 3.56

GC-MS Total Ion Current Chromatograms
of the VC Hexamer HPLC Fractions

GC-MS conditions given in Section 2.11.2
Peaks due to VC Hexamer Isomers are Assigned

*Figure 3.34
Figure 3.52
Figure 3.53
Figure 3.54
Figure 3.55
Figures 3.57 to 3.61

GC-MS Total Ion Current Chromatograms of the VC Heptamer HPLC Fractions

GC-MS conditions given in Section 2.11.2

Peaks due to VC Heptamer Isomers are Assigned

Only the Fractions that were found to contain VC Heptamer Isomers are shown

*Figure 3.32
Figure 3.57
VC Heptamer Fraction 8

VC Heptamer Fraction 9

VC Heptamer Fraction 10

VC Heptamer Fraction 12

VC Heptamer Fraction 13

Figure 3.58
Figure 3.59
Figure 3.60
Figure 3.61
HPLC Fraction 3 (GC Peak 366 - Figure 3.47)

HPLC Fraction 4 (GC Peak 146 - Figure 3.48)

HPLC Fraction 5 (GC Peak 105 - Figure 3.48)

Figure 3.62 Mass Spectra of VC Tetramer Isomers

GC-MS conditions given in Section 2.11.2
HPLC Fraction 3 (GC Peak 88 - Figure 3.49)

HPLC Fraction 4 (GC Peak 81 - Figure 3.49)

HPLC Fraction 5 (GC Peak 95 - Figure 3.50)

Figure 3.63  Mass Spectra of VC Pentamer Isomers

GC-MS conditions given in Section 2.11.2
HPLC Fraction 6 (GC Peak 78 - Figure 3.50)

HPLC Fraction 7 (GC Peak 88 - Figure 3.50)

HPLC Fraction 8 (GC Peak 85 - Figure 3.50)

Figure 3.64  Mass Spectra of VC Pentamer Isomers

GC-MS conditions given in Section 2.11.2
HPLC Fraction 9 (GC Peak 89 - Figure 3.51)

HPLC Fraction 10 (GC Peak 91 - Figure 3.51)

HPLC Fraction 11 (GC Peak 92 - Figure 3.51)

Figure 3.65  Mass Spectra of VC Pentamer Isomers

GC-MS conditions given in Section 2.11.2
Figure 3.52  Mass Spectra of VC Hexamer Isomers

GC-MS conditions given in Section 2.11.2
Figure 3.67 Mass Spectra of VC Hexamer Isomers

GC-MS conditions given in Section 2.11.2
HPLC Fraction 17 (GC Peak 105—Figure 3.55)

HPLC Fraction 19 (GC Peak 110—Figure 3.55)

HPLC Fraction 22 (GC Peak 111—Figure 3.56)

Figure 3.56  Mass Spectra of VC Hexamer Isomers

GC-MS conditions given in Section 2.11.2
HPLC Fraction 4 (GC Peak 195—Figure 3.57)

HPLC Fraction 10 (GC Peak 198—Figure 3.58)

HPLC Fraction 15 (GC Peak 213—Figure 3.59)

Figure 3.69 Mass Spectra of VC Heptamer Isomers

GC-MS conditions given in Section 2.11.2
HPLC Fraction 17 (GC Peak 214 - Figure 3.59)

HPLC Fraction 21 (GC Peak 215 - Figure 3.60)

HPLC Fraction 26 (GC Peak 220 - Figure 3.60)

Figure 3.70 Mass Spectra of VC Heptamer Isomers

GC-MS conditions given in Section 2.11.2
HPLC Fraction 11 (GC Peak 223 - Figure 3.61)

HPLC Fraction 18 (GC Peak 229 - Figure 3.61)

HPLC Fraction 29 (GC Peak 243 - Figure 3.61)

Figure 3.71  Mass Spectra of VC Heptamer Isomers

GC-MS conditions given in Section 2.11.2
3.10 Structural characterisation of the Lucovyl RB 8010 VC oligomer isomers by $^1$H NMR

Isomers of the Lucovyl RB 8010 VC oligomers heptamer, pentamer and tetramer, which had been isolated by HPLC (Sections 2.10 and 3.6.3), were analysed by $^1$H NMR as described in Section 2.12. The 200 MHz $^1$H NMR spectra of three VC heptamer isomers (HPLC fractions 11, 18 and 29 - Figure 3.32), nine VC pentamer isomers (HPLC fractions 3-11 incl. - Figure 3.35) and three VC tetramer isomers (HPLC fractions 3-5 incl. - Figure 3.36) are shown in Figures 3.72 to 3.74, 3.75 to 3.83 and 3.84 to 3.86, respectively.

The Lucovyl RB 8010 VC trimer fraction prepared by HPSEC (Sections 2.7 and 3.5) (Figure 3.24) could not be resolved into its two constituent isomers by HPLC (Figure 3.37) and so the HPSEC trimer fraction was analysed directly by $^1$H NMR as described in section 2.12. The 200 MHz $^1$H NMR spectrum of the VC trimer fraction is shown in Figure 3.87.
Figure 3.72

'H NMR Spectrum of VC Heptamer Fraction 11 in the Region 2-6 PPM

Analysis conditions given in Section 2.12
Other Possible Partial Structures shown in Section 4.6.5

* Figure 3.32
Figure 3.73

'H NMR Spectrum of VC Heptamer Fraction 18* in the Region 2-6.8 PPM

Analysis conditions given in Section 2.12
Other Possible Partial Structures shown in Section 4.6.5

*Figure 3.32
Figure 3.74

$^{1}H$ NMR Spectrum of VC Heptamer Fraction 29$^x$ in the Region 1.8-6 PPM

Analysis conditions given in Section 2.12
Other Possible Partial Structures shown in Section 4.6.5

$^x$Figure 3.32
Figure 3.75

'H NMR Spectrum of VC Pentamer Fraction 3* in the Region 1.8-6.4 PPM

Analysis conditions given in Section 2.12

*Figure 3.35
Figure 3.76

1H NMR Spectrum of VC Pentamer Fraction 4\textsuperscript{x}
in the Region 2–6.4 PPM

Analysis conditions given in Section 2.12

\textsuperscript{x} Figure 3.35
Figure 3.77

"H NMR Spectrum of VC Pentamer Fraction 5\textsuperscript{x} in the Region 1.8-6.6 PPM

Analysis conditions given in Section 2.12

\textsuperscript{x}Figure 3.35
Figure 3.78

$^1$H NMR Spectrum of VC Pentamer Fraction 6* in the Region 2.4-6.6 PPM

Analysis conditions given in Section 2.12

*Figure 3.35
Figure 3.79

$^1$H NMR Spectrum of VC Pentamer Fraction 7* in the Region 1.8-6.6 PPM

Analysis conditions given in Section 2.12

*Figure 3.35
\[ -\text{CH}_2\text{CH=CH-CL} \]
\[ -\text{CH-CH}_2\text{Cl} \]
\[ >\text{CH-CH}_2\text{Cl} \]

**Figure 3.80**

\( ^1\text{H NMR Spectrum of VC Pentamer Fraction 8}^{x} \)

in the Region 2.8–6.8 PPM

Analysis conditions given in Section 2.12

\(^x\text{Figure 3.35} \)
\[ \text{CL-CH}_2\text{-CH}_2\text{-CH-CH-CH}_2\text{-CH-CH}_2\text{-CH=CH-CH}_2\text{-Cl} \]

**Figure 3.81**

\(^1\text{H NMR Spectrum of VC Pentamer Fraction 9}^x\)

in the Region 1.8-6 PPM

Analysis conditions given in Section 2.12

* Figure 3.35
Figure 3.82

'$^1$H NMR Spectrum of VC Pentamer Fraction 10$^x$

in the Region 1.8 - 6 PPM

Analysis conditions given in Section 2.12

$^x$Figure 3.35
Figure 3.83

$^1$H NMR Spectrum of VC Pentamer Fraction 11

in the Region 1.8-6 PPM

Analysis conditions given in Section 2.12

*Figure 3.35
Figure 3.84

$^1$H NMR Spectrum of VC Tetramer Fraction 3

in the Region 0.8-7.8 PPM

Analysis conditions given in Section 2.12

*Figure 3.36
Figure 3.85

'H NMR Spectrum of VC Tetramer Fraction 4\textsuperscript{\times}
in the Region 1.8-6 PPM

Analysis conditions given in Section 2.12

\textsuperscript{\times} Figure 3.36
Figure 3.86

'H NMR Spectrum of VC Tetramer Fraction 5* in the Region 2-6 PPM

Analysis conditions given in Section 2.12

*Figure 3.36
Figure 3.87

'H NMR Spectrum of VC Trimer Fraction in the Region 3-7.4 PPM

Analysis conditions given in Section 2.12

*Figure 3.24
3.11 Structures of Lucovyl RB 8010 VC oligomer isomers

The GC-MS (Sections 2.11.2 and 3.9) and \(^1\)H NMR (Sections 2.12 and 3.10) analysis of the VC oligomer isomers that had been isolated from Lucovyl RB 8010 (Section 3.7) enabled the complete structures of two VC tetramer isomers (HPLC fractions 4 and 5 - Figure 3.36) and five VC pentamer isomers (HPLC fractions 3, 5, 7, 9 and 11 - Figure 3.35) to be elucidated. These are shown overleaf.
VC tetramer isomers  (Section 4.6.2)

i) HPLC fraction 4

CH₂Cl

\[
\begin{array}{c}
\text{CH₂CH=CH-CH₂-CH-CH-CH₂} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

ii) HPLC fraction 5

CH₂CH=CH-CH₂-CH-CH-CH₂-CH₂

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

VC pentamer isomers  (Section 4.6.3)

i) HPLC fraction 3

\[
\begin{array}{c}
\text{CH₂CH=CH-CH₂-CH₂-CH=CH-CH₂} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{CH₂Cl} \\
\end{array}
\]

ii) HPLC fraction 5

\[
\begin{array}{c}
\text{CH₂CH=CH-CH₂-CH₂-CH=CH₂-CH₂} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{CH₂Cl} \\
\end{array}
\]
From the spectroscopic data it was possible to assign partial structures for the other VC oligomer isomers and these are given in Section 4.6.
CHAPTER FOUR

Discussion

4.1 VC oligomer sources

Because the aim of this work was to characterise VC oligomers that had a potential to migrate into food, only food grade PVC base resins were considered as oligomer sources. The type of food packaging that the PVC is going to be processed into determines the molecular weight of the base resin used. For example, PVC film is produced from a high molecular weight resin ($\bar{M}_n \approx 6.5 \times 10^4$) whereas PVC bottles originate from a low molecular weight resin ($\bar{M}_n \approx 3.7 \times 10^4$). It has been shown by Gilbert et al.\textsuperscript{15} that as the molecular weight of a PVC resin decreases the amount of extractable low molecular weight material increases. In order to maximise the yield of VC oligomers the lowest molecular weight (K-value) bottle grade PVC base resins were used (Section 2.1). Table 3.1 gives the molecular weight data, obtained by HPSEC (Section 2.3), for each PVC base resin used in this work.

PVC base resins contain a number of compounds that can be coextracted with the VC oligomers under Soxhlet conditions\textsuperscript{16} (Section 1.8). One such compound is the stabiliser that is added to the resin to inhibit degradation during the drying process etc. An example of such a material is butylated hydroxy toluene (BHT). A large concentration of phthalate impurity is found in low molecular weight fractions derived from mass polymerised PVC resins (Section 3.8) (Figure 3.44) due to such compounds being used as solvents for the polymerisation initiator, which is added to the polymerisation autoclave in a solution form. Phthalates have been discovered in suspension PVC extracts.
due to their use as plasticisers in elastomeric seals that are present in the polymerisation autoclave structure.\textsuperscript{131}

To enable a valid comparison to be made between the VC oligomers inherent in a PVC base resin and those existing in a fabricated PVC food packaging article, PVC bottles were analysed that had been produced from a formulation based on the same batch of one of the base resins investigated (Norvinyl VY 80/30). The manufacturers, Norsk Hydro, were requested to supply bottles that had been produced from their least complicated formulation in order to keep the number of potential VC oligomer coextractants to a minimum. As much information as possible regarding the formulation was solicited and the following list of ingredients provided:

Norvinyl VY 80/30 PVC base resin
Methyl methacrylate copolymer (Process aid)
Dioctyl thioglycollate (tin: stabiliser)
Epoxy soya bean oil
Waxes.

4.2 Soxhlet extraction of PVC base resins and PVC bottles
The initial extraction work was carried out on Corvic S57/116. Two criteria were used in the choice of solvent. First, only solvents with boiling points below the glass transition temperature of PVC ($81^\circ$C) were considered in order to minimise particle fusion which could occur with soft particles, resulting in a significant reduction of surface area. Second, the liquid should be regarded as a poor solvent or non-solvent for PVC at room temperature so that selective dissolution of oligomers occurred at the extraction temperature. Although some of the liquids chosen have solubility parameters close to that of PVC ($9.5$ (cal/cm$^3$)$^{1/2}$), its limited solubility due to its polar,
partly crystalline character results in these liquids being poor solvents at room temperature. The other liquids are non-solvents for PVC at room temperature due to the difference in solubility parameters (Section 1.2.2). There is no HPSEC data in Table 3.2 for some of the high yield extracting solvents because such solvents are of little use for this work due to the high quantity of long chain PVC that is present in their extracts. Only the Mₚ HPSEC data is provided for the methanol extract because the multi-peaked chromatogram could not be characterised by the computer programme developed for the other single peak chromatograms. Since only VC oligomers having molecular weights below 500 are of interest in this work, the results in Table 3.2 show that, of the liquids evaluated, only diethyl ether and methanol are suitable extracting solvents, as they alone provide oligomer extracts containing low quantities of long chain PVC. The inherent instability of PVC has already been discussed (Section 1.7) along with the change in the colour of the polymer that accompanies its degradation. This discolouration commences at very low levels of degradation and so is a useful indicator of the state of the extract. PVC base resins do contain a stabiliser (Section 4.1) but from the colour of the extracts shown in Table 3.2 it is evident that the majority have undergone thermal degradation. This is undesirable due to the possible structural changes that the VC oligomers could undergo under such circumstances. The most likely possibility is the loss of hydrogen chloride which would result in extra double bonds being present in the molecules. The amount of thermal degradation was found to be dependent on both the extraction temperature and the liquid used. Some liquids that had a low boiling point still produced extracts that were degraded, possibly due to the liquid having a catalytic effect on the degradation.
The initial extraction work had shown that only two liquids were capable of providing extracts containing a reasonable proportion of VC oligomers: diethyl ether and methanol, although only diethyl ether had combined this property with a low state of thermal degradation. In order to maximise the yield of VC oligomers, a large Soxhlet was obtained and extractions performed on Corvic S57/116 using diethyl ether and methanol. Both the extracts were found to be contaminated with a substance that appeared to be insoluble in THF, the methanol extract to a much greater extent. The insolvability in THF indicated that this substance was not a PVC fraction as even high molecular weight PVC is soluble in THF at room temperature. One probable source of the contamination was the Soxhlet thimble which was made of a cellulosic material. Such a contaminant would not be visible in the small scale Soxhlet extracts due to the much smaller extraction thimble employed. The HPSEC chromatogram of a methanol extract of an extraction thimble (Figure 3.4) has a large peak corresponding to a molecular weight of 300. Such a peak is also present in the HPSEC chromatogram of a methanol extract of Corvic S57/116 under standard Soxhlet conditions (Figure 3.2). Several pre-extraction procedures were carried out on the extraction thimble in an attempt to stop it contaminating the oligomer fraction, but these were not successful which indicated that a continuous breakdown of the thimble was taking place. The Soxhlet was therefore modified (Section 2.2.3) to enable it to be used without an extraction thimble. Figure 3.5 gives a HPSEC chromatogram for a methanol extract of Corvic S57/116 obtained using the modified Soxhlet and it can be seen that the peak due to cellulosic material \( (M_p \sim 300 \text{ g mol}^{-1}) \) is not present. However, there was still visible in the extract some material that was apparently insoluble in the THF which had
been coextracted with the VC oligomers. Acting on the premise that this material was dispersing agent originating from the surface of the PVC particles, small scale extractions were carried out on two commercial dispersing agents used in the suspension polymerisation of PVC to test their solubility in diethyl ether and methanol under Soxhlet conditions. The results obtained (Section 3.2.1) showed that it was possible that the dispersing agent was being stripped from the PVC particle surface by either solvent during the course of an extraction. The dispersing agents were only sparingly soluble in THF. However, from a HPSEC chromatogram of the fraction of the as-received dispersing agent which is soluble in THF it can be seen (Figure 3.1) that there is a large peak corresponding to a molecular weight of 600 g mol$^{-1}$. A peak having a similar molecular weight (700 g mol$^{-1}$) is a feature of the HPSEC chromatograms given in Figures 3.2 and 3.5, which strongly suggests that each of the oligomer fractions contains dispersing agent. To corroborate this assertion a mass polymerised PVC was obtained from ICI and extracted with methanol using the modified Soxhlet. The HPSEC chromatogram of the resulting extract (Figure 3.6) does not have any peak corresponding to a molecular weight of ~700 g mol$^{-1}$.

The methanol extraction results have been cited to illustrate the origin of two potential VC oligomer fraction contaminants because it was very efficient at solvating the materials in question. Both the cellulosic and dispersing agent contaminants were visibly present in the diethyl ether extracts, although at a much lower concentration when compared to the methanol extracts. These large scale Soxhlet extraction results showed that the purity of the oligomer fraction could be enhanced by carrying out the PVC base resin extractions in a Soxhlet which had been modified to remove the need for an extraction thimble, and by using
mass polymerised PVC as the VC oligomer source. With the large scale Soxhlet, both the diethyl ether and methanol extracts appeared darker in colour than their small scale analogues, which could indicate a greater degree of degradation. However, it seems more likely that the much greater mass of material present gave a truer indication of the amount of thermal degradation that had taken place. Diethyl ether was finally chosen in preference to methanol for the routine Soxhlet extraction work because it yielded oligomer extracts that had undergone less thermal degradation.

A further mass polymerised PVC, Lucovyl RB 8010, was evaluated as a source for VC oligomers and as Table 3.4 shows the oligomer yield obtained with diethyl ether was higher than for the ICI mass PVC. In addition to the higher oligomer purity conferred by mass polymerised PVC compared with suspension polymerised PVC, a comparison of Table 3.3 with Table 3.4 reveals that a higher yield of oligomers is obtained from the mass polymerised polymer with either solvents. This is due to the peracellular skin that surrounds suspension PVC particles, which hinders solvent penetration and hence oligomer dissolution. In view of these results, the Lucovyl RB 8010 resin was chosen as the source for the VC oligomers. To see if the oligomer yield could be improved, diethyl ether extractions were performed on Lucovyl RB 8010 as a function of time, giving dry extract yields of 0.80, 0.89 and 0.91% after 20, 40 and 60 hours extraction respectively. Although these results do demonstrate some increase in the yield for longer extraction times, the possibility that a higher degree of thermal degradation would result, and the fact that the separation of oligomers would appear to be sufficiently efficient for a 20 hour extraction, resulted in this extraction time being used.
After the VC oligomers that had been obtained from Lucovyl RB 8010 had been studied it was considered desirable to analyse the VC oligomers present in a fabricated PVC food packaging article to investigate the effect that processing had on them. PVC bottles that had been stretch blow moulded from a formulation based on Norvinyl VY 80/30 suspension resin were obtained along with a sample of the base resin itself. Both of these were extracted with diethyl ether in the modified Soxhlet. A relatively low yield of VC oligomers was obtained from the Norvinyl VY 80/30 base resin compared with the Corvic 557/116 suspension resin (Table 3.3) which, although no information regarding the porosity of the resin particles was available, would seem to indicate a lower level of porosity. The PVC bottle extract was a viscous, grey coloured oil due to the high concentration of additives (Section 4.1) that had been co-extracted with the VC oligomers. The yield of VC oligomers was low compared to the base resins because of the much lower surface area that the cut up bottles presented to the extracting solvent and because fused PVC was involved and not individual, porous particles. The VC oligomers that were present in the bottle extract were solvated by the co-extracted additives. These additives can be clearly seen in the HPSEC chromatogram of the bottle extract (Figure 3.11).

4.3 Low molecular weight PVC fractions obtained from diethyl ether Soxhlet extracts of PVC base resins and PVC bottles

Although the VC oligomer sources had been fractionated by diethyl ether Soxhlet extraction (Sections 3.2.2 and 4.2), the resulting extract still contained a very large concentration of long chain PVC. Tables 3.3 and 3.4 show that PVC molecules having molecular weights of up to 20,000 g mol\(^{-1}\) are present in the diethyl ether extracts of the PVC base resins and Figure 3.11 reveals the molecular weight range
of the diethyl ether PVC bottle extract extending to 4000 g mol$^{-1}$. To facilitate the characterisation of VC oligomers having molecular weights up to 500 g mol$^{-1}$ it is desirable to remove a large proportion of this long chain PVC. Two techniques were utilised for this purpose: preparative gel filtration and fractional precipitation. The preparative gel filtration route was similar to that followed by Gilbert et al.\textsuperscript{5} the main difference being that only one stage was used instead of two in order to speed up the fractionation process. The gel chosen, Bio-Beads S-X8, had a molecular weight exclusion limit of 1000 g mol$^{-1}$ which meant that the majority of the diethyl ether extract should have been excluded from the gel pores and should have passed straight down the column. A low molecular weight exclusion limit was desirable because it helped to reduce the amount of long chain PVC that carried over into the $< \text{578}$ molecular weight fraction. Such a phenomenon is experienced with gel filtration columns because they have less resolving power than HPSEC columns due to the much larger gel particles and a broad gel particle size range. This dispersing of the extract as it passes down the column can be clearly seen in Figure 3.12 where it is not obvious that most of the analyte is greater in molecular weight than the exclusion limit of the packing, i.e. there is no sharp peak. This carryover of long chain PVC into the $< \text{578}$ molecular weight fraction is the reason why this fraction represents $\sim 40\%$ of the Soxhlet extract loaded onto the column. For the two mass polymerised polymers, Lucovyl RB 8010 and ICI, there is a secondary peak in the chromatogram situated in the $< \text{578}$ molecular weight fraction. The GC-MS analysis of the Lucovyl RB 8010 $< \text{578}$ molecular weight fraction (Section 3.8) had revealed that it contained a high concentration of phthalates and it is possible that this peak is due to these compounds.
This analysis had also located a number of other compounds in the fraction (Figure 3.44), some of which could be identified using a mass spectrometer data base (Table 3.10). The origin of some of these compounds can be traced. In the mass polymerisation process the initiator is usually added in the form of a solution and the solvent normally used is a phthalate compound. This practice results in the final PVC base resin containing a quantity of phthalate which can be extracted. A very common initiator used in the polymerisation of VCM is lauryl peroxide, and the impurities dodecanoic acid and undecyl dodecanoate are derivatives of this initiator. Gilbert et al\textsuperscript{16} found some of these impurities in a GC-MS analysis of a <500 molecular weight fraction isolated from a suspension polymerised PVC base resin. Upon routine preparative use the gel filtration column became discoloured and its efficiency dropped due to the gel pores becoming blocked by adsorbed material, possibly other compounds which had been extracted from the PVC base resin or degraded PVC.

This resulted in more long chain PVC being carried over into the <578 molecular weight fraction and a need for the column to be recalibrated with the polystyrene 580 standard. Eventually, the column had to be repacked with fresh BioBeads S-X8 packing. In addition to discovering and, in some cases, identifying impurities in the <578 molecular weight fraction the GC-MS analysis revealed important information regarding the VC oligomers themselves (Section 3.8). The presence of a series of VC oligomers ranging from the trimer to the heptamer was shown (Figure 3.44); the higher oligomers were not volatile enough to elute from the gas chromatograph before they had undergone thermal degradation. There was no evidence of a VC dimer species being present in the <578 molecular weight fraction. It is probable that most of this VC oligomer species is lost
during the VCM stripping procedure (Section 1.1.4), since the temperatures involved approach it's theoretical boiling point (136°C for the 1,3 dichlorobutane VC dimer analogue). Each VC oligomer was found to exist as a number of structural isomers, the number increasing with increasing chain length (Figure 3.44).

The second technique used to isolate low molecular weight fractions from diethyl ether Soxhlet extracts was fractional precipitation. The main advantage of this technique is the rapidity with which a Soxhlet extract can be fractionated and the dried low molecular weight fraction obtained. With the preparative gel filtration technique a single Soxhlet extract (~2g) cannot be fractionated in one procedure due to the finite column loading capacity. The result of this is that it is a very time consuming process due to both the long fractionated times (~90 minutes) and the amount of relatively high boiling point solvent (~60 mls of toluene per fractionation) that had to be removed to achieve a dry fraction. However, with fractional precipitation one or more Soxhlet extracts can be fractionated in one operation and, by a judicious choice of solvent, the dried fraction obtained quickly. For a solvent to be of use for this technique it had to be primarily a non-solvent for PVC, so that only the VC oligomers remained in solution, and furthermore have a relatively low boiling point to facilitate solvent removal at, or near, room temperature. High temperatures could not be employed to dry fractions as they would cause thermal degradation of the VC oligomers. Solubility parameters were used to select an appropriate solvent. Pentane was chosen as its solubility parameter of 6.3 (cal/cm³)½ makes it a non-solvent for PVC and its low boiling point (36°C) easy to remove. Pentane proved to be very effective at isolating a low molecular weight fraction.
that had a similar molecular weight range to the <578 molecular weight fraction prepared using preparative gel filtration. The diethyl ether Soxhlet extract was not taken to dryness before being added to the pentane because of the possibility that a quantity of the desired VC oligomers could remain trapped in the bulk of the extract. Although diethyl ether is regarded as a poor solvent for PVC, it is a better one than pentane, and so small differences in the volume in which the Soxhlet extract remained solvated in (Section 2.5) altered the molecular weight range that was precipitated. The actual volume of the concentrated Soxhlet extract was not monitored stringently before addition to the pentane because there was no chance of vital VC oligomers, i.e. those with molecular weights below 500, being lost if the volume was kept around 20 ml due to their solubility, and other fractionation steps were to follow which would remove any additional long chain PVC left in the diethyl ether/pentane precipitating solution. The diethyl ether Soxhlet extract of the PVC bottles contained a high concentration of additives and possibly oligomers of the methylmethacrylate (MMA) copolymer (Section 4.1). With the possible exception of the MMA copolymer oligomers these compounds have relatively low molecular weights and so it is highly probable that they will remain in solution when the PVC bottle extract is added to the pentane. For this reason the fractional precipitation technique does not yield low molecular weight fractions from such extracts that are any purer than those prepared by alternative techniques such as preparative gel filtration. Due to the relatively low quantity of long chain PVC in the PVC bottle extract (Figure 3.11) much less precipitation was observed compared with the PVC base resin extracts.
4.4 Separation of the VC oligomers in the low molecular weight PVC fractions by HPSEC

4.4.1 Low molecular weight PVC fractions prepared by preparative gel filtration

Preliminary separation experiments were carried out using a 30cm x 7.7 mm HPSEC column containing 10μm, 50Å PL gel packing but the column was found to be incapable of resolving the VC oligomers present in the low molecular weight fraction. HPSEC columns containing 5μm packing had been shown in trade literature to be capable of separating oligostyrene standards (Polymer Laboratories, Church Stretton, Shropshire) and so two 60cm x 7.7 mm columns containing 5μm, 50Å PL gel were obtained to evaluate their ability to separate VC oligomers. Although Lucovyl RB 8010 had been selected on the basis of initial experiments as the PVC base resin to provide the VC oligomers for eventual structural characterisation (Section 4.2), other PVC base resins, Corvic S57/116 and ICI mass PVC, were also analysed to enable a comparative study to be carried out. The two HPSEC columns were used in series and Figures 3.18 and 3.16 show that the chromatograms obtained for the two mass polymerised resins, Lucovyl RB 8010 and ICI, are very similar indicating that the two low molecular weight fractions have a similar composition. The chromatogram of the low molecular weight fraction obtained from the suspension polymerised resin, Corvic S57/116 (Figure 3.17), is anomalous and illustrates, as initial experiments had (Section 4.2), that oligomer fractions from such polymers contain a greater number of low molecular weight contaminants than those from mass polymers. The main feature of each chromatogram is a very large peak which eluted at a volume corresponding to a VC tetramer species (polystyrene calibration). By carrying out a separate analysis, this peak...
was tentatively identified as being due to the THF stabiliser, quinol, relatively large quantities of which would have been deposited in the <578 molecular weight fraction with the removal of the gel filtration eluent ~60 ml containing 0.1% quinol. The eluent for both the gel filtration and HPSEC systems was changed to unstabilised THF and the complete procedure repeated. The same predominant peak was observed in the HPSEC chromatograms which was considered to be the phthalate impurity detected in the <578 molecular weight fraction by GC-MS (Section 3.8). To circumvent this problem, the eluent in both chromatographic systems was changed to toluene. Toluene was chosen because of its stability and, as refractive index detection was being employed, its refractive index of 1.4961 was almost the same as that of dibutyl phthalate (1.4900) which was considered to be the main phthalate impurity. This rendered the phthalate impurity almost undetectable and, as Figure 3.19 illustrates, a HPSEC chromatogram of a <578 molecular weight Lucovyl RB 8010 fraction obtained using: toluene as the eluent has no massively predominant peak. This chromatogram shows a higher quantity of long chain PVC in the <578 molecular weight fraction.

Figures 3.16 to 3.19 show VC oligomer peaks that are separated from one another to a greater or lesser extent. They have been assigned with respect to the degree of polymerisation of each oligomer by using a calibration curve that was constructed by analysing VC oligomers prepared by HPSEC during the course of this work (Figures 3.22 and 3.24). Before these oligomers were available an attempt was made to calibrate the HPSEC chromatograms using a polystyrene calibration curve but this proved troublesome because in this molecular weight range two oligomers having the same molecular weight but different molecular structures can
have quite different molecular volumes and hence elution times. This did not matter so much in the gel filtration work where such accuracy was not required. Because of the reliance on polystyrene calibration at the time that Figure 3.19 was produced it was thought that the peaks were due to the VC oligomer series trimer to octamer.

It is evident from Figures 3.16 to 3.19 that the two column HPSEC system did not have the required resolution to produce a good separation of the VC oligomer species. As previously discussed (Section 1.3) the limited peak capacity of SEC systems can be overcome by employing a recycle technique. Because the existing equipment could be easily modified to accommodate it, the recycle technique used in this work was the alternate pumping type. Figures 3.19 to 3.22 demonstrate clearly that as the length of gel bed increases the separation of the individual oligomer species also increases. It is evident that a gel bed length of 480 cm (Figure 3.22) is required to separate each oligomer effectively. Increasing the length of the gel bed also results in shoulders becoming apparent on the oligomer peaks, which could be indicative of the presence of isomers. Having achieved an acceptable degree of oligomer separation, low molecular weight Lucovyl RB 8010 fractions were routinely fractionated as shown in Figure 3.22 in order to obtain a sufficient mass of each VC oligomer for further characterisation. The characteristic mass spectra of VC oligomers up to the heptamer were known and so GC-MS was employed in an attempt to unambiguously identify each of these VC oligomer fractions. As in the GC-MS analysis of the <578 molecular weight fraction (Section 4.3) VC oligomers greater in molecular weight that the heptamer did not elute from the gas chromatograph due to thermal decomposition. However, it was possible to obtain mass
spectrometry data on the VC oligomer fractions pentamer to heptamer (Section 3.8) and with this to confirm that the HPSEC fractions in Figure 3.22 corresponded to the VC oligomer species pentamer to decamer.

4.4.2 Low molecular weight PVC fractions prepared by fractional precipitation and then purified by adsorption liquid chromatography

As discussed in Section 4.3, a low molecular weight fraction can be isolated from a Soxhlet extract more effectively by fractional precipitation than preparative gel filtration. The HPSEC chromatogram of a low molecular weight fraction obtained in this way is very similar to a chromatogram of such a fraction isolated by preparative gel filtration, a small increase in the long chain PVC component being the only difference (Figure 4.1). With the discovery that the HPSEC scheme described in Section 4.4.1 had not enabled the VC tetramer and trimer species to be prepared a second, improved scheme was designed. The use of toluene as the HPSEC eluent coupled with refractive index detection and the presence of a large concentration of impurities, particularly phthalates, had caused problems in detecting the lower VC oligomers, i.e. tetramer to dimer (if present). The toluene had also been difficult to remove from the oligomer fractions at room temperature. To enable dichloromethane, a low boiling point (40°C) solvent having a refractive index of 1.4242, to be used as the HPSEC eluent the low molecular weight fraction had to be purified to remove the phthalates and other impurities that obscure the VC oligomers with such refractive index detection - eluent combinations. Most of the impurities found by GC-MS analysis of the <578 molecular weight fraction (Section 3.8) were more polar in character than VC oligomers. A preparative adsorption liquid chromatography column with a mobile phase of hexane - MTBE (95:5) proved successful in removing impurities from the low molecular weight fraction.
Figure 4.1

HPSEC Chromatogram of a Lucovyl RB 8010 Unpurified Low Molecular Weight Fraction

Chromatographic System given in Section 2.7.1
Mobile Phase: Dichloromethane
Flow Rate: 1 ml min⁻¹
120 cm PL gel 5 μm, 50 Å
derived from Lucovyl RB 8010. The chromatogram obtained (Figure 3.13) reveals the concentration of phthalate present in the fraction by the size of the assigned peak. It is also clear from the chromatogram that, as well as removing more polar impurities, this purification stage also serves to reduce the quantity of long chain PVC in the fraction. This explains the reduced molecular weight range observed on HPSEC analysis of the purified fraction (Figure 3.23) compared to the impure (Figure 4.1). Having purified the Lucovyl RB 8010 low molecular weight fraction, the HPSEC system, with dichloromethane as the eluent, was used to fractionate it. Prior to the analysis the HPSEC system had been calibrated using the VC oligomers decamer to pentamer that had been prepared by the method discussed in Section 4.4.1 (Figure 3.22) and the VC dimer analogue 1,3 dichlorobutane. The HPSEC chromatogram shown in Figure 3.23 has a large peak, corresponding to a VC trimer species, which on analysis using 480 cm of gel bed (Figure 3.24) is resolved into two components, one present in a large quantity and now no longer at an elution volume which corresponds to a VC trimer species and a much smaller one that does. GC-MS analysis of these two components revealed that the one present in a large concentration was butylated hydroxy toluene (BHT), a PVC base resin stabiliser (Section 4.1), and the other the VC trimer species. The structure of BHT (shown below)

![Structure of BHT](image)

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reveals how it came to elute from the adsorption liquid chromatography column with the VC oligomers. The tert-butyl groups in positions 2 and 6 shield the hydroxy group and so inhibit it interacting with the silica packing. The chromatogram differs from the one obtained with toluene as the eluent (Figure 3.22) in that there are no shoulders present on the oligomer peaks. This implies that at least some of the shoulders were not due to VC oligomer isomers but impurities. GC-MS analysis of the other fractions designated in Figure 3.24 also enabled the VC oligomer species pentamer and tetramer to be identified. The fractions A and B were collected, although no material appeared to be present in them, in order to see if the sensitive GC-MS technique could detect the presence of any VC dimer. Use of the dimer analogue had indicated that, if present, the VC dimer would elute at a volume corresponding to fraction B. Unfortunately, no evidence of the VC dimer species could be found in either fraction. This was not very surprising because in the research programme carried out by MAFF on VC oligomers 15-19 (Section 1.8), a VC dimer species had not been located in any of the PVC base resins analysed. It is thought that the high temperatures used to strip VCM from the base resins also remove most of the VC dimer, and that the rest is eliminated by the solvent removal processes that are required in the procedure used to acquire the low molecular weight fraction. This particular HPSEC technique was used to accumulate quantities of the two VC oligomers, tetramer and trimer, that could not be prepared by the HPSEC system using toluene as the eluent.

Low molecular weight fractions of Norvinyl VY 80/30 suspension PVC were analysed on this HPSEC system because this PVC base resin was used in the PVC bottle formulation (Section 4.1) and its oligomers had to be characterised if the effect that processing had on such oligomers was to be
ascertained. An HPSEC analysis of the unpurified low molecular weight fraction (Figure 4.2) revealed that it did not contain the large quantity of phthalate that was present in the unpurified low molecular weight fraction derived from Lucovyl RB 8010 PVC base resin (Figure 4.1). Nevertheless, the fraction was still put through the adsorption liquid chromatography procedure (Section 2.6) to remove any other impurities that might be present (Figure 3.14). The HPSEC chromatogram of the purified low molecular weight fraction (Figure 3.25) differs from Figure 3.23 in one major respect: there is no peak eluting at a volume corresponding to a VC trimer species. This demonstrates that the polymerisation stabiliser, BHT, was not present in the original PVC base resin and that the VC trimer species is present in only very low concentrations, if at all. More severe VCM stripping procedures are used for suspension PVC than mass PVC (Section 1.1.4) and this could account for the lower concentration of VC trimer observed in the suspension polymer. The purified low molecular weight Norvinyl VY 80/30 fraction was fractionated as displayed in Figure 3.26 and enough mass of each fraction obtained for HPLC analysis (Section 2.10). Characteristic HPLC chromatograms were obtained (Section 3.6.3) which enabled the collected fractions to be identified as the VC oligomer species hexamer to tetramer. Unfortunately, time did not permit a GC-MS analysis of each collected HPSEC fraction or a search using that technique for any presence of the VC trimer and dimer species in later eluting fractions.

It was hoped that adsorption liquid chromatography would provide a method for separating the VC oligomers from the additives in the low molecular weight PVC bottle fraction. Unfortunately, as Figure 3.15 shows, the additives and the
Figure 4.2

HPSEC Chromatogram of a Norvinyl VY 80/30 Unpurified Low Molecular Weight Fraction

Chromatographic System given in Section 2.7.1
Mobile Phase: Dichloromethane
Flow Rate: 1 ml min⁻¹
120 cm PL gel 5 μm, 50 Å
VC oligomers coeluted, there being no chromatographic window in which the oligomers could be isolated. Nevertheless, a similar fraction that had been isolated from the low molecular weight PVC base resin fraction was collected from the low molecular weight PVC bottle fraction (Section 2.6.4) and analysed by HPSEC with dichloromethane as the eluent. The resulting chromatogram (Figure 3.27) is totally different to the HPSEC chromatograms of the purified low molecular weight PVC base resin fractions obtained using the same system (Figures 3.23 and 3.25) due to the presence of low molecular weight additives, i.e. there is no distinguishable series of oligomer peaks. A portion of the chromatogram was recycled and, after 480 cm of gel bed had been used, fractions were taken which corresponded to the elution volume range within which each VC oligomer was known to elute at (Figure 3.28) since the individual oligomer peaks were not visible. These fractions were then analysed by HPLC (Section 2.10) and it was found that this high performance system was capable of separating the isomers of each VC oligomer from any attendant additive impurities. Once again, the characteristic HPLC chromatograms obtained (Section 3.6.3) enabled the VC oligomer present in each fraction to be identified. In this way the presence of the VC oligomer species tetramer to hexamer in the low molecular weight PVC bottle fraction was shown. Time again did not allow any GC-MS analysis of the HPSEC fractions to be attempted or a search for the VC trimer and dimer in later eluting fractions. It was not expected that these two lower oligomers would be apparent in the low molecular weight PVC bottle fraction since they did not appear in the low molecular weight fraction obtained from the same batch of PVC base resin (Norvinyl VY 80/30) that the bottles were made from.
4.5 Separation of the VC oligomers into their isomeric forms

The GC-MS analysis of the VC oligomer fractions that had been prepared by HPSEC and the <578 molecular weight fraction isolated by preparative gel filtration had shown that each VC oligomer existed in a number of isomeric forms, the number of isomers increasing with chain length (Section 3.8). The same observation was made by Gilbert et al. from a GC-MS analysis of an oligomer fraction isolated from a suspension polymerised PVC. Before an attempt could be made to structurally characterise the VC oligomers using techniques such as NMR, each oligomer had to be separated into its constituent isomers. HPSEC had proved very effective in separating the VC oligomers according to chain length, but it is not a suitable technique for separating isomer mixtures where there is very little, if any, difference in molar volume between the species. GC had demonstrated sufficient resolving power to separate the isomers of the lower VC oligomers but had managed only partial isomer separations with the higher (ie. hexamer and above) oligomers for which a large number of isomeric forms existed. Although it might have been possible to find conditions under which GC could separate the isomers of each VC oligomer of interest in this work, ie. up to the octamer, the fact that the inherently thermally unstable oligomers would be subjected to high temperatures was undesirable and so the technique was rejected. Two chromatographic techniques that were of interest, due to their ability to function at ambient temperature and on a preparative scale, were TLC and HPLC.

4.5.1 VC oligomer fractions isolated by HPSEC from the Lucovyl RB 8010 <578 molecular weight fraction

In addition to having a potential to separate VC oligomer isomers, it was hoped that TLC would be successful in
separating the isomers from the phthalate impurity which had been identified in each fraction, particularly the hexamer, by GC-MS (Section 3.B). Because the VC hexamer fraction contained the greatest concentration of phthalate impurity, the TLC work was concentrated on this fraction. The GC-MS analysis had not yielded an unambiguous identification of the phthalate compound present in the hexamer fraction and so two common phthalates, dibutyl and di(2-ethyl hexyl), were analysed along with the hexamer fraction under the same conditions. In addition, several chlorinated standards were analysed in an attempt to elicit information regarding the chemical nature of the hexamer isomers. Table 3.6 shows that with toluene development the silica plates were capable of separating the VC hexamer fraction into three clearly defined chlorine containing moieties. The detection technique used to locate the chlorine compounds on the plate (Section 2.B.2) is not a very sensitive one and it also results in the plate darkening in colour. Because of these factors other, smaller chlorine containing moieties, might have been present on the plate but were indistinguishable from the motled greyish coloured background. From Table 3.6 it can be seen that the phthalate impurity in the VC hexamer fraction is either dibutyl phthalate or a phthalate possessing a very similar chemical nature; the GC-MS results (Table 3.12 in Section 3.B) corroborate this assertion. Also, the phthalate and the first chlorinated moiety have similar $R_f$ values and a visual analysis of their respective spots revealed a significant amount of plate area where the two coexisted. The chlorinated standards gave $R_f$ values which indicated that the chlorinated moiety of the fraction having the largest $R_f$ value corresponded to a straight chain structure whereas the other two chlorine containing moieties could be cyclic or branched. These inferences are extremely
tentative due to the disparity in molecular weight between
the chlorinated standards and the hexamer isomers. The VC
pentamer fraction was also analysed using toluene as the
developing solvent and, as Table 3.7 shows, two chlorinated
moieties were observed, the first not completely separated
from the phthalate impurity. In both hexamer and pentamer
cases the chlorinated moiety having the largest $R_f$ value
was present in the highest concentration. The GC-MS
analysis of both the <578 molecular weight fraction and VC
oligomer fractions had shown the presence of at least four
isomer species for the pentamer and hexamer (Figure 3.44
and Tables 3.11 and 3.12) and so it was apparent that this
TLC technique was not giving complete isomer separations.
In an attempt to improve the isomer separation obtained with
the silica plates, further work was carried out on the VC
hexamer fraction with hexane containing varying amounts of
either MTBE or ethyl acetate as the developing solvent.
These liquids were chosen because of their relatively low
boiling points and due to the promise that a hexane - MTBE
mobile phase was showing at the time for separating VC
oligomer isomers with a silica packed HPLC column. The re­s­
ults displayed in Tables 3.8 and 3.9 show that much better
separations were achieved with both of these combinations
than had previously been obtained with toluene. It can be
seen from Table 3.8 that with 5% of MTBE in the developing
solvent the chlorine containing compounds in the VC hexamer
fraction were represented by a single spot and two broad
bands. Upon increasing the MTBE content to 10% these
compounds were distributed among three spots and two broad
bands. This result suggests that more VC hexamer isomers
exist than the quantity shown by GC-MS. Further increases
in the MTBE concentration increased the separation between
the spots and the bands but did not result in any additional
chlorinated components being resolved. The phthalate
constituent of the hexamer fraction was associated with some of the chlorinated moieties for each of the developing solvents evaluated. The experiments conducted with ethyl acetate as the modifier in the developing solvent produced inferior separations to those obtained with MTBE modifier and a complete isolation of the phthalate impurity from the chlorinated moieties was never achieved. TLC was eventually discarded as a possible technique for separating the isomers of the VC oligomers because of the difficulty experienced in separating the large number of isomers existing for the higher oligomers. Although no TLC work was done on the VC tetramer and trimer, the results obtained with the hexamer suggest that satisfactory separations might be possible for such relatively simple isomer mixtures.

HPLC was regarded as the most likely chromatographic technique to effect an acceptable VC oligomer isomer separation due to its high peak capacity and potential for subtle specificity variations. Microbore HPLC came to be used in this project because of the aim to utilise a liquid chromatography-electron capture (LC-EC) detector to facilitate detection of the VC oligomer isomers, which are not amenable to high sensitivity liquid chromatography detection because they do not contain a strong UV chromophore. As already mentioned (Section 2.9.2) the LC-EC detector could not be used due to malfunction but preliminary work had shown that a standard UV detector set at 200nm could be used to adequately detect VC oligomer isomers. Of the VC oligomers of interest the largest represent the hardest analytical task in the separation of their isomers due to the large number existing. Because the VC heptamer was the largest oligomer for which GC information was available, it was chosen as the first oligomer to be analysed on the microbore HPLC system using an S5W silica packed
column. Hexane was chosen as the mobile phase because its low wavelength cut off point (195nm) enabled the UV detector to be used at 200nm. The resulting chromatogram (Figure 3.29) consists of a number of peaks, the initial ones representing the solvent front which is a feature of low wavelength UV detection. There is, however, no series of peaks which would be indicative of VC heptamer isomers. A further analysis was performed with a mobile phase of hexane - MTBE (95:5). In the chromatogram obtained (Figure 3.30) there is a series of peaks after the solvent front that are not present in Figure 3.29. It is possible that these presumptive VC heptamer isomer peaks had not been discernable with hexane as the mobile phase because of complete retention of the compounds on the column, or a very slow bleeding off. To attain information on these peaks a standard size HPLC column containing S5W silica packing was procured and the procedure scaled up. An analysis of the VC heptamer fraction was performed under the same conditions as those used with the microbore system, but the series of peaks (Figure 3.31) were separated to a much lesser extent. A succession of experiments were then carried out, with the amount of MTBE modifier in the mobile phase being decreased to promote interaction between the heptamer isomers and the column packing and hence improve the peak separation. The results obtained showed that a mobile phase consisting of hexane - MTBE (99:1) afforded the best isomer separation (Figure 3.32). As with the microbore system, when pure hexane was utilised as the mobile phase the series of isomer peaks obtained with the presence of the MTBE modifier were not apparent. A semi-preparative analysis was conducted with 2 mg of VC heptamer fraction being loaded onto the column and each peak collected (see Figure 3.32 for peak collection programme). To ascertain which peaks were due to VC heptamer isomers, each of these HPLC fractions was subjected to three
investigative tests: chlorine detection, GC and GC-MS (Section 2.10.3). These showed that the peaks within the fraction range 3-29 were due to isomers of the VC heptamer by virtue of them registering a positive chlorine test, having very similar GC retention times and giving characteristic VC heptamer mass spectra.\textsuperscript{125} The number of isomers found to exist for the VC heptamer by this HPLC technique was surprisingly large, since the analytical evidence available prior to this analysis, such as that yielded by GC (Figure 3.44 and Table 3.13), had indicated far fewer. The problem of elucidating the structure of VC oligomer isomers from mass spectrometer data alone has been discussed in the literature\textsuperscript{16,18,19} and so to accumulate a sufficient mass of each isomer so that a characterisation could be attempted using \textsuperscript{1}H NMR, the VC heptamer fraction was routinely fractionated. As discussed in Section 2.10.4, gradient elution HPLC would be a more efficient chromatographic technique than isocratic HPLC for dealing with this type of analytical problem, but with 200 nm UV detection it is not practically possible. Gradient elution HPLC was palpably essential if a satisfactory separation of the isomers of the largest VC oligomer of interest in this work, the octamer, was to be achieved. The HPLC chromatogram (Figure 3.33) of the VC octamer fraction, obtained under the same chromatographic conditions used for the heptamer, does not show a series of well resolved isomer peaks. The population of isomers present in the chromatogram is not as great as that predicted by reference to the heptamer due to the difficulty in eluting these larger isomers from the column under such conditions. Work on the VC octamer fraction proceeded no further than the production of this HPLC chromatogram because gradient elution HPLC was not available, because there was a limited mass available for fractionation which would have resulted in only tiny
quantities of each isomer being prepared due to the large number existing, and due to the difficulty in obtaining structural information on such large molecules by $^1$H NMR analysis.

The other two VC oligomer fractions obtained from the Lucovyl RB 8010 <578 molecular weight fraction, the hexamer and pentamer, were analysed using the same HPLC procedure. The chromatograms obtained (Figure 3.34 and 3.35) were simpler when compared to the heptamer chromatogram, which was expected. There was also better correlation with regard to the number of major isomers found by this technique and the GC-MS analysis of the Lucovyl RB 8010 <578 molecular weight fraction and Lucovyl RB 8010 VC pentamer and hexamer fractions (Figure 3.44 and Tables 3.11 and 3.12). By consulting the reference VC hexamer mass spectrum the peaks within the fraction range 3-25 for the hexamer chromatogram (Figure 3.34) were identified as isomers of the VC hexamer. Using the same approach, the peaks within the fraction range 3 to 11 for the pentamer chromatogram (Figure 3.35) were found to be due to VC pentamer isomers. As in the case of the VC heptamer fraction, the VC hexamer and pentamer fractions were routinely fractionated in an attempt to accumulate enough mass of each isomer for an effective $^1$H NMR analysis.

In addition to detecting which HPLC fractions contained VC oligomer isomers and characterising the isomers with respect to chain length, the GC-MS analysis yielded other valuable information on the fractions (Section 3.9). It revealed if what appeared to be a single peak on the HPLC chromatogram, i.e. a symmetrical peak, was or not a single species. In actual fact for none of the three VC oligomers fractionated by HPLC was there an instance where two components were found in an isolated symmetrical peak by GC-MS. The HPLC
technique used to separate the isomers of the VC oligomers had not completely resolved all of the isomers to the baseline and as a consequence some of the HPLC fractions contained more than one isomer. The GC-MS analysis of the HPLC fractions gave a measure of the purity of each isomer. The GC-MS chromatograms given in Section 3.9 show that the purity of the HPLC fractions obtained from each VC oligomer vary greatly; the complexity of the GC-MS chromatograms is directly related to the relative resolution of isomer species.

Due to the very small quantities of each isomer prepared by routine HPLC fractionation of the VC oligomers it was not possible to accurately obtain a yield for each one by a standard weighing technique. Subsequent $^1$H NMR studies did reveal that in no case did the amount of a VC oligomer isomer collected exceed 500μg and in most cases the mass was substantially less than this.

### 4.5.2 VC oligomer fractions isolated by HPSEC from the purified low molecular weight fraction obtained from Lucovyl RB 8010, Norvinyl VY 80/30 and PVC bottles

The separation work performed on the VC oligomers octamer to pentamer, which had been isolated from the <578 molecular weight Lucovyl RB 8010 fraction, had resulted in a HPLC system being developed that was capable of fractionating such oligomers into their respective isomers (Section 2.10). This technique was applied to the VC oligomer species tetramer and trimer, which could not be prepared from Lucovyl RB 8010 by the same scheme as the higher oligomers, but were isolated using the purified low molecular weight fraction route (Section 4.4.2). The VC tetramer fraction gave the chromatogram shown in Figure 3.36 and, by analysing each of the fractions designated by GC-MS, fractions 3, 4 and 5 were identified as VC
tetramer isomers. The concentration of polar modifier, MTBE, in the mobile phase had been reduced to 0.25% because it was found that this improved the tetramer isomer separation. At the 1% level utilised for the higher oligomers the tetramer isomers were not interacting with the column packing to the same extent, which resulted in a shorter elution time and inferior resolution. The discovery of only three tetramer isomers was consistent with the observation that the number of isomers existing for a given VC oligomer decreases rapidly with chain length. As much of each of these three isomers was obtained as possible by routine fractionation of the VC tetramer fraction and submitted for \textsuperscript{1}H NMR analysis.

The VC trimer fraction was not amenable to HPLC analysis under the conditions used for the other VC oligomers. Even at a reduced modifier concentration of 0.25% the two trimer isomers, which were known to exist in the fraction from the GC-MS analysis of the <578 molecular weight fraction (Figure 3.44), could not be separated from the solvent front and were indistinguishable from it on the HPLC chromatogram (Figure 3.37). The molecular weight of the trimer isomers was too low and a sufficient degree of interaction with the column packing could not be obtained with this mobile phase composition. An analysis was performed with pure hexane as the mobile phase but again only the solvent front was apparent on the chromatogram. Unfortunately, there was no time remaining to do any further separation work on this VC oligomer and so an \textsuperscript{1}H NMR had to be attempted on the unfractionated HPSEC fraction (Section 3.10).

The last phase of work carried out involved the analysis of the VC oligomers present in a suspension PVC base resin, Norvinyl VY 80/30, and PVC bottles produced from a
formulation based on this resin. The HPLC technique developed for the fractionation of the VC oligomers isolated from Lucovyl RB 8010 could be used to characterise the VC oligomers obtained from Norvinyl VY 80/30 and the PVC bottles with respect to degree of polymerisation and to compare the isomers existing for each oligomer because of the very specific chromatograms that had been produced for each oligomer species. This was particularly useful as there was not enough time to carry out GC-MS investigations of the VC oligomer fractions themselves or the HPLC fractions of each oligomer species. Thus it can be seen from Figures 3.38 to 3.40 that the VC oligomers isolated from Norvinyl VY 80/30 by HPSEC (Figure 3.26) range from the hexamer to the tetramer. The HPLC chromatograms of the tetramer and pentamer species are virtually identical to those of the same oligomers isolated from Lucovyl RB 8010 (Figures 3.36 and 3.35). The mobile phase composition was kept at hexane - MTBE (99:1) for the analysis of the Norvinyl VY 80/30 tetramer since only a fingerprint chromatogram was required and so the slight improvement which results in decreasing the MTBE concentration to 0.25% was of no significance. For both these oligomers the same number of isomers exist in each case as well as there being a very similar distribution of the total mass of oligomer amongst the isomers, ie. a true fingerprint isomer chromatogram exists for the VC tetramer and pentamer. The VC hexamer species is not such an easily understood case. The HPLC chromatogram of the Norvinyl VY 80/30 hexamer (Figure 3.38) has an initial set of isomer peaks that are mirrored in the isomer chromatogram of the Lucovyl RB 8010 hexamer (Figure 3.34) but there are only a few isomer peaks after these, unlike Figure 3.34 where many more hexamer isomers are shown. It would seem unlikely that the Norvinyl VY 80/30 hexamer should differ
so much from the Lucovyl RB 8010 hexamer when it has been shown that the pentamer and tetramer species isolated from both resins are almost indistinguishable from one another. For a VC hexamer species to exist in fewer isomeric forms than a pentamer isolated from the same base resin would also be against the established pattern of an increasing number of isomers with chain length. An explanation for this observation is that the hexamer isomers that would have eluted from the HPLC column after those present in Figure 3.3B have been lost, possibly at the adsorption liquid chromatography stage. Further work carried out on VC hexamer fractions isolated from this and other PVC base resins would soon clarify this situation.

It was known that the VC oligomer fractions that had been obtained from the PVC bottles contained a high concentration of additives relative to the VC oligomers themselves (Section 4.4.2). For this reason it was not possible to predict if the HPLC analysis of these oligomer fractions would give intelligible chromatograms or, since no other analysis such as GC-MS had been carried out on these fractions, if there was even any VC oligomer isomers in these so-called oligomer fractions (Section 4.4.2). There has been no published work on the study of VC oligomers present in fabricated PVC products and so it was not known if the high temperatures used in the blow moulding technique (Section 1.6.3) resulted in the VC oligomers being 'lost' due to chemical reactions with other PVC molecules or additives such as stabilisers. However, when analysed by HPLC the HPSEC fractions that were regarded as corresponding to the VC oligomers hexamer to tetramer (Figure 3.2B) gave chromatograms that could be interpreted (Figures 3.41 to 3.43). In fact a number of interesting facts were discernible from the chromatograms. The HPLC technique had accomplished what the adsorption liquid chromatography system had failed
to do, i.e. separate the VC oligomers from the bottle additives. It can be seen in Figures 3.42 and 3.43 that there is a large impurity peak after the VC oligomer isomer peaks. This on-column purification resulted in the VC oligomer isomer peaks being clearly discernable and so, as in the Norvinyl VY 80/30 case, because fingerprint chromatograms were revealed the VC oligomer fractions were positively identified as the oligomer species hexamer to tetramer. The hexamer chromatogram (Figure 3.41) is very similar to the Norvinyl VY 80/30 hexamer chromatogram (Figure 3.38) which is to be expected as the same oligomer preparation scheme was followed in each case and does not resolve the question as to whether the later eluting isomers present in the Lucovyl RB 8010 hexamer chromatogram (Figure 3.34) were present in the Norvinyl VY 80/30 base resin to start with. The pentamer chromatogram (Figure 3.42) is directly comparable to the Norvinyl VY 80/30 pentamer chromatogram (Figure 3.39) and the Lucovyl RB 8010 pentamer chromatogram (Figure 3.35), the isomer fingerprint being the same in each case. In the tetramer chromatogram (Figure 3.43) only the two major characteristic isomers are immediately discernable, there is however a very slight leading shoulder to the first isomer which could be indicative of the characteristic minor isomer, present at a reduced concentration to that previously observed with the PVC base resins. Apart from this discrepancy, the three HPLC chromatograms of the VC tetramer obtained from each of the three sources (Figures 3.36, 3.40 and 3.43) have the same isomer features. Collectively, these HPLC results strongly indicate that for a given VC oligomer the same number of isomers with the same relative mass distribution exist in both mass and suspension polymerised PVC resins and that the processing stages used to produce a PVC product do not alter the number of isomers or isomer mass distribution to any great extent.
4.6 Structural characterisation of the VC oligomers isolated from Lucovyl RB 8010 PVC base resin

Although chromatographic characterisation work was performed on VC oligomers that had been obtained from a number of sources, spectroscopic structural characterisations were only carried out on VC oligomers that had been isolated from Lucovyl RB 8010. Two spectroscopic techniques were employed in an attempt to derive structures for the VC oligomer isomers: mass spectrometry (MS) and $^1$H NMR. GC-MS was used in preference to a straight MS analysis because of the inherent advantage that the technique has in the analysis of samples that are known, or suspected, to contain more than one compound. The GC-MS technique was therefore ideal for analysing the VC oligomer fractions prepared by HPSEC (Section 3.8) and enabled unadulterated mass spectra to be obtained of the main isomer present in any partially resolved VC oligomer HPLC fractions (Section 3.9). The GC-MS study of VC oligomers carried out by Gilbert et al.\textsuperscript{16} has already been alluded to (Section 1.8) and the spectra produced in that study have been very useful in first identifying VC oligomer species in the HPLC fractions etc. and then discriminating between them with respect to chain length. However, because an oligomer mixture was the analyte in that work the mass spectra obtained for the higher oligomers are not pure due to the incomplete resolution of the isomers achieved by the GC under the conditions used. A similar analysis has been performed in this work and this point is illustrated in Figure 3.44. More representative spectra have been achieved in this work because, with the exception of the trimer, the isomers of each oligomer have been isolated prior to GC-MS analysis. This means that each isomer can be analysed using the optimum GC conditions to ensure the minimum amount of interference from other compounds present in the same fraction.
In spite of this, for a given VC oligomer the mass spectra of its isomers are still, as reported by Gilbert et al, essentially the same. The discovery of a series of characteristic fragment ions for VC oligomers was also reported by Gilbert et al and this is corroborated by this study. Most of these ions are formed by the successive elimination of chlorine or HCl from the molecular ion. This can be illustrated by reference to the VC tetramer isomers (Figure 3.62). The molecular ion is at m/e 250 and a successive loss of chlorine or HCl (\(^{35}\text{Cl}\) or \(^{37}\text{Cl}\) in both instances) gives rise to fragment ions at the following: m/e 214, 177, 139, 101 and 65. Most of the other primary fragment ions result from the elimination of chlorine or HCl from other precursor ions, for example, m/e 115 from m/e 151 and m/e 54 from m/e 89. The other prominent feature in the mass spectra of the VC oligomers, the clusters of ions due to \(^{35}\text{Cl} - ^{37}\text{Cl}\) isotope combinations, has also been observed by Gilbert et al. The complexity of these clusters is enhanced by overlapping patterns caused by the loss of either chlorine or HCl from the same precursor ion. Using the VC trimer isomers as examples (Figure 3.46), loss of chlorine from the molecular ion (m/e 186) gave a fragment at 150 and loss of HCl an ion at 151. The 150 ion gave rise to isotope peaks at 152 and 154, and the 151 ion fragments at 153 and 155. This phenomenon resulted in a characteristic cluster of ions at every mass from 150 to 155. A further similarity in the results of this study and the one conducted by Gilbert et al is the low intensity of the higher mass ions in each VC oligomer isomer spectrum. As there are no analogous standards available it cannot be stated unambiguously that the highest ion present in each spectrum is the molecular ion, although in the case of the trimer and tetramer it is very likely. This could have a significant effect in the
structural characterisation of the pentamer isomers (Section 4.6.3) where MS data has been very influential. Gilbert et al concluded from the GC-MS results that the isomers of each VC oligomer existed in either of two structural forms, straight chain or cyclic. In this study there has been no evidence of any cyclic structures, which could indicate that the GC component of the GC-MS technique has altered the structure of some of the oligomers due to their inherent poor thermal stability; the disparity in the number of isomers of each oligomer shown by GC analysis with that by HPLC has already been mentioned (Section 4.5). From the results of the comparative study of VC oligomers isolated from different sources carried out in this work it would seem unlikely that the oligomers analysed by Gilbert et al differed greatly from those characterised here.

The structure of the VC oligomers could not be elucidated from MS data alone and so NMR was employed. A 200 MHz Fourier transform $^1$H NMR instrument was used because it offered the following advantages over less sophisticated instruments: higher resolution, and a relatively low mass requirement. The high resolution was important as it was anticipated that some complex signal splitting would be present in the spectra due to chiral centres. The Fourier transform facility enabled a spectrum to be recorded from a small amount of material and this was vital as it was always recognised that a major problem would be the accumulation of even milligram quantities of each oligomer isomer. As it turned out the main limiting factor in the characterisation of the oligomers by NMR was the small quantity (<1mg) of each isomer available. In spite of this it was possible to assign partial structures for most of the isomers submitted and, in a few cases, full structures could be proposed. The $^1$H NMR spectra were interpreted by

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Dr J Mitchell (see Acknowledgements) and it is his assignments, which are based on the work published by a number of authors on model PVC compounds,\textsuperscript{83, 86, 87, 89, 124, 135, 136} that are cited in this thesis.

4.6.1 VC trimer

The HPLC technique was not capable of resolving the VC trimer fraction into its constituent isomers and so it was only possible to obtain MS and NMR data by analysing the whole fraction by \textsuperscript{1}H NMR and GC-MS. The GC-MS analysis revealed the presence of two isomers in the fraction (Figure 3.45) which were sufficiently resolved to enable an authentic mass spectrum to be produced for each (Figure 3.46). This analysis also revealed the presence of BHT in the fraction, a consequence of incomplete resolution of the two entities by HPSEC (Figure 3.24). Unfortunately, the trimer fraction gave a weak NMR spectrum (Figure 3.87) from which, aside from the NMR solvent CDCl\textsubscript{3} and perhaps BHT, only very weak signals that could be assigned as the vinyl end group\textsuperscript{124}

\[-\text{CH-CH}=\text{CH}_2,\text{ appear at 5.8, 5.0 and 4.1 ppm;}
\]

\[\text{Cl}
\]

with possibly some CHCl resonance at 4.7 ppm. As usual the mass spectra of the two isomers (Figure 3.46) are virtually identical and no definite structural information can be ascertained from them. However, from the partial and complete structures determined for the other oligomers, the existence of an end group such as \(-\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}\) or \(-\text{CH}_2-\text{CHCl}-\text{CH}=\text{CH}_2\) in one or both of the isomers is probable. Such groups would possibly give an ion fragment at m/e 89, which is present in both mass spectra. Another end group commonly found in the oligomers is \(-\text{CHCl}-\text{CH}_2\text{Cl}\). Combining these inferences with the NMR data acquired
and the observance of a molecular ion at m/e 186 can lead to the proposal of two possible trimer isomer structures.

\[
\text{CH}_2-\text{CH-CH}_2-\text{CH-CH=CH}_2
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

and

\[
\text{CH}_2-\text{CH-CH}_2-\text{CH=CH-CH}_2
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

It is unlikely that either of the trimer isomers is branched because of the limited number of carbon atoms in the molecule.

4.6.2 VC tetramer

The three tetramer isomers separated by HPLC (fractions 3, 4 and 5 in Figure 3.36) were analysed by GC-MS (Figures 3.47, 3.48, and 3.62) and \(^1\)H NMR (Figures 3.84 to 3.86). The GC-MS results (Figure 3.47) showed that fraction 3 contained some VC pentamer as well as a quantity of fraction 4. The occurrence of both of these species in the fraction can be traced to the chromatographic separations: pentamer due to incomplete HPSEC separation of the oligomers (Figure 3.24) and the other tetramer isomer because of incomplete resolution of fraction 3 and 4 by HPLC (Figure 3.36). In comparison to fraction 3, fractions 4 and 5 were extremely pure. Although good mass spectra could be obtained for each of the tetramer isomers, only the major isomers (fractions 4 and 5) were present in sufficient quantities to provide NMR spectra. For fraction 3 (Figure 3.84) so little mass was present that no signals were observed after protracted scanning, except for those due to solvent or water.

The NMR spectrum for fraction 4 (Figure 3.85) shows signals in good agreement with those reported\(^{63, 86, 107, 135}\) for the structural moieties
From Figure 3.85 a very reasonable structure for this tetramer isomer is:

\[
\text{VC tetramer isomer A}
\]

\[
\begin{array}{ccccccc}
1 & 2 & 3 & 4 & 5 & 6 & 7 \\
\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 & - & - & - & - & - & \text{CH}_2 \\
& & & & & & \text{Cl} \\
& & & & & & \text{C}_1 \\
& & & & & & \text{Cl} \\
\end{array}
\]

This structure combines the two fragments and takes into account additional shifts and integrals at ~4.1 and 2.0 ppm. Further evidence for this structure is given by the mass spectrum of this isomer (Figure 3.62) which has a molecular ion cluster at m/e 250. The proton resonances can be assigned as follows.

<table>
<thead>
<tr>
<th>Position</th>
<th>Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.0 doublet, J=6Hz, 2H</td>
</tr>
<tr>
<td>2</td>
<td>5.89 multiplet, 2H</td>
</tr>
<tr>
<td>3</td>
<td>2.55 triplet, J=6Hz, 2H</td>
</tr>
<tr>
<td>4</td>
<td>1.90 - 2.32 multiplet, 1H</td>
</tr>
<tr>
<td>5</td>
<td>4.13 - 4.45 multiplet, 3H</td>
</tr>
<tr>
<td>6</td>
<td>3.52 - 3.83 multiplet, 2H</td>
</tr>
</tbody>
</table>
The observed integral is close to that expected, although the \( \text{CH}_2, \text{CH} \) integral is too high, possibly due to differences in nuclear relaxation.

<table>
<thead>
<tr>
<th>Proton environment</th>
<th>Expected Integral</th>
<th>Observed Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HC} = \text{CH} )</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>( \text{CH}_2, \text{CH} )</td>
<td>3</td>
<td>3.4</td>
</tr>
<tr>
<td>( \text{CHCl}, \text{CHCl} )</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

It is possible to countenance an alternative structure (B) from the NMR spectrum of fraction 4, which is:

**VC tetramer isomer B**

\[
\begin{array}{cccccccc}
1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\
\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2 \\
\mid & \mid & \mid & \mid \\
\text{Cl} & \text{Cl} & \text{Cl} & \text{Cl} \\
\end{array}
\]

The evidence against this structure is that the expected integral would be 2:4:6, which is a worse correlation than that experienced with the other structure, and the fact that an additional triplet would be present in Figure 3.85 for position 6. In view of these facts, structure A is the preferred structure for the tetramer isomer present in fraction 4.

In common with fraction 4, fraction 5 recorded a strong enough NMR spectrum to enable a complete isomer structure to be assigned. Figure 3.86 shows signals in good agreement with those reported for the end group

\(-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl} \quad \text{(trans)}\)

along with shifts reasonable for

\(-\text{CH}-\text{CH}_2-\text{CH}_2 \mid \mid \text{Cl} \text{Cl} \)
as reported by Darricades-Llauro et al. With a molecular ion cluster at m/e 250 (Figure 3.62), a reasonable structure is:

**VC tetramer isomer C**

\[
\begin{array}{cccccccc}
1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\
\text{CH}_2\text{-C=CH-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH}_2 \\
\text{Cl} & & \text{Cl} & & \text{Cl} & & \text{Cl} \\
\end{array}
\]

The spectrum in Figure 3.86 exhibits shifts and integrals that are in reasonable agreement with this structure.

<table>
<thead>
<tr>
<th>Proton environment</th>
<th>Expected integral</th>
<th>Observed integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>H:C=CH</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>CH_2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>CHCl_2 CH_2 Cl</td>
<td>6</td>
<td>7</td>
</tr>
</tbody>
</table>

As in the case of fraction 4, relaxation of the various protons may greatly differ, altering the expected integrals. Proton assignment are as follows:

<table>
<thead>
<tr>
<th>Position</th>
<th>Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.03</td>
</tr>
<tr>
<td>2</td>
<td>5.88</td>
</tr>
<tr>
<td>3</td>
<td>2.35 - 2.60</td>
</tr>
<tr>
<td>4</td>
<td>4.03 - 4.27</td>
</tr>
<tr>
<td>5</td>
<td>2.13 - 2.28</td>
</tr>
<tr>
<td>6</td>
<td>3.66 - 3.85</td>
</tr>
<tr>
<td>7</td>
<td>4.03 - 4.27</td>
</tr>
<tr>
<td>8</td>
<td>2.13 - 2.28</td>
</tr>
</tbody>
</table>

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Both the preferred isomer structure for fraction 4 (A) and the structure derived for fraction 5 (C) contain at least two chiral centres and as a result the spectra of both fractions are complicated due to the many splittings of the resonance positions.

Gilbert et al. analysed a VC tetramer isolated from a suspension PVC resin and, from NMR and MS data, assigned the end group

\[-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}\]

This end group has been located in the tetramer isomer structures proposed for fractions 4 and 5. In addition, Gilbert et al. carried out an epoxidation on the tetramer and the derivative produced indicated that the structure of the original tetramer was analogous to that proposed for fraction 5 in this work.

4.6.3 VC Pentamer

All of the HPLC fractions that were shown by GC-MS to contain pentamer isomers (fractions 3-11 incl. in Figure 3.35) were analysed by $^1$H NMR. The main obstacle in achieving unambiguous full structural characterisations was insufficient isomer mass, although partial structures could be determined in all cases. For five of the fractions (3, 5, 7, 9 and 11) a reasonable structure could be proposed by utilising both MS and NMR data. The structures given are, however, more tentative than those assigned for the tetramer isomers and it is not possible to give such a complete exposition of the NMR data, ie. all the shifts and integral values.
For fraction 3 (Figure 3.75) the following partial assignments can be made:

\[ -\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 \]
\[ \text{Cl} \]

\[ -\text{CH}_2-\text{CH}_2 - -\text{CH}-\text{CH}_2 \]
\[ \text{Cl} \text{ Cl} \text{ Cl} \]

A reasonable composite structure based on the reported shifts of model PVC systems and the appropriate integrals would be:

\[ \text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 \]
\[ \text{Cl} \text{ Cl} \text{ CH}_2 \text{ Cl} \]
\[ \text{CH}_2\text{Cl} \]

The molecular formula of this isomer is \( \text{C}_{16}\text{H}_{16}\text{Cl}_4 \) which agrees with the MS data (Figure 3.63) because the highest mass ion cluster occurs at m/e 276.

For fraction 4 (Figure 3.76) only the following structural moieties can be assigned

\[ -\text{CH}-\text{CH}_2 \]
\[ \text{Cl} \text{ Cl} \]

\[ -\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2 \]
\[ \text{Cl} \]

Although the NMR spectrum of fraction 5 (Figure 3.77) is weak the following partial assignment can be made:

\[ -\text{CH}-\text{CH}_2 \]
\[ \text{Cl} \text{ Cl} \]
with there being no indication of

\[ \text{CH}_2-\text{CH} = \text{CH}-\text{CH}, \]

\[ \text{Cl} \]

The following structure is not inconsistent with the observed MS data (the highest mass ion cluster occurs at m/e 276 - Figure 3.63) and NMR data for an isomer with a molecular formula of C_{10}H_{16}Cl_{4}.

\[
\begin{array}{c}
\text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH} = \text{CH}_2 \\
\text{Cl} & \text{Cl} & \text{CH}_2 & \text{Cl} \\
\text{CH}_2 \text{Cl} \\
\end{array}
\]

For fraction 6 (Figure 3.78) only partial assignments are possible. The structure does not contain the end group

\[ \text{CH}_2-\text{CH} = \text{CH}-\text{CH}_2 \]

\[ \text{Cl} \]

but may contain

\[ \text{CH} = \text{CH}-\text{CH}_2 \]

\[ \text{Cl} \]

\[ \text{Cl} \]

\[ \text{CH}_2-\text{CH}_2 \]

\[ \text{Cl} \]

A more intense NMR spectrum could be obtained for fraction 7 in which it was possible to locate the presence of the following end groups:
An isomer structure consistent with both the NMR data (Figure 3.79 has two distinct alkene regions at 5.8 and 6.2 ppm) and MS data (Figure 3.64 shows the highest mass ions to be around m/e 276) for the molecular formula C_{10}H_{14}Cl_{4} is:

\[-\text{CH}_2\text{-CH}=\text{CH}=\text{CH}_2\]
\[\text{Cl} \]
\[\text{CH}_2\text{-CH}=\text{CH}-\text{CH}_2\]
\[\text{Cl} \quad \text{CHCl} \quad \text{CH}_2\text{Cl} \]

For fraction 8 (Figure 3.80) a very weak spectrum was recorded and only partial assignments could be made. The fraction does not contain the end group:

\[-\text{CH}_2\text{-CH}=\text{CH}_2\]
\[\text{Cl} \]

but may contain

\[-\text{CH}_2\text{-CH}=\text{CH}\]
\[\text{Cl} \]

\[-\text{CH}_2\text{-CH} \quad \text{CH}_2\text{-CH}_2\]
\[\text{Cl} \quad \text{Cl} \quad \text{Cl} \]

Fraction 9 (Figure 3.81) gave a better spectrum with the following groups being discernable:
There was no indication of the end group:

\[ \text{-CH-CH,} \]

\[ \begin{array}{c}
| \vspace{1cm} \\
\text{Cl} & \text{Cl}
\end{array} \]

A reasonable structure for the isomer is therefore:

\[ \text{CH}_{3}\text{-CH}_{2}\text{-CH-CH-CH, -CH-CH-CH, -CH=CH-CH,} \]

\[ \begin{array}{c}
| \vspace{1cm} \\
\text{Cl} & \text{Cl} & \text{Cl}
\end{array} \]

The molecular formula is \( \text{C}_{10}\text{H}_{15}\text{Cl}_{5} \), which is in agreement with the MS data (Figure 3.65) where the highest mass ion cluster occurs at m/e 310.

Only a very weak NMR spectrum was given by fraction 10 (Figure 3.82) and, as a result, the only structural information gained was that the isomer contained the end group:

\[ \text{CH, -CH=CH-CH,} \]

\[ \begin{array}{c}
| \\
\text{Cl}
\end{array} \]

The NMR spectrum obtained for fraction 11 (Figure 3.83) was intense enough for the following partial assignments to be possible:

\[ \text{-CH, -CH=CH-CH,} \]

\[ \begin{array}{c}
| \\
\text{Cl}
\end{array} \]
From the observed integral the second group occurred twice in the structure. An isomer structure consistent with this end group analysis is:

\[ \text{CH}_2-\text{CH-CH-CH-CH}_2-\text{CH} = \text{CH-CH}_2 \]

\[ \begin{array}{cccc}
\text{Cl} & \text{Cl} & \text{CHCl} & \text{Cl} \\
\text{CH}_2\text{Cl}
\end{array} \]

However, the MS data for this fraction (Figure 3.65) does not indicate a molecular ion at a high enough mass (m/e 310) to support this assignment.

Collectively these structural assignments are not controversial; most of the end groups reported have been well documented and there is no doubt as to their existence in PVC. There are, however, one or two unusual structures, namely, the dichloroethyl branch

\[ \text{--CH} \]

\[ \begin{array}{c}
\text{CHCl} \\
\text{CH}_2\text{Cl}
\end{array} \]

and the end group.

\[ \text{--CH}_2-\text{CH}=\text{CH} \]

\[ \begin{array}{c}
\text{Cl}
\end{array} \]

It is surprising that none of these isomer structures has as an end group

\[ \text{--CH}_2-\text{C} = \text{CH}_2 \]

\[ \begin{array}{c}
\text{Cl}
\end{array} \]

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which is known to occur as a result of a transfer to monomer reaction followed by chain propagation (Section 1.5.2). One major potential source of error in the deriving of the complete structures by a composite technique is the reliance on the MS data. The pentamer isomers were prior to this study considered to have a molecular weight of 310, i.e. a molecular formula of C₁₀H₁₅Cl₅.¹⁶ If this is in fact still the case and that molecular ions are not present in the MS data (only fraction 9 gives an ion at m/e 310, and this is extremely weak), then the structures that have been proposed on the basis that the ions at m/e 276 are the molecular ions (fractions 3, 5, 7) are wrong. It is clear that only a study of analogous standards can clarify this point.

4.6.4 VC hexamer

The VC heptamer was the first VC oligomer for which isomers were submitted for ¹H NMR analysis. The results of this analysis (Section 4.6.5) revealed two major problems: there was not enough mass of each isomer to give a good spectrum, and the large number of protons in the molecule made those signals that were discernable hard to interpret. Because the VC hexamer species itself existed in numerous isomeric forms (Figure 3.34) and the mass available for fractionation was similar to the heptamer and, in addition contained only three hydrogen atoms less than the heptamer species, no NMR work was attempted on this oligomer. The mass spectra obtained for the HPLC fractions (Figures 3.66 to 3.68) display a very similar range of fragment ions, as was expected. A noticeable feature is the absence of any ions above m/e 350. There is an ion cluster at m/e 338 in each spectrum which, if it represents the molecular ion, corresponds to a molecular formula of C₁₂H₁₈Cl₅. This would mean that the isomers contain one less chlorine atom than expected.
4.6.5 VC heptamer

Three HPLC fractions (11, 18 and 29 in Figure 3.32) of the VC heptamer, which had been shown by GC-MS (Figure 3.61) to be reasonably pure isomers were analysed by $^1$H NMR. Despite intensive routine preparation procedures only very small quantities of each isomer could be accumulated and so protracted scanning, eg. >10,000 transients, was required in order to produce informative spectra. The $^1$H NMR spectra proved hard to interpret due to the large number of protons present in the molecules; a large amount of splitting occurred in the resonance positions. As a consequence of this, coupled with the fact that the spectra were weak in the first place, complete structures could not be determined, although enough signals were discernable to enable possible end groups to be assigned and certain structural moieties discounted altogether.

By comparison with other $^1$H NMR reports on model PVC systems, the following structural types could be discounted for all three fractions:

\[ -\text{CH-CH=CH}_2 \quad \text{Cl} \]
\[ -\text{CH-C=CH} \quad \text{Cl} \quad \text{Cl} \]
\[ -\text{CH-CH-CH=CH} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \]
\[ -\text{CH}_2-\text{CH-CH}_2-\text{C}=\text{CH}_2 \quad \text{Cl} \quad \text{Cl} \]
\[ -\text{CH}=\text{CH}-\text{CH}_2 \quad \text{Cl} \]
\[ -\text{CH}=\text{C}-\text{CH}_2 \quad \text{Cl} \quad \text{Cl} \]

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For the individual fractions 11, 18 and 29, the following partial structures are likely as end groups.

**Fraction 11 (Figure 3.72)**

\[
\begin{align*}
\text{-CH}_2\text{-CH}_2\text{-CH=CH-CH}_2 \\
\text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{-CH-CH}_2\text{-CH=CH} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

**Fraction 18 (Figure 3.73)**

\[
\begin{align*}
\text{-CH}_2\text{-CH}_2\text{-CH=CH-CH}_2 \\
\text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{-CH=CH-CH-CH}_2 \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{-CH-CH}_2 \text{-CH}_2 \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{-CH-} \\
\text{CH}_2\text{Cl}
\end{align*}
\]

**Fraction 29 (Figure 3.74)**

\[
\begin{align*}
\text{-CH}_2\text{-CH}_2\text{-CH=CH-CH}_2 \\
\text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{-CH=CH-CH-CH}_2 \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{-CH-CH}_2 \text{-CH}_2 \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{-CH-} \\
\text{CH}_2\text{Cl}
\end{align*}
\]
With each heptamer isomer being only 14 carbon atoms long it is obviously impossible for all the end groups postulated for fractions 18 and 29 to be present in the molecules. Due to the frequency with which the \( \text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl} \) end group has been encountered in studies on PVC\(^{50,137} \) and in this investigation it would be reasonable to propose that the discovery of this structural moiety in each fraction is not spurious. The chloromethyl branches found in fractions 18 and 29 are also reported extensively in the literature\(^{86,101} \) and so cannot be discounted. The end group,

\[
\begin{array}{c}
\text{CH}_2-\text{CH}-\text{CH}_2 \\
\mid \\
\text{Cl} & \text{Cl}
\end{array}
\]

identified in the fractions 18 and 19 is also well documented\(^{86,139} \) Two surprise omissions are the end groups

\[
\begin{array}{c}
\text{C}=\text{CH}_2 \\
\mid \\
\text{Cl}
\end{array} \quad \text{and} \quad \begin{array}{c}
\text{CH}-\text{CH}=\text{CH}_2 \\
\mid \\
\text{Cl} & \text{Cl}
\end{array}
\]

which are considered to be present in PVC molecules\(^{139} \)

The mass spectra obtained for these three HPLC fractions (Figure 3.71) are virtually identical, with the characteristic series of fragment ions present in each. The highest mass detail on the spectra occurs at m/e 400 which, if it represents the molecular ion, corresponds to a molecular formula of \( \text{C}_{14}\text{H}_{21}\text{Cl}_6 \). This would mean that the isomers contain one less chlorine atom than expected.

4.7 The formation of VC oligomers

It has been possible, by using \(^1\)H NMR and GC-MS to elucidate partial and, in some cases, complete structures for isomers of VC oligomers (Section 4.6). Of the complete structures presented, those for the two tetramer isomers are with the greatest degree of certainty as to their
authenticity. Although five complete isomer structures have been elucidated for the VC pentamer, there is some doubt as to the substitution positions in the centre of the molecules. Because of this only the two tetramer isomers will be used to illustrate how VC oligomers can be formed in the polymerisation of VCM. None of the oligomer isomers characterised have initiator moieties as end groups. From the impurities identified in the <578 Lucovyl RB 8010 fraction by GC-MS (Table 3.10) it was evident that the initiator used in the production of this polymer was Lauryl peroxide (molec. wt. 398). This initiator results in the following end group being present in some of the PVC chains.

\[ CH_{3}-(CH_{2})_{10}-C_{10} \]

molec. wt. 199

This end group attached to a single monomer unit would give a species having a molecular weight of 262, which is similar to a VC tetramer. Likewise, two monomer units terminated at one end with this group would have a molecular weight closely resembling that of a pentamer. It is therefore possible that species such as these are present in the VC oligomer fractions tetramer and above which were prepared by HPSEC. However, there are two reasons why they do not register in any structural characterisation of the HPLC fractions: only 30% of the PVC molecules contain initiator end groups to start with (Section 1.5.4) and so oligomers containing such groups would be present in low concentrations; and such a molecule is more polar than the VC oligomers, due to the ester group, and so could be separated from them by the HPLC technique used to fractionate the oligomers (Section 2.10). It is therefore
apparent that some other species acted as an initiator. Two species that are present in the polymerisation of VCM and which could give rise to VC oligomers are chlorine radicals and VCM radicals. The chlorine radicals are present in the reaction mixture due to double bond formation in the molecules, for example:

\[
\begin{align*}
-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}- \quad & \text{chain radical caused by hydrogen abstraction} \\
\quad & \text{Cl} \quad \text{Cl} \\
\downarrow \\
-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}- + \text{Cl}. \\
\quad & \text{Cl}
\end{align*}
\]

A feature of VCM polymerisation is the great amount of transfer to monomer that occurs. This produces VCM radicals, i.e.

\[
\begin{align*}
-\text{CH}_2-\cdot + \text{CH}_2=\text{CH} \quad & \rightarrow -\text{CH}_2-\text{CH}_2 + \text{CH}_2=\text{C}. \\
\quad & \text{Cl} \quad \text{Cl} \\
\quad & \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\end{align*}
\]

The following reaction mechanisms are proposed to account for the formation of the two tetramer isomers for which complete structures could be assigned (Section 4.6.2).

**VC tetramer isomer A**

\[
\begin{align*}
\text{CH}-\text{CH}-\text{CH}=\text{CH}-\text{CH}_2 \\
\quad & \text{Cl} \quad \text{Cl} \quad \text{CH}_2\text{Cl} \quad \text{Cl}
\end{align*}
\]
Step 1  Reinitiation by a chlorine radical\textsuperscript{130}

\[
\text{Cl} \cdot + \text{CH}_2=\text{CH} \rightarrow \text{CH}_2-\dot{\text{CH}}
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

Step 2  Head-to-head addition\textsuperscript{96}

\[
\text{CH}_2-\dot{\text{CH}} + \text{CH}_2=\text{CH} \rightarrow \text{CH}_2-\text{CH}-\text{CH}-\dot{\text{CH}}_2
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

Step 3  1,2 chlorine migration\textsuperscript{94}

\[
\text{CH}_2-\text{CH}-\text{CH}-\dot{\text{CH}}_2 \rightarrow \text{CH}_2-\dot{\text{CH}}-\text{CH}-\text{CH}_2
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

Step 4  Addition of monomer unit\textsuperscript{94}

\[
\text{CH}_2-\dot{\text{CH}}-\text{CH}-\text{CH}_2 + \text{CH}_2=\text{CH} \rightarrow \text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-\dot{\text{CH}}
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{CH}_2\text{Cl} \quad \text{Cl}
\]

Step 5  Head-to-head addition\textsuperscript{96}

\[
\text{CH}_2-\dot{\text{CH}}-\text{CH}-\text{CH}_2-\dot{\text{CH}} + \text{CH}_2=\text{CH} \rightarrow \text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-\dot{\text{CH}}
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{CH}_2\text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{CH}_2\text{Cl} \quad \text{Cl} \quad \text{Cl}
\]
Step 6  1,2 chlorine migration

\[ \text{CH}_2\text{-CH-CH-CH}_2\text{-CH-CH-CH}_2 \]
\[ \begin{array}{cccccc}
\text{Cl} & \text{Cl} & \text{CH}_2\text{Cl} & \text{Cl} & \text{Cl} \\
\end{array} \]
\[ \rightarrow \]

\[ \text{CH}_2\text{-CH-CH-CH}_2\text{-CH-CH}_2 \]
\[ \begin{array}{cccccc}
\text{Cl} & \text{Cl} & \text{CH}_2\text{Cl} & \text{Cl} & \text{Cl} \\
\end{array} \]

Step 7  Production of a chlorine radical

\[ \text{CH}_2\text{-CH-CH-CH}_2\text{-CH-CH}_2 \]
\[ \begin{array}{cccccc}
\text{Cl} & \text{Cl} & \text{CH}_2\text{Cl} & \text{Cl} & \text{Cl} \\
\end{array} \]
\[ \rightarrow \]

\[ \text{CH}_2\text{-CH-CH-CH}_2\text{-CH-CH}_2 + \text{Cl}^\cdot \]
\[ \begin{array}{cccccc}
\text{Cl} & \text{Cl} & \text{CH}_2\text{Cl} & \text{Cl} \\
\end{array} \]

VC tetramer isomer C

\[ \text{CH}_2\text{-CH}_2\text{-CH-CH-CH}_2\text{-CH-CH}_2 \]
\[ \begin{array}{cccccc}
\text{Cl} & \text{Cl} & \text{Cl} & \text{Cl} \\
\end{array} \]

Step 1  Reinitiation by a chlorine radical

\[ \text{Cl}^\cdot + \text{CH}_2\text{=CH} \rightarrow \text{CH}_2\text{-CH} \]
\[ \begin{array}{cccc}
\text{Cl} & \text{Cl} & \text{Cl} \\
\end{array} \]
Step 2  Head-to-tail addition
\[ \text{CH}_2-\cdot\text{CH} + \text{CH}_2=\text{CH} \rightarrow \text{CH}_2-\text{CH}-\text{CH}_2-\cdot\text{CH} \]
\[ \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \]

Step 3  Hydrogen abstraction
\[ \text{CH}_2-\text{CH}-\text{CH}_2-\cdot\text{CH} \rightarrow \cdot\text{CH}-\text{CH}_2-\text{CH}_2 \]
\[ \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \]

Step 4  Head-to-tail addition
\[ \text{CH}_2-\cdot\text{CH}_2-\cdot\text{CH} + \text{CH}_2=\text{CH} \]
\[ \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \]
\[ \downarrow \]
\[ \text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\cdot\text{CH} \]
\[ \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \]

Step 5  Head-to-head addition
\[ \text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\cdot\text{CH} + \text{CH}_2=\text{CH} \]
\[ \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \]
\[ \downarrow \]
\[ \text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}-\cdot\text{CH}_2 \]
\[ \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \]
Step 6 1,2 chlorine migration

\[
\text{CH}_2\text{-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH}_2
\]

\[
\| \| \| \| \| \|
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

\[
\downarrow
\]

\[
\text{CH}_2\text{-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH}_2
\]

\[
\| \| \| \| \| \|
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

Step 7 Production of a chlorine radical

\[
\text{CH}_2\text{-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH}_2
\]

\[
\| \| \| \| \| \|
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

\[
\downarrow
\]

\[
\text{CH}_2\text{-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH}_2 + \text{Cl}^+\text{.}
\]

\[
\| \| \| \| \| \|
\]

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

A salient feature of both the reaction mechanisms is the occurrence of the head-to-head monomer addition step. This mode of monomer addition is not very prevalent in the polymerisation of VCM as a whole, as shown by the low concentration of head-to-head structures found in the polymer (Section 1.5.5). The termination step in both cases is the expulsion of a chlorine radical and this is a common feature of many of the VC oligomer isomers characterised (Section 4.6). The hydrogen abstraction reaction shown in the synthesis of isomer C (Step 3) is analogous to a 'back-biting' mechanism in a polymer molecule. Such a reaction in the long chain PVC molecules would result in chlorinated n-propyl branches, a type of branch which has not been identified in PVC. Such a reaction, however, would not be as likely to occur in a polymer molecule because the common backbone structure...
\[
\begin{array}{ccc}
\gamma & \beta & \alpha \\
-\text{CH} & -\text{CH} & -\text{CH} \\
\text{Cl} & | & \text{Cl}
\end{array}
\]

has a methylene group in the \( \gamma \) position, from which a hydrogen abstraction would be less favourable. All the other steps in the two reaction mechanisms are accepted reactions for growing PVC molecules and the references in which the reactions are reported are given alongside the step numbers.
CHAPTER FIVE

Conclusions and suggestions for further work

5.1 Conclusions

5.1.1 Soxhlet extraction of PVC materials

This work has optimized the process of obtaining low molecular weight Soxhlet extracts from PVC base resins with respect to three important areas: extract yield, contamination and degradation. It has been shown that for a given extracting solvent a mass polymerised PVC will give a higher extract yield than a suspension polymerised PVC having a similar molecular weight (K-value). This has been attributed to the pericellular skin that surrounds suspension PVC particles and hinders oligomer dissolution. Two major sources of extract contaminants were identified: the cellulose extraction thimble that is used in a standard Soxhlet apparatus, and the dispersing agents which are used in the suspension polymerisation process and remain on the surface of the PVC resin particles. These impurities were eradicated from the extract by modifying the Soxhlet so that it could function without a thimble and utilising PVC produced by the mass polymerisation process. Most of the solvents evaluated as extracting agents gave an extract that was highly coloured due to thermal degradation. It was essential that the structure of the VC oligomers in the extract was altered as little as possible and so for this reason diethyl ether, which provided extracts that were the least degraded, was the preferred extractant.

Diethyl ether Soxhlet extracts were obtained from PVC bottles, the bottles being comminuted finely to present the largest possible surface area to the extractant. The bottles had been produced from a formulation containing a number of additives and it was found that these were co-extracted with the VC oligomers. This situation resulted
in an extract that was mostly comprised of additives, with the VC oligomers being a minority component. Because most additives are of a low molecular weight and not chemically bound to the PVC molecules this situation is impossible to avoid and will be experienced whenever a fabricated PVC product is extracted with a relatively non-discriminating solvent.

5.1.2 Procurement of a low molecular weight PVC fraction from the diethyl ether Soxhlet extracts

The intermediate fractionation stage that involved acquiring a low molecular weight fraction from a diethyl ether Soxhlet extract that was suitable for HPSEC analysis had two basic functions: removal of unwanted long chain PVC and purification. Preparative gel filtration was initially used to remove the redundant long chain PVC but was later discarded because of its inefficiency in dealing with large quantities of Soxhlet extract. The preferred choice due to its speed of operation, fractional precipitation, was a less precise technique in that the molecular weight distribution of the low molecular weight fraction was more variable. However, this was unimportant as the molecular weight range of interest (up to 500 g mol\(^{-1}\)) was unaffected and the performance of the subsequent HPSEC system not compromised. The impurities in the low molecular weight fraction were found to hinder the detection and, hence, separation of the VC oligomers by HPSEC and so an adsorption liquid chromatography technique was employed in an attempt to remove them. With the fractional precipitation - adsorption liquid chromatography combination it was possible to efficiently prepare reasonably pure low molecular weight fractions from Soxhlet extracts of PVC base resins. It was not possible, however, to separate the VC oligomers from the
additives in the low molecular weight PVC bottle fraction using the adsorption liquid chromatography technique.

5.1.3 Separation of VC oligomers

An HPSEC system based on columns containing 5μm, 50 Å PL gel packing was found to be capable of separating the VC oligomers trimer to decamer from low molecular weight PVC fractions. To resolve the VC oligomer species a gel bed length of 480 cm was required and this was achieved by employing an alternate pumping recycle technique. Refractive index detection for this kind of separation gave problems because of the close proximity of the lower oligomer peaks to the ubiquitous detector peaks that are a feature of this type of detection system with HPSEC. Another problem encountered was that of calibration. In this molecular weight range the HPSEC calibrating standards, polystyrenes, were found to give misleading peak assignments and so GC-MS had to be employed for an unambiguous identification. For a given eluent the elution volume range for each VC oligomer was found to be constant, which enabled the oligomers present in the low molecular weight fraction obtained from the PVC bottles to be isolated even though their peaks were obscured by bottle additives. The HPSEC analysis of the suspension PVC resin, Norvinyl VY 80/30, revealed that it contained far less (if any) trimer species compared to the mass PVC resin, Lucovyl RB 8010. This is due to the harsher conditions, ie. higher temperatures, used to strip VCM from suspension polymers. There was no evidence of a VC dimer species in any of the PVC materials analysed and this can also be attributed to the VCM stripping procedure.
5.1.4 Separation of the VC oligomer isomers

Two chromatographic techniques were evaluated for the separation of VC oligomer isomers: TLC and HPLC. TLC proved capable of achieving a partial resolution of the isomers of the oligomer species hexamer and pentamer, the best separations resulting from a developing solvent consisting of hexane-MTBE (75:25). An HPLC system based on a 55W silica column and a mobile phase of hexane containing 1% v/v MTBE modifier produced good isomer separations for the VC oligomers heptamer to pentamer. The modifier content was reduced to 0.25% to resolve the isomers of the tetramer species. With the VC octamer only a partial isomer separation was achieved due to the copious number of isomers existing for that species. The two isomers of the VC trimer were found to be indistinguishable from the solvent front that is inherent with low wavelength UV detection. A useful quality of the HPLC system was its ability to separate the weakly polar VC oligomer isomers from other, more polar, compounds. It was this attribute that enabled VC oligomer isomer chromatograms to be obtained from the additive contaminated VC oligomer fractions isolated from the PVC bottles. The HPLC analysis of the VC oligomers obtained from different sources revealed that the number of isomeric forms existing for each oligomer increased rapidly with chain length and that, for a given oligomer, the same number of isomers with the same relative mass distribution exist in both mass and suspension polymerised PVC resins. Also, the processing stages used to produce a PVC bottle do not alter the number of isomers or isomer mass distribution of each oligomer to any great extent.
5.1.5 Structural characterisation of VC oligomers

By using GC-MS and 200 MHz $^1$H NMR it has been possible to derive the structures of two VC tetramer isomers. A mechanism for the formation of each isomer has been proposed by utilising accepted reaction pathways. The same techniques have enabled tentative structures of five pentamer isomers to be assigned along with partial structures for four other pentamer isomers and three heptamers. Very little structural information could be elucidated from the mass spectrum of each isomer and so a heavy reliance was placed on the $^1$H NMR assignments which were dependent on work previously published on model PVC systems. The major limiting factor on the structural information that could be obtained from $^1$H NMR was the limited quantity of each isomer that was available for analysis. The majority of the structural moieties assigned by $^1$H NMR for the VC oligomer isomers are well documented from the numerous studies carried out on PVC. However, there were a few, previously unpublished, partial structures whose presence in the oligomers would have to be corroborated by further work before they could be proposed with confidence.

5.2 Suggestions for further work

The scope of this work included VC oligomers from the dimer to octamer species. The oligomers tetramer to heptamer were characterised the most fully by the analytical procedures developed. The other three oligomers, the dimer, trimer and octamer were either partially or, in the case of the dimer, not characterised. It would appear that these oligomers require a different approach to the one that has been successful with the other oligomers. Because the vast majority of the VC dimer is lost in the VCM removal process, it will never be present in the PVC base resins in sufficient quantities for a structural characterisation to be possible by NMR analysis. However, a technique such as
headspace GC could be attempted on a low molecular weight PVC fraction to see if the VC dimer could at least be located, something which has not been possible to date. The HPLC technique utilised in this work was unsuitable for separating the isomers of the VC trimer and octamer (Section 5.1.4) and so other HPLC column-mobile phase systems that are compatible with low wavelength UV detection could be evaluated. Also, a more specific detector, for example an LC-EC, could be employed to extend the range of options available. In the case of the trimer, where only two isomers exist, the TLC techniques used in this work would be worth investigating as they showed some promise in separating the higher VC oligomer isomer mixtures. If it were possible to find methods to separate the isomers of the VC trimer and octamer, then the characterisation could be continued to eventually obtain structural information by the use of spectroscopic techniques.

The amount of structural information that could be obtained on each VC oligomer isomer was limited due to the very small quantities available. To circumvent this problem the isomer preparation programme could be modified in order to facilitate the accumulation of much larger quantities of each species. If approximately 20 mg of each isomer could be prepared, $^{13}$C NMR could be employed in addition to $^1$H NMR which would result in much fuller characterisations being accomplished. The stages in the VC oligomer isomer preparation programme that were the least efficient were the HPSEC (oligomer separation) and HPLC (isomer separation) stages. Both of these could be carried out more efficiently if preparative columns were utilised instead of the analytical type; the very high cost involved, particularly for the preparative HPSEC columns, ruled out this option in this work. In addition to repeating the structural characterisation of the VC oligomer isomers
analysed in this work, the process could be extended to include the isomers that were separated but not analysed by $^1$H NMR, ie. the hexamer isomers and the remaining isomers of the heptamer.

Although a number of VC oligomer sources have been used in this work, the analysis of oligomers from other sources, such as alternative mass, suspension and emulsion polymerised PVC base resins and a variety of fabricated PVC articles, would demonstrate if the statements made regarding the isomer populations of VC oligomers and the effect of processing on the oligomers (Section 5.1.4) were truly authoritative. In addition, it would be interesting to analyse the VC oligomers using SFC to see how the isomer chromatograms obtained compared with those procured by HPLC.

The analytical procedures developed in this work have enabled the complete structures of two VC tetramer isomers and five VC pentamer isomers to be elucidated. It would be very instructive to synthesis these oligomers and then analyse them using the same chromatographic and spectroscopic techniques. This would enable a comparison of the analysis behaviour of the two sets of oligomers to be made and, more importantly, it would reveal whether the proposed isomer structures are authentic or not.
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