Characterisation of oligomers and additives from polymeric materials

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Characterisation Of Oligomers And Additives From Polymeric Materials

by

Alexander Hayk Celik. B.Sc. (Hons)

Supervisor: Professor J. V. Dawkins

A Doctoral Thesis

Submitted in partial fulfilment of the requirements

for the award of

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ABSTRACT

Characterisation Of Oligomers And Additives From Polymeric Materials

Alexander H. Celik

A multi-stage scheme was developed for the separation of vinyl chloride (VC) oligomers. A low molecular weight fraction was isolated from poly(vinyl chloride) by Soxhlet extraction. The presence of VC oligomers up to decamer was demonstrated by high-performance size exclusion chromatography (HPSEC). Removal of polar impurities was accomplished by preparative adsorption liquid chromatography of the low molecular weight fraction. Recycle HPSEC with repeated injections permitted the accumulation of fractions of VC pentamer oligomers which were resolved into their isomers by high-performance liquid chromatography (HPLC) off-line. These results were duplicated utilising a coupled column system comprising of recycle HPSEC connected on-line to HPLC. This coupled technique was then applied to the hexamer and heptamer oligomers which were resolved into their constituent isomers.

Multi-stage schemes were then developed for the extraction, characterisation and quantification of low molecular weight compounds from nitrile (NBR), ethylene-propylene-diene monomer (EPDM) and silicone elastomers. Low molecular weight fractions were isolated from these elastomers by Soxhlet extraction. HPLC and SEC analysis was performed on these extracts followed by gas chromatography-mass spectrometry (GC-MS). Extracts from these elastomers were shown to contain various phthalates, diamines, phenols, hydrocarbons and thiazoles. In addition, analysis of the low molecular weight extract from the silicone elastomer disclosed the presence of a number of cyclic and linear silicone oligomers.

CONTENTS

6. APPENDIX

1. Introduction

1.1 Background

Many polymers have applications as food contact materials. A range of species may migrate from these materials into food with consequential concerns about possible health effects[1]. Whilst monomer residues have received particular attention, and regulations for levels of monomers in thermoplastics are well documented[2], the gathering of data on potential migrants is much less complete for other low molecular weight compounds such as oligomers and additives. Food contact materials often contain many components in addition to the base polymer such as additives, oligomers and polymerisation residues. Consequently, the final product can contain a multitude of components at all levels from traces to perhaps 20-30% by weight[3], and despite considerable effort, many of these potential migrants remain uncharacterised.

Oligomeric species which are produced in all polymerisation processes often contain terminal functionality similar to a monomer unit and are also present in substantially higher concentrations than the monomer. Intentional additives include plasticisers, antioxidants, flame retardants, heat and ultra-violet stabilisers, slip and anti-blocking additives for plastics, and antioxidants, oil extenders, accelerators, activators, soap and sulphur for vulcanised rubbers. Analytical methods for low molecular weight compounds must therefore consider a very varied range of chemical types. It is also important that the oligomer fraction and additives in polymer based packaging be evaluated with regard to potential for migration[4].

1.2 Purpose of investigation

1.2.1 Major aim

To establish chromatographic and spectroscopic methods in order to characterise and quantify oligomers and additives in plastics, rubbers and elastomers used in food contact applications.

1.2.2 Objectives

Chromatographic and spectroscopic characterisation techniques were established in order to quantify oligomer and additive levels in the following polymers:

1. Poly(vinyl chloride) (PVC)
2. Nitrile Rubber (NBR)
3. Ethylene-Propylene-Diene-Monomer (EPDM)
4. Silicone Rubber

The main objectives of this work have been:

1. To develop methods for the extraction of low molecular weight compounds (<1000) from food contact polymers.

2. To develop chromatographic methods for the separation of compounds from low molecular weight fractions and to utilise various spectroscopic techniques to characterise the low molecular weight compounds isolated.

3. To establish a coupled column chromatographic technique to separate oligomers and additives in appropriate polymers (e.g. PVC).

1.3 Polymerisation of vinyl chloride

1.3.1 Polymerisation kinetics

The kinetics[5,6] that apply to mass and suspension polymerisations are the same and these are described here. As PVC products manufactured by emulsion polymerisation were not used in this work, the kinetics of emulsion polymerisation will not be discussed.

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 reaction due to chain transfer to monomer which increases more rapidly with temperature than does the chain propagation reaction. As a consequence, the molecular weight of the resultant PVC is determined by the polymerisation temperature and is less effected by the initiator concentration.

Initiation in the presence of an initiator I may be considered in two steps: first, the rate-determining decomposition of the initiator into free radicals R·,

$$I \xrightarrow{k_d} 2R\cdot \qquad (1.1)$$

and second, the addition of a monomer unit to form a chain radical M_1·,

$$R\cdot + M \xrightarrow{k_i} M_1\cdot \qquad (1.2)$$

where the rate constants, k, in these and subsequent equations have subscripts designating the reactions to which they refer. The successive steps in propagation:

$$M_1\cdot + M \xrightarrow{k_p} M_2\cdot$$
$$M_2\cdot + M \xrightarrow{k_p} M_3\cdot$$
$$M_X\cdot + M \xrightarrow{k_p} M_{X+1}\cdot \qquad (1.3)$$

are all assumed to have the same rate constant k_p, since radical reactivity is presumed to be independent of chain length.

The termination step involves combination

$$M_X\cdot + M_y\cdot \xrightarrow{k_{tc}} M_{x+y} \qquad (1.4)$$

or disproportionation

$$M_X\cdot + M_y\cdot \xrightarrow{k_{td}} M_X + M_y \qquad (1.5)$$

Except where it is necessary to distinguish between the two mechanisms, the termination rate constant is denoted k_t.

The rates of the three steps may be written in terms of the concentrations [in brackets] of the species involved and the rate constants. The rate of initiation is

$$R_i = \left(\frac{d[M\cdot]}{dt}\right)_i = 2fk_d\,[I] \qquad (1.6)$$

where f represents the initiator efficiency, i.e. the proportion of initiator radicals that initiate a chain.

The rate of termination is

$$R_t = -\left(\frac{d[M\cdot]}{dt}\right)_t = 2\,k_t\,[M\cdot]^2 \tag{1.7}$$

In many cases of interest, the concentration of free radicals [M·] becomes essentially constant very early in the reaction due to the fact that radicals are formed and destroyed at identical rates. In this *steady-state* condition $R_i = R_t$ and equations 1.6 and 1.7 may be equated to solve for [M·]:

$$[M\cdot] = \left(\frac{fk_d[I]}{k_t}\right)^{0.5} \tag{1.8}$$

The rate of propagation is essentially the same as the overall rate of disappearance of monomer, since the number of monomers used in reaction 1.2 must be small compared to that used in reaction 1.3 if high polymer is obtained. Then

$$R_p = -\frac{d[M]}{dt} = k_p\,[M][M\cdot] \tag{1.9}$$

or with substitution from equation 1.8

$$R_p = k_p \left(\frac{fk_d\,[I]}{k_t}\right)^{0.5} [M] \tag{1.10}$$

Thus, the overall rate of polymerisation should, in the early stages of the reaction, be proportional to the square root of the initiator concentration and, if f is independent of [M], to the first power of the monomer concentration. This is true if the initiator efficiency is high. With very low efficiency, f may be proportional to [M], making R_p proportional to $[M]^{3/2}$.

1.3.2 Degree of polymerisation and chain transfer

1.3.2.1 Kinetic chain length

The *kinetic chain length* v, is defined as the number of monomer units consumed per active centre. It is therefore given by $R_p/R_i = R_p/R_t$, and so from equations 1.7 and 1.9, v is given by

$$v = \frac{k_p}{2k_t}\frac{[M]}{[M\cdot]} \tag{1.11}$$

By eliminating the radical concentration by means of equation 1.9, the general expressions are obtained

$$v = \frac{k_p^{\,2}}{2k_t}\frac{[M]^2}{R_p} \tag{1.12}$$

$$v = \frac{k_p}{2(f\,k_d\,k_t)^{0.5}}\frac{[M]}{[I]^{0.5}} \tag{1.13}$$

When no reactions take place other than those already discussed, the kinetic chain length should be related to x_n, the degree of polymerisation. It therefore follows for termination by combination that $x_n = 2v$, and for disproportionation that $x_n = v$. Whilst this is found to be true for some systems, for others, wide deviations are noted in the direction of more polymer molecules than active centres. These deviations are the results of chain transfer reactions:

$$M_x\cdot + RH \longrightarrow M_xH + R\cdot$$

$$R\cdot + M \xrightarrow{k_{tr}} RM\cdot$$

etc.

where R may be monomer, initiator, solvent, or other added chain transfer agent. (Transfer to polymer is omitted, since no new polymer molecule is produced.)

The degree of polymerisation is therefore

$$x_n = \frac{\text{rate of growth}}{\Sigma \text{ rates of all reactions leading to dead polymer}}$$

$$x_n = \frac{R_p}{f\,k_d[I] + k_{tr,M}[M][M\cdot] + k_{tr,S}[S][M\cdot] + k_{tr,I}[I][M\cdot]} \qquad (1.14)$$

where the terms in the denominator represent termination by combination and transfer to monomer, solvent, and initiator, respectively. If termination is disproportionation, the first term becomes $2 f k_d[I]$. If transfer constants are defined as

$$C_M = \frac{K_{tr,M}}{k_p} \quad C_S = \frac{K_{tr,S}}{k_p} \quad C_I = \frac{K_{tr,I}}{k_p} \qquad (1.15)$$

then (assuming termination by combination):

$$\frac{1}{x_n} = \frac{k_t}{k_p^2}\frac{R_p}{[M]^2} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{k_t\ R_p^{\,2}}{k_p^{\,2} f k_d\ [M]^3} \qquad (1.16)$$

The above analysis assumes that the radical formed in the transfer process is approximately as reactive as the original chain radical, otherwise retardation or inhibition results.

In viscous VCM/PVC mixtures, polymer molecule production by chain transfer to monomer is far more frequent than production by the two termination reactions where bulky molecules are involved.

This results in $k_{tr} >> k_t$ and so equation 1.16 simplifies to

$$x_n = \frac{k_p}{k_{tr}} \tag{1.17}$$

Kuchanov and Bort[7] have obtained a value of 9.2 x 10^{-3} exp 7400/RT for k_p/k_{tr} implying a degree of polymerisation of 950 (number average molecular weight, M_n = 59000) at 50°C, 670 (M_n = 42000) at 60°C and 482 (M_n = 30000) at 70°C. Freeman and Manning[8] have produced experimental data which corroborate these values and confirm that equation 1.17 is an accurate measure of the molecular weight achieved.

1.3.3 Polymerisation methods

Commercially, VCM is polymerised by a free radical mechanism using the following methods[9]:

1. Suspension polymerisation
2. Mass or bulk polymerisation
3. Emulsion polymerisation

1.3.3.1 Suspension polymerisation

Suspension polymerisation is a heterogeneous process consisting of a dispersed phase (VCM) and dispersion medium (water). The identity of the dispersed phase droplets converted to particles is maintained by vigorous stirring and the action of dispersing agents. Partially hydrolysed polyvinyl acetate is used extensively as a protective colloid. Because it is in 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 because (a) the dispersion medium (water) is both cheap and non-hazardous; and (b) the polymerisation can be carried to almost complete exhaustion of monomer before being stopped.

Suspension PVC resin particles are usually irregular in shape, with a mean size of 100-150 μm and are porous in structure. The resin particles possess a skin which hinders the absorption of diffusants such as plasticisers. This is the most widely employed technique for the production of PVC, accounting for approximately 85% of the worlds production. A typical suspension polymerisation recipe for a 10 m^3 autoclave is given below.

Table 1. VCM polymerisation at 60°C for up to 6 hours

Ingredient	Weight (kg)
Water	5000
Dispersing Agent	3.5
Buffer	0.7
Initiator	1.5
VCM	3500

1.3.3.2 Mass or bulk polymerisation

The mass polymerisation process is simple and no elaborate isolation or purification step is needed. The reaction mixture contains only monomer and initiator. However, as the reaction is exothermic, hot spots tend to develop when heat removal is inefficient. Auto-acceleration occurs in the highly viscous medium making control difficult and efficient monomer conversion is impeded. The main advantages of the technique are the optical clarity of the product and its freedom from contamination, which make it ideal for food contact use.

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%. With bulk polymerisations, the polymerisation has to be ended at ~80% conversion to avoid excessive heat build-up.

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

1.3.3.3 Emulsion polymerisation

In this process, the liquefied monomer is emulsified in water containing a water soluble initiator. It is, therefore, a heterogeneous system like the

suspension process. 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.

1.3.4 Molecular weight

An inherent feature of addition and condensation polymerisations is that a distribution of molecular weights exists in the final polymer product. This can vary greatly depending upon the polymerisation mechanism used: anionic mechanisms can give polymers with very narrow distributions, whilst free radical mechanisms resulting in a very broad distribution of molecular weights[10].

The molecular weight distribution (MWD) of a polymer may be characterised by utilising its average molecular weights. There are several average molecular weights that can be determined, but the two most commonly used are the number average molecular weight (M_n) and weight average molecular weight (M_w). The number average molecular weight is found by dividing the total mass of polymer (W) by the total number of moles (N_i). If W_i is the weight of the species with the molecular weight M_i then

$$W = \sum_{1=1}^{\infty} N_i M_i \tag{1.18}$$

and M_n is defined by

$$M_n = \frac{W}{\sum_{1=1}^{\infty} N_i} = \frac{\sum_{1=1}^{\infty} W_i}{\sum_{1=1}^{\infty} N_i} = \frac{\sum_{1=1}^{\infty} N_i M_i}{\sum_{1=1}^{\infty} N_i} \tag{1.19}$$

A value for M_n can be determined experimentally by using vapour pressure or osmometry techniques[10].

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.

$$M_W = \frac{\sum_{1=1}^{\infty} W_i M_i}{\sum_{1=1}^{\infty} W_i} = \frac{\sum_{1=1}^{\infty} N_i M_i^{\,2}}{\sum_{1=1}^{\infty} N_i M_i} \qquad (1.20)$$

A value for M_w is determined in the laboratory by using light scattering[10]. By using the two expressions for the number and weight average molecular weights the width of the MWD is characterised by the polydispersity (M_w/M_n).

$$\frac{M_W}{M_n} = \frac{\sum_{1=1}^{\infty} N_i M_i^{\,2}}{\sum_{1=1}^{\infty} N_i M_i} \Bigg/ \frac{\sum_{1=1}^{\infty} N_i M_i}{\sum_{1=1}^{\infty} N_i} \qquad (1.21)$$

The value of the polydispersity gives an insight into the molecular weight range existing in the polymer, being unity for a completely monodisperse and 2 for a most probable distribution such as a polymer produced by a free radical polymerisation with chains formed by chain transfer reactions.

The molecular weights for most commercial PVC polymers are in the range M_w = 100000-200000; M_n =45000-64000. The polydispersity is usually about 2, although it may be larger for the higher molecular weight grades. For commercial purposes, the molecular weight is generally 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:

$$[\eta] = K^1 M^{\alpha} \qquad (1.22)$$

where K^1 and α are referred to as Mark-Houwink constants, M is the molecular weight (M_v), and $[\eta]$ is the intrinsic viscosity for the polymer in a known solvent at a fixed temperature. The intrinsic viscosity is found by plotting $(\eta-\eta_0)/\eta_0$ c against c, where η is the viscosity of the polymer solution, η_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 to quote an actual figure for molecular weight. The K value is found by using the following equation:

$$\log_{10} \eta_{rel} = \left[\frac{75K^2 \times 10^{-6}}{1 + 1.5\, Kc \times 10^{-3}} \right] + (K \times 10^{-3}) \qquad (1.23)$$

where η_{rel} is the relative viscosity (η/η_0) and c is the polymer concentration in g/100 ml.

1.3.5 Removal of VCM from PVC resins

The kinetics of the polymerisation of VCM make it impossible to polymerise all the VCM because the rate of polymerisation falls rapidly at high conversion[9]. As a consequence, the PVC resin contains substantial quantities of unreacted VCM. Due to its toxicity, the residual level of monomer present in the resin has to be drastically reduced, but how this is achieved is dependent on the process concerned. The procedures used to strip VCM from the PVC resin will also reduce the concentration of vinyl

chloride (VC) oligomers, particularly the lower species such as dimer and trimer.

1.3.5.1 Stripping VCM from suspension PVC

The unreacted VCM is removed in two stages:

1. 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 higher. Both of these processes result in PVC resins containing approximately 3% of unreacted VCM.

2. The residual level of VCM is reduced to the permissible limit by purging the aqueous PVC slurry with steam. The steam heats the slurry to temperatures between 80 and 120°C and the resulting steam/VCM mixture is then drawn off to reduce the level of VCM in PVC resins to less than 1 ppm.

1.3.5.2 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 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. The difficulties in obtaining good large scale vacuums economically has resulted in higher, although still acceptable levels of VCM being present in mass resins compared to suspension resins.

1.3.5.3 Stripping VCM from emulsion PVC

The same basic stripping processes used for suspension PVC is also applied to emulsion PVC. The small size of the particles means that their loss of VCM diffusion is rapid. This advantage is, however, out-weighed 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 usually has a VCM level of less than 150 ppm w/v after stripping, but drying and milling operations reduce this to 10 ppm.

1.3.6 The structure of PVC

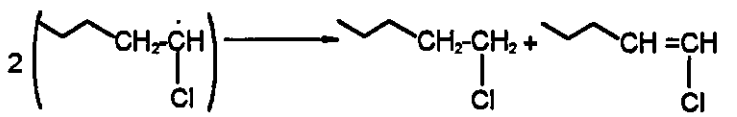
There is evidence that commercial PVC does not have the regular head-to-tail structure based on the repeat unit $-CH_2-CHCl-$[11]. There are a number of structural anomalies present in the polymer which have the undesirable effect of reducing thermal stability. The analytical technique most frequently employed for the elucidation of the structure of PVC is nuclear magnetic resonance (NMR) spectroscopy. 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

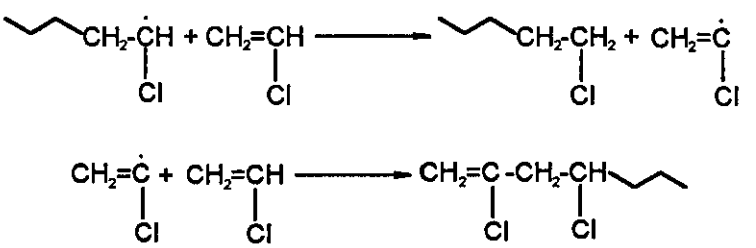
1.3.6.1 Unsaturation

There are several mechanisms whereby a double bond in a PVC chain arises.

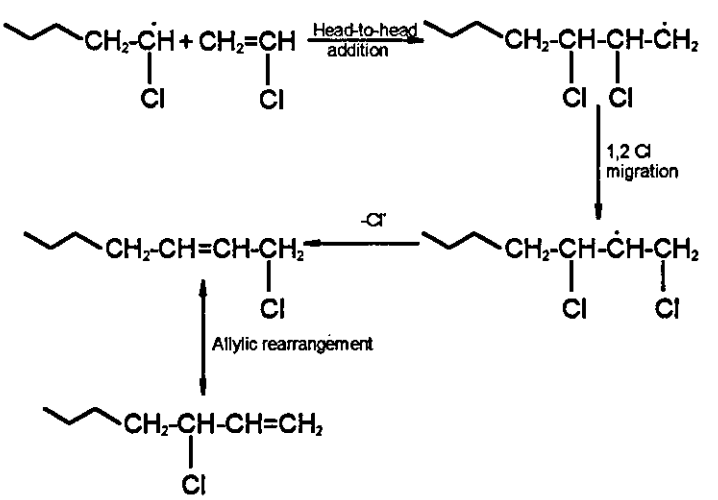
1. Termination by disproportionation



2. Chain transfer to monomer

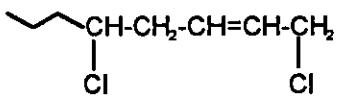


3. Mechanism proposed by Bezadea *et al.*[12]



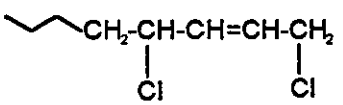
The concentration of double bonds in PVC using liquid phase bromination, with an incidence of 2 x 10^{-3} double bonds per monomer unit has been observed[13].

Low molecular weight extracts obtained from mass PVC by proton NMR 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[14].

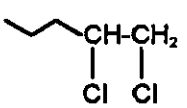


1,5 dichloro-3-pentyl

A low molecular weight fraction (M_n = 1500) was obtained by extracting mass PVC with methanol and analysing it using proton and carbon 13 NMR. In addition to 1,5 dichloro-3-pentyl, 2,5 dichloro-3-pentyl and 1,2 dichloroethyl structures were also found, their ratios per molecule being 2:1:5, respectively[15].



2,5 dichloro-3-pentyl



1,2 dichloroethyl

Confirmation of the presence of these three structures has been provided by Maddams[16]. Examination of PVC samples produced by Suspension polymerisation PVC samples with proton and carbon 13 NMR have shown 1,5 dichloro-3-pentyl to be the main unsaturated chain end structure and 1,2 dichloroethyl to be the main saturated chain end structure. Other unsaturated structures have been found in small quantities[17].

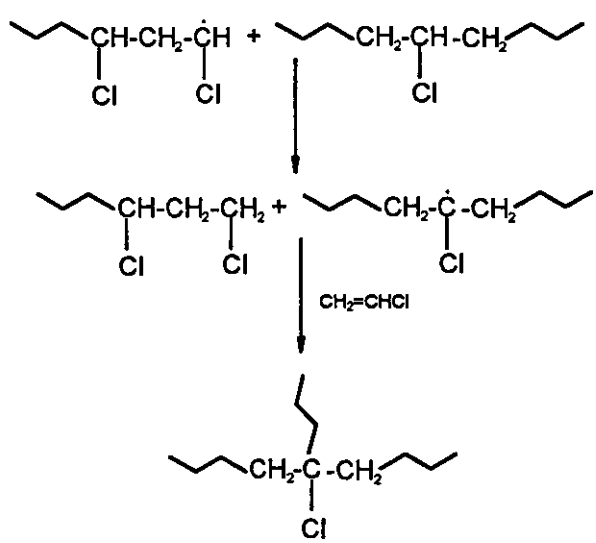
To characterise the double bond content of PVC, an infra-red (IR) spectroscopy method was developed by Simak[18]. Good agreement was established between the double content found this way and by the

chemical method described by Hildebrand[19]. To determine the double bond content of PVC, several other chemical methods have been developed. The internal double bond concentration has been evaluated by measuring changes in molecular weight resulting from oxidative double bond scission caused by reacting PVC with N-dimethyl acetamide. Using this method Braun and Quarge[20] calculated 0.3 x 10^{-3} to 2.5 x 10^{-3} double bonds per monomer unit from the change in intrinsic viscosity. By measuring the molecular weight change after ozonolysis, there were 0.2 double bonds per 1000 monomer units in a suspension PVC sample[21].

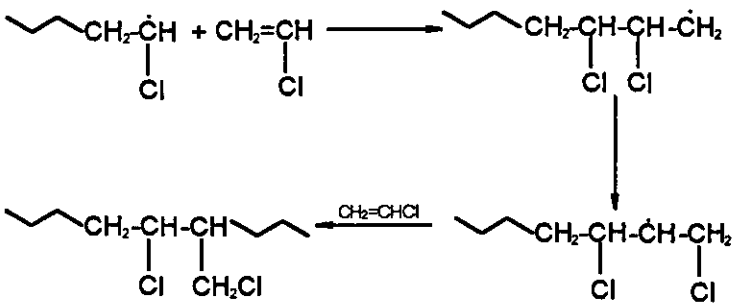
1.3.6.2 Branching

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

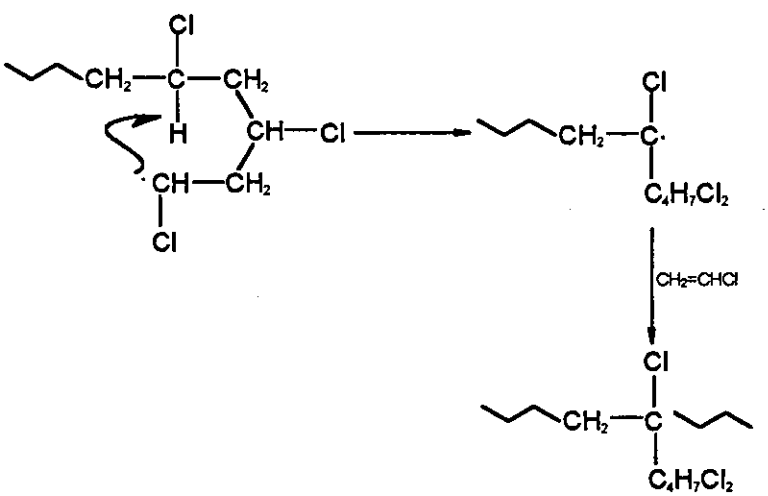
1. Transfer to polymer



2. Head-to-head addition followed by a 1,2 chlorine atom shift[22].



3. Back-biting



Production of dichlorobutyl branches has been attributed to a back-biting mechanism analogous to that proposed for low density polyethylene[23]. Long branches arise during polymerisation by the transfer of hydrogen from within the polymer to growing radicals. The most labile hydrogen atoms in PVC are those in the -CHCl- groups since the resultant free radical has resonance stability.

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. Levels of branching in the range 1.8 to 16 per 1000 monomer units have been found by Baker *et al.*[24]. By using high field NMR techniques 4 to 5 branches per chain of

high molecular weight PVC have been reported[25]. The mechanism for the production of chloromethyl branches in PVC was originally proposed by Rigo *et al.*[22]. A comprehensive examination by carbon 13 NMR of the branch structures present in a number of PVC samples has been reported[26]. The following branches were found in varying concentrations depending on the polymer: long chain, butyl, ethyl and methyl.

1.3.6.3 Initiator end-groups

During polymerisation reactions initiator moieties may be 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[27]. The chemical nature of the end-group 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.

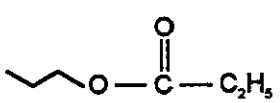
1.3.6.4 Head-to head structures

Head-to-head units in PVC can either be formed through termination by combination or by head-to-head addition during propagation. 2.5 to 7.0 head-to-head structures per 1000 monomer units are found, the number increasing with the polymerisation temperature[28]. With the method followed by Mitani[28] various PVC samples gave a measure of the content of saturated 1,2 dichloroethyl chain end-groups, and indicated a lower

concentration of 0 to 0.2 head-to-head structures per 1000 monomer units[29].

1.3.6.5 Oxygen containing defects

Oxygen containing structures can arise in PVC molecules either by a reaction with traces of oxygen present during polymerisation or by oxidation during storage or treatment of the polymer in the air. Another prime source of oxygen is initiator residues present at the chain ends. Virgin PVC has been found to contain up to 500 ppm of peroxide[30]. The presence of an ethoxycarbonyloxy structure in a molecular weight fraction of a commercial suspension PVC resin has been suggested[31].



Ethoxycarbonyloxy structure

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

1.3.6.6 Tacticity

X-ray studies reveal that commercial PVC is substantially amorphous although a small amount (about 5%) of crystallinity is present. NMR studies show[32] that ordinary PVC is about 55% syndiotactic in structure, the rest being atactic. Syndiotacticity may by increased by lowering the polymerisation temperature: for example, polymer prepared at -50°C is 66% syndiotactic. A completely syndiotactic polymer has been obtained

by use of a urea canal complex[33]. Compared to the atactic material, syndiotactic polymers are more difficult to process and give brittle products; they have not, therefore, become of commercial importance.

1.3.7 Stability of PVC

The stability of the polymer is not given lengthy consideration here as this work is concerned with the separation of VC oligomers in PVC base resins. However, by analogy with PVC, there are possible structural changes that the VC oligomers could undergo during processing and service life. The inherent instability of PVC, 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[34,35].

1.3.8 Vinyl chloride oligomers

VC oligomers are short chain homologues of VCM. VC oligomers which have 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 into foodstuffs.

Although extensive characterisation studies have been carried out on oligomers of other plastics, particularly oligostyrenes, very little work has been published on the structural characterisation of VC oligomers obtained from PVC. Initially, a low molecular weight fraction was isolated from food grade PVC resins using Soxhlet extraction followed by size exclusion chromatography, and estimations of oligomer levels were made on the

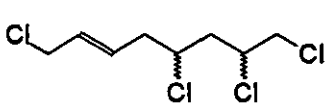
basis of gravimetric measurements and microchlorine detection[36]. These results assumed that all the oligomers had the same empirical formula as VCM and that all the available chlorine was present as oligomers rather than as alternative chlorinated organic compounds. The quantity of oligomers found of molecular weight less than approximately 600 ranged from 100 to 350 mg kg^{-1} depending upon base resin.

Further analysis of the low molecular weight fractions using gas chromatography-mass spectrometry (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. Mass spectrometry data obtained from hydrogenation studies indicate that 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}Cl - ^{37}Cl combinations and fragment ions due to the sequential loss of hydrogen chloride from the molecular ion.

It was apparent that mass spectrometry only provided partial information and that NMR would need to be employed to elucidate the structure of the VC oligomers. The disadvantage of NMR is that a few milligrams of

relatively pure compound are required to facilitate analysis. To provide sufficient quantity, one particular VC oligomer, a straight chain tetramer, had to be prepared for proton analysis. A multi-stage chromatographic procedure was developed Gilbert *et al.*[37], 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 size exclusion chromatography to give a 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[38]. Only a partial characterisation was possible due to complex overlapping signals thought to be due to impurities which hindered interpretation of the spectrum.

Dawkins *et al.*[39,40], reported a procedure for the separation of oligomers from a low molecular extract of PVC using a recycle high-performance size exclusion chromatographic technique. This system was capable of resolving oligomers in the range of pentamer to decamer; however, no structural determinations were made. This technique was incorporated into a separation scheme directed to the isolation of tetrameric oligomers which utilised HPLC to separate the tetramer oligomer into its constituent isomers (Dawkins *et al.*,[41]). These isomers then underwent 400 MHz proton and carbon 13 NMR characterisation which indicated that the VC tetramer was composed of two diastereomers of the structure shown below:



1.4 Nitrile rubber

Acrylonitrile-butadiene rubbers (NBR) may be most concisely described as speciality rubbers with a conventional technology. With good chemical resistance, particularly to aliphatic hydrocarbons, nitrile rubbers have grown steadily in importance. First prepared in 1930, pilot plant production of this rubber commenced in 1934 with a full scale production starting in Germany in 1937.

1.4.1 Emulsion polymerised NBR

The development of a free-radical initiated emulsion polymerisation process for the production of NBR closely parallels that for styrene-butadiene rubber (SBR)[42]. 'Low', 'medium' and 'high' solvent resistant grades of copolymer, respectively containing approximately 25, 30 and 40% by weight of acrylonitrile, are commonly produced. The butadiene content of a copolymer is made up of *trans*-1,4-, *cis*-1,4- and 1,2-units. Both 'hot' and 'cold' processes may be employed but now only 'cold' processes (using temperatures in the range 5-30°C) are operated commercially. Copolymers prepared by 'hot' and 'cold' processes differ in that the later are less branched and have a narrower molecular weight distribution. The theory and process of emulsion polymerisation have been the subject of a number of reviews (Alexander *et al.*[43]; Blackley [44]; Ugelstad *et al.*[45].

1.4.2 NBR produced by Ziegler-Natta systems

Butadiene-acrylonitrile copolymers with a predominantly alternating structure were produced using Ziegler-Natta systems in the late 1960s[46, 47]. Although bulk and solution polymerisation processes were the first to be developed, superior results were obtained using a suspension

polymerisation system (Takamatsu *et al.*[48]). A typical catalyst consisted of trimethyl aluminium, aluminium chloride and vanadyl chloride, whilst polymerisation is carried out at 0°C with *n*-hexane as diluent.

1.4.3 Structure and properties of NBR

As the acrylonitrile content is increased, the polymer becomes less hydrocarbon and more polar. The primary properties affected are the glass transition temperature (T_g) and the solubility parameter, δ, which both increase with increasing percentage acrylonitrile content, and influence rubber properties and solvent resistance.

The butadiene may be wholly or partly replaced with a substituted butadiene i.e. isoprene, piperylene or dimethyl butadiene, but the polymers with higher values of T_g brought about by the stiffening effect of the methyl side groups are generally more leatherlike. The molecular weight is controlled (in the case of common emulsion polymers) by the use of modifiers such as *t*-dodecyl mercaptan. Due to the branching that occurs during polymerisation the molecular distribution is fairly broad, the cold NBR, being less branched, having narrower distributions. Number average molecular weights are of the order of 10000. For technological purposes, the molecular weight is usually characterised by the Mooney viscosity[49] although this value will also be influenced by the molecular weight distribution and by branched structures.

In commercial processes the mercaptan modifiers are introduced gradually during conversion in order to give a more uniform chain length[50]. The increased tendency to branch and cross-link at high conversions must

increase both the average molecular weight and the breadth of the molecular weight distribution.

1.4.4 Vulcanisation of NBR

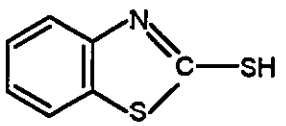
Vulcanisation is the process by which mainly plastic-rubber is converted into an elastic-rubber or a hard-rubber state. From a chemical perspective, vulcanisation is principally a process of cross-linking whereby the discreet rubber chains are converted into a three-dimensional network. In this way, the chains are prevented from slipping passed one another when the sample is stressed and can return to their original conformations when the stress is removed.

1.4.4.1 Accelerated sulphur vulcanisation

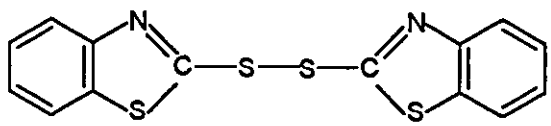
Technologically, the most important methods of vulcanising NBR are by the use of accelerated sulphur systems. The interaction between NBR and sulphur is highly complex and has been the subject of extensive investigations. In this thesis, it is only possible to give a brief account of the main conclusions of such work; more detailed reviews many be found elsewhere[51-54].

The reaction between NBR and elemental sulphur is relatively slow at the temperatures normally used for vulcanisation, i.e. about 150°C. The rate of reaction may be substantially increased by the addition of one or more organic compounds known as 'accelerators', the more important being the following:

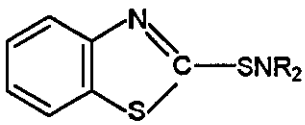
1. Thiazoles, e.g. mercaptobenzothiazole (MTB), benzothiazyl disulphide (mercaptobenzothiazole disulphide, MTBS) and sulphenamides
2. Thiurams, e.g. tetramethylthiuram disulphide (TMTD)
3. Dithiocarbamates, e.g. zinc dimethyldithiocarbamate (ZD_MC)



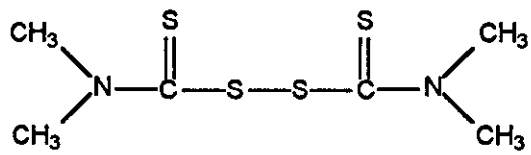
MTB



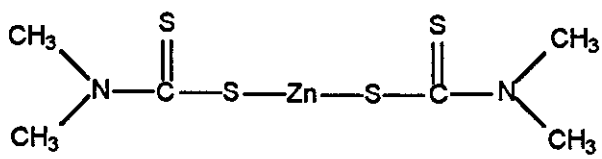
MTBS



Sulphenamide



TMTD



ZD_MC

The action of accelerators is enhanced by the presence of 'activators'; in general, a combination of zinc oxide and a fatty acid is nearly always used. The activator increases the efficiency of the vulcanisation system so that only about 5 sulphur atoms are combined for each cross-link formed. As a consequence, the vulcanisate shows improved physical properties, ageing characteristics and appearance (less sulphur bloom). The use of accelerator-activator systems is standard practice in rubber compounding and a typical formulation might be as follows:

Table 2. Typical NBR formulation with a 30 minute cure time at 140°C

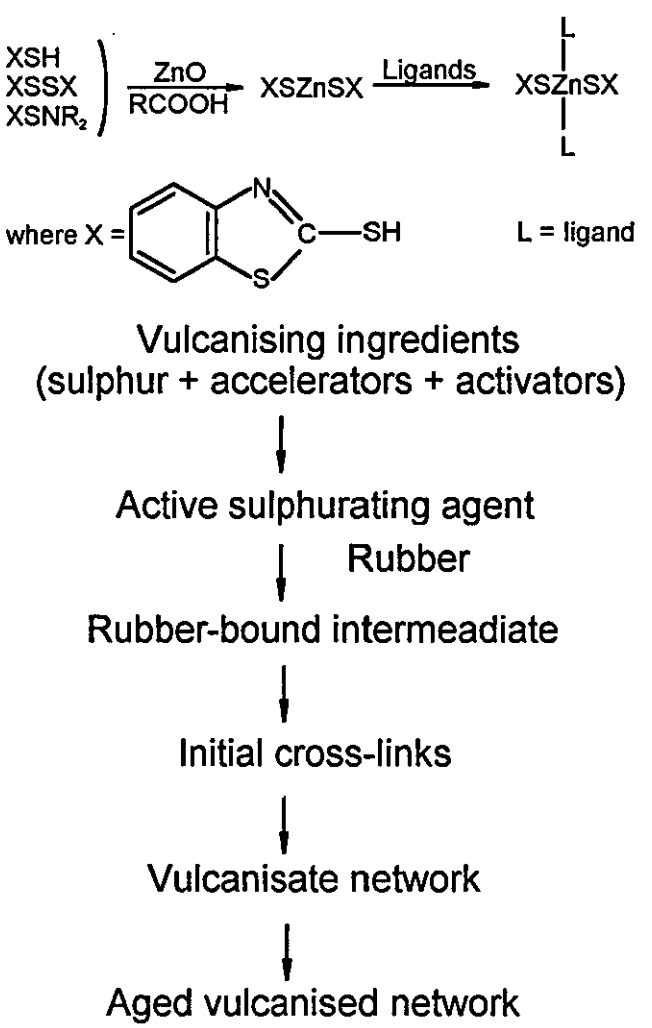
Compound	Parts By Weight
NBR	100
Carbon black	47.5
MTBS	0.85
Zinc oxide	5.0
Stearic acid	3.0
Sulphur	1.5

It is considered[52] that accelerated sulphur vulcanisation follows the general pathway shown in Figure 1. The various steps involved in this scheme are considered below.

1.4.4.2 Formation of the active sulphonating agent

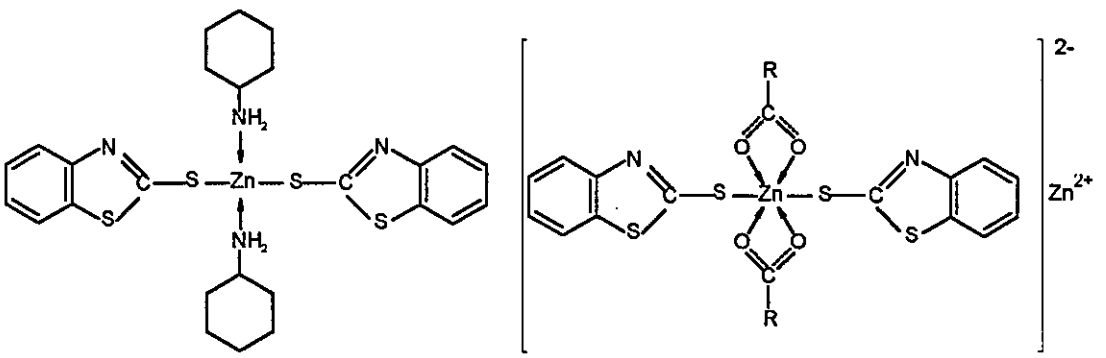
In this step, the accelerators and activators interact to give a species which then reacts with sulphur to form the sulphonating agent. In the case of the thiazole-zinc oxide-fatty acid system, the initial step may be represented as follows:

Figure 1. ***Pathway of accelerated sulphur vulcanisation of NBR***

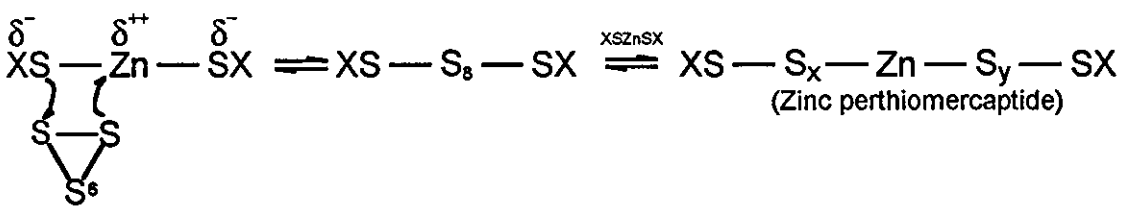


The initial zinc mercaptide (XSZnSX) is sparingly soluble in rubber but is rendered very soluble through co-ordination with nitrogen bases (either present in the polymer or added as accelerator) or zinc carboxylates; examples of complexes involving co-ordination of amine (a) and carboxylate ligands (b) are as follows:

(a) (b)



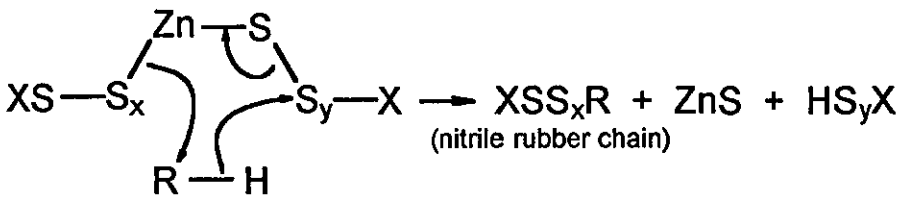
In the next stage, the zinc mercaptide complexes (represented below, for simplicity, as XSZnSX) are thought to react with sulphur to form zinc perthiomercaptides by means of a series of equilibria involving sulphur insertion and interchange:



The average values of x and y in the perthiomercaptides will be determined by the relative concentrations of sulphur and zinc mercaptide complexes. Zinc perthiomercaptide complexes are believed to be the actual sulphonating agents in the vulcanisation process.

1.4.4.3 Formation of the rubber-bound intermediate

The mechanism by which a zinc pertiomercaptide complex reacts with rubber is not known with certainty. It is possible that reaction involves nucleophilic attack of a terminal perthiomercaptide sulphur atom on an α-methylic carbon atom in the rubber hydrocarbon (R-H):



$$2HS_yX \xrightleftharpoons{ZnO} XS_yZnS_yX + H_2O$$

As a result of this reaction, pendant polysulphide groups terminated by accelerator moieties are attached to the NBR chain and zinc perthiomercaptide is regenerated and is available for further reaction.

1.4.4.4 Formation of initial cross-links

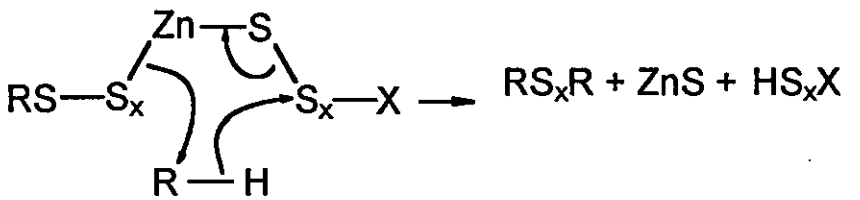
The third step in the vulcanisation sequence is considered to be the formation of polysulphide cross-links. The most probable route for the conversion of the rubber-bound intermediate into cross-linked polysulphides is by disproportionation reactions, involving cleavage of S-S bonds; these reactions may be initiated by mercaptide ions (XS^-) derived from zinc mercaptide:

$$RS_xSX + XS^- \rightleftharpoons RS^-_a + XS_bX$$

$$RS^-_a + RS_xSX \rightleftharpoons RS_zR + XS^-_c \quad \text{etc.}$$

A further possibility is interchange between the rubber-bound intermediate and zinc perthiomercaptide followed by sulphonation of another NBR chain:

$$RS_xSR + XSS_xZnS_ySX \rightleftharpoons XSS_ySX + RS_xZnS_xSX$$

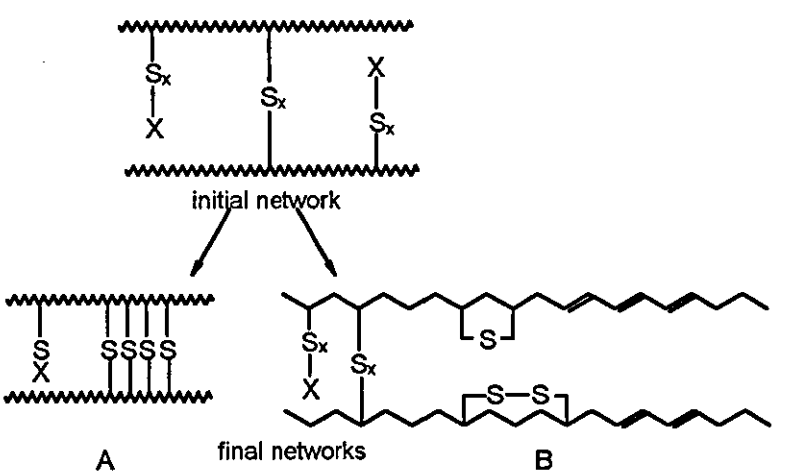


The structure of the initial network so obtained is illustrated in Figure 2.

1.4.4.5 Formation of vulcanisate network

In this step, initial polysulphide cross-links undergo further transformations (so called 'maturing process').

Figure 2. Structural features of networks formed in accelerated sulphur vulcanisation[55,56]



A. Network obtained with high accelerator to sulphur ratio

B. Network obtained with low accelerator to sulphur ratio

Two competing reactions are thought to be involved, namely desulphonation and decomposition. The desulphonation process results in progressive shortening of the cross-links, leading in the limit to

monosulphide cross-links. Desulphonation is effected by the zinc mercaptide complexes:

$$RS_xR + XSZnSX \longrightarrow RSR + XSS_mZnS_nSX$$

The zinc perthiomercaptide produced is able to form further cross-links. Decomposition of polysulphide cross-links appears to be an uncatalysed thermal process and leads to cyclic mono- and di-sulphides, conjugated dienes and trienes, and zinc sulphate. The mechanisms of these reactions are not known, but intramolecular hydrogen transfer may be involved.

1.4.4.6 Formation of aged vulcanisate network

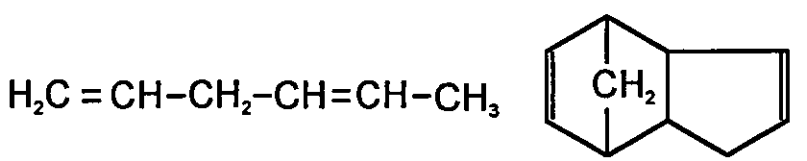
The changes depicted in Figure 2 may continue to occur after formal vulcanisation is complete. The reactions may continue whilst the vulcanisate is in service, particularly if elevated temperatures are encountered. Monosulphide cross-links are thermally stable and hence vulcanisated of type A (Figure 2) show relatively little change on ageing. Conversely, polysulphide cross-links are thermally unstable and vulcanisates of type B undergo reversion (loss of cross-links) and main chain modification with corresponding changes in physical properties.

1.5 Ethylene-propylene-diene monomer elastomer (EPDM)

1.5.1 Polymerisation of EPDM

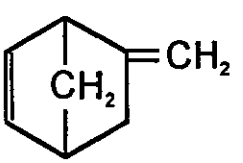
Copolymerisation of propylene with ethylene yields non-crystalline products that have rubbery behaviour and are chemically inert because of their saturation; consequently vulcanisation by conventional techniques is not possible. This limitation may be overcome by introducing unsaturation

into the polymer by the use of a third monomer in the copolymerisation process (Ziegler-type initiation). The third monomer is a non-conjugated diene; one of its double bonds enters into the polymerisation process becoming incorporated in the main polymer chain whilst the other double bond does not react and is left on a side chain and is available for subsequent vulcanisation; the resulting terpolymers are known as ethylene-propylene-diene monomer (EPDM) elastomers. The following are examples of commercial compounds used as the third monomer[53,54].



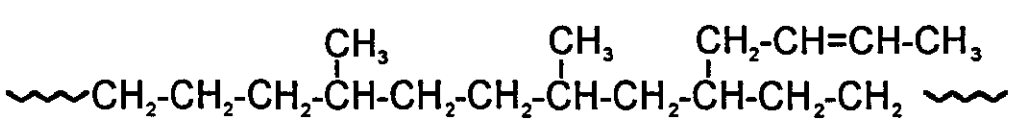
1,4-hexadiene

dicyclopentadiene



2-methyl-5-norbornene

(In the latter two, it is the double bond on the far left that is more favourable to polymerisation). The fraction of unsaturation introduced is generally within the range of 2-15 double bonds per 1000 carbon atoms, distributed randomly throughout the polymer. The structure of an ethylene-propylene-1,4-hexadiene terpolymer might therefore be represented as follows:



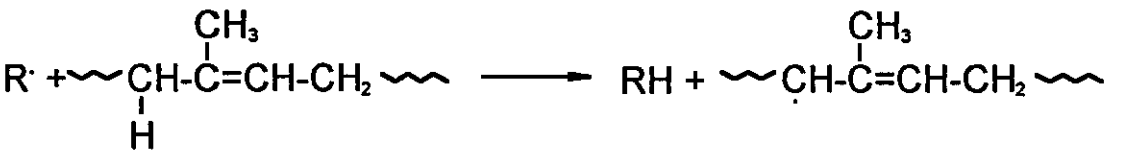
1.5.2 Vulcanisation of EPDM

Although it is common place for EPDM to be vulcanised using sulphur curatives, the EPDM samples used in this investigation have undergone peroxide curing (Section 2.3). The activation effect from the incorporated

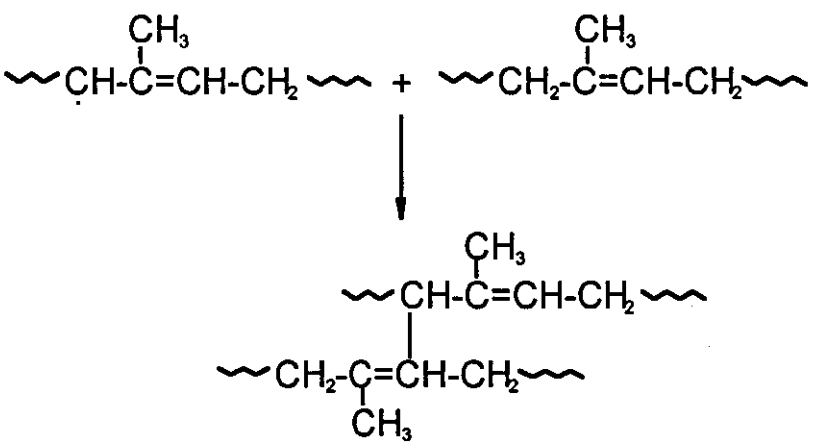
diene is postulated to play a role in the vulcanisation of EPDM according to the following scheme:

a. A free radical R· is formed by the decomposition of the curing agent, which is usually either di-*tert*-alkyl or di-*tert*-aryl peroxides (e.g. 1,3 bis-(*tert* butyl-peroxy-isopropyl) benzene).

b. This free radical initiates vulcanisation by abstracting a hydrogen atom from one of the α-methylene groups.



c. The rubber free radical then attacks a double bond in an adjacent polymer chain. This results in the formation of a cross-link and the regeneration of a free radical in a reaction analogous to propagation in an addition polymerisation (Section 1.3):



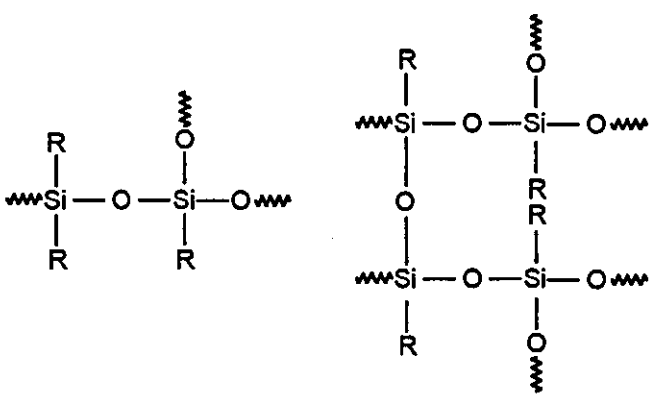
Vulcanisation may continue by several such propagation steps. Chain transfer may also occur. Termination probably occurs by reaction of the rubber free radical with a free radical fragment of the curing agent. In contrast to addition polymerisation in a fluid system, the termination reaction between two rubber free radicals is considered unlikely because

of the low probability of two such radicals coming into position to react, owing to the high viscosity of the medium.

1.6 Silicone rubber

1.6.1 Polymerisation techniques

Silicones can be defined as polymers comprising alternate silicon and oxygen atoms in which the silicon atoms are joined to organic groups [55,56]. The following types of structure come within this definition:



and both linear and network silicones find technological use. It is convenient to classify the silicones which are of commercial interest into three groups, namely fluids, elastomers and resins. Only elastomers will be examined in this section.

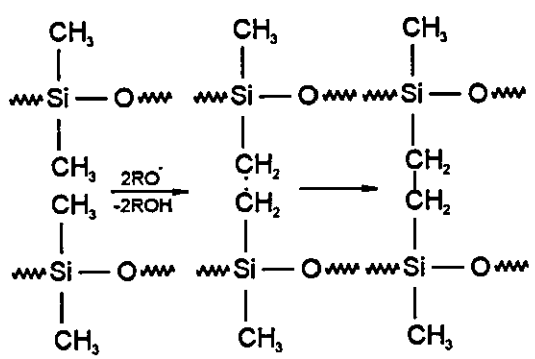
1.6.2 Commercial production of silicones

The basis of commercial production of silicones is that chlorosilanes readily react with water to give silanols which are unstable and condense to form siloxanes. Both the functionality of the chlorosilane and the conditions used for hydrolysis have a decisive influence on the structure of the siloxane which is obtained[57-59]. Dichlorosilanes tend to form the basis of most silicone elastomers. Normally, hydrolysis of dimethyldichloro-

silane leads to a mixture of linear and cyclic polymers. The ratios of cyclic and linear polymers are determined by the reaction conditions. Silicone elastomers are based on linear polymers. As with other elastomeric materials, it is necessary to cross-link linear polymers in order to obtain characteristic elastic properties. General purpose elastomers are based on polydimethylsiloxanes.

1.6.3 Vulcanisation of dimethyl silicone

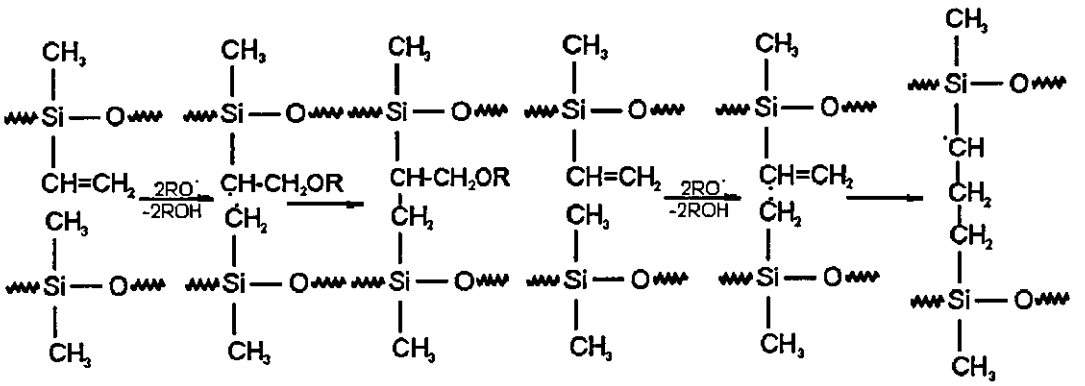
Dimethyl silicones are normally vulcanised by heating with organic peroxides such as bis(2,4-dichlorobenzoyl)peroxide at temperatures in the range 110-175°C. Thermal decomposition of the peroxides gives rise to a free radical (Section 1.3) which abstracts hydrogen from a methyl group; combination then results in ethylene cross-links.



Support for this mechanism comes from the finding that treatment of octamethylcyclotetrasiloxane with benzoyl peroxide gives 1,2-bis(heptamethylcyclotetrasiloxanyl)ethane[60].

Vinyl silicones which have been studied during this investigation are very similar to dimethyl silicones except for the incorporation of a small number of methylvinylsiloxane groups (about 0.1-0.5% w/w). The vinyl groups are particularly reactive toward peroxides and the polymers are readily vulcanised. Since the presence of so few vinyl groups is sufficient to give

an adequate level of cross-linking, it is unlikely that vinyl-to-vinyl linking occurs. It has been suggested that (a) 1,2-propylene and (b) trimethylene links are formed [61].



(a) (b)

1.7 Fractionation of polymers by solubility

Solubility relations in polymer systems are more complex than those among low-molecular weight compounds, because of the size differences between polymer and solvent molecules, the viscosity of the system and the effects of molecular weight of the polymer. In turn, the level of solubility as conditions (such as the nature of the solvent, or the temperature) are varied can give much more information about the polymer. From what has already been said, it is clear that the structure of the polymer is highly important in determining its solubility.

1.7.1 The solution process

Dissolving a polymer is a slow process that occurs in two stages. Firstly, solvent molecules slowly diffuse into the polymer to produce a swollen gel. This may be all that happens if, for example, the polymer-polymer intermolecular forces are high because of cross-linking, crystallinity, or strong hydrogen bonding. But if these forces can be overcome by the

introduction of strong polymer-solvent interactions, the second stage of solution can take place. Here the swollen gel gradually disintegrates into a true solution. Only this stage can be materially speeded by agitation. Even so, the solution process can be quite slow (days or weeks) for materials of very high molecular weight.

1.7.2 Solubility parameters

Solubility occurs when the free energy of mixing

$$\Delta G = \Delta H - T\Delta S \qquad (1.24)$$

is negative. It is generally presumed that the entropy of mixing ΔS is always positive, and therefore the sign of ΔG is determined by the sign and magnitude of the heat of mixing ΔH. For reasonably non-polar molecules and in the absence of hydrogen bonding, ΔH is positive and was assumed to be similar to that derived for the mixing of small molecules. For this case, the heat of mixing per unit volume can be approximated [62] as:

$$\Delta H = v_1 v_2 (\delta_1 - \delta_2)^2 \qquad (1.25)$$

where v is volume fraction and subscripts 1 and 2 refer to solvent and polymer respectively. The quantity δ^2 is the cohesive energy density or, for small molecules, the energy of vaporisation per unit volume. The quantity δ is known as the solubility parameter.

It can be seen from equation 1.25 that when δ_1 is equal or very similar to δ_2, ΔH will be zero or almost zero and it follows from equation 1.24 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[63]. The solubility parameter defines only the heat of mixing of liquids or amorphous polymers. A non-crystalline polymer will therefore dissolve in a solvent of similar δ without the need of solvation, chemical similarity, association or any specific interaction. The high entropy change that results from the dissolution of polymers is a sufficient reason for it to occur.

1.7.3 Methods of fractionating polymers

1.7.3.1 Poly(vinyl chloride)

There are a number of ways in which PVC can be fractionated[64,65] by solubility. However, in this work, fractional precipitation was chosen since it was considered the most practical method. There are three methods by which this technique can be carried out:

1. Addition of non-solvent

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

2. Lowering the temperature

The successive precipitation of polymer species from a solution by controlled cooling.

3. Solvent volatilisation.

The successive precipitation of polymeric species from a solution of the polymer in a solvent/non-solvent mixture by controlled evaporation of the more volatile solvent.

Commercial PVC is about 55% syndiotactic and as a consequence has been shown by X-ray diffraction methods to be about 5% crystalline[66]. PVC has very limited solubility with a solubility parameter for PVC of $9.5(cal/cm^3)^{0.5}$. 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 tetrahydrofuran (THF) and methyl ethyl ketone (MEK). A comprehensive list of solvents and non-solvents for PVC at ambient temperatures is available[63].

1.7.3.2 NBR, EPDM and silicone rubber

Cross-linked polymers do not dissolve, but only swell if indeed they interact with the solvent at all. In part, at least, the degree of this interaction is determined by the extent of cross-linking. Lightly cross-linked rubbers swell extensively in solvents in which the unvulcanised material would dissolve, but hard rubbers may not swell appreciably in contact with any solvent.

The absence of solubility does not imply cross-linking however. Other features such as sufficiently high intermolecular forces may prevent solubility. The presence of crystallinity is a common example. Many crystalline polymers do not dissolve except at temperatures near their melting points. Because crystallinity decreases as the melting point is approached, and the melting point is itself depressed by the presence of the solvent, solubility can often be achieved at temperatures significantly below the melting point.

1.8 The separation of additives and oligomers

Oligomers are loosely defined in polymer chemistry as compounds consisting of a series of repeat units whose molecular weights total less than 10000 g/mol. This definition is broad enough to describe the molecular weight region in which small-organic-molecule character disappears and measurable polymer physical properties become evident. Additives on the other hand should be treated as low molecular weight organic molecules. The majority of this section will concentrate on the isolation, separation and characterisation of oligomers and additives utilising various chromatographic techniques.

A widely used technique has been SEC for the separation of oligomer species in low molecular weight polymer fractions. Techniques such as 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 GC can be used. Although not extensively used for oligomer analysis, TLC has been evaluated for the separation of oligomer standards.

One technique that is increasingly used to separate oligomers is SFC since it is a powerful separating method for analysing substances that are not amenable to GC analysis. CCC is now being considered as a technique in its own right rather than a hybridisation of two or more other techniques. It is ideally used for the separation of complex mixtures and analysis of copolymers according to molecular weight distribution and chemical composition distribution.

Although most of the published work has been concerned with the separation of oligostyrenes, a variety of other oligomer species have also received attention. The following sections will briefly outline the major techniques utilised for the chromatographic fractionation of polymers emphasising the separation of oligomers and additives.

1.9 Chromatographic fractionation of polymeric materials

1.9.1 Size exclusion chromatography (SEC)

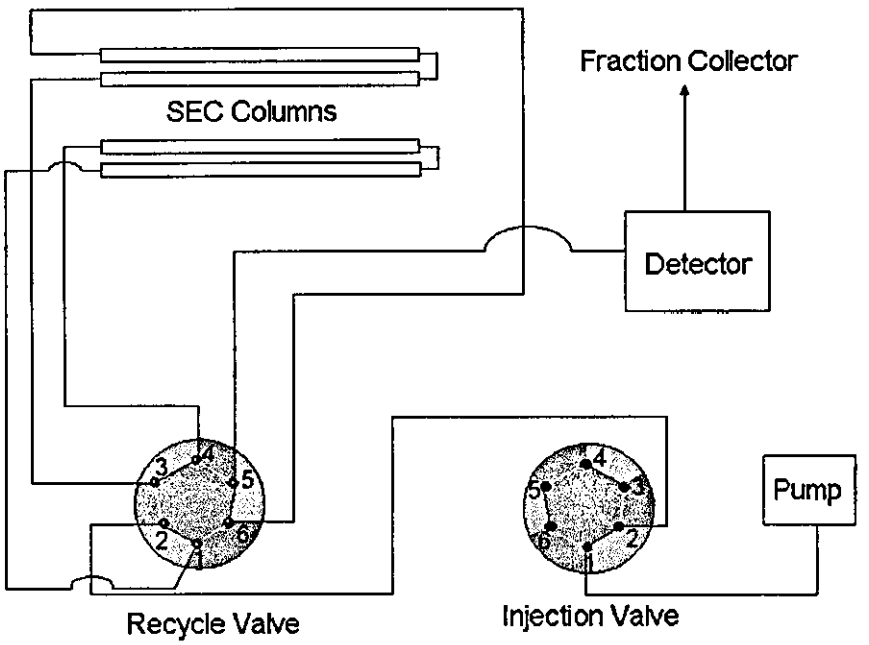
In 1959, Porath and Flodin[67] were the first to effectively demonstrate that macromolecules could be separated according to their molecular size by their degree of penetration into a porous packing. This technique was known as gel filtration chromatography (GFC) and utilised dextran gels. Dextran gels tend to be very soft and consist of lightly cross-linked polymer networks. They are highly swollen by water and have low mechanical stability, which deteriorates as pore size increases. These disadvantages were overcome by Moore[68], who introduced rigid porous cross-linked polystyrene gels, covering a wide range of pore sizes, which were suitable for separations of synthetic polymers in organic media. These gels undergo limited or no swelling with the solvent and have good mechanical stability for separations 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.

Recently, the term size exclusion chromatography (SEC) has been adopted at the expense of GPC, due to its more accurate description of the separation mechanism. In high performance SEC (HPSEC) columns

containing porous particles with diameters of 5 or 10 μm are used in conjunction with high performance solvent delivery pumps. This results in high separation efficiencies and relatively short run times (<30 minutes). Due to the nature of these porous cross-linked gels, there is a limit to the amount of back pressure that they can withstand. This imposes a finite limit to the length of the gel bed that can be utilised for a separation carried out on a standard system. If the sample contains a large number of components, the limited peak capacity of SEC can be overcome by using a recycle technique. This modification to the standard HPSEC system uses a switching valve that diverts the analyte away from the outlet and recycles it through the column(s). The two main techniques employed are the alternate pumping recycle technique[69] and the closed loop technique[70]. The simplest recycle concept places the sample, pump, column and detector in a closed loop[71]. However, due to peak dispersion and skewing which occurs in the pump chamber and associated hydraulic damping circuits, this approach is not completely satisfactory. A better approach to recycling a sample in SEC uses an alternate pumping principle to eliminate problems associated with the closed loop approach[72].

Alternate pumping (Figure 3) has two major advantages over closed-loop pumping. Most importantly the sample does not have to pass through the pump chamber, therefore keeping dead volume to a minimum; and also, a flowing reference cell can be maintained while recycling the sample through the column system. It is this technique that has been used in this work.

Figure 3. Alternate pumping recycle technique



1.9.1.1 Separation mechanism

The separation of a solute of a given size in solution is determined by a distribution coefficient K_{SEC} 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:

$$V_R = V_0 + K_{SEC}V_i \qquad (1.26)$$

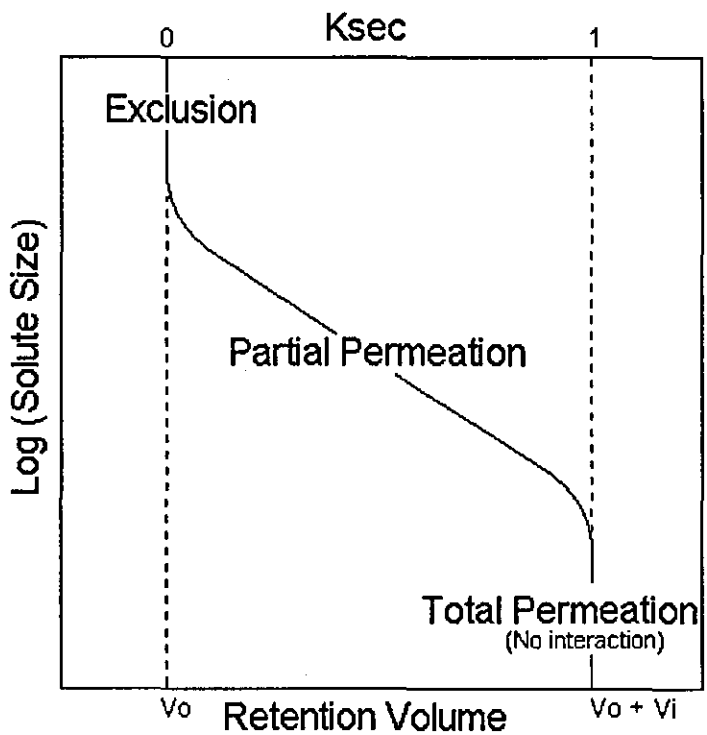
where V_0 is the volume of the mobile phase which is accessible to all molecules (the void volume), and V_i is the volume of the solvent in the porous gel particles. At slow flow rates, an equilibrium distribution of solute between the two phases takes place enabling the dependence of K_{SEC} on V_R 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:

$$K_{SEC} \propto \exp(-\ell/2) \qquad (1.27)$$

where 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, i.e. $K_{SEC} = 0$. Very small molecules have free access to both the stationary phase solvent in the pores and the mobile phase, i.e. $K_{SEC} = 1$. When solvent is pumped down the column the large molecules are eluted first followed by molecules of decreasing size that 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 4 which shows an example of a size exclusion calibration curve.

Figure 4. Size exclusion calibration curve



1.9.1.2 Plate height and plate number

A measure of the efficiency of a chromatography column is the height equivalent to a theoretical plate or plate height H[73]. The plate height for an experimental chromatogram is calculated from the expression:

$$H = L/N \tag{1.28}$$

where L is the column length and N is the plate number. If the chromatograms are symmetrical, corresponding to a normal error function, then N may be determined from:

$$N = 5.54(V_R/w_{0.5})^2 \tag{1.29}$$

where $w_{0.5}$ is the width of the peak at half its height.

1.9.1.3 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, u, has been investigated and the following relationship proposed for monodisperse polymers.

$$H = 2\lambda dp + [R(1-R)udp^2/30\ D_s] \tag{1.30}$$

in which λ is a constant close to unity that depends upon the column packing and is numerically close to unity; dp is the particle diameter; R is the ratio of solute zone velocity to mobile phase velocity; 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.

1.9.1.4 Resolution

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

$$R= (V_2 - V_1)/(W_1 + W_2) \quad (1.31)$$

here V_1 and V_2 are the peak elution volumes of compound 1 and 2 respectively; and W_1 and W_2 are the baselines 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_i/V_0), and on the column length. In SEC, resolution is restricted by limited peak capacity due to the fact that the analyte must elute between the total exclusion and total permeation volumes, i.e. K_{SEC} is always between 0 and 1. The number of components, n, that can be resolved in one separation is given by:

$$n \cong (1 + 0.2N^{0.5}) \quad (1.32)$$

1.9.1.5 Separations involving SEC

Gilbert *et al.*[36], obtained low molecular weight fractions of PVC by Soxhlet extraction followed by fractionation by gel filtration. The size distribution of components in these fractions was assessed by high-performance size exclusion chromatography (HPSEC) using cross-linked

polystyrene gels (particle size 10 μm) having exclusion limits below 500 Å. Analysis of these low molecular weight fractions by gas chromatography-mass spectroscopy (GC-MS)[74] enabled the oligomer species from trimer to hexamer to be separated, with some evidence of the heptamer and octamer. A separation scheme was devised[37] in which an alternate pumping recycle HPSEC technique[39], followed by routine high-performance liquid chromatographic (HPLC) fractionation was capable of resolving the VC pentamer fraction present in a low molecular weight fraction into its constituent isomers. With this method, it was possible to isolate 0.5 mg of VC pentamer from a PVC polymer for proton NMR analysis. In another paper, a VC tetramer fraction was isolated into its constituent isomers[41]. A technique for the simultaneous determination of the molecular weight distribution of PVC and polystyrene and the measurement of additives has also been reported[75].

Polystyrene standards have been used extensively in oligomer work mainly due to their availability, stability and their strong chromophore making UV detection easy. If the correct system is chosen, it is possible to separate the lower molecular weight standards into their constituent oligomers. A recycle technique based on SEC has been employed to separate a polystyrene (PS) PS600 standard into 13 peaks, corresponding to the oligomer species dimer to tetradecamer[76] and dimer to pentamer[77]. The purity of each fraction collected was assessed by re-injecting it into the same system. The oligomers were characterised using 60 MHz ^{1}H NMR[77].

Kuo *et al.*[78], used SEC for the characterisation of oligomers used in the coatings systems based on epoxy-ester, acrylic resins, melamine resins and polyester urethanes.

Methanol extracts obtained from a series of poly(etherurethane urea) (PEUU) materials were analysed quantitatively by SEC. The extractables were found to consist of low molecular weight PEUU polymer, 4,4'-methylenebis(phenyl isocyanate) (MDI) rich oligomer, the additives Santowhite and Methacrol, and aniline[79].

An industrial polyether-polyol mixture used for the manufacture of polyurethane foams was fractionated by SEC and it was possible to quantitatively analyse the oligomers present[80].

The identification of oligomers in the reaction of polyols with isocyanates has been carried out using SEC in conjunction with ^{13}C NMR. The results enabled kinetic and mechanistic schemes to be derived for the reaction[81].

Shodex KF800 series columns have been used to separate the oligomers present in a PS474 standard and Epikote 1001, an epoxy resin. Good resolution of 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 columns connected in series having exclusion limits of $5x10^3$ and $2x10^4$ g/mol 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 increased[82]. A micro-SEC technique has also been used to study the oligomers of polystyrenes as well as epoxy resins, phenol-formaldehyde resins and methylated melamine-formaldehyde resins[83-85].

In a paper by Quinn[86], SEC and reversed phase HPLC methods were used to measure the level of elemental sulphur in an uncured, compounded NBR formulation. It was found that both chromatographic techniques yielded results that were comparable in precision and level of sulphur recovered. Cheng *et al.*[87], also reported the use of SEC and HPLC for the analysis of residual homopolymer and unreacted monomers from the grafting of dimethylsiloxane and styrene. Following on from this work, SEC and HPLC were used to analyse oligomeric dimethylsiloxanephenyl-silesquioxanes[88] and trifunctional methylphenylsiloxane oligomers[89]. SEC, with a refractive index (RI) and ultra-violet (UV) and IR detectors, was applied to the analysis of oligomeric carbonate group containing methylphenyl-siloxanes[90]. Reyx *et al.*[91], used SEC to characterise heptamethyl-2-phenyltrisilane and octamethyl-2,3-diphenyltetrasilane.

Anderson *et al.*[92], quantified polydimethylsiloxane present in pharmaceutical formulations utilising SEC with RI detection. Holohan *et al.*[93], characterised monofunctional polydimethylsiloxane oligomers used in graft polymerisation by SEC, NMR, thermogravimetric analysis, differential scanning calorimetry and IR spectroscopy.

In a paper by Shunk *et al.*[94], SEC was used with HPLC to enable a compositional distribution characterisation of poly(methylmethacrylate)-*graft*-polydimethylsiloxane copolymers utilising Fourier-transform infra red (FT-IR) spectroscopy and evaporative light-scattering detection. Cazaux *et al.*[95] used SEC to characterise polydimethylsiloxanes with vinyl ether end-groups in order to ascertain the effect of excess divinyl ether addition on end properties of the polymer. SEC has also been applied to hydroxyl-terminated polybutadieines, phenolic-uncapped end groups in

Bisphenol A polycarbonate[96], poly(ethylene oxide) surfactants[97] and for separations of star-branched styrene-butadiene diblock elastomers[98].

In a paper by Martin and Balke[99] room temperature SEC for poly(ethylene terephthalate) (PET) was developed using a mobile phase mixture of 5% hexafluoroisopropanol in methylene chloride. Calibration was carried out with three different approaches, each time with and without considering the presence of cyclic oligomer in PET samples and standards. At typical concentrations of cyclic oligomer a calibration curve generated from a chromatogram truncated to eliminate the oligomer peak had its slope distorted such that it gave molecular weight average values inaccurate by up to 8%, whereas correcting for the oligomer explicitly resulted in average errors of about 1%.

Analytical characterisation, utilising SEC and HPLC, of road bitumins was reviewed by Joly *et al.*[100]. A method for obtaining molecular size distribution of asphalts was presented by Bishara and McReynolds[101]. A TLC-SEC method was developed for the analysis of bitumens of different grades from different refineries[102]. SEC has also been used for the characterisation of asphaltenes[103,104], coal hydrogenation[105] and pyrolysis products[106], coal-tar pitch fractions[107], natural gas condensates[108], shale oil residues[109], and heavy and extra heavy crude oils[110].

SEC is a useful technique for separating low molecular weight compounds from interfering oligomeric or polymeric matrices. Automated robotic workstations were described for SEC cleanup[111,112]. A technique for on-line extraction of pollutants from environmental and biogenic matrices by supercritical fluid extraction and cleanup by SEC was presented by

Stalling *et al*[113].Tangential ultrafiltration coupled with SEC was described to fractionate dissolved organic matter from water[114].

Applications using SEC include removal-cleanup of pesticides from fruits[115,116], foods[117-119], hops[120], oils and fats[121-123], soil[124-126], lanolin waxes[127], and animal tissues[128]; polycyclic aromatic compounds from environmental samples[129,130]; polychlorinated napthalenes from polychlorinated biphenyl products[131]; and polychlorinated biphenyls from environmental samples[132].

1.9.2 High performance liquid chromatography (HPLC)

HPLC has undergone considerable development over the past 25 years, so that today rapid and efficient separations can be achieved. Such improvements have been brought about by reducing the packing particle size (3-5 μm particles are most commonly used) 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 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: a hydrocarbon bonded phase (reversed-phase), an ion exchange material, a polar bonded phase or silica. Other bonded phases that encourage specific interactions have been developed for specialised areas, such as the resolution of optical enantiomers (chiral bonded phase).

The term normal-phase chromatography was coined by Howard and Martin in 1950 when liquid chromatography was usually performed on a polar stationary phase with a less polar eluent. If a gradient was used, it would have been one of increasing polarity. This procedure was normal at that time. The term reversed-phase chromatography should indicate separations using a stationary phase of moderate polarity and a more polar eluent, and in the case of gradient elution, the decreasing polarity of the mobile phase. Currently, about 80% of all HPLC separations are conducted in reversed-phase mode but, nevertheless, the chromatography on polar stationary phases is referred to as normal.

1.9.2.1 Particle size to pore diameter

Most of the common packing materials for liquid chromatography are porous, usually about 10 nm in diameter. The molecular size of substances of low molecular weight is of the order of 1 nm, i.e. a high ratio of pore diameter to solute dimensions is characteristic of small-molecule chromatography. Polymer size can be characterised by coil dimensions, e.g. by the radius of gyration, or in the case of polymers with a tertiary structure, by the length of the three characteristic axes. Above 10000 g/mol, the threshold of polymer behaviour, the dimensions of molecules are equal to or larger than the pores of common liquid chromatography (LC) packings. Polymer chromatography can be subdivided into size exclusion chromatography and separation by non-exclusion mechanisms. The ratio of solute to pore size and the energy of interaction between the solute and the surface of the column packing decide whether exclusion or the non-exclusion phenomena would predominate. For non-exclusion chromatography, wide-pore packings are recommended. The pores should

be spacious enough to give even the largest solute molecules access to the active inner surface. Interference of non-exclusion with exclusion mechanisms is in the most cases detrimental to straightforward separation strategies. On the other hand, the pore diameter should not be too large because this would reduce the surface area and thus the chromatographic activity of the packing.

1.9.2.2 Inter-linked groups

A characteristic of small-molecule liquid chromatography is the reversibility of molecular contacts with the stationary phase. The distribution constant determines the duration of molecular residence in the stationary phase and, thus, the retention of the solute. The principles of chromatographic retention are identical for polymers and low-molecular solutes. Every adsorbed repeat unit of a polymer is reversibly attached to the stationary phase- but adjacent units are linked to each other through covalent bonding. The probability is small that all units of an adsorbed chain can desorb simultaneously. The retention factor or its mass distribution constant K', of the solute allows the straightforward comparison of results obtained with different apparatus. A molecule with several independently adsorbed units in a chain can migrate only if all of them are free. For the adsorption of n units with a constant K'_u for each unit the retention factor for the whole chain becomes:

$$K'_{TOTAL} = (K'_u + 1)^n - 1 \qquad (1.33)$$

The logarithmic form of equation 1.33 gives a relation similar to the Martin rule for members of a homologous series with carbon number n and a group-specific contribution:

$$\log K'_{MARTIN} = A + Bn \qquad (1.34)$$

The linearity proposed by equation 1.34 has been proven for a great many homologues. Recent work with polystyrene oligomers showed adherence to the Martin equation for solute with no more than 19 repeat units.

1.9.2.3 Gradient requirements

Strongly adsorbed and flexible macromolecules will be generally not desorbed on lowering the concentration of the solute. This apparent irreversibility is the consequence of the inter linkage of the segments which in themselves are reversibly adsorbed. The removal of adsorbed macromolecules requires displacement by a stronger component; thus gradient elution is typical of polymer liquid chromatography.

1.9.2.4 Column packings

Gradient elution requires packing materials that can withstand the accompanied changes in solvent composition. Another requirement is the accessibility of the active surface. A pore size of 30-50 nm is adequate in most cases of interactive polymer chromatography. As previously mentioned, uncontrolled superposition of size exclusion and interactive retention must be avoided since the order of separation in both types of chromatography is different. Large-pore packings provide a chance to avoid interference as all the molecules of the solute can penetrate. Another

possibility is given through the use of packings with small pores inaccessible to all the large solute molecules.

1.9.2.5 Separations involving HPLC

Lai *et al.*[133], have used normal nitrile-bonded phase liquid chromatography with UV and fluorescence detection to separate styrene oligomers in PS600 and PS730 standards. In addition, it was shown that the nitrile phase, in polar solvents such as dichloromethane, performed size exclusion. In another paper by Lai *et al.*[134], it was demonstrated how phenyl-containing room temperature vulcanisable (RTV) silicone raw material and polystyrene polymers can be separated on a phenyl-bonded phase HPLC column using both UV and fluorescence detection. In pure THF eluent, size exclusion behaviour is observed for both samples. In THF : H_20 gradient elution, polymers are retained and elute according to their solubility in the mobile phase.

Schou *et al.*[135], 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. In this investigation, styrene oligomers from n=1 to 18 were isolated with a purity from 95 to 99.5% using analytical columns containing the same packing (ODS (Me_2)-silica).

The adsorption chromatography of anionically and cationically prepared polystyrene oligomers using 5 μm silica with *n*-hexane : dichloromethane mobile phases was investigated by Mourey[136]. It was found that the end-group differences between the two samples produced significant differences in the retention of oligomers of equivalent size. He also

analysed narrow molecular weight polystyrene standards on 6 and 50 nm pore diameter silica with *n*-hexane : tetrahydrofuran (THF), *n*-hexane : ethyl acetate and *n*-hexane : dichloromethane gradients. Eluents containing tetrahydrofuran and ethyl acetate gave separations according to the number of oligomer units and eluents containing dichloromethane further separated the stereoisomers of individual oligomers[137].

The effects of various allyl, phenyl and fluorinated stationary phases on the selectivity towards stereoisomers of polystyrene oligomers using acetonitrile : water gradients in reversed-phase HPLC have been investigated[138]. All allyl phases tested from trimethylsilyl (C_1) to an octadecylsilyl (C_{18}) stationary phase separated stereoisomers. An increased chain length of the allyl ligand made only a minor contribution to the resolution. Stationary phases containing phenyl and fluorinated, however, gave little or no isomer selectivity.

The separation of styrene oligomers on silica gel using 1,4 dioxane : *n*-heptane and tetrahydrofuran : *n*-heptane mobile phases were compared[139]. Both isocratic and gradient elution liquid chromatography was performed. 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. It can also be used as the basis of calculations of retention volumes under isocratic and gradient elution conditions. The application of a convex gradient of dioxane in *n*-heptane enables at least partial separation of individual oligostyrenes having up to 25-30 oligomer units and the concentration ratios of the individual oligomers in the polystyrene samples can be estimated.

Lai *et al.*[140], showed that styrene oligomers present in a PS600 sample can be separated isocratically on phenyl-bonded phases using THF : water, THF : *n*-hexane and acetonitrile : water eluents. With pure *n*-hexane as eluent, partial resolution of the stereoisomers of the individual oligomers was achieved, corresponding to their syndiotactic, isotactic and atactic microstructures. Addition of THF to the *n*-hexane mobile phase diminishes the resolution of the stereoisomers, and only the separation of oligomers can be observed.

In a theoretical paper, Jandera[141] described the retention behaviour of an oligomer series in reversed phase systems with respect to the number of repeated structural units and the mobile phase compositions. He showed that they can be described by the same set of equations as for a homologous series, but the constants of these equations were strongly dependent on the structure of both the repeat structural unit and the structural residue in the molecule.

Kawai *et al.*[142] reported the compositional fractionation of poly (methyl methacrylate)-*graft*-polydimethylsiloxane (PMMA-*graft*-PDMS) by reversed phase HPLC. Samples of PMMA-*graft*-PDMS were eluted from the components of higher PDMS contents to those of lower PMMA contents, according to reversed phase adsorption. These graft copolymers were separated according to their chemical compositions.

In a paper by Sugita[143], a method was developed for the determination of residual monomers, bisphenol A and diphenylcarbonate, and polymerization regulators, phenol, 4-tert-butylphenol and 4-(1,1,3,3-

tetramethylbutyl) phenol in polycarbonate by HPLC using a reversed-phase column with UV detection. PC resin was dissolved in dichloromethane and polymers were precipitated with acetone. The clear upper layer was taken and evaporated. The concentrate was dissolved in acetonitrile and water was added to precipitate oligomers. Monomers and polymerization regulators were separated by a linear gradient method using an acetonitrile : water mixture as a mobile phase. The monomers and polymerization regulators were detected by absorbance measurement at 217 nm.

HPLC has been used for the separation of hydrogen-capped polymethylmethacrylate oligomers into their constituent stereoisomers on a silica gel column using gradient elution of 1% acetonitrile : butyl chloride to 20% acetonitrile in 20 minutes[144]. Alexander *et al.*[145], demonstrated that underivatised silica and partially derivatised silica with octadecyl groups produced improved separations of oligomers of nonylphenol-oligo(ethylene glycol) than a more extensively derivatised silica packing.

In a paper by Dulio *et al.*[146], low-molecular-weight compounds were extracted from recycled PET from post-consumer soft-drink bottles, and characterised by HPLC, SEC and desorption chemical ionization/mass spectrometry (DCI/MS). Among these products, cyclic and linear oligomers were identified, and their distribution was determined.

Guryanova and Pavlov[147] investigated the concept of polymer chromatography under 'critical conditions' that allows the separation of oligomers by virtue of their functionality. Several types polycondensation

oligomers were studied and their molecular weight distribution and functional type distribution determined.

Van der Maeden *et al.*[148], gave examples of oligomer separations with epoxy resins, novolak resins, poly(2,6-diphenyl-*p*-phenylene oxide), PET and poly(ethylene oxide) derivatives. Gradient elution with various mobile phases was used in all cases in conjunction with columns containing octadecyl and amine stationary phases. However, the resolution obtained with gradient elution HPLC was found to be adversely affected by size exclusion effects and sample solubilities.

Bodmeier *et al.*[149], developed a single reversed phase HPLC method to identify plasticisers commonly used with polymers present in pharmaceutical applications. These included the quantification of plastisicers in polymer-coated sugar beads and in leaching studies of water soluble plastics from polymeric films into simulated intestinal fluids.

Mengerink *et al.*[150], used an evaporative light-scattering detector in reversed-phase HPLC of oligomeric surfactants. The sensitivity of the evaporative light scattering detector was found to be dependent on the analyte concentration and the organic modifier concentration. Lee *et al.*[151], used a systematic experimental design to optimise the separation conditions in HPLC of selected plasticisers, namely phthalates, using an overlapping resolution mapping technique.

In a paper by Barkby and Lawson[152], UV spectrophotometery, HPLC and liquid chromatography coupled to mass spectroscopy (LC-MS) were used to identify and quantify oligomers extracted with boiling water from two

different nylon 6 films used in boil-in-bag food packaging. The results indicated the loss of up to 1.5% of the original nylon film weight, into the boiling water, as caprolactam and cyclic oligomers up to the nonamer. Extraction time, thickness and type of film used, were found to be parameters which affected the levels of these migrants.

In a theoretical paper, Boehm and Martire[153] investigated the application of homopolymer and oligomer separations to gradient elution liquid chromatography. They suggested improved treatments for the determination of the solvent-stationary phase adsorption isotherm and the solvent-entrained solute expansion factors. An investigation of the effects that sample concentration has on the retention behaviour of oligomers and homopolymers was also performed.

Marquez *et al.*[154], attempted optimisation of HPLC conditions to analyse widely distributed ethoxylated alkylphenol surfactants. These surfactants are composed of a mixture of oligomers with different ethylene oxide numbers (EON). The different oligomers were separated by various HPLC techniques. It was shown that isocratic elution on a silica column allowed the separation of oligomers up to EON = 10; gradient programming extended the limit to EON = 15. For higher EON values (up to 25) a NH_2 stationary phase column was used. Extreme separations of oligomers with widely distributed ethylene oxide numbers was possible when the silica and NH_2 columns were placed in series.

Bledzki *et al.*[155], used normal phase HPLC as the main chromatographic technique in order to separate methyl methacrylate oligomers and used ^1H NMR for the analysis of their diastereoisomers. It was observed that the

separation did not only proceed in accordance with the molecular weight of the oligomers, but also with their tacticity as well. The results demonstrated that free radical oligomerisation is a process in which syndiotactic structures are favoured above isotactic ones.

Begley *et al.*[156], used C_8 reversed phase HPLC with gradient elution for the determination of migrating PET oligomers in corn oil. The oligomers were extracted with *n*-hexane : acetonitrile, the extract was evaporated almost to dryness, and the concentrate was diluted with dimethylacetamide for separation and quantitation of the oligomers by HPLC.

In a paper by Dorn *et al.*[157], a system was developed which combined HPLC with the detective capabilities of inductively coupled plasma atomic emission spectroscopy (ICP-AES) for the determination of a wide range of organosilicon compounds. Samples analysed included water and extracts of sludge and soils. It was found that the detection limit for PDMS was approximately 4-5 ng of Si.

Staal *et al.*[158] developed an on-line extraction method for polymers, oligomers, additives and monomers involving multiple solvents on HPLC columns containing octadecyl derivatised silica for reversed phase separations. The principle of this method was to dissolve the sample in a good solvent and precipitate or suspend the polymer sample on the column packing with a non-solvent. The precipitate or suspension would adsorb onto a column guard made of the same material as the main column. By adding a solvent to the adsorbed suspension with the aid of a gradient system, the monomers, oligomers, polymers and additives would re-dissolve and elute from the column.

1.9.3 Supercritical fluid chromatography (SFC)

SFC was first reported in 1962 by Klesper *et al.*[159], 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:

1). Extraction and solvation effects allow the migration of materials of high molecular weight.

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

3). The low viscosity means that the pressure drop across the column is greatly reduced for a given flow rate.

4). 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 gas chromatography in that it can be used to analyse compounds that are thermally labile. The main limitation of SFC is the limited solubility of

analytes containing polar groups with mobile phases such as carbon dioxide.

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. 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 that 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 flame ionisation and UV detectors. A pressure restrictor is located after the detector to ensure supercritical conditions.

1.9.3.1 Separations involving SFC

In 1978, Klesper and Hartmann[160] modified an HPLC system for use with supercritical fluids and then used oligostyrenes to analyse its performance. This is one of the earliest separations of oligomers by SFC. However, it was not until gradient elution techniques became established that SFC became widely used for the separation of low molecular weight polymers and oligomers. One of the earliest reported uses of gradient elution in SFC for the separation of oligomeric species was presented by Schmitz and Klesper[161]. Three oligostyrene standards PS800, PS2200 and PS4000 were fractionated on a column of silica 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.

Schmitz *et al.*[162], have investigated the effect that a number of mobile phase compositions have in the separation of 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.*[163]. A silica stationary phase was used with *n*-pentane : 1,4 dioxane gradients. Separations were found to occur not only with respect to the 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.

Schmitz *et al.*[164], investigated the optimisation of oligomer separations with SFC. The oligomers used were from a PS800 standard and an oligo(2-vinyl naphthalate) sample prepared by anionic polymerisation. Temperature programming was shown to be applicable if the appropriate temperature region was chosen. Optimisation strategies were also given for both pressure programmed separations and for separations using gradient elution, in particular multiple gradient techniques were demonstrated to be capable of enhancing the efficiency of oligomer separations.

Hirata[165] studied the retention behaviour of samples having different polarities using columns containing silica and an octadecylsilyl bonded phase with *n*-hexane as the eluent. Separations were also carried out with

n-hexane : ethanol (90:10) as the mobile phase. For a given oligomer series, the separation achieved varied markedly depending upon the column and mobile phase used.

Schmitz and Gemmel[166] used SFC as a means for monitoring the preparation of macromers. It was shown that separations by SFC yield different retentions for oligomer series depending on their end-groups, enabling it to be utilised for monitoring the preparation and subsequent reaction of oligomers of the macromer type.

Bartle *et al.*[167], used supercritical fluid extraction and chromatography for the determination of oligomers in PET films, both off-line and on-line. Models for continuous (off-line) and discontinuous (on-line) extraction from films were developed and also a model for continuous extraction with a non-uniform initial concentration of extractable material across the film.

Schmitz *et al.*[168], used high-performance liquid and supercritical fluid chromatographic separations of vinyl oligomers by gradient elution with various eluent pairs on a silica stationary phase. For the HPLC of vinylpyridine oligomers, changing the primary component (in which the solute was less soluble) of the eluent mixture distinctly influenced the separation. In SFC, the separation efficiency was greatly influenced by the column temperature and/or pressure and by the eluent composition.

Ute *et al.*[169], obtained isotactic and syndiotactic pentacontamers (50mers) of methyl methacrylate by fractionation with preparative SFC using carbon dioxide : ethanol as a mobile phase and silica gel as the stationary phase. Schmitz *et al.*[170], separated different oligomers by SFC using gradient

elution over a wide molecular weight range. For separating oligomers which absorb only at low wavelengths, a carbon dioxide : acetonitrile mobile phase was used which allowed UV detection down to 200 nm.

In a paper by Dilettato *et al.*[171], Soxhlet extracts of a polyolefin were investigated by capillary SFC using flame ionization detection. Separation and detection of every polymer additive (antioxidants, antistatic agents, etc.) present in the plastic were possible, sometimes in a single SFC run. Identification of coextracted low mass oligomers and certain of the alteration products of Irganox 1010 was confirmed by GC-MS.

Just *et al.*[172], used SFC to study linear and cyclic components in technical silicone oils. Accurate assignment of linear and cyclic PDMS was possible by coupling SFC with mass spectroscopy or by using standard compounds. In another paper, Just *et al.*[173], used SFC in combination with mass spectroscopy for determining cyclic siloxanes beside linear methyl and hydroxyl "end-capped" siloxanes.

1.9.4 Gas chromatography (GC)

GC is the most powerful separating technique of the chromatographic techniques currently available. Although a powerful method, the use of GC is restricted by two factors: firstly, the sample to be analysed must be sufficiently volatile to be eluted from the chromatograph; and secondly, the analyte must possess a minimum degree of thermal stability. Generally, there are two types of column currently available: 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 (WCOT) and porous layer open tubular (PLOT). In such columns, the walls, made from stainless steel or fused silica, act as support. The stationary phases used in gas-liquid chromatography (GLC), the most popular form of GC, are involatile liquids. The mobile phase, e.g. helium, transports the volatised analyte along the heated column where it interacts with the stationary phase. The separation obtained depends upon the relative solubilities and adsorption potentials of the compounds with respect to the stationary phase. In gas-solid chromatography (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 that a compound will take to elute from the chromatograph. For a given column, held at a given temperature, 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. This method is used to resolve oligomer mixtures. Programmes are chosen so that the lower oligomers are well separated and higher oligomers appear as sharp peaks in practical analysis times.

The standard detector used in GC is the flame ionisation detector (FID), although an electron capture detector can be used for the selective

detection of halogen containing compounds. GC is often coupled to a mass spectrometer. With this arrangement, the high resolving power of GC is used to separate compounds in a mixture, and identification is possible from their mass spectrum.

1.9.4.1 Separations involving GC

Gilbert *et al.*[174], used GC-MS to identify VC oligomers and other low-molecular-weight components in PVC resins for food packaging applications. Analysis by packed-column gas chromatography using hall electrolytic conductivity detection showed the presence of a series of chlorinated components which by subsequent GC-MS were identified as VC oligomers ranging from trimer to octamer. Other non-chlorinated compounds identified in the resin included mixed phthalates, alkanes, nonylphenol, and undecyl dodecanoate, the latter being derived from the polymerisation initiator lauryl peroxide.

Schwenk *et al.*[175], investigated 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 was analysed by GC-MS. The results showed that low molecular weight paraffins in the sample consisted of a sequence of even-numbered homologues. Compounds up to C_{24} were separated from one another.

Garner *et al.*[176], used capillary GC for the analysis of low molecular weight tertiary butoxide initiated or bornyl oxide initiated fluoral, chloral or bromal, acetate end-capped oligomer mixtures. Unlike the gas

chromatography of such mixtures on packed columns, which gave only partially resolved peaks, capillary GC gave near full resolution.

Aldissi *et al.*[177], 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 which was capable of resolving oligomers up to C_{28}.

In a paper by Abrantes[178], GC-MS identification of polystyrene oligomers in polystyrene plastic for milk packaging was performed using a headspace and solution injection technique. Twenty compounds were determined by GC-MS in polystyrene used for milk packaging. The major components identified in milk were styrene and its dimer.

Lai and Locke[179] 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. Orav *et al.*[180], studied the analysis of reaction by-products in ethylene oligomers by capillary GC. A method using temperature-programmed polydimethylsiloxane (PDMS) (bonded phase) and poly(phenyl ether) (5 rings) capillary columns was developed. Keohan *et al.*[181], used GC to assess selective degradation of silicone copolymers and networks. GC was used along side SEC to determine the degree of cross-linking in the networks. In a paper by Kappler *et al.*[182], low-molecular vaporizable components in silicone resins were identified by GC-MS. A number of cyclic and linear siloxanes were identified.

Materials used in the manufacture of silicone breast prostheses were analysed by SFC and by high temperature GC coupled with direct deposition FT-IR detection[183]. The chromatographic resolution and deposition quality were found to be unsatisfactory for SFC/FT-IR; however, high temperature GC/FT-IR produced satisfactory results.

1.9.5 Thin layer chromatography (TLC)

In TLC, a stationary phase of uniform thickness is supported by a solid surface. The stationary phase can be normal phase (silica or alumina) or reversed (non-polar) phase. 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 pressure TLC). In comparison with HPLC, TLC is less accurate, sensitive and reproducible. However, it does approach HPLC for selectivity and the apparatus is simpler and less complicated to use.

To obtain the best performance possible from a system, the sample should be spotted onto a plate with the least amount of spreading that is practically possible. TLC results are represented in the form of Rf values. The Rf 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.

$$Rf = a/b \qquad (1.35)$$

The Rf value for a given compound depends on the activity of the plate, spot size and developing conditions and is not a definite analytical value.

For this reason, calibration tests 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 HPLC. The only criteria is that it must be possible to remove all the solvent by drying.

1.9.5.1 Separations involving TLC

Hudgins *et al.*[184], reported a number of TLC systems used to resolve individual species of three separate oligomers of PET, 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 a single and multiple direction development. Separations were achieved between cyclic and linear oligomers of equal molar mass. The separations were regarded as being superior to those previously reported.

Cserháti *et al.* [185], used a thin layer chromatographic separation of some tributylphenyl ethylene oxide oligomers according to the length of the ethylene oxide chain. The separation was carried out on precoated alumina thin-layer plates using various tetrachloromethane : acetonitrile mixtures as the eluent. It was found that the optimum separation of surfactant oligomer pairs with longer ethylene oxide chains required a higher eluent strength (higher acetonitrile concentration).

In another paper, Cserháti[186] investigated solvent strength and selectivity in TLC separations of ethylene oxide oligomers. The separations of various non-ionic tensides consisting of ethylene oxide oligomer mixtures were carried out in 55 different TLC systems. The solvent strength and selectivity were calculated for each system and correlated with the

physicochemical parameters of the solvents. It was found that selectivity was higher on alumina than on silica and both strength and selectivity depended significantly on the dielectric constant and refractive index of the solvents.

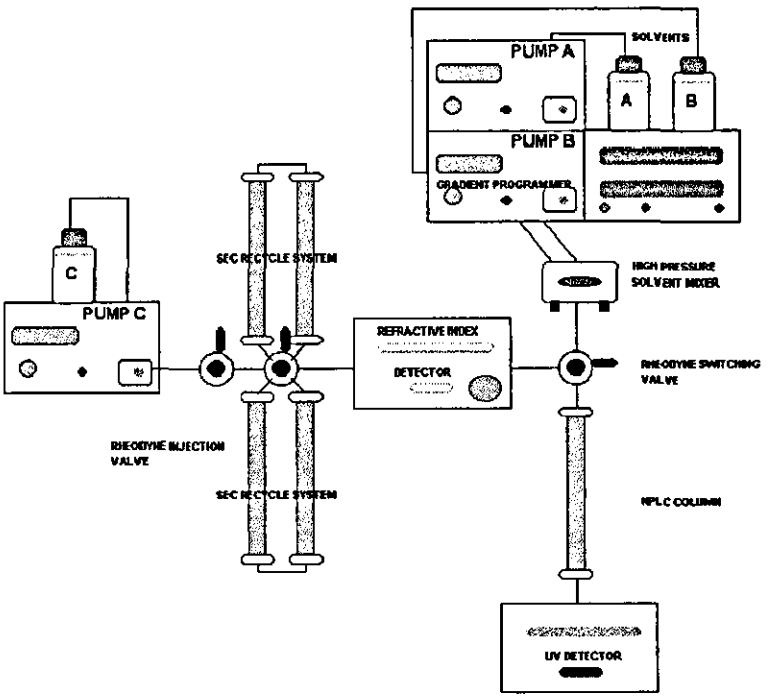
Bui *et al.*[187], used reversed phase TLC to separate low molecular weight standards of polyisoprene, polystyrene and poly(ethylene oxide). The performance of reversed phase TLC was compared to gradient elution HPLC and SEC. It was found that TLC had from two to five times the resolving power of SEC for the molecular weight range investigated. As expected, the HPLC system exhibited the greatest resolving power.

Kundu[188] developed a method based upon the separation of silicones present in vegetable oils by TLC and visualisation of the spots developed by means of the Rhodium B reagent.

1.9.6 Coupled column chromatography (CCC)

Coupled column chromatography is a method of using two or more chromatographic systems to analyse complex molecules. To accomplish the desired fractionation, two chromatographs are coupled together so that the eluent from the first flows through the injection valve of the second. Figure 5 shows this arrangement. The first instrument is operated by conventional SEC. The second is operated as HPLC in a isocratic or gradient mode. The desired detection is attained by utilising a variety of detectors, notably UV, at the exit of the second instrument. The basic principles underlying CCC are discussed in the following sections.

Figure 5. Assembly of CCC system



1.9.6.1 Cross-fractionation

Complex polymers contain more than one broad property distribution. If molecular weight and composition are the only two property distributions present, then an example of cross-fractionation would be the separation of the polymer first according to molecular weight (or molecular size) by SEC and the separation of each single molecular weight fraction obtained according to composition. This cross-fractionation provides a two-dimensional answer to a two-dimensional distribution problem. It has typically been accomplished for polymers using adsorption liquid chromatography

1.9.6.2 Multi-dimensional chromatography

Multi-dimensional chromatography is the term used to describe a variety of methods where fractions from one chromatographic system are each

transferred to another for further separation. Combinations of SEC with thin-layer chromatography have been shown to enable separation of copolymers by composition in a 'cross-fractionation'. CCC utilises a combination an SEC coupled to an HPLC in a cross-fractionation approach.

1.9.6.3 The mechanism of column switching

In CCC, SEC utilises conventional separation by molecular size exclusion. However, adsorption phenomena take place in the second system. SEC separates the polymer according to molecular size in solution. At any desired retention time, the flow in the first instrument is stopped and an injection made into the second instrument of a single 'slice' of the chromatogram. This slice is then separated by conventional HPLC.

A large number of factors play a role in the development of a column-switching procedure; these include the separating power of the chromatographic columns, mobile phase compositions and the nature and number of the analytes. Method development in CCC is generally performed by trial-and-error experiments and can, therefore be quite laborious and expensive.

There is considerable interest in CCC because of its potential for additional selectivity and resolution. These benefits are particularly of interest in the characterisation and analysis of low molecular extracts from plastic materials. The CCC experimental work in this thesis is based on a combination of SEC and isocratic normal phase HPLC. It has the advantage that a final elution can be carried out with multiple detection,

thus providing additional information with reference to the composition of the fractions investigated.

1.9.6.4 Separations involving CCC

Venkatramani *et al.*[189], developed a two-dimensional gas chromatograph in which a thermal modulator serially coupled two columns containing dissimilar stationary phases. The secondary column generated a series of high-speed secondary chromatograms from the sample stream formed by the chromatogram eluting from the primary column. This series of secondary chromatograms formed a two-dimensional gas chromatogram with peaks dispersed over a retention plane rather than along a line. The entire primary column chromatogram was transmitted through the secondary column. The temperature program reduced the retentive power of the secondary column as a function of progress of the primary chromatogram such that the retention mechanism of the primary column was eliminated from the second dimension. Retention of a substance in the second dimension was then determined by the difference in its interaction with the two stationary phases

Schulz *et al.*[190], determined the functionality and molecular weight distribution of 1,3,6-trioxocane polymers by coupled column chromatography. This method included a preparative chromatographic separation of the polymer followed by SEC and liquid adsorption chromatography under "critical conditions". The results, advantages and problems of this type of CCC were discussed.

Cortes *et al.*[191], performed quantitative determination of acrlyonitrile-butadiene-styrene (ABS) terpolymer additives using a CCC system consisting of a micrcolumn SEC coupled on-line to a capillary GC and to a conventional liquid chromatography system. The results obtained were compared to conventional sample preparation procedures consisting of dissolution of the polymer followed by precipitation and analysis of the supernatant. Results obtained for two polymer systems studied indicated losses for some additives using the precipitation approach.

In a paper by Welsch *et al.*[192], the selectivity tuning of serially coupled columns in HPLC was investigated. Two columns with different retention characteristics were coupled in series via a T-piece and the relative retention of components chromatographed on the system were changed by varying the individual flow rates in the coupled columns. This has been demonstrated by using different column combinations to separate several mixtures containing chlorophenols, nitroaromatic compounds, and aromatic hydrocarbons.

Grainger *et al.*[193], examined isomer differentiation of chlorinated dibenzo-*p*-dioxin (CCD) isomer pair components by three orthogonal chromatographic (gas chromatography, liquid chromatography, and micellar electrokinetic chromatography) techniques and three orthogonal spectroscopic (FT-IR and carbon-13 and proton NMR) techniques. Synthetic CCD isomer pair mixtures from the same sample set were separated by methods using independent partitioning dynamics and identified by spectroscopic methods using independent energy/structure transformations.

In a paper by Barth[194], an overview was presented on recent developments in the use of hyphenated multidimensional separation and detection techniques for the characterisation of polymeric materials. Multidimensional hyphenated techniques, such as orthogonal chromatography, temperature-rising elution fractionation-SEC, and SEC-HPLC, were briefly discussed.

Ogan *et al.*[195], applied CCC to the analysis of polycyclic aromatic hydrocarbons in coal liquids and oils. The method incorporated three chromatographic steps: HPLC coupled to SEC which was designed for preliminary fractionation of the mixture. Individual compounds were then identified in a final high resolution HPLC step.

In a number of papers and reviews, Balke *et al.*[196-201], have discussed the used of coupled column chromatography for polymer cross-fractionation using combinations of SEC-SEC and SEC-HPLC.

Nerín *et al.*[202], have developed a coupled column procedure for determining antioxidants and UV stabilisers in PET consisting of an SEC column connected in series to a normal phase HPLC column. An automatic three-way switching valve was placed between the two columns. The SEC column separated the bulk polymer from the antioxidants and UV stabilisers. These compounds were then separated and analysed using the HPLC column. The behaviour of the SEC column in different organic phases was also studied.

Monteiro *et al.*[203], used coupled SEC-HPLC to determine antioxidants and UV stabilisers in PET bottles. In a single run, it was possible to separate and quantify a synthetic mixture of the stabilisers.

In a review by Dawkins[204], it is stated that copolymers having composition and molar mass distributions can be characterised with one or more concentration detectors on-line to a chromatographic system based on SEC. For more detailed information on composition heterogeneity, two approaches were reviewed. An SEC method involving on-line concentration detection together with on-line low-angle laser light scattering is described to demonstrate how heterogeneity parameters permit a distinction between block copolymers and polymer blends. Coupled column chromatography with two chromatographic systems in which fractions from an SEC column are injected into a second column containing a polymer-based packing where retention is determined by non-exclusion mechanisms is described.

In a paper by Dawkins *et al.*[205], CCC was performed on statistical copolymers of styrene and *n*-butyl methacrylate with two chromatographic systems in which fractions from SEC are injected into a column were retention is determined by non-exclusion mechanisms. Separations dependent on copolymer composition as a function of the non-solvent component in the mobile phase and the polarity of the stationary phase in the second column system were accomplished by isocratic elutions.

In a paper by Mori[206], the use of SEC and non-exclusion liquid-chromatography for the characterisation of styrene copolymers was examined. It was stated that SEC dual detector systems cannot give an

accurate chemical composition distribution for copolymers; therefore, non-exclusion liquid chromatography (NELC) is required. Several NELC techniques that separate copolymers according to composition were reviewed: liquid adsorption chromatography (LAC), high-performance precipitation liquid chromatography, normal-and reversed-phase chromatography, orthogonal chromatography, and LAC at the critical point.

2. Experimental

2.1 Poly(vinyl chloride)

2.1.1 PVC polymer

The PVC polymer was Lucovyl RB8010 with a K value (solution viscosity parameter used by PVC manufacturers) of 56. This was a mass-polymerised sample kindly provided by Atochem (UK).

2.1.2 Reagents

Diethyl ether, tetrahydrofuran (THF), dichloromethane, *n*-hexane, *n*-pentane, methyl *tert.*-butyl ether (MTBE) and *iso*-propanol (all HPLC grade) were supplied by Fisons (UK) and used as received.

2.1.3 Chromatographic columns

Polymer Laboratories (UK) provided HPSEC columns containing the following packings: PL gel 5 μm, 50 Å (30 cm x 7 mm) and PL mixed gel B (60 cm x 7 mm and 30 cm x 7 mm). A semi-preparative adsorption liquid chromatography column (31 cm x 25 mm) containing LiChroprep Si60 (40-63 μm) packing was procured from Merck (Germany). HPLC columns containing Spherisorb S5W (25 cm x 4.6 mm) were supplied by Phase Separations (UK).

2.1.4 Solvent delivery pumps

Model 64 analytical HPLC pumps (Knauer, Germany) with a gradient programmer were used in this investigation.

2.1.5 HPLC detectors

A differential refractometer (no. 98.00) (Knauer, Germany), a PU 4025 UV detector (Pye Unicam, UK), a 8800 series variable UV detector (Dupont, USA) and a diode array UV detector (Pharmacia Sweden) were used in this study.

2.1.6 Chromatographic valves and tubing

The chromatographic valves used in this investigation are supplied by Rheodyne (UK) (7125 injection valve, 7010 and 7000 switching valves). For the HPLC systems, zero dead volume connectors and narrow bore (0.15 mm) stainless steel tubing (Valco, UK) were used for all the essential connections. This ensured that dead volume, and hence peak broadening, was kept to a minimum.

2.1.7 Standards

A set of polystyrene standards (Mn = 580-2100000) were supplied by Polymer Laboratories (UK).

2.1.8 Chromatographic computer software

All detectors were connected to a PL Caliber Data Station supplied by Polymer Laboratories (UK).

2.1.9 Molecular weight characterisation of PVC base resin

Samples were prepared by adding 12.5 mg of PVC to 25 ml of THF in a three-necked 100 ml flask containing a magnetic stirrer and equipped with a nitrogen inlet and condenser. Stirring was allowed to continue overnight. The flask was then placed in a water bath thermostated at 60° C for 75

minutes (no stirring). The flask was finally removed and the solution, with stirring, was allowed to attain room temperature.

2.1.9.1 Chromatographic system

SEC was performed at room temperature using a mixed gel B column (60 cm x 7.5 mm). After the solution was allowed to cool to room temperature, toluene (5 µl) was added as an internal standard and the solution (5% w/v) was loaded into a Rheodyne 7125 injection valve containing a 200 µl loop. The solution was then injected onto the mixed gel column fitted with a 2 µm pre-filter. The sample was eluted with unstabilised THF using a Knauer 64 HPLC pump at a flow rate of 1.0 ml/min. Detection was accomplished using a Knauer differential refractometer connected to a chart recorder. The column was calibrated (with toluene as a reference) using 10 polystyrene standards with narrow molecular weight distributions and peak molecular weights in the range of 580 to 2100000.

The chromatograms were evaluated by a computer program to produce number average molecular weight Mn, weight average molecular weight Mw, peak maxima molecular weight Mp and Mw/Mn, the polydispersity.

2.1.10 Large-scale Soxhlet extraction of PVC

In order to maximise the yield of oligomers, a modified Soxhlet extractor (chamber volume 700 ml) using diethyl ether as the extractant was constructed.

It was claimed that extractions using a conventional Soxhlet extraction thimble were unsatisfactory because the extraction process extracted

material from the thimble[207]. In order to use the Soxhlet without the thimble, a layer of glass wool was placed in the bottom of the Soxhlet chamber to a depth sufficient to cover the siphon outlet. The outlet was partially blocked to retain the polymer particles in the chamber but allowing the solvent to drain out. A glass tube was then pushed through the glass wool to a position approximately 2 cm from the siphon outlet; when the chamber was full of PVC, the tube allowed air to reach the outlet and break the siphon once the solvent had drained away. If the tube was placed too near the outlet, the siphon would break prior to complete solvent drainage; too far away and the siphon will never be broken. A second layer of glass wool was then placed in the bottom of the chamber to ensure that the insertion of the glass rod in the first layer had not opened a route of escape for the PVC particles. A final layer of glass wool was then placed on the surface to prevent 'splashing' of the particles. Typical extraction conditions were PVC (250 g), solvent (500 ml), extraction time (20 hours), cycle time (30 minutes) with water bath heating at a temperature of 60°C.

2.1.11 Isolation of low molecular weight Soxhlet extracts

The diethyl ether Soxhlet extract was reduced to approximately 20 ml on a rotary evaporator and added to 350 ml of *n*-pentane at room temperature. The mixture was left for 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 utilising first a rotary evaporator and then a vacuum oven at room temperature.

2.1.12 Molecular weight characterisation PVC Soxhlet extract

SEC was performed using the technique described in Section 2.1.9.1

2.1.13 Fractionation by adsorption liquid chromatography

The low molecular weight PVC fraction was purified and further fractionated on a Merck Lobar size B column (31 cm x 25 mm I.D.) containing LiChroprep Si 60 (40-63 μm) packing. A Model 64 HPLC pump was used in conjunction with a 8800 series variable UV detector operated at 200 nm and a Rheodyne Model 7125 injection valve fitted with a 200 μl loop.

The mobile phase employed was *n*-hexane containing MTBE modifier (5.0%) at a flow rate of 3.0 ml/min. Aliquots (75 w/v) of the low molecular weight fraction were injected into the chromatograph and the fraction within the elution volume range 0-420 ml was collected. The bulk of the solvent was removed using a rotary evaporator, final dryness being achieved in a vacuum oven at room temperature.

2.1.14 Analysis of low molecular weight fraction by SEC

Individual oligomer species were separated from the low molecular weight PVC fraction using a SEC system based on 4 PL gel 5 μm 50 Å columns (30 cm x 7 mm). The columns were used in conjunction with a Knauer Model 64 pump and a Knauer differential refractometer. An alternate pumping recycle system[69] was set up using a Rheodyne Model 7000 switching valve and a Rheodyne Model 7125 injection valve fitted with a 200 μl loop. Dichloromethane, the mobile phase, was delivered at a rate of 1.0 ml/min. A separation was performed by injecting an aliquot (5 w/v) and passing it with recycling (1½ recycles) through 300 cm of gel bed.

Oligomers corresponding to resolved oligomer peaks were collected manually and the dry oligomer fractions were obtained using a vacuum oven at room temperature.

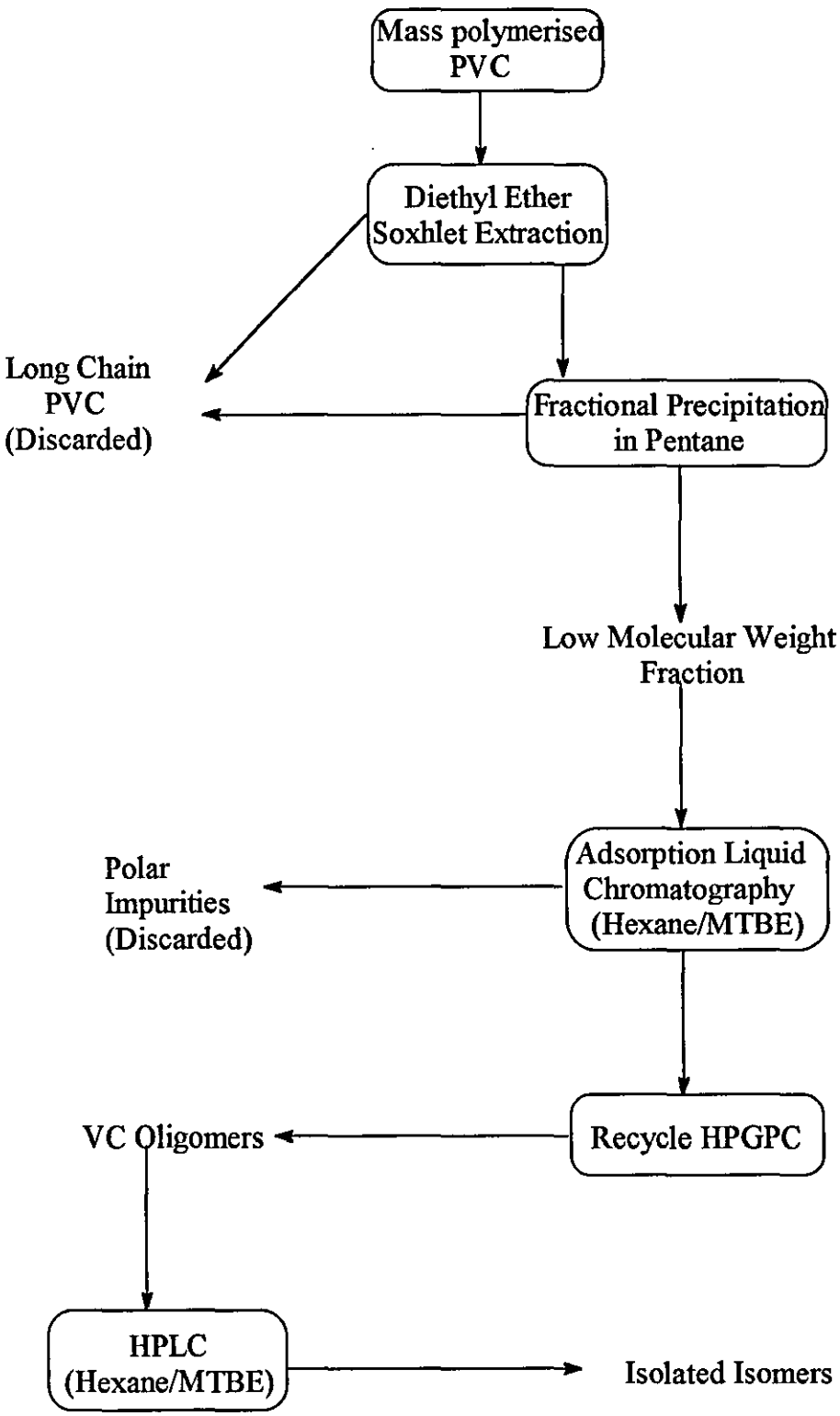
2.1.15 Separation of VC oligomers into isomeric forms

Oligomers prepared by recycle HPSEC were separated into their isomeric forms by normal phase HPLC. The chromatography consisted of a Knauer Model 64 pump, a 25 cm x 4.6 mm I.D. column containing Spherisorb S5W silica packing, a 8800 series variable UV detector operated at 200 nm and a Rheodyne Model 7125 injection valve fitted with a 200 µl loop. The mobile phase employed was *n*-hexane containing MTBE modifier (1.0%) at a flow rate of 1.0 ml/min. Routine fractionation was carried out by injecting aliquots (1% w/v) and the fractions blown to dryness using nitrogen. A schematic illustration of the muti-stage procedure for the separation of VC oligomers from a PVC polymer is shown in Figure 6.

Using this separation scheme it was possible to isolate 0.5 mg of VC pentamer with repeat fractionation by HPLC from the Lucovyl RB 8010 PVC polymer. The principle limitation of this scheme was the small amount of VC oligomer available and the requirement for repeated fraction collection to obtain sufficient mass if successful structural studies were to be performed using NMR. These limitations were minimised by the application of a coupled column system where the SEC was coupled directly on-line to the HPLC chromatograph bypassing the need for any additional sample handling. By eliminating sample waste, the efficiency of the analysis increased reducing the need for multiple fraction collection. It was possible to duplicate the results obtained for the pentamer fraction by

the use of a coupled column system and then apply this coupled technique to the hexamer and heptamer fractions of the low molecular weight extract.

Figure 6. ***Separation scheme***



2.1.16 Assembly of CCC system

The coupled column chromatograph comprised of two dimensions. SEC, the first dimension, consisted of a Model 64 pump, a Model 98 refractive index detector, a Model 7125 injection valve and 4 PL gel 5 μm 50 Å columns (30 cm x 7 mm) with a Model 7000 recycle valve. SEC was used to fractionate the PVC extract into its constituent oligomeric and additive portions with the aid of a recycle technique (1½ recycles). HPLC, the second dimension, consisted of a Model 64 pump, a 25 cm x 4.6 mm I.D. column containing Spherisorb S5W silica packing and a Model 8800 variable UV detector set at 200 nm. The two dimensions were connected via a Model 7010 switching valve. As the desired oligomer fraction eluted from the SEC chromatograph, the switching valve was rotated diverting the eluting peak into the HPLC system. Once this was accomplished, the switching valve was rotated back. Aliquots (15 w/v) of the low molecular extract in HPLC grade dichloromethane were injected via a 200 μl injection loop onto the first chromatographic system (SEC). The mobile phase in the first column system was dichloromethane at a flow rate of 1.0 ml/min. The second system (HPLC) employed a *n*-hexane mobile phase containing *iso*-propanol modifier (2.0-4.0% v/v). The flow rate varied between 0.6 and 1.0 ml/min. Both detectors were connected to a Caliber data station which displayed the chromatograms in "real-time".

2.2 Nitrile rubber

2.2.1 NBR compound

NBR rubber test sheets supplied by Rapra Technology Ltd, (UK) were compression moulded under the following conditions: 3 minutes at 165°C.

Formulation information is shown in Table 3.

2.2.2 Reagents

Iso-propanol, tetrahydrofuran, toluene, *n*-hexane, *iso*-octane and *n*-pentane (all HPLC grade) were supplied by Fisons, (UK) and were used as received.

2.2.3 Chromatographic columns

SEC columns containing PL mixed gel B columns (60 cm x 7 mm and 30 cm x 7 mm) were supplied by Polymer Laboratories (UK). HPLC columns containing Spherisorb S5W (25 cm x 4.6 mm and 30 cm x 7.8 mm) were supplied by Phase Separations, (UK) and HPLC cartridge columns containing Nova-pak C_{18} 60 Å 4μm (15 cm x 3.9 mm) were supplied by Waters Millipore Corporation, (USA). GC low bleed DB5MS columns (15 m, I.D. 0.25 mm, film 0.25 μm) were supplied by J&W Scientific, (USA).

Table 3. NBR formulation information

Compound	PHR*
Krynac 34-50 (rubber polymer)	100.0
Zinc oxide (cure activator)	5.0
MC Sulphur (curative)	1.5
Stearic acid /long chain carboxylic acids (cure activator)	1.0
Di-2 ethyl hexyl phthalate (plastisicer)	10.0
SRF N762 Carbon Black (reinforcing filler)	30.0
Stockalite Clay (aluminium silicate)	20.0
IPPD (N-isopropyl-N'-phenyl-*p*-phenylenediamine) (antiozanant)	1.0
Santowhite crystals (antioxidant)	1.0
Astorstag wax (antiozonant)	2.0
MBTS (2-mercaptobenzothiazyl disulphide) (curative accelerator)	1.0
TMTD(tetramethyl thiuram disulphide) (curative accelerator)	0.25

*Parts per hundred rubber

2.2.4 HPLC detectors

A Knauer differential refractometer (type no. 98.00), Dupont 8800 series variable UV detector and LKB Bromma 2140 rapid spectral detector were used.

2.2.5 HPLC fraction collector

Fractions were collected with a Frac-100 fraction collector supplied by Pharmacia Fine Chemicals (Sweden).

2.2.6 GC system

Separations were performed with a GC 8000 series gas chromatograph connected to a MD 800 mass spectrometer (both Fisons Instruments UK).

2.2.7 Chromatographic valves and tubing

The HPLC valves were supplied by Rheodyne (7125 injection valve, 7010 and 7000 switching valves). Zero dead volume connectors and narrow bore (0.15 mm) stainless steel tubing were used to make all the essential connections (Valco UK).

2.2.8 Chromatographic computer software

All detectors were connected a PL Caliber Data Station supplied by Polymer Laboratories (UK).

2.2.9 Large-scale Soxhlet extraction of NBR

A modified Soxhlet extractor (chamber volume 700 ml) using *n*-hexane or *iso*-octane as the extractant of a similar type to that used in Section 2.1.10. Typical extraction conditions were NBR (30 g shredded), solvent (200

ml), extraction time (12 hours), cycle time (10 minutes) with water bath heating at a temperature of 100°C.

2.2.10 Isolation of low molecular weight Soxhlet extracts

When an extraction was complete, the extract was filtered to remove any rubber particles. The solvent was removed with a rotary evaporator. The extract was then dried in a vacuum oven at room temperature.

2.2.11 Molecular weight characterisation NBR Soxhlet extract

SEC was performed at room temperature using a PL mixed gel B column (60 cm x 7.5 mm). Toluene (5 µl) was added as an internal standard and the solution (5% w/v) was loaded into a Rheodyne 7125 injection valve containing a 200 µl loop. The solution was then injected onto the mixed gel column fitted with a 2 µm pre-filter. The sample was eluted with unstabilised THF using a Knauer 64 HPLC pump at a flow rate of 1.0 ml/min. Detection was accomplished using a Knauer differential refractometer. The column was calibrated (with toluene as a reference) using 10 polystyrene standards with narrow molecular weight distributions and peak molecular weights in the range of 580 to 2100000.

The chromatograms were evaluated by a computer program to produce number average molecular weight Mn, and weight average molecular weight Mw and peak maxima molecular weight Mp.

2.2.12 HPLC of the NBR low molecular weight fraction

Normal phase and reversed phase experiments were performed on analytical scale HPLC equipment which consisted of a Knauer binary programmable gradient HPLC system with high pressure solvent mixing.

This instrumentation comprised two Knauer 64 pumps connected to a Knauer gradient programmer, a high pressure solvent mixer, a Rheodyne 7125 injection valve fitted with a 200 µl loop used in conjunction with a Dupont 8800 variable UV detector. A range of wavelengths between 200 and 254 nm was utilised. 1-5% w/v aliquots were injected and the fractions dried at room temperature in a vacuum oven. A range of wavelengths between 200 and 254 nm were utilised. The eluents were degassed after every run using a sonic bath to avoid the formation of bubbles in the UV detector flow.

The reversed phase system consisted of a HPLC cartridge column (15 cm x 3.9 mm) containing Nova-pak C_{18} 60 Å 4 µm packing which was used with a range of mobile phase compositions consisting of THF : water in isocratic and gradient elution modes at a flow rate of 1.0 ml/min. The eluents were degassed after every run using a sonic bath to avoid the formation of bubbles in the UV detector flow cell. Optimum conditions consisted of a THF : water gradient which ran from 50% THF to 100% THF in 30 mins at 1.0 ml/min with UV detection set at 254nm. 1% w/v aliquots were injected onto the system.

The normal phase system comprised of a column (25 cm x 4.6 mm) containing Spherisorb S5W silica packing which was used with a range of mobile phase compositions consisting *n*-hexane : *iso*-propanol and *n*-hexane : THF in isocratic and gradient elution modes at a flow rate between 0.3 and 1.1 ml/min. It was found that the best separation of the components within the NBR sample was obtained using a normal phase Spherisorb 25 cm x 4.6 mm column containing S5W silica packing with

the following gradient elution shown in Table 4 at a flow rate of 1.0 ml/min with UV detection set at 254 nm.

In order to increase the efficiency of the separation, a semi-preparative HPLC column containing Spherisorb S5W packing was incorporated into the HPLC system. The system was assembled as follows. A Knauer 64 pump was used in conjunction with a Dupont 8800 variable UV detector and a Rheodyne 7125 injection valve fitted with a 2 ml loop. A column (30 cm x 7.8 mm) containing Spherisorb S5W silica packing was used with the gradient conditions shown in Table 5 at a flow rate of 2.0 ml/min. UV detection was set at 254 nm. This procedure was repeated 15 times.

Table 4. Gradient elution conditions

Time/Mins	% Hexane	% THF
0	100	0
25	100	0
85	50	50

Table 5. Gradient elution conditions

Time/Mins	% Hexane	% THF
0	100	0
35	100	0
180	50	50

The chromatographic system was connected to a Frac-100 fraction collector. 10% w/v aliquots were injected and the collected fractions dried at room temperature in a vacuum oven.

2.2.13 NBR extract fraction identification by GC-MS

Capillary column GC-MS analysis of the bulk low molecular weight NBR extract and fractions from HPLC was carried out with a GC system Fisons

Instruments GC 8000 series gas chromatograph connected to a Fisons Instruments MD 800 mass spectrometer. The gas chromatograph was fitted with a GC low bleed DB5MS column (15 m, I.D. 0.25 mm, film 0.25 μm). The velocity of the carrier gas, helium, was set at a flow rate of 30 cm/sec. Analysis of the low molecular weight NBR fractions from HPLC was performed by injecting 5 μl of a 20% w/v solution with the injector at 250°C. The interface temperature between the GC and the mass spectrometer was set at 250°C. The source conditions were: pressure 30 Pa; temperature 200°C; source current 3287 μA; electron energy 70 eV; trap current 183 μA; filament current 4.2 A. Temperature programming in each case was as follows: 50°C-250°C in 25 minutes. All spectra were processed using a Fisons Mass Labs work station connected directly to the GC-MS. Spectra were produced by scanning the range 20 to 600 m/z. Perfluortri-*n*-butylamine (*Heptacosa*) was used to calibrate the mass spectrometer.

2.2.14 Quantitative analysis of target compounds

Quantitative HPLC analysis was performed on 4 target compounds specified by the Ministry of Agriculture, Fisheries and Food, MAFF, present as *iso*-octane extractables from NBR, as shown in Table 6.

Table 6. MAFF "target compounds"

Compound	Function/Origin
Di-2 ethyl hexyl phthalate	(plastisicer)
Tetratetracontane $CH_3(CH_2)_{42}CH_3$	(process wax)
Benzo-thiazole	(breakdown product of MBTS)
N-isopropyl-N'-phenyl-*p*-phenylenediamine	(from antiozanant)

The chromatographic system comprised of a Knauer 64 pump, a Dupont 8800 variable UV detector and a Rheodyne 7125 injection valve fitted with a 100 µl loop. A column (25 cm x 4.6 mm) containing Spherisorb S5W silica packing was used with the gradient elution conditions shown in Table 7 at a flow rate of 1.0 ml/min. UV detection set at 254 for di-2 ethyl hexylphthalate, benzo-thiazole, *n*-isopropyl-*n*'-phenyl-*p*-phenylenediamine and 203 nm for tetratetracontane.

Table 7. Gradient elution conditions

Time/Mins	% Hexane	% THF
0	100	0
25	100	0
85	50	50

A HPLC calibration was performed using the external standard method utilising Caliber HPLC calibration software. Calibrants were obtained by fractionating the desired compound identified from GC-MS data present in the extract by HPLC. Calibration curves were then constructed and quantitative data was obtained.

2.3 Ethylene-propylene-diene monomer elastomer

2.3.1 EPDM rubber compound

EPDM rubber test sheets supplied by Rapra Technology Ltd. (UK) were compression moulded under the following conditions: 25 minutes at 170°C then post-cured for 5 hours at 165°C in an autoclave (steam). Formulation information is shown in Table 8.

Table 8. EPDM formulation information

Compound	PHR*
Keltan 720 (ethylene-propylene-diene-terpolymer)	100.0
SRF N762 Carbon Black (reinforcing filler)	50.0
Perkadox 1440 1,3 bis-(tert butyl-peroxy-isopropyl) benzene (curative)	4.0
Zinc oxide (cure activator)	5.0
Strukpar 2280 paraffinic oil (plasticiser)	8.0

* Parts per hundred rubber

2.3.2 Reagents

Iso-propanol, tetrahydrofuran, toluene, *n*-hexane and *n*-pentane (all HPLC grade) were supplied by Fisons, (UK) and used as received.

2.3.3 Chromatographic columns

SEC columns containing PL mixed gel B columns (60 cm x 7 mm and 30 cm x 7 mm) were supplied by Polymer Laboratories (UK). HPLC columns containing Spherisorb S5W (25 cm x 4.6 mm and 30 cm x 7.8 mm) were supplied by Phase Separations, (UK) and HPLC cartridge columns containing Nova-pak C_{18} 60 Å 4 μm (15 cm x 3.9 mm) were supplied by Waters Millipore Corporation, (USA). GC low bleed DB5MS columns (15 m, I.D. 0.25 mm, film 0.25 μm) were supplied by J&W Scientific, (USA).

2.3.4 Solvent delivery pumps

Knauer Model 64 analytical HPLC pumps with a gradient programmer were used in this investigation.

2.3.5 HPLC detectors

A Knauer differential refractometer (type no. 98.00), Dupont 8800 series variable UV detector and LKB Bromma 2140 rapid spectral detector were used.

2.3.6 HPLC fraction collector

Fractions were collected with a Frac-100 fraction collector supplied by Pharmacia Fine Chemicals (Sweden).

2.3.7 GC system

Separations were performed with a GC 8000 series gas chromatograph connected to a MD 800 mass spectrometer (both Fisons Instruments UK).

2.3.8 Chromatographic valves and tubing

The HPLC valves were supplied by Rheodyne (7125 injection valve, 7010 and 7000 switching valves). Zero dead volume connectors and narrow bore (0.15 mm) stainless steel tubing were used to make all the essential connections (Valco UK).

2.3.9 Chromatographic computer software

All detectors were connected a PL Caliber Data Station supplied by Polymer Laboratories (UK).

2.3.10 Large-scale Soxhlet extraction of EPDM

A modified Soxhlet extractor (chamber volume 700 ml) using *iso*-propanol as the extractant was of a similar type to that used in Section 2.1.10. Typical extraction conditions were EPDM (30 g shredded), solvent (200

ml), extraction time (12 hours), cycle time (10 minutes) with water bath heating at a temperature of 100°C.

2.3.11 Isolation of Soxhlet extracts

When an extraction was complete, the extract was filtered to remove any rubber particles. The solvent was removed with a rotary evaporator. The extract was then dried in a vacuum oven at room temperature.

2.3.12 Molecular weight characterisation EPDM Soxhlet extract

SEC was performed at room temperature using a PL mixed gel B column (60 cm x 7.5 mm). Toluene (5 µl) was added as an internal standard and the solution (5%w/v) was loaded into a Rheodyne 7125 injection valve containing a 200 µl loop. The solution was then injected onto the mixed gel column fitted with a 2 µm pre-filter. The sample was eluted with unstabilised THF using a Knauer 64 HPLC pump at a flow rate of 1.0 ml/min. Detection was accomplished using a Knauer differential refractometer. The column was calibrated (with toluene as a reference) using 10 polystyrene standards with narrow molecular weight distributions and peak molecular weights in the range of 580 to 2100000.

The chromatograms were evaluated by a computer program to produce number average molecular weight Mn, and weight average molecular weight Mw and peak maxima molecular weight Mp.

2.3.13 HPLC of the low molecular weight fraction

Normal phase and reversed phase experiments were performed on analytical scale HPLC equipment which consisted of a Knauer binary

programmable gradient HPLC system with high pressure solvent mixing. This instrumentation comprised two Knauer 64 pumps connected to a Knauer gradient programmer, a high pressure solvent mixer, a Rheodyne 7125 injection valve fitted with a 200 µl loop used in conjunction with a Dupont 8800 variable UV detector. A range of wavelengths between 200 and 254 nm was utilised. 1% w/v aliquots were injected and the fractions dried at room temperature in a vacuum oven.

The reversed phase system consisted of a HPLC cartridge column (15 cm x 3.9 mm) containing Nova-pak C_{18} 60 Å 4 µm packing which was used with a range of mobile phase compositions consisting of water: THF in isocratic and gradient elution modes at a flow rate of 1.0 ml/min. The eluents were degassed after every run using a sonic bath to avoid the formation of bubbles in the UV detector flow cell. Optimum conditions consisted of a water : THF gradient which ran from 98% water to 70% water in 30 mins at 1.0 ml/min with UV detection set at 254 nm. 1% w/v aliquots were injected onto the system.

Normal phase chromatography was performed with a Spherisorb 25 cm x 4.6 mm column containing S5W silica packing which used a range of mobile phase composition consisting of *n*-hexane : *iso*-propanol and *n*-hexane : THF in isocratic and gradient elution modes. Flow rates were between 0.3 and 1.1 ml/min. The eluents were degassed after every run using a sonic bath to avoid the formation of bubbles in the UV detector flow cell.

It was found that separation of the components within the EPDM fraction was optimised using a normal phase 25 cm x 4.6 mm column containing

Spherisorb S5W silica packing with a mobile phase composition consisting of *n*-hexane : *iso*-propanol (97:03) operating isocratically at 1.0 ml/min.

In order to increase the efficiency of the separation, a semi-preparative HPLC column containing Spherisorb S5W packing was incorporated into the HPLC system. The system was assembled as follows. A Knauer 64 pump was used in conjunction with a Dupont 8800 variable UV detector and a Rheodyne 7125 injection valve fitted with a 2 ml loop. A column (30 cm x 7.8 mm) containing Spherisorb S5W silica packing was used with 5% v/v *iso*-propanol in *n*-hexane as a mobile phase at a flow rate of 2.0 ml/min. UV detection was set at 254 nm. The chromatographic system was connected to a Frac-100 fraction collector. 10% w/v aliquots were injected and the collected fractions dried at room temperature in a vacuum oven.

2.3.14 Analysis of the low molecular weight fraction by GC-MS

Capillary column GC-MS analysis of the bulk low molecular weight EPDM extract and fractions from HPLC were carried out with a Fisons Instruments GC 8000 series gas chromatograph connected to a Fisons Instruments MD 800 mass spectrometer. The gas chromatograph was fitted with a GC low bleed DB5MS column (15 m, I.D. 0.25 mm, film 0.25 μm). The velocity of the carrier gas, helium, was set at a flow rate of 30 cm/sec. Analysis of the low molecular weight EPDM fractions from HPLC and the additives were performed by injecting 5 μl of a 20% w/v solution with the injector at 250°C. The interface temperature between the GC and the mass spectrometer was set at 250°C. The source conditions were: pressure 30 Pa; temperature 200°C; source current 3287 μA; electron energy 70 eV; trap current 183 μA; filament current 4.2 A.. Temperature programming in each case was as follows: 50°C-250°C in 25

minutes. All spectra were processed using a Fisons Mass Labs work station connected directly to the GC-MS. Spectra were produced by scanning the range 20 to 600 m/z. Perfluortri-*n*-butylamine (*Heptacosa*) was used to calibrate the mass spectrometer.

2.4 Silicone rubber

2.4.1 Silicone rubber compound

This compound was supplied as a compression moulded sheet by Rapra Technology Ltd (UK)

2.4.2 Silicone rubber formulation

Silastic New GP 600 silicone rubber was a polydimethyl vinyl siloxane containing vinyl at 0.5% w/w, incorporating precompounded fumed silica and proprietary process additives to a 60 Shore A general purpose compound. The curative was bis(2,4-dichlorobenzoyl)peroxide 50% at an addition level of 1.2%. Cure conditions were 5 minutes at 116°C with 4 hour at 200°C postcure.

2.4.3 Reagents

Tetrahydrofuran, toluene, *n*-hexane and (all HPLC grade) were supplied by Fisons, (UK) and were used as received.

2.4.4 Chromatographic columns

Polymer Laboratories (UK) provided SEC columns containing the following packing: PL gel 5 μm, 50 Å (30 cm x 7 mm). HPLC columns (250 x 4.6 mm and 300 x 7.8 mm) containing Spherisorb S5W were

supplied by Phase Separations, (UK) and a GC low bleed DB5MS column (15 m, I.D. 0.25 mm, film 0.25 μm) was supplied by J&W Scientific, (USA).

2.4.5 Solvent delivery pumps

Knauer 64 analytical HPLC pumps with a gradient programmer were used in this investigation.

2.4.6 HPLC detectors

A Knauer differential refractometer (type no. 98.00), Dupont 8800 series variable UV detector and LKB Bromma 2140 rapid spectral detector were used in this work.

2.4.7 HPLC fraction collector

Fractions were collected with a Frac-100 fraction collector supplied by Pharmacia Fine Chemicals (Sweden).

2.4.8 GC system

Separations were performed with a GC 8000 series gas chromatograph connected to a MD 800 mass spectrometer (both Fisons Instruments UK).

2.4.9 Chromatographic valves and tubing

The HPLC valves were supplied by Rheodyne (7125 injection valve, 7010 and 7000 switching valves). Zero dead volume connectors and narrow bore (0.15 mm) stainless steel tubing were used to make all the essential connections (Valco UK).

2.4.10 Chromatographic computer software

All detectors were connected a PL Caliber Data Station supplied by Polymer Laboratories (UK).

2.4.11 Large-scale Soxhlet extraction of silicone rubber

A modified Soxhlet extractor (chamber volume 700 ml) using *n*-hexane as the extractant was constructed similar to the type used in Section 2.1.10. Typical extraction conditions were silicone rubber (30 g shredded), solvent (200 ml), extraction time (12 hours), cycle time (10 minutes) with water bath heating at a temperature of 100°C.

2.4.12 Isolation of low molecular weight Soxhlet extracts

When an extraction was complete, the extract was filtered to remove any rubber particles. The solvent was removed with a rotary evaporator. The extract was then dried in a vacuum oven at room temperature.

2.4.13 HPLC of the low molecular weight fraction

Normal phase experiments were performed on analytical scale HPLC equipment which consisted of a Knauer binary programmable gradient HPLC system with high pressure solvent mixing. This instrumentation comprised two Knauer 64 pumps connected to a Knauer gradient programmer, a high pressure solvent mixer, a Rheodyne 7125 injection valve fitted with a 200 µl loop used in conjunction with a Dupont 8800 variable UV detector. A column (25 cm x 4.6 mm) containing Spherisorb S5W silica packing was used with a range of mobile phase compositions consisting of *n*-hexane : THF in isocratic and gradient elution modes at a flow rate between 0.3 and 1.1 ml/min. It was found that the best separation of the components within the silicone rubber fraction was obtained with a

mobile phase composition consisting of *n*-hexane : THF (90:10) run isocratically at 1.0 ml/min. This procedure was then scaled up to include a semi-preparative HPLC column (30 cm x 7.8 mm) containing S5W silica packing and a 2 ml injection loop. The mobile phase consisted of *n*-hexane : THF (90:10). The flow rate was set at 2.0 ml/min with UV detection at 203 nm. 10% w/v aliquots were injected and the fractions dried at room temperature in a vacuum oven.

2.4.14 SEC of the Silicone low molecular fraction

Individual species were separated from the low molecular weight silicone rubber fraction using a SEC system based on four 30 cm x 7.5 mm columns containing 5 μm, 50 Å PL gel. The columns were used in conjunction with a Knauer model 64 pump, a Knauer 98 RI detector and a Rheodyne 7125 injection valve fitted with a 200 μl loop. The chromatographic system was connected to Frac-100 fraction collector. Toluene, the mobile phase was delivered at a rate of 1.0 ml/min. 5% w/v aliquots were injected onto the system and the fractions dried at room temperature in a vacuum oven.

2.4.15 Silicone rubber extract fraction identification by GC-MS

Capillary column GC-MS analysis of the bulk Soxhlet extract and low molecular weight silicone fractions from SEC and HPLC were carried out with a GC system Fisons Instruments GC 8000 series gas chromatograph connected to a Fisons Instruments MD 800 mass spectrometer. The gas chromatograph was fitted with a GC low bleed DB5MS column (15 m, I.D. 0.25 mm, film 0.25 μm). The velocity of the carrier gas, helium, was set at a flow rate of 30 cm/sec. Analysis of the bulk Soxhlet extract and low molecular weight silicone fractions from SEC and HPLC were

performed by injecting 5 μl of a 20% w/v solution with the injector at 250°C. The interface temperature between the GC and the mass spectrometer was set at 250°C.The source conditions were: pressure 30 Pa; temperature 200°C; source current 3287 μA; electron energy 70 eV; trap current 183 μA; filament current 4.2 A. Temperature programming in each case was as follows: 50°C-250°C in 25 minutes. All spectra were processed using a Fisons Mass Labs work station connected directly to the GC-MS. Spectra were produced by scanning the range 20 to 600 m/z. Perfluortri-*n*-butylamine (*Heptacosa*) was used to calibrate the mass spectrometer.

3. Results and Discussion

3.1 Poly (vinyl chloride)

3.1.1 SEC analysis of Lucovyl RB8010 PVC resin

Lucovyl RB8010 was characterised using the method described in Section 2.1.9. The SEC chromatogram is given in Figure 7. Table 9 gives the molecular weight data obtained for the Lucovyl RB8010 PVC resin.

Figure 7. SEC analysis of Lucovyl RB8010 PVC resin

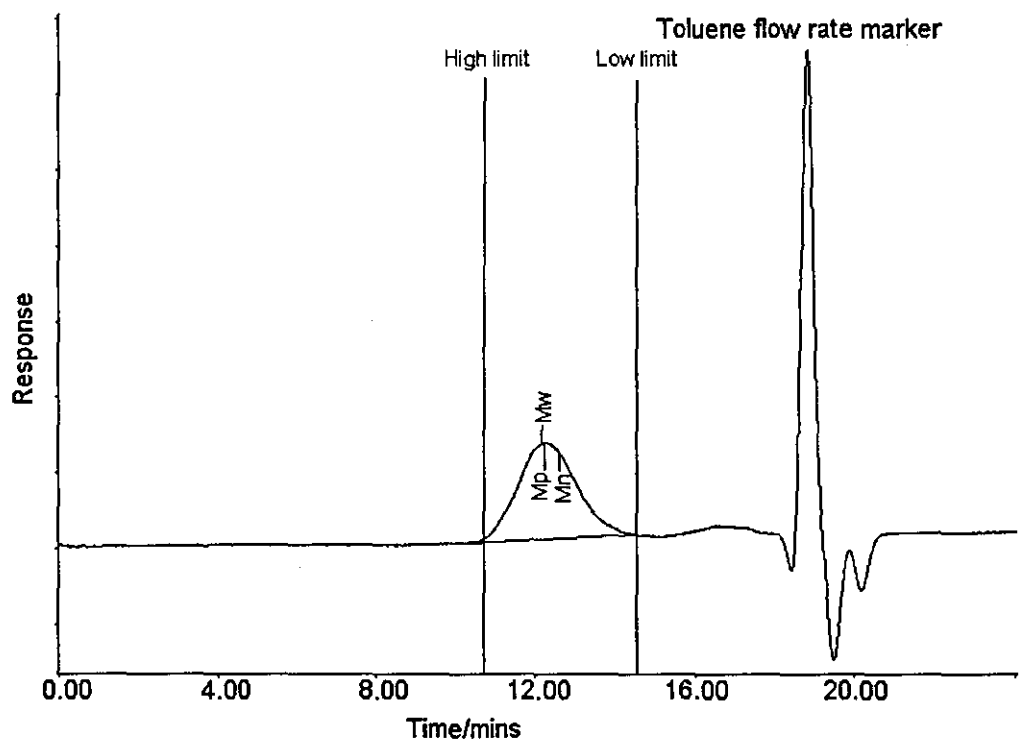


Table 9. SEC molecular weight data of Lucovyl RB8010.

SAMPLE	Mn	Mw	Mp	Mw/Mn
Lucovyl RB8010	37313	76165	53310	2.04

3.1.2 Large scale Soxhlet extractions

Large scale Soxhlet extractions were performed on Lucovyl RB8010 using methods described in Section 2.1.10. The extraction results are shown in Table 10.

Table 10. Large scale extraction results of Lucovyl RB8010.

Sample	Solvent	Boiling point/°C	Solubility parameter $(Cal/cm^3)^{0.5}$	Yield/%	Colour
RB8010	Diethyl ether	34	7.4	1.08	Light yellow

The low molecular weight fraction that was obtained from the filtrate after fractional precipitation of the diethyl ether extract with *n*-pentane (Section 2.1.11) constituted 1.08% by weight of the original.

Two criteria were used in the choice of solvent. Firstly, only solvents with boiling points below the glass transition temperature of PVC (81°C) were considered in order to minimise particle fusion which could occur with soft particles, resulting in a significant reduction of surface area. Secondly, 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 many liquids have solubility parameters close to that of PVC[63] (9.5 $(cal/cm^3)^{0.5}$), the limited solubility of PVC due to its polar, partially crystalline character results in these liquids being poor solvents at room temperature. It was only diethyl ether that was considered as a suitable extracting solvent since it provided oligomer extracts containing low quantities of PVC having molecular weights

greater than 1000. The inherent instability of PVC has already been discussed (Section 1.3.7) 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. From the colour of the extract shown in Table 10, it is evident that the PVC sample has undergone some thermal degradation. This is undesirable due to the possible structural changes that the VC oligomers could undergo during such circumstances. The most likely possibility is the loss of hydrogen chloride which would result in extra double bonds being present in the molecules.

3.1.3 Removal of long chain PVC by fractional precipitation

Although the sample of Lucovyl RB8010 had been fractionated by diethyl ether Soxhlet extraction, it had previously been established[207] that the resulting extract still contained a high concentration of PVC having molecular weights of up to 20000. To facilitate the characterisation of VC oligomers having molecular weights up to 500 it was desirable to remove a large proportion of this long chain PVC. This was accomplished by fractional precipitation. The immediate advantage of this technique is the rapidity with which a Soxhlet extract can be fractionated and then dried to obtain the low molecular weight fraction. For a solvent to be used for this technique, it had to be primarily a non-solvent for PVC, so that only the VC oligomers remained in solution. Furthermore, it had to have a relatively low boiling point to facilitate solvent 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 for the VC oligomers[63]. Pentane was

chosen as its solubility parameter of 6.3 $(cal/cm^3)^{0.5}$ makes it a non-solvent for PVC and its low boiling point (36°C) enables it to be easily removed by rotary evaporation techniques.

Pentane proved to be very effective at isolating a low molecular weight fraction. 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 solvent than pentane. The small differences in volume in which the Soxhlet extract remained solvated (Section 2.1.11) 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 little 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.

3.1.4 Molecular weight determination of Lucovyl RB8010 Soxhlet extracts

The PVC Soxhlet extract was characterised using the method described in Section 2.1.12. Molecular weight data (polystyrene equivalent) are given in Table 11.

Table 11. Molecular weight data for the Lucovyl RB8010 Soxhlet extracts after fractional precipitation.

Sample	Extraction solvent	Mn	Mw	Mp
RB8010	Diethyl ether	578	616	525

3.1.5 Purification of the low molecular weight PVC fraction isolated from the diethyl ether Soxhlet extract

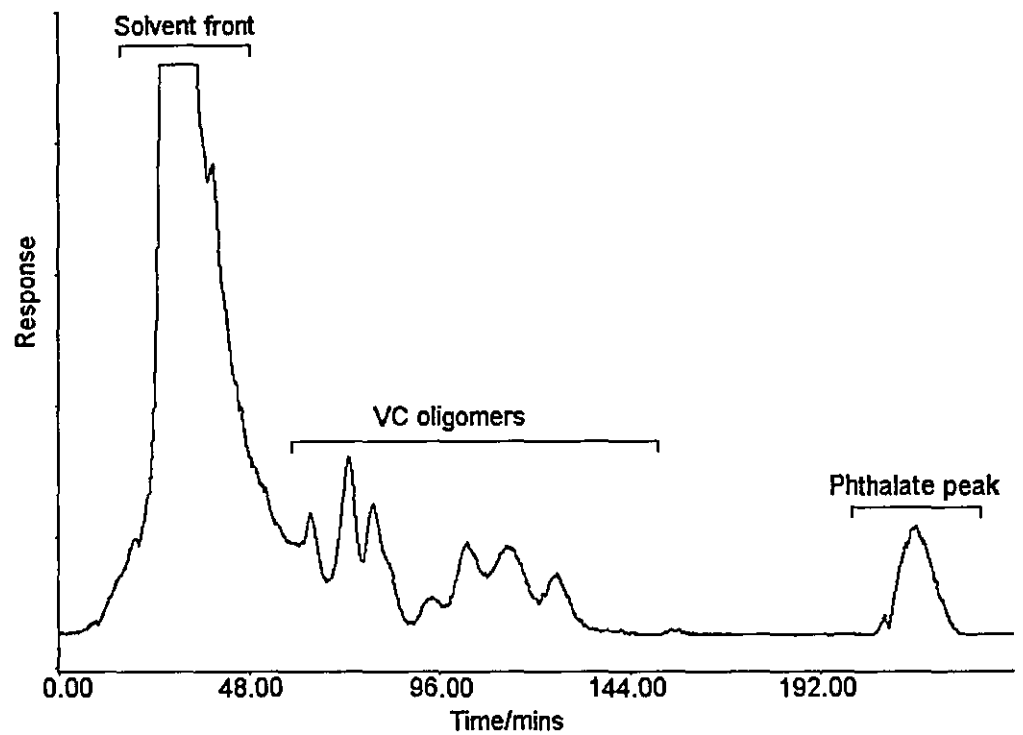
It was known[207] that SEC was incapable of resolving the VC oligomers in the low molecular fraction because of impurities from the PVC co-eluting with the VC oligomers. An impurity previously identified was a phthalate compound. The fractions due to VC oligomers had also been identified[40]. The absence of any discernible concentration of VC dimer and trimer were considered to be due to the monomer stripping process (Section 1.3.5.2). It was possible to assign the oligomeric peaks by using VC oligomers as calibrants because the pentamer to decamer oligomers had been prepared and described in previous work[37].

Further chromatographic techniques were then employed to purify the low molecular weight extract prior to SEC analysis. A semi-preparative adsorption liquid chromatographic system, which is described in Section 2.1.13, was used to separate the VC oligomers in the low molecular weight fraction which had been isolated from the diethyl ether Soxhlet extracts by fractional precipitation (Section 2.1.11). The chromatogram obtained for the low molecular weight PVC fraction is shown in Figure 8.

It can be seen that the phthalate impurity and oligomer fractions collected are well separated owing to the greater polarity, and hence longer retention time of the phthalate compound. The quantity of MTBE modifier in the mobile phase was set at 5% v/v. To enable separations to be carried out in reasonable times whilst maintaining sufficient oligomer-phthalate resolution, the elution volume range designated in Figure 8 for collection was derived by determining the volume required for all of the VC decamer isomers to elute from the column. As elution time is proportional to

oligomer chain length, this ensured that none of the isomers of the oligomers of greatest interest, i.e. pentamer, hexamer and heptamer were missed.

Figure 8. Preparative adsorption liquid chromatography of low molecular weight fraction from n-pentane filtrate. Mobile phase: n-hexane : MTBE (95:5) at 3.0 ml/min



3.1.6 SEC analysis of the low molecular weight fraction obtained by Soxhlet extraction

After the low molecular weight fraction had been purified by adsorption liquid chromatography, SEC was performed on the low molecular weight fraction with dichloromethane as the eluent (Section 2.1.14). An SEC chromatogram of the low molecular weight fraction obtained from Lucovyl RB8010 using 120 cm of gel bed is shown in Figure 9.

With an alternate pumping recycle technique[69], resolution of the VC oligomers was improved using 300 cm (1½ recycles) of gel bed. The chromatogram obtained is shown in Figure 10, where the oligomer species from tetramer to decamer are well separated.

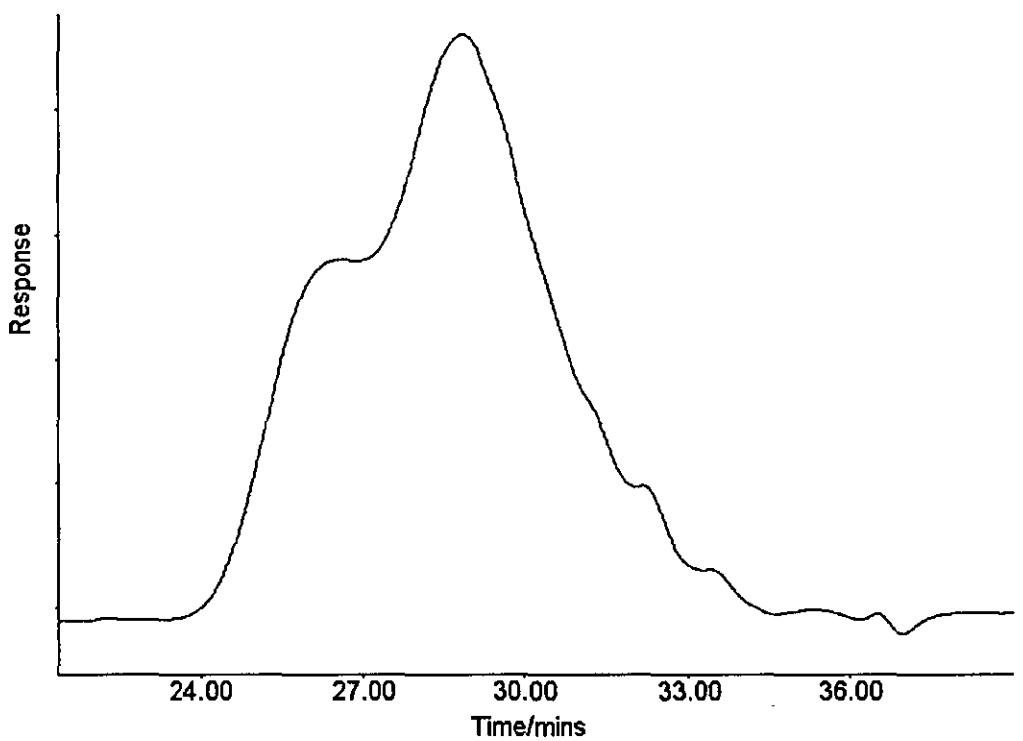
The assignments of the oligomer peaks in Figure 10, were confirmed by referring to data that had been published previously[74] and by direct comparison with chromatograms and retention time data with SEC analysis performed on the Lucovyl RB 8010 PVC sample utilising identical conditions in previous work[207]. To investigate this further, the pentamer was accumulated by fractionating the purified low molecular weight fraction designated in Figure 10. The polyisomeric nature of the VC oligomers necessitated the development of a chromatographic technique for resolving each entity prior to an attempted structural characterisation by NMR. Such a combination of HPLC and ^{13}C NMR analysis has been reported for 2-vinyl pyridine oligomers[208]. Liquid-solid chromatography had also been used for isomer separation[209].

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. Owing to the non-polar nature of the VC oligomers, a normal-phase HPLC silica column containing Spherisorb S5W was chosen in conjunction with a variable UV detector. Hexane was chosen as the mobile phase because its low UV cut-off point (195 nm) enabled the UV detector to be used at 200 nm. A succession of experiments was then carried out by varying the amount of MTBE modifier in the mobile phase in order to find the ratio of *n*-hexane : MTBE which promoted interaction between the pentamer isomers and the

column packing optimising isomer separation. The results showed that a mobile phase composition consisting of *n*-hexane : MTBE (99:1) afforded the best isomer separation as illustrated in Figure 11.

The chromatogram in Figure 11 shows four well-resolved peaks. The initial peaks in the chromatogram represent the solvent front which is a feature of low wavelength UV detection. The four peaks were fractionated and have been analysed by GC-MS[207].

Figure 9. SEC of low molecular weight fraction from n-pentane after semi-preparative adsorption liquid chromatography. Column, 120 cm PL gel (5 mm, 50 Å), eluted with dichloromethane at 1.0 ml/min



Having established which fractions represented VC pentamer isomers, HPLC fractionation of the VC pentamer from SEC was carried out by repeated injections to accumulate a sufficient mass of each isomer for NMR analysis.

Figure 10. SEC of low molecular weight fraction from n-pentane after semi-preparative adsorption liquid chromatography. Column, 300 cm PL gel (5 μm, 50 Å), eluted with dichloromethane at 1.0 ml/min

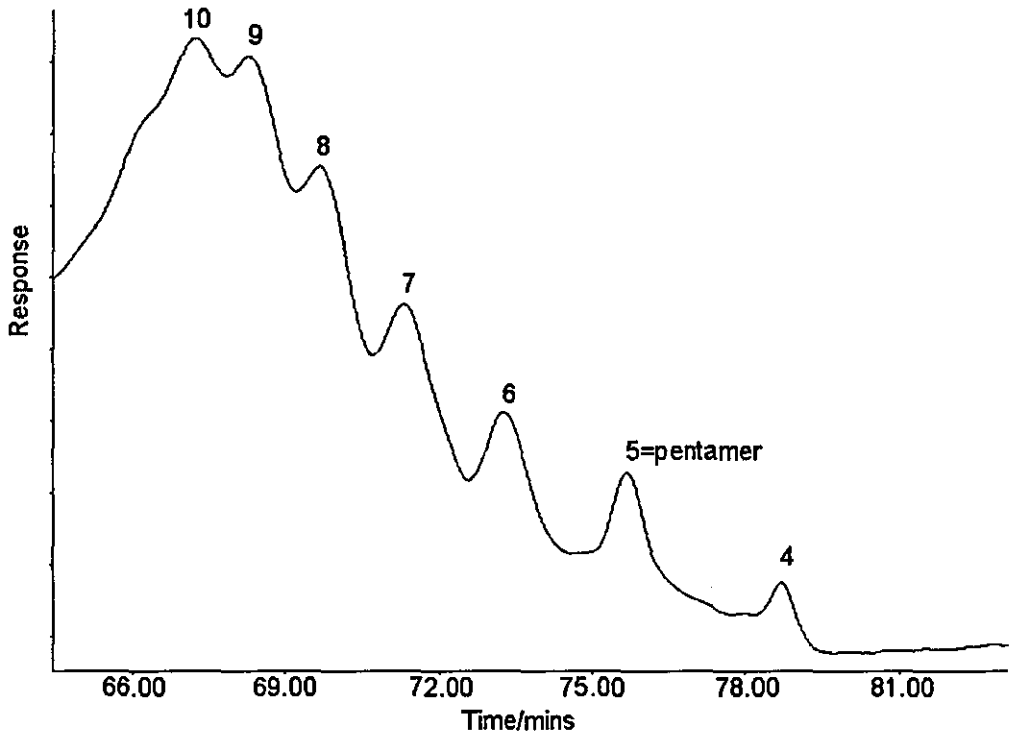
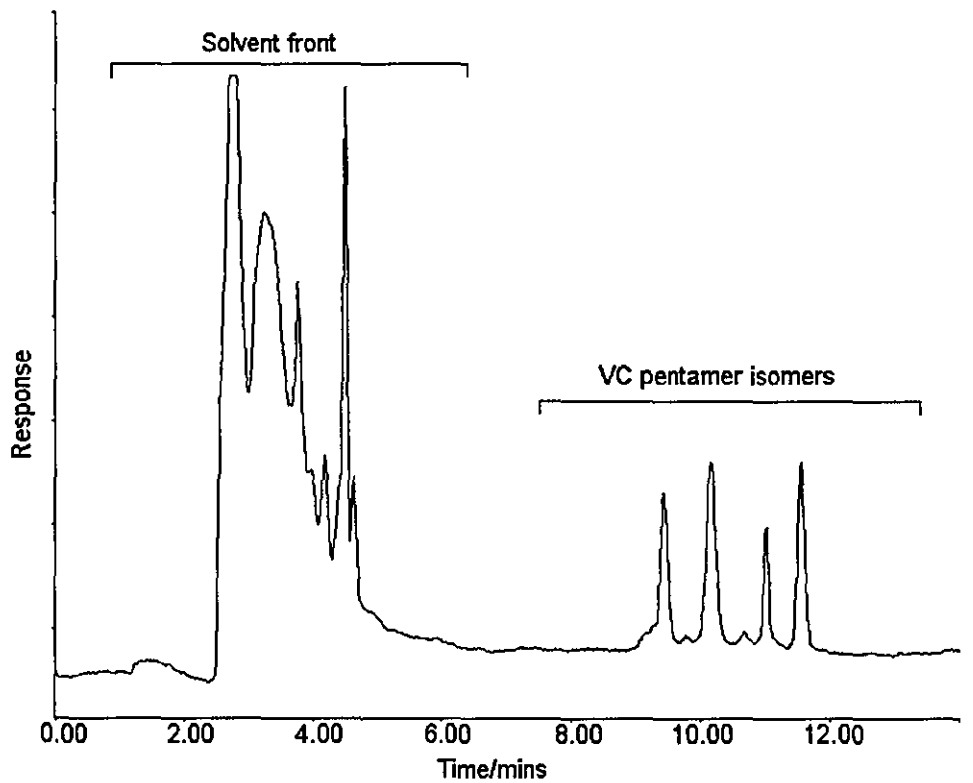


Figure 11. HPLC of the VC pentamer fraction. Mobile phase: n-hexane : MTBE (99:1) at 1.0 ml/min



This method proved to be very time consuming because of the large number of steps involved, the considerable sample handling and the small mass of oligomer available. Another consideration was the inherent thermal instability of VC oligomers and so only chromatographic techniques that functioned at ambient temperatures could be utilised. Regrettably, insufficient isomer was collected to allow NMR studies to be performed.

3.1.7 Separation of oligomers present in Lucovyl RB8010 by coupled column chromatography

The principle limitation of the previous method was the small amount of VC oligomer available and the requirement for repeated fraction collection to obtain sufficient mass if successful structural studies were to be performed using NMR. It was attempted to improve and extend the separation scheme so that it would be possible to achieve a full structural characterisation of VC oligomers from pentamer to heptamer. Because of the requirements of NMR, the existing separation scheme was modified to incorporate a coupled column system.

This system comprised an SEC apparatus which was coupled directly on-line to the HPLC chromatograph bypassing the need for any additional sample handling. By eliminating sample waste, the efficiency of the analysis increased reducing the need for multiple fraction collection. Efforts were directed at duplicating the results obtained for the pentamer fraction by the coupled column system and then applying this coupled technique to the hexamer and heptamer fractions of the low molecular weight extract.

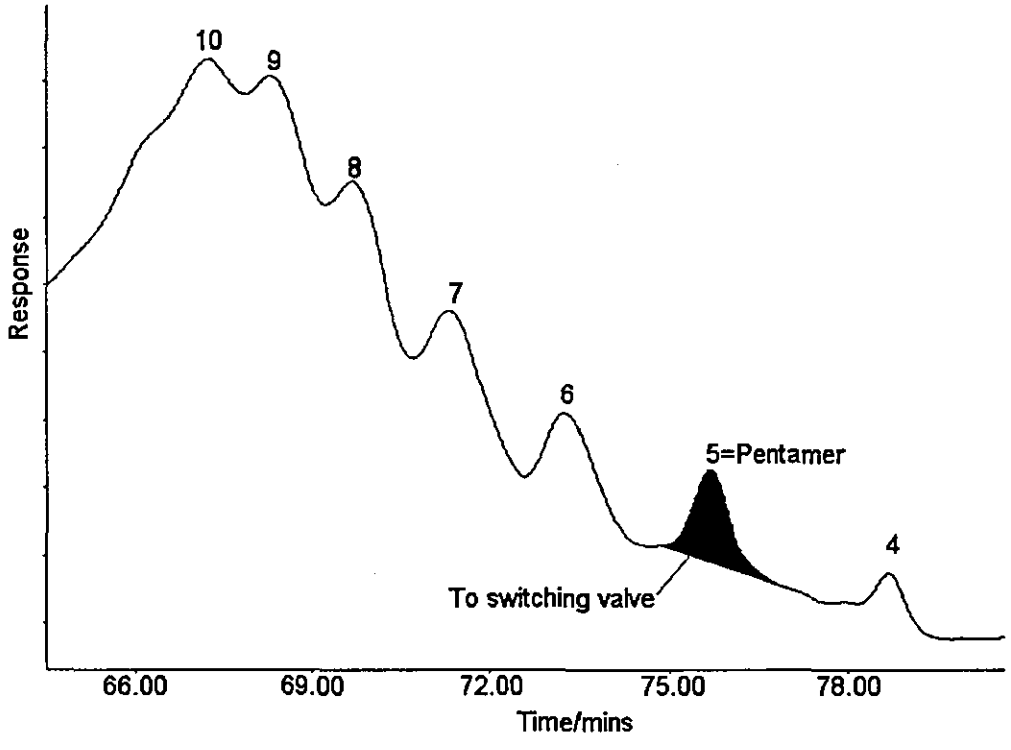
The coupled column work initially utilised MTBE as the modifier in the HPLC system. However, when this work was performed, the laboratory room temperature was above normal (due to faulty heating) at about 30°C. This caused considerable volatilisation of the solvents resulting in gassing of the *n*-hexane : MTBE eluent in the HPLC solvent delivery system. This had the effect of creating pumping and detection problems. In order to progress as rapidly as possible, an alternative solvent to MTBE was required. The alternative solvent needed to have a similar UV cut-off point (210 nm) and polarity index (2.5) to MTBE but have a higher boiling point (55°C) in order to minimise volatilisation. A number of solvent systems were evaluated. However, a *n*-hexane : *iso*-propanol system proved stable at these elevated temperatures and was subsequently used (*iso*-propanol: b.p. 82°C, UV cut-off 210 nm, polarity index 3.9). (Note: the polarity index is an arbitrary scale from 0.0 to 9.0 which is gaining considerable usage in HPLC. Hydrocarbons such as *n*-hexane have a value of 0.0 whereas water has a maximum value of 9.0).

Because of the resulting change in mobile phase composition, a new method had to be developed for the pentamer oligomer isomer separation. The normal-phase HPLC column containing Spherisorb S5W silica was retained with UV detection set at 200 nm. A succession of experiments were then carried out by varying the amount of *iso*-propanol modifier in the mobile phase in order to find the ratio of *n*-hexane : *iso*-propanol which promoted interaction between the pentamer isomers and the column packing optimising isomer separation. The results showed that a mobile phase composition consisting of *n*-hexane : *iso*-propanol (96:4) at a flow rate of 0.9 ml/min afforded the best isomer separation. As in the previous method, the low molecular weight fractions isolated from Lucovyl RB8010

base resin by diethyl ether Soxhlet extraction followed by fractional precipitation were analysed by recycle SEC as shown in Figure 12.

As the pentamer fraction eluted from the SEC chromatograph, the switching valve that connected the SEC to the HPLC was rotated diverting the eluting peak into the HPLC system. Once this was accomplished, the switching valve was rotated back. The chromatogram obtained for the pentamer isomers is shown in Figure 13.

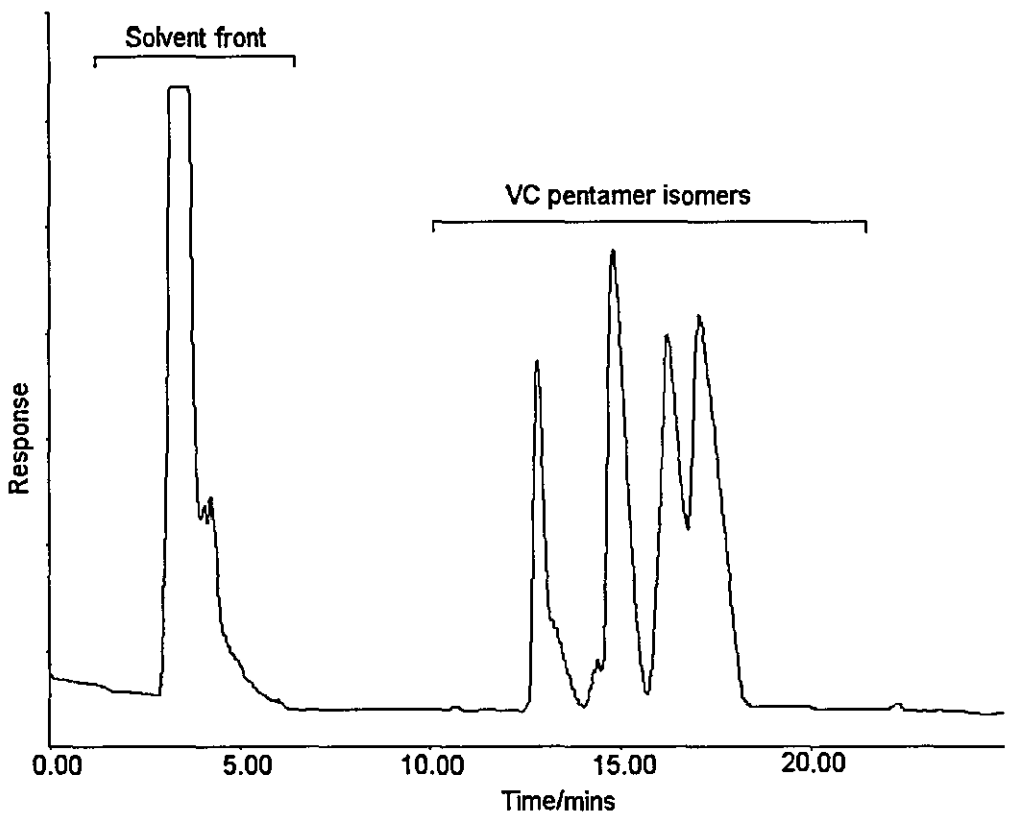
Figure 12. SEC of low molecular weight fraction from n-pentane filtrate utilising coupled column technique. Column, 300 cm PL gel (5 μm, 50 Å), eluted with dichloromethane at 1.0 ml/min



It is evident by comparing Figures 10 and 11 with Figures 12 and 13 that there is good agreement between the two techniques. The slight increase in retention times of the isomers in Figure 13 compared to Figure 11 can be attributed to the participation of dichloromethane, the eluent from the SEC system, the use of *iso*-propanol (4.0%) as the modifier rather than MTBE

and differences in the void volumes of the two systems. These results indicate that the choice of *iso*-propanol as a modifier for the coupled column system provided comparable resolution to MTBE.

Figure 13. HPLC of the VC pentamer fraction obtained by coupled column technique. Mobile phase: n-hexane : iso-propanol (96:4) at 0.9 ml/min



The coupled column technique was then applied to the hexamer and heptamer oligomer fractions as shown by the chromatograms in Figures 14 and 15. Preliminary studies indicated the presence of isomeric species.

It was found that the hexamer isomer separation improved if the concentration of the polar modifier, *iso*-propanol, was decreased to 2% and the mobile phase flow rate decrease to 0.6 ml/min.

Figure 14. HPLC of the VC hexamer fraction obtained by coupled column technique. Mobile phase: n-hexane : iso-propanol (98:2) at 0.6 ml/min

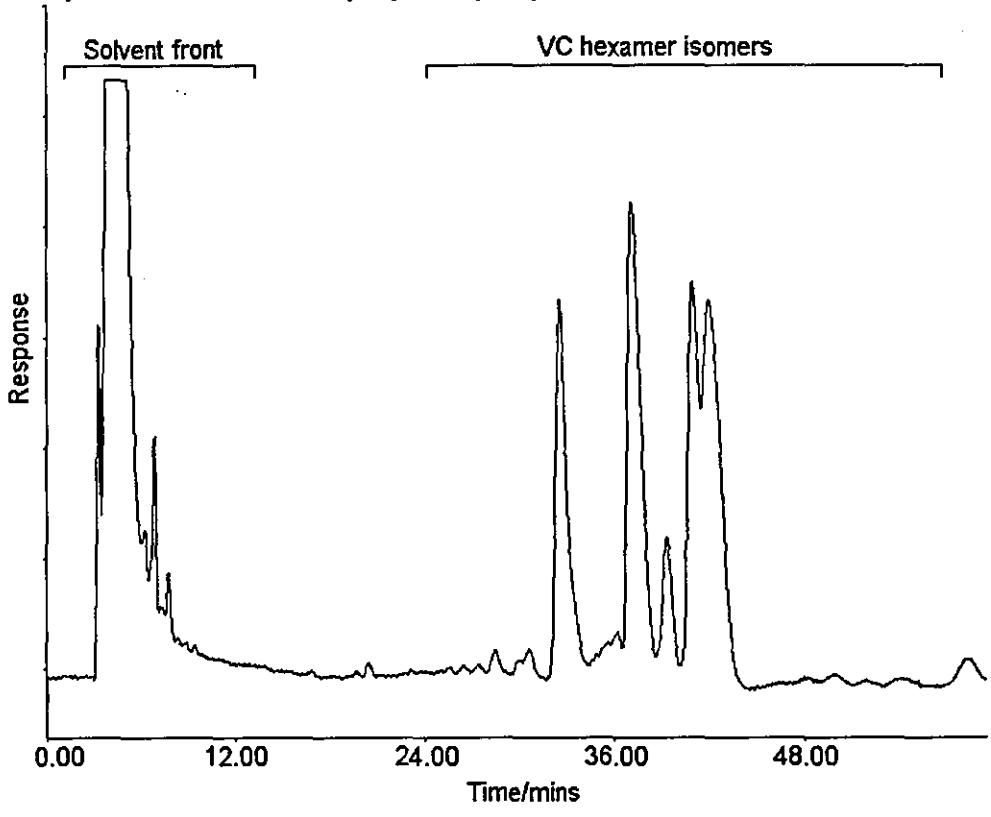
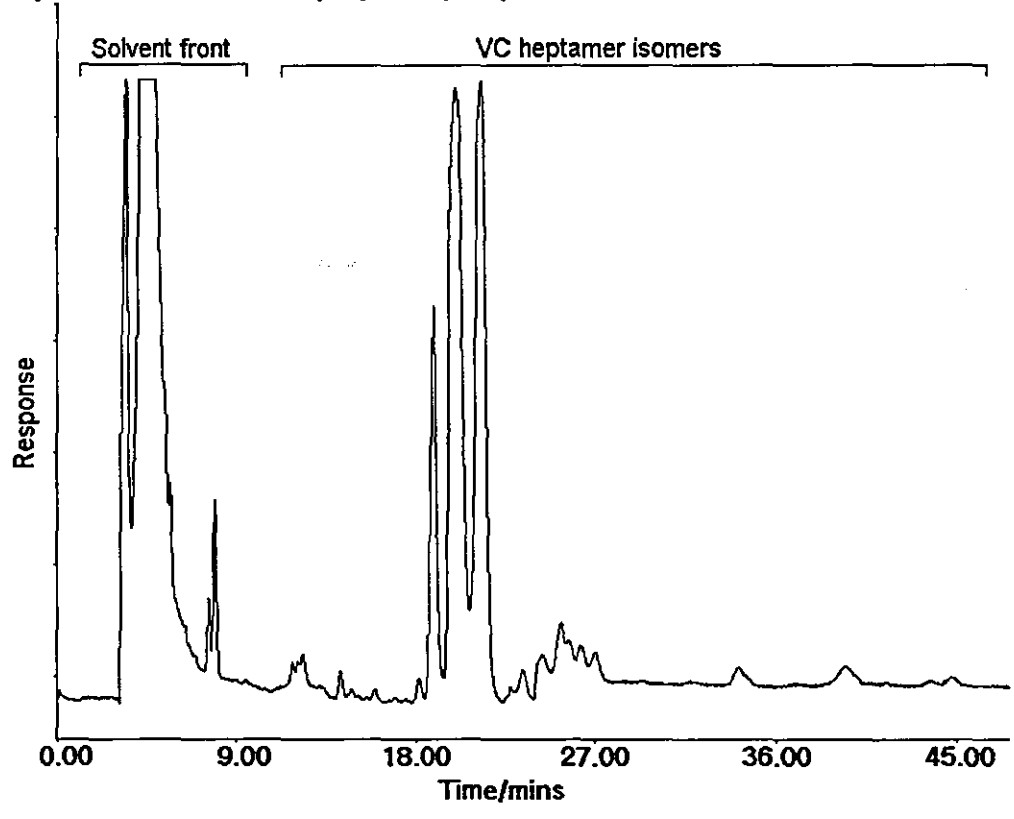


Figure 15. HPLC of the VC heptamer fraction obtained by coupled column technique. Mobile phase: n-hexane : iso-propanol (96:4) at 1.0 ml/min



At the 4% level utilised for the pentamer and heptamer oligomer fractions, the hexamer isomers were not interacting with the column packing to the same extent, which resulted in inferior resolution. The results obtained for the hexamer and heptamer fractions using this coupled column technique are consistent with data obtained utilising other techniques[207].

However, it has been demonstrated, by a series of fractionation procedures utilising a number of chromatographic techniques, relatively pure VC oligomer isomers can be isolated from a PVC polymer. The results show that, even for the VC oligomer pentamer, at least four isomeric forms exist. By using this preparation scheme, it is possible to accumulate a sufficient quantity of each VC oligomer to enable NMR to be employed as a characterisation method. This work has also shown that coupled column chromatographic techniques are feasible and could be used for the analysis of targeted species within complex samples. PVC oligomers from pentamer to heptamer have been resolved successfully into their constituent isomers. Further work is planned to characterise these isomers fully.

3.2 Nitrile rubber

3.2.1 Large scale extraction of NBR

Large scale Soxhlet extractions were performed on a sample of NBR using methods described in Section 2.2.10. The extraction results are shown in Table 12.

Table 12. Large scale extraction results of NBR.

Sample (30 g)	Solvent	B.P./°C	Extract/ %	Extract Colour
NBR	*n*-hexane	68	15.66	Dark Yellow
NBR	*iso*-octane	99	15.00	Yellow

3.2.1.1 Hexane extractables

The total amount of material Soxhlet extracted with *n*-hexane from finely shredded NBR was 15.66% (duplicate values of 15.71 and 15.61).

3.2.1.2 Iso-octane extractables

The total amount of material Soxhlet extracted with *iso*-octane from finely shredded NBR was 15.00% (duplicate values of 14.91 and 15.09). The theoretical extract based on the level of additive addition and assuming that all of the sulphur is present in the polymer network is 9.4%. These results indicate that solubles associated with the polymer have also been extracted.

3.2.2 Molecular weight determination of NBR Soxhlet extracts

The NBR Soxhlet extract was characterised using the method described in Section 2.2.11. Molecular weight data (polystyrene equivalent) for the *n*-hexane and *iso*-octane Soxhlet extracts are given in Table 13.

Table 13 Molecular weight data for the *n*-hexane and *iso*-octane Soxhlet extracts.

Sample	Extraction Solvent	Mn	Mw	Mp
NBR	*n*-hexane	542	633	508
NBR	*iso*-octane	505	620	475

Both extracts appear to have a molecular weight less than 700. Only the *iso*-octane Soxhlet extracts from NBR will be the subject of further investigation in this section, since *iso*-octane is a specified non-polar solvent used in studies of migration from food contact polymers.

3.2.3 GC-MS analysis of NBR low molecular weight extract

GC-MS analysis was performed upon the NBR Soxhlet extract using the method described in Section 2.2.13. The chromatogram and identified mass spectra obtained for the major components in the extract are given in Figures 16-20. A summary of this information is given in Table 14. The main mass fragmentations associated with the mass spectra have also been assigned.

Table 14. Identified components present in *iso*-octane Soxhlet extract of NBR by GC-MS.

Retention Time/ Mins	Assignment
21.853	N-isopropyl-*n*'-phenyl-*p*-phenylenediamine
24.404	2,2' -methylenebis (4-methyl-6-tert.butylphenol)
25.979	Di 2-ethylhexylphthalate
28.230	4,4'-thio-bis-(3-methyl-6-tert.-butylphenol)

Figure 16. GC of NBR low molecular weight extract

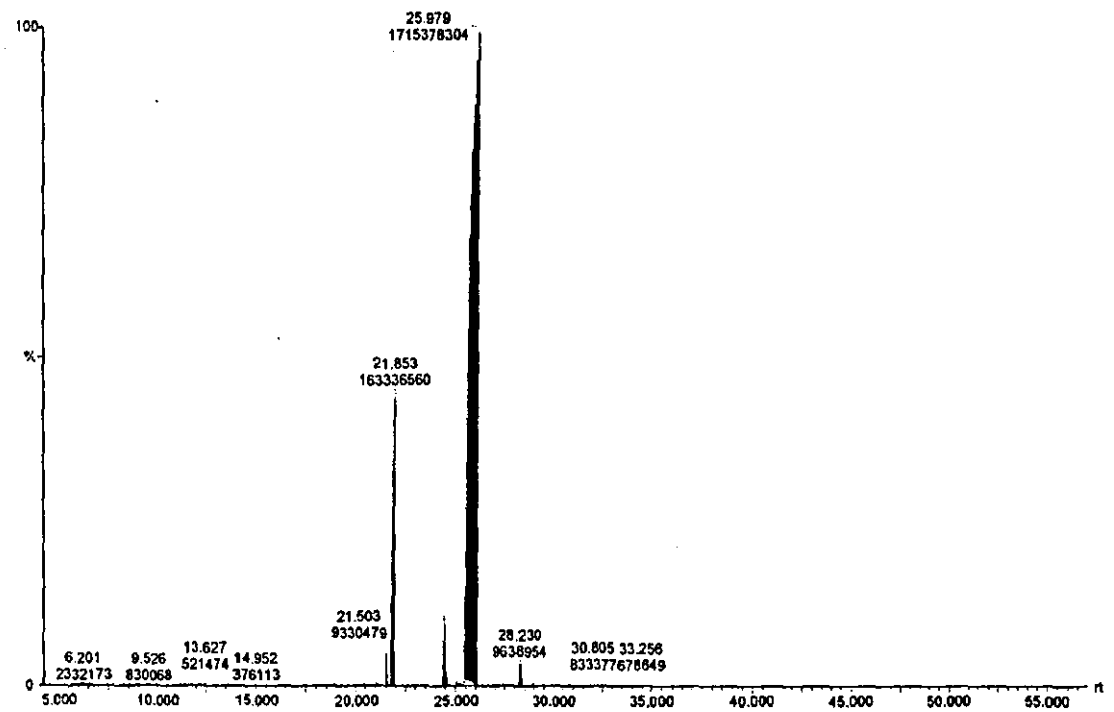
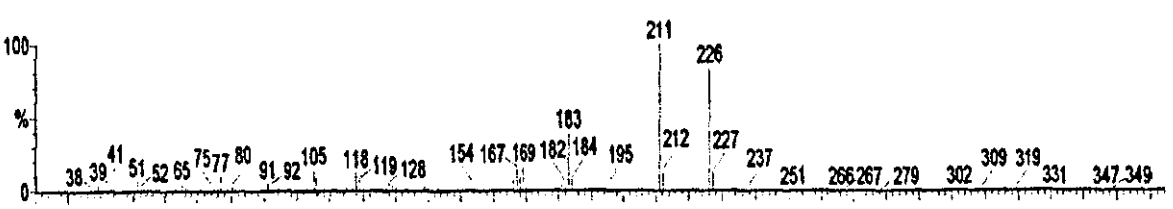


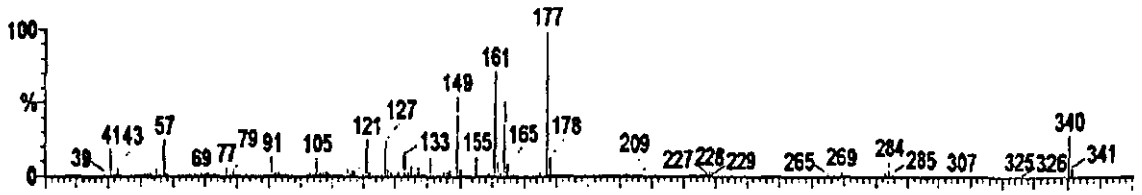
Figure 17. Mass spectra of N-isopropyl-n'-phenyl-p-phenylenediamine (RT 21.853)



m/z*	Structure	m/z	Structure	m/z	Structure
226	$CH_3CH(CH_3)NHC_6H_4NHC_6H_5$)	183	$^+NHC_6H_4NHC_6H_5$	168	$C_6H_5N^+C_6H_5$
211	$^+CH(CH_3)NHC_6H_4NHC_6H_5$	169	$C_6H_5NH^+C_6H_5$		

**** m/z - mass of the ion divided by its charge (usually unity)***

Figure 18. Mass spectra of 2,2' -methylenebis (4-methyl-6-tert.butylphenol) (RT.24.404)



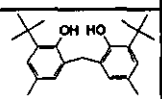
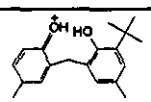
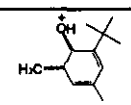
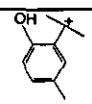
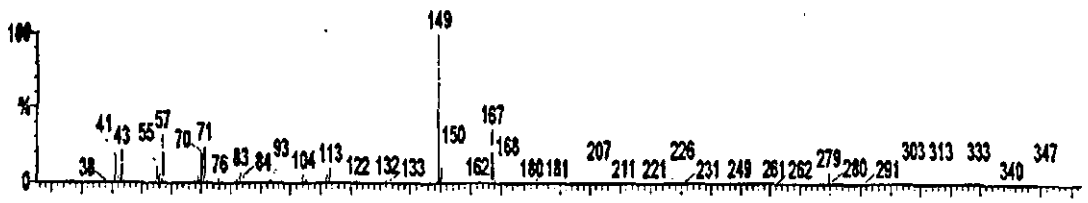
m/z	Structure	m/z	Structure	m/z	Structure	m/z	Structure	m/z	Structure
340		284		177		164		149	

Figure 19. Mass spectra of di 2-ethylhexylphthalate (RT 25.979)



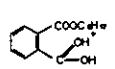
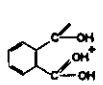
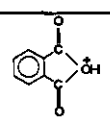
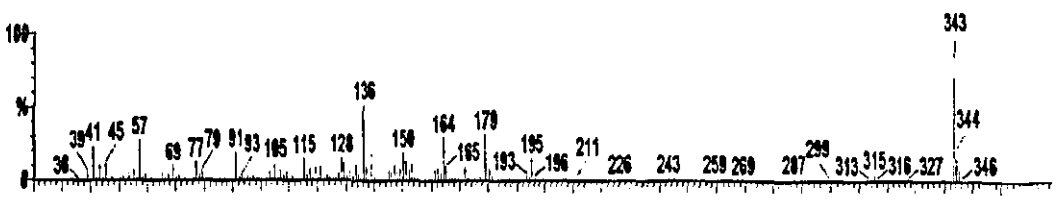
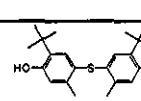
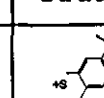
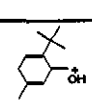
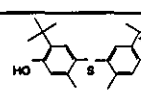
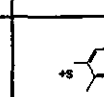
m/z	Structure	m/z	Structure	m/z	Structure
279		167		149	

Figure 20. Mass spectra of 4,4'-thio-bis-(3-methyl-6-tert.-butylphenol) (RT 28.230)



m/z	Structure	m/z	Structure	m/z	Structure
358		195		164	
343		179		136	

It can be seen from the chromatogram in Figure 16 that the peak corresponding to di 2-ethylhexylphthalate has the largest response. The

peak height ratioing performed by the GC-MS computer software had the effect of increasing the signal to noise ratio of the scan so that most of the other peaks detected were lost in the base-line noise. It was decided therefore that direct GC-MS analysis was not appropriate for this sample due to the high phthalate content. In order to overcome this problem, the extract was fractionated using HPLC with UV detection. GC-MS was then performed on the fractions collected to aid identification of the species present in the extract.

3.2.4 Analysis of NBR low molecular weight Soxhlet extractables by HPLC

From the GC-MS data obtained for the extract in Section 3.2.3, it was uncertain whether reversed phase or normal phase chromatography would provide the best separation of the components in the extract. This uncertainty was mainly due to the wide range of functionalities that were known to be present. It was therefore decided to try both chromatographic techniques to find an optimum separation method. A number of key papers and standard methods of particular relevance to the HPLC of NBR vulcanisation agents and their reaction products isolated via Soxhlet extraction have been identified in the literature as reviewed over-page. Although the presence of these compounds went undetected during the initial GC-MS analysis of the NBR soxhlet extract, it was known that they can be observed in extracts from cured rubber materials. Such products can be reactive and are frequently thermally labile. Because of this, examination of accelerator residues is normally undertaken using HPLC with UV detection. References to reverse phase chromatography using C_{18} or phenyl bonded silica columns and acetonitrile : water, methanol : water or THF : water mixtures predominate in the literature.

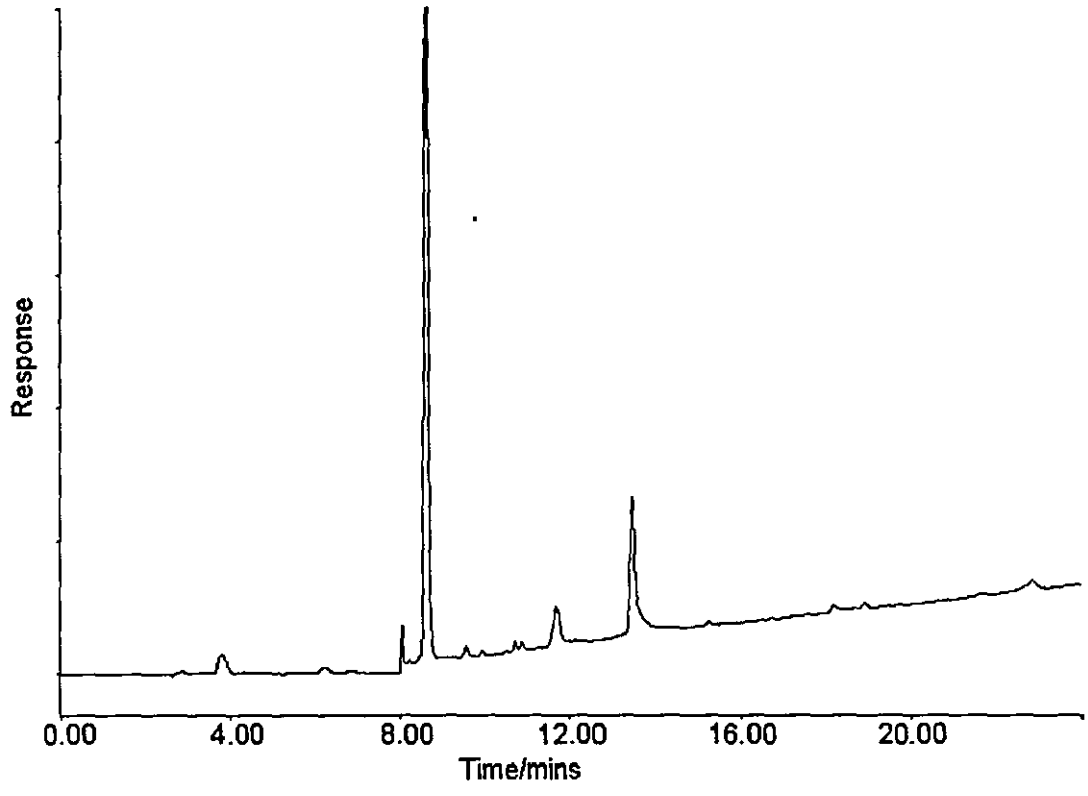
Datta and Basu[210] reported the separation on C_{18} silica columns with 70:30 acetonitrile water eluent of the mercaptobenzothiazole disulphide accelerator present in the NBR formulation (Section 2.2). Kretzschmar *et al.*[211] also examined the reaction products of the thiuram accelerator tetra methylthiuram (TMTD) disulphide using C_{18} columns and methanol : phosphate buffer gradients (pH 7).

Hann *et al.*[212] examined the cure products from a natural rubber sample cured with N-t.butyl-2-benzothiazole sulphenamide) using C_{18} with acetonitrile : water : 0.005M acetic acid mobile phase.

It has also been reported[213] that accelerators in cured and un-cured compounds were identified utilising GC and TLC procedures. In addition to the analysis of cured products present in NBR by HPLC, procedures for determining mineral hydrocarbon migration into various food types have been published[214]. Wax migration from NBR could be examined by the procedures described. A paper has also been published[215] which outlines procedures employed in a survey of di 2-ethylhexylphthalate in various dairy products. These procedures could be used for the determination of di 2-ethylhexylphthalate in the *iso*-octane Soxhlet extract.

Reversed phase studies were performed with a HPLC cartridge column (15 cm x 3.9 mm) containing Nova-pak C_{18} 60 Å 4μm supplied by Waters Millipore Corporation, (USA). These separations were performed both isocratically and in gradient mode. After a succession of experiments utilising a range of mobile phase compositions, optimum separation conditions were found which consisted of a THF : water gradient (50-100% THF) at 1 ml/*min* with UV detection between 200 and 254 nm.

Figure 21. HPLC of NBR extract using a C_{18} column with a THF : water gradient (50-100% THF) in 30 mins at 1 ml/min with UV detection set at 254nm with 1% w/v aliquots injected onto the system

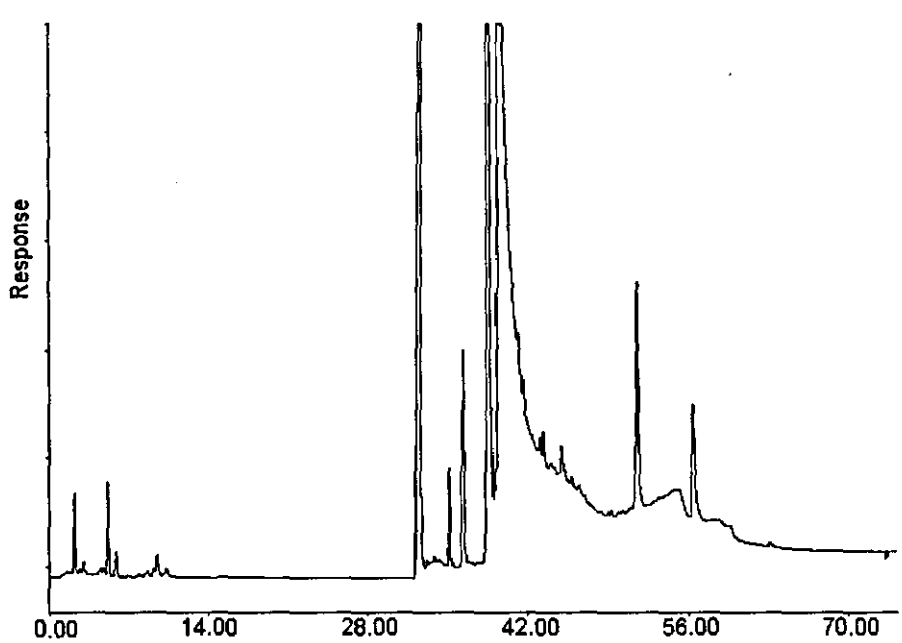


Initial studies demonstrated that reversed phase chromatography provided reasonable extract separation. It can be seen in the reversed phase chromatogram, Figure 21, there are five well resolved peaks but also many smaller peaks. It order to speed up the fractionation procedure, the injected concentration was doubled to 2% w/v. This however had the effect of overloading the column and resulted in a poor separation. Although reasonable separations were obtained using 1% w/v injection concentrations, the major limitation with this method was the lengthy process of fractionation. Ideally, the analytical separation should have been scaled up to incorporate a preparative scale column. Unfortunately there were no C_{18} preparative scale columns available.

In order to progress as rapidly as possible with fraction collection, there was a need for preparative scale chromatography. Although, no C_{18} preparative columns were available, there were a number of normal phase semi-preparative columns available in the laboratory. It was decided therefore to direct all efforts towards developing an analytical scale normal phase chromatographic method for the separation of the NBR extract and then to scale up the procedure to incorporate a semi-preparative column.

Normal phase studies were performed with an analytical HPLC column (25 cm x 4.6 mm) containing Spherisorb S5W. These separations were performed isocratically and in gradient mode. A series of experiments were carried out and optimum separation conditions were found to consist of a *n*-hexane : THF gradient (100% *n*-hexane at 25 mins-50% *n*-hexane at 85 mins) at 1 ml/min with UV detection at 254 nm with 5% w/v aliquots injected onto the system.

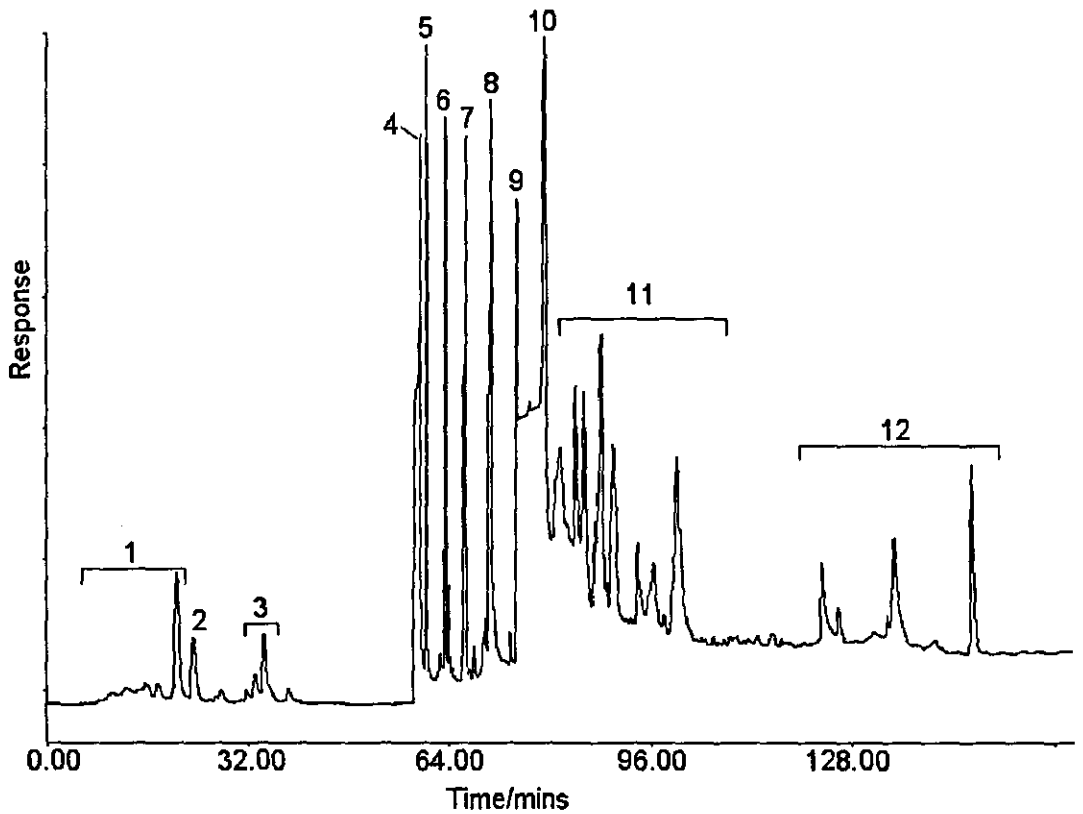
Figure 22. Separation of NBR extract using a S5W analytical column with a n-hexane : THF gradient (100% n-hexane at 25 mins-50% n-hexane at 85 mins) at 1 ml/min with UV detection at 254 nm with 5% w/v aliquot sample



It can be seen from Figure 22 that the normal phase separation of the NBR extract provided a more complex elution profile than the reversed phase separation. The two stage elution profile enabled the non-polar fractions to be separated isocratically in the first half of the separation with 100% *n*-hexane. A gradient was then applied which ran to 50% *n*-hexane at 85 minutes allowing the separation of the more polar compounds. The chromatogram is composed of a number of well resolved peaks and a very broad region which overloaded the detector between 40 and 55 minutes. This broadening effect could be associated with the higher injection volume (5% w/v) in the normal phase separation and increased interaction with the silica stationary phase. There is also, however, a large response from one well resolved peak in the reversed phase chromatogram (Figure 21 at 8.5 mins) which may be attributed to the same species.

It was decided to proceed with normal phase separations and incorporate a semi-preparative scale S5W normal phase column (30 cm x 7.8 mm) into the system with a 2 ml injection loop. The optimum conditions consisted of a *n*-hexane : THF gradient (100% *n*-hexane at 35 mins-50% *n*-hexane at 300 mins) at 2 ml/min with UV detection at 254 nm. The chromatographic system was connected to a Frac-100 fraction collector. Aliquots (10% w/v) were injected and the fractions were then dried in a vacuum oven at room temperature. This procedure was repeated 15 times.

Figure 23. Separation of NBR extract using a semi-preparative S5W column with a n-hexane : THF gradient (100% n-hexane at 35 mins-50% n-hexane at 300 mins) at 2 ml/min with UV detection at 254 nm with 10% w/v aliquots injected onto the system. The collected fractions are indicated on the chromatogram



3.2.5 NBR extract fraction identification from HPLC by GC-MS

The HPLC chromatogram (Figure 23) was fractionated as described in Section 3.2.4. The collected fractions then underwent GC-MS analysis with the conditions described in Section 2.2.13. Figures 24-51 show the respective GC chromatograms with associated mass spectra. It can also be seen that some chromatograms contain species carried over from the previous fraction. When this occurs, it is indicated beneath the respective chromatogram. Table 15. shows a summary of the proposed structures present in the NBR extract.

Table 15. Proposed structures present in the NBR Soxhlet extract

Fraction	Identification By GC-MS
1	Alkanes C_{10}-C_{45} major component tetratetracontane
2	Pyrene
3	Butyl hexadecanoate, Octadecanoic acid, 2-methylpropyl ester
4	Di 2-ethylhexylphthalate
5	2,2' -methylenebis (4-methyl-6-tert.butylphenol)
6	2-tert.-butyl-4-(dimethylbenzyl)phenol
7	Benzothiazole
8	2,4-dimethyl 2,4-heptadienal
9	4,4'-thio-bis-(3-methyl-6-tert.-butylphenol)
10	N-isopropyl-n'-phenyl-*p*-phenylenediamine
11	Various siloxanes
12	Unidentified

It is evident from the following figures that the compounds in fraction 1 produce similar mass spectra. This resulted in only tentative identifications which were obtained from an on-line spectral library search. However, it is possible to state with confidence that the species present in fraction 1 are all alkanes.

Figure 24. GC chromatogram of extract fraction 1

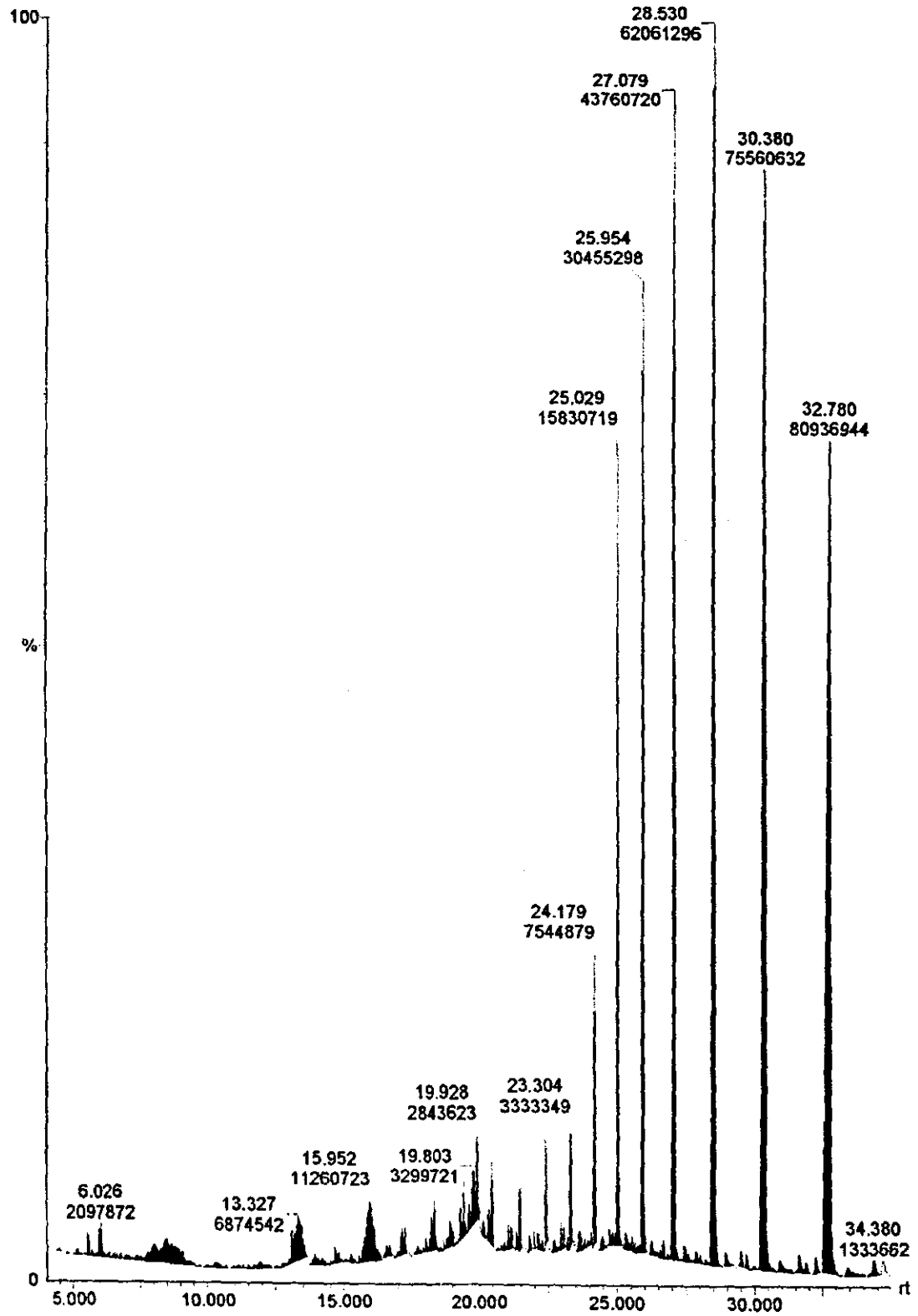


Figure 25. Mass spectra of pentatriacontane (RT 25.029)

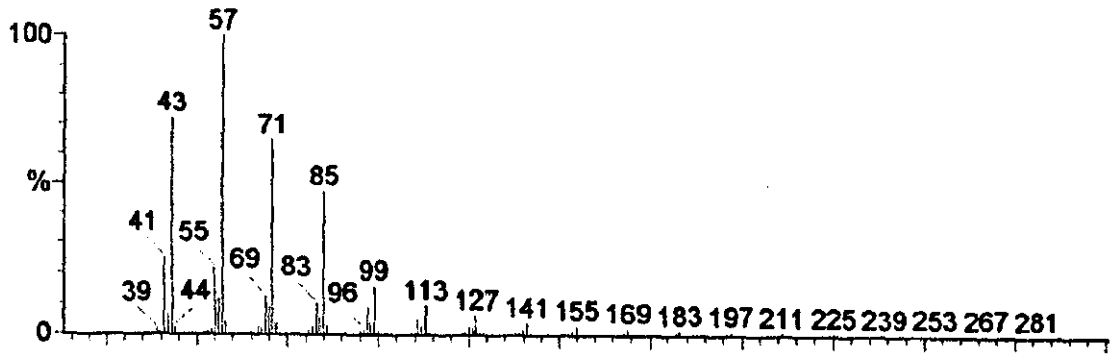


Figure 26. Mass spectra of hexatricontane (RT 27.029)

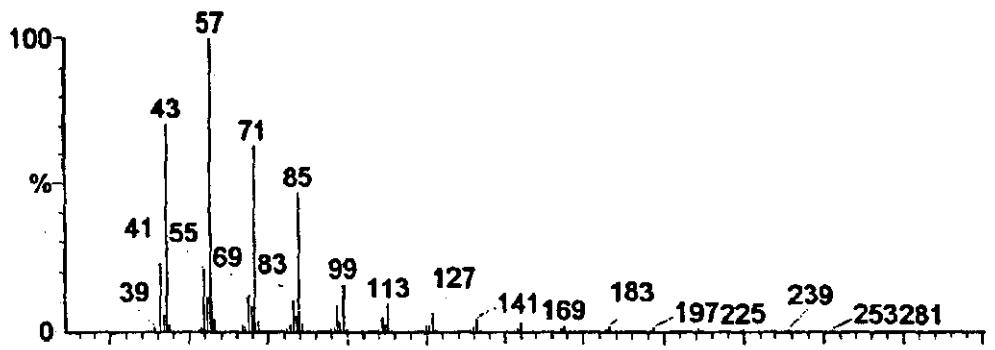


Figure 27. Mass spectra of tetratetracontane (RT 28.530)

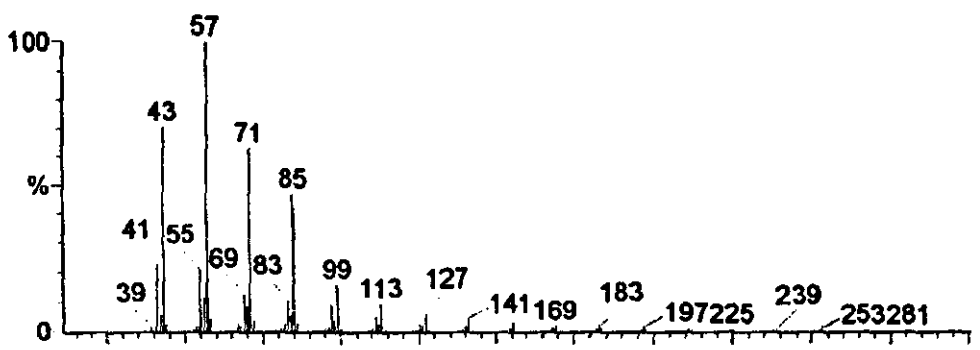


Figure 28. Mass spectra of henicosane (RT 30.380)

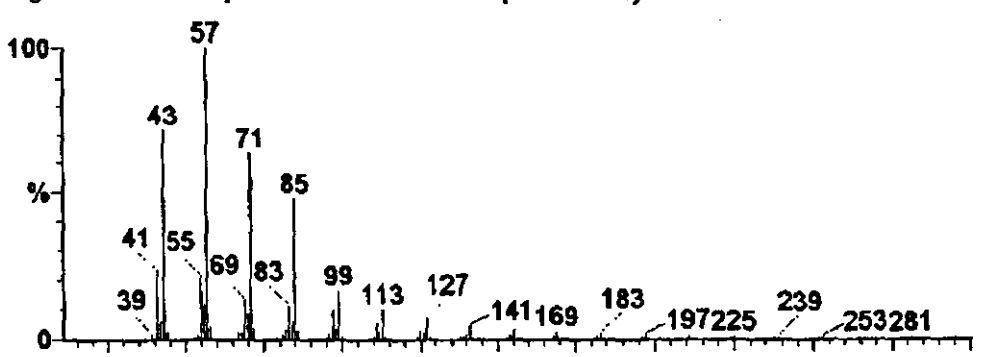


Figure 29. GC chromatogram of extract fraction 2

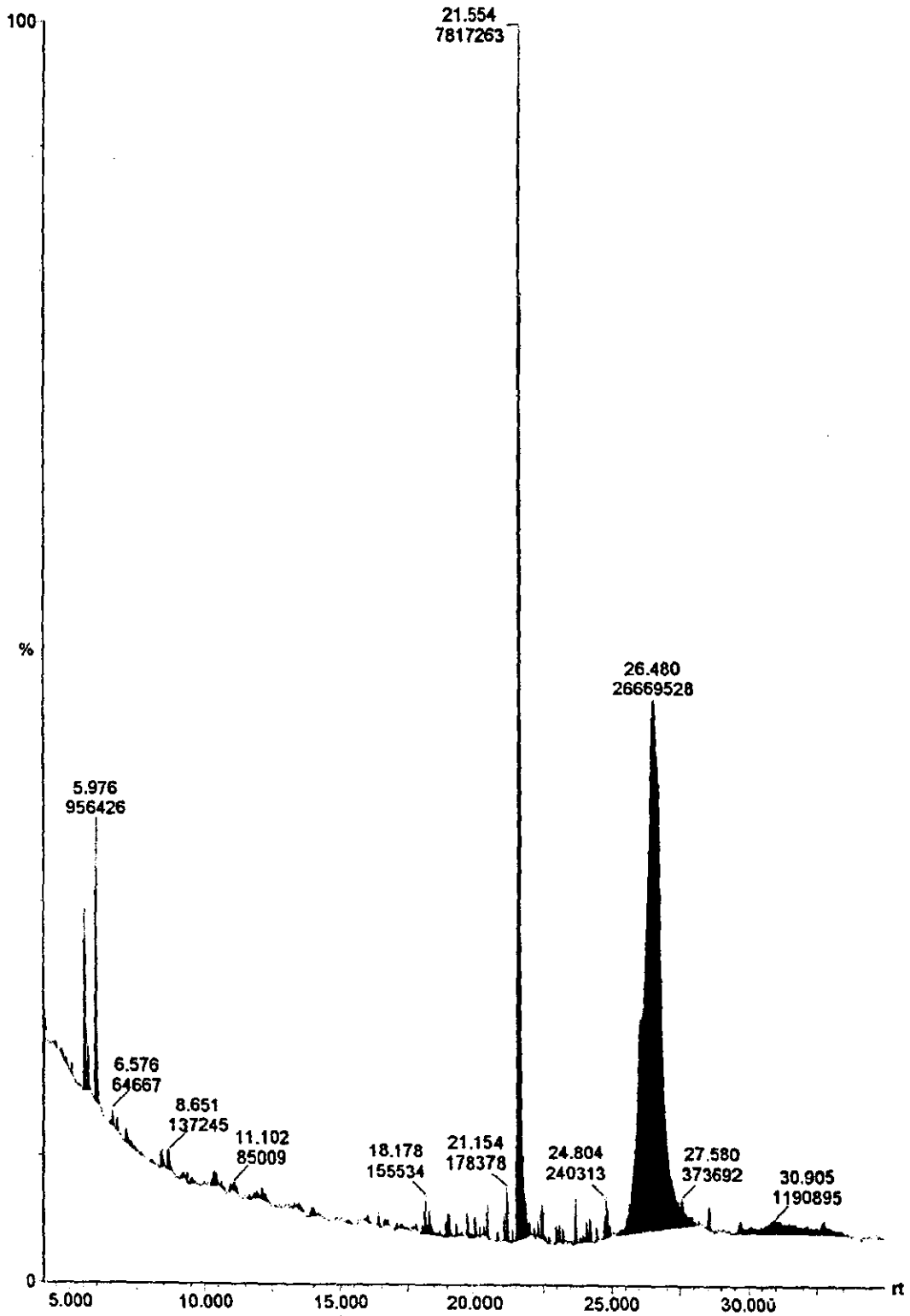
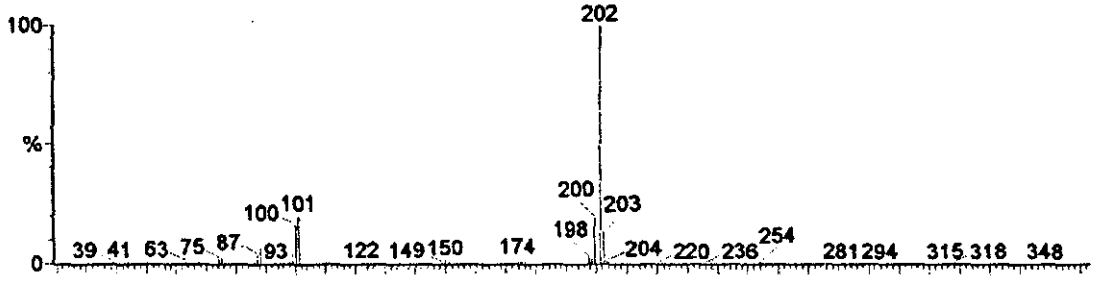


Figure 30. Mass spectra of pyrene (RT 21.554) (tetratetracontane impurity at 26.480 mins)



m/z	Structure	m/z	Structure
202		101*	

*mz 101 Doubly charged molecular ion (m/2z)

Figure 31. GC chromatogram of extract fraction 3

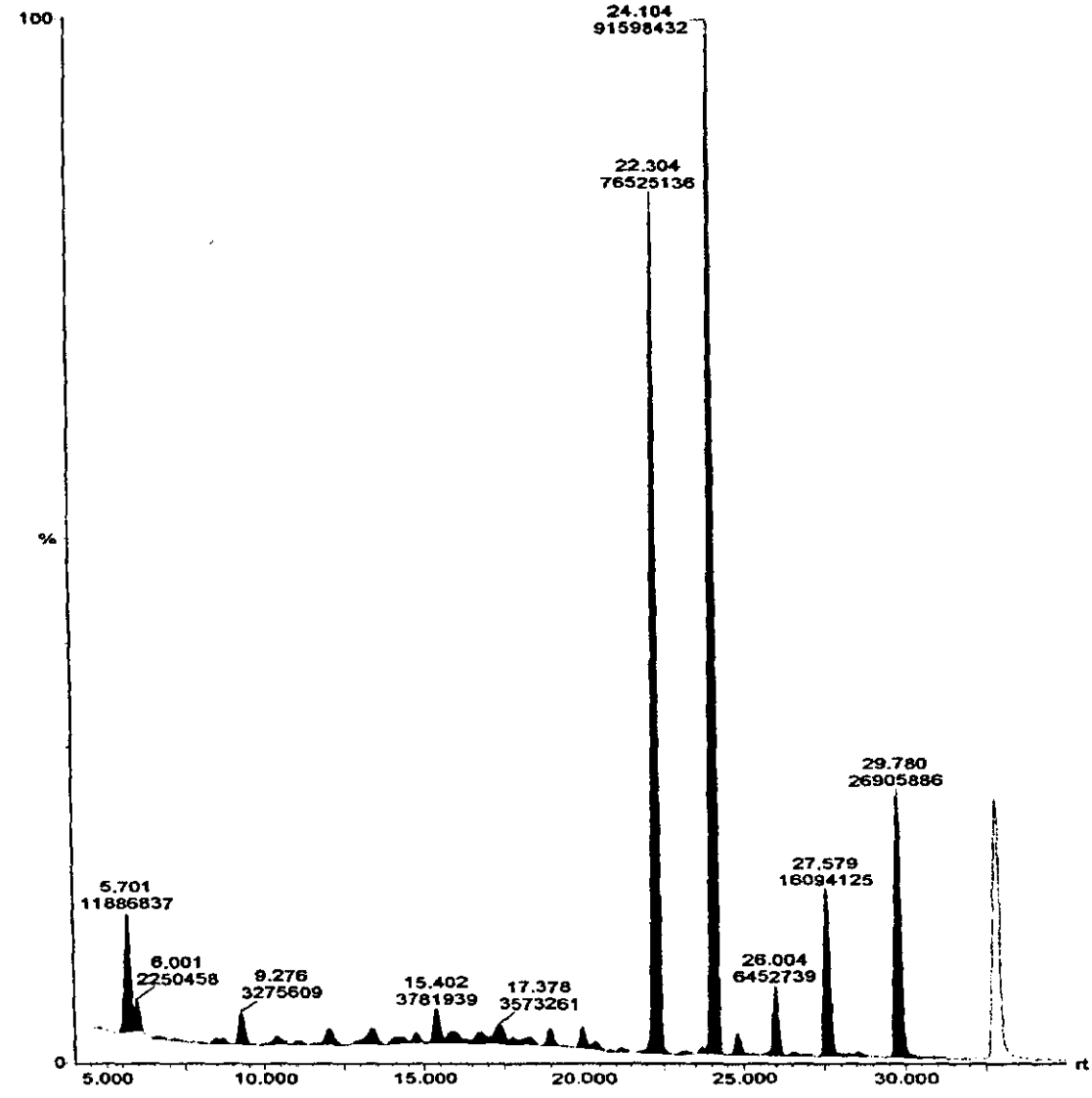
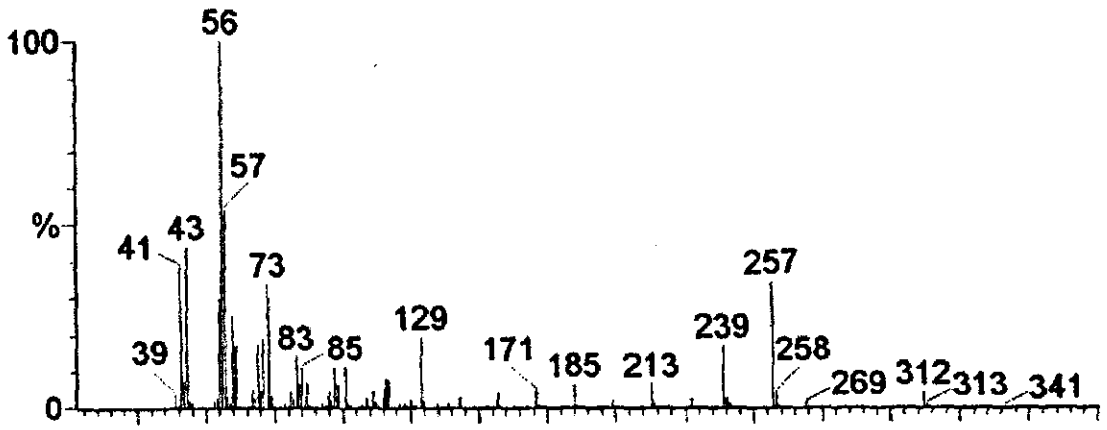
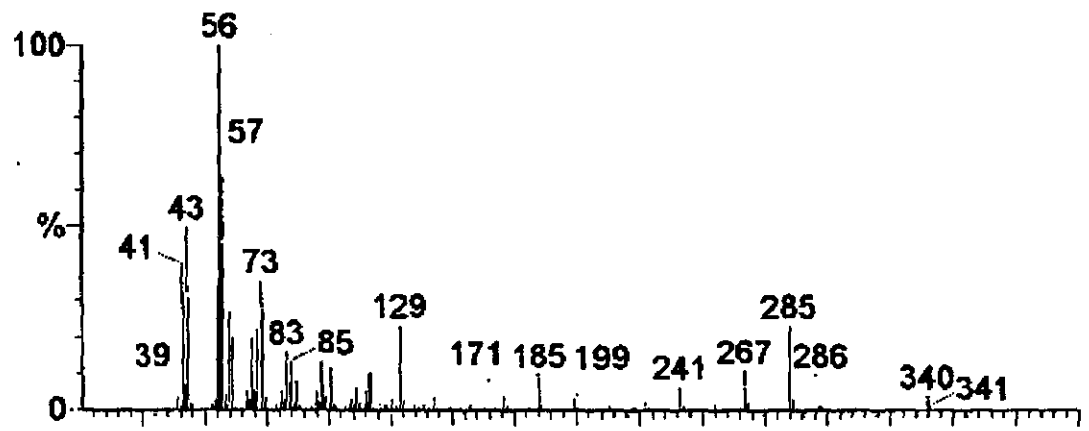


Figure 32. Mass spectra of butyl hexadecanoate (RT 22.304)



m/z	Structure	m/z	Structure	m/z	Structure
312	$CH_3(CH_2)_{14}COO(CH_2)_3CH_3$	239	$CH_3(CH_2)_{14}CO^+$	56	$CH_3(CH_2)_2CH^+$
257	$CH_3(CH_2)_{14}C(OH)O^+H$	57	$(CH_3)_3C^+$		

Figure 33. Mass spectra of octadecanoic acid, 2-methylpropyl ester (RT 24.104)



m/z	Structure	m/z	Structure	m/z	Structure
340	$CH_3(CH_2)_{16}COOCH_2(CH_3)CH_3$	239	$CH_3(CH_2)_{18}CO^+$	56	$CH_3(CH_2)_2CH^+$
257	$CH_3(CH_2)_{16}C(OH)O^+H$	57	$(CH_3)_3C^+$		

Figure 34. GC chromatogram of extract fraction 4

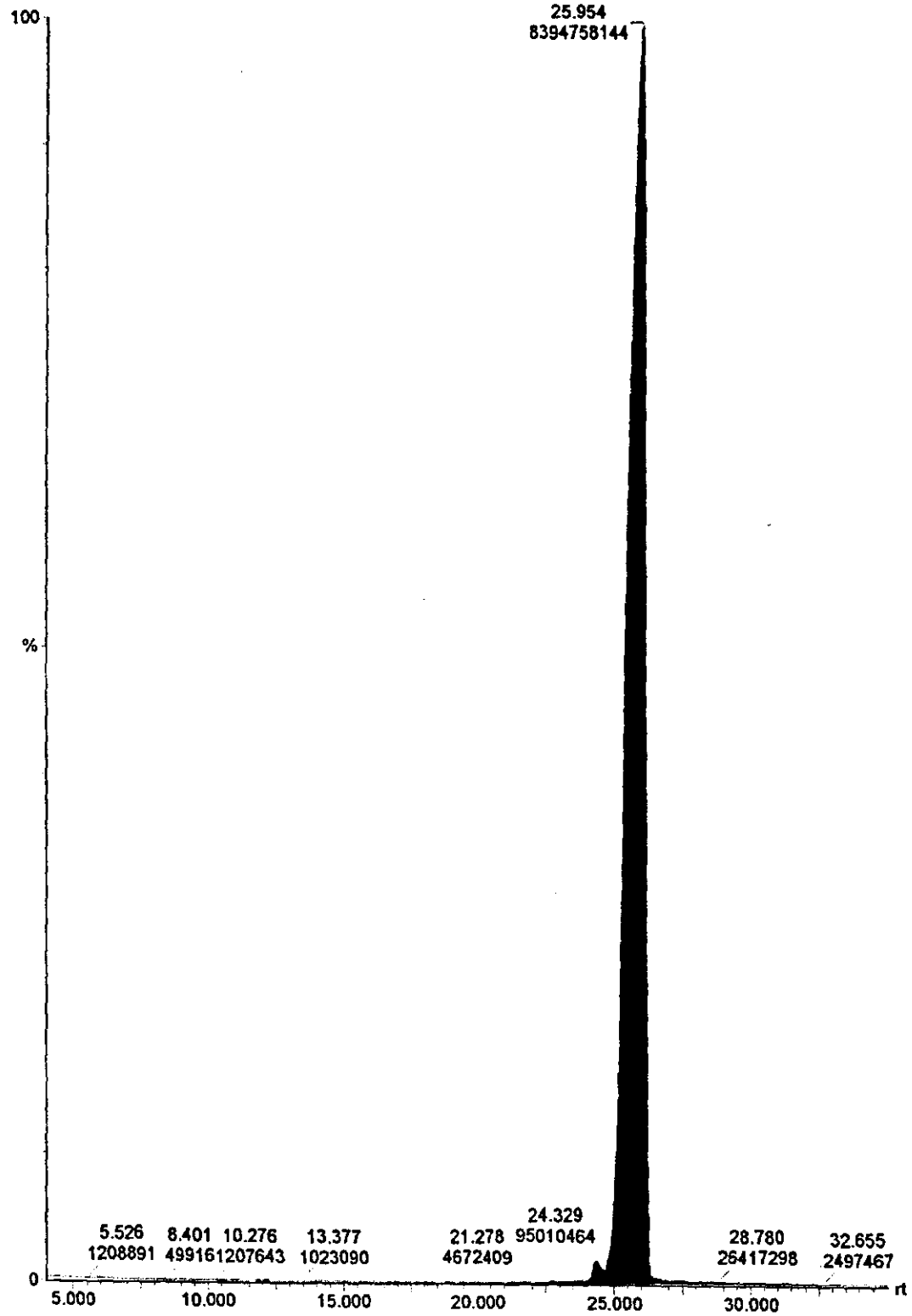
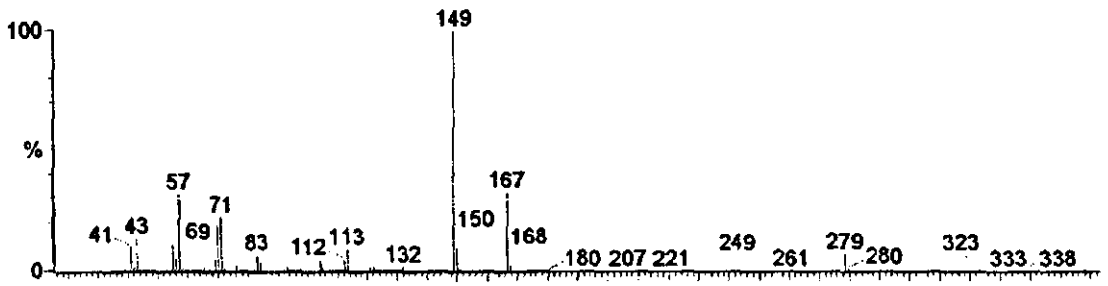


Figure 35. Mass spectra of di 2-ethylhexylphthalate (RT 25.594)



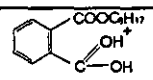
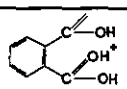
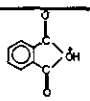
m/z	Structure	m/z	Structure	m/z	Structure
279		167		149	

Figure 36. GC chromatogram of extract fraction 5

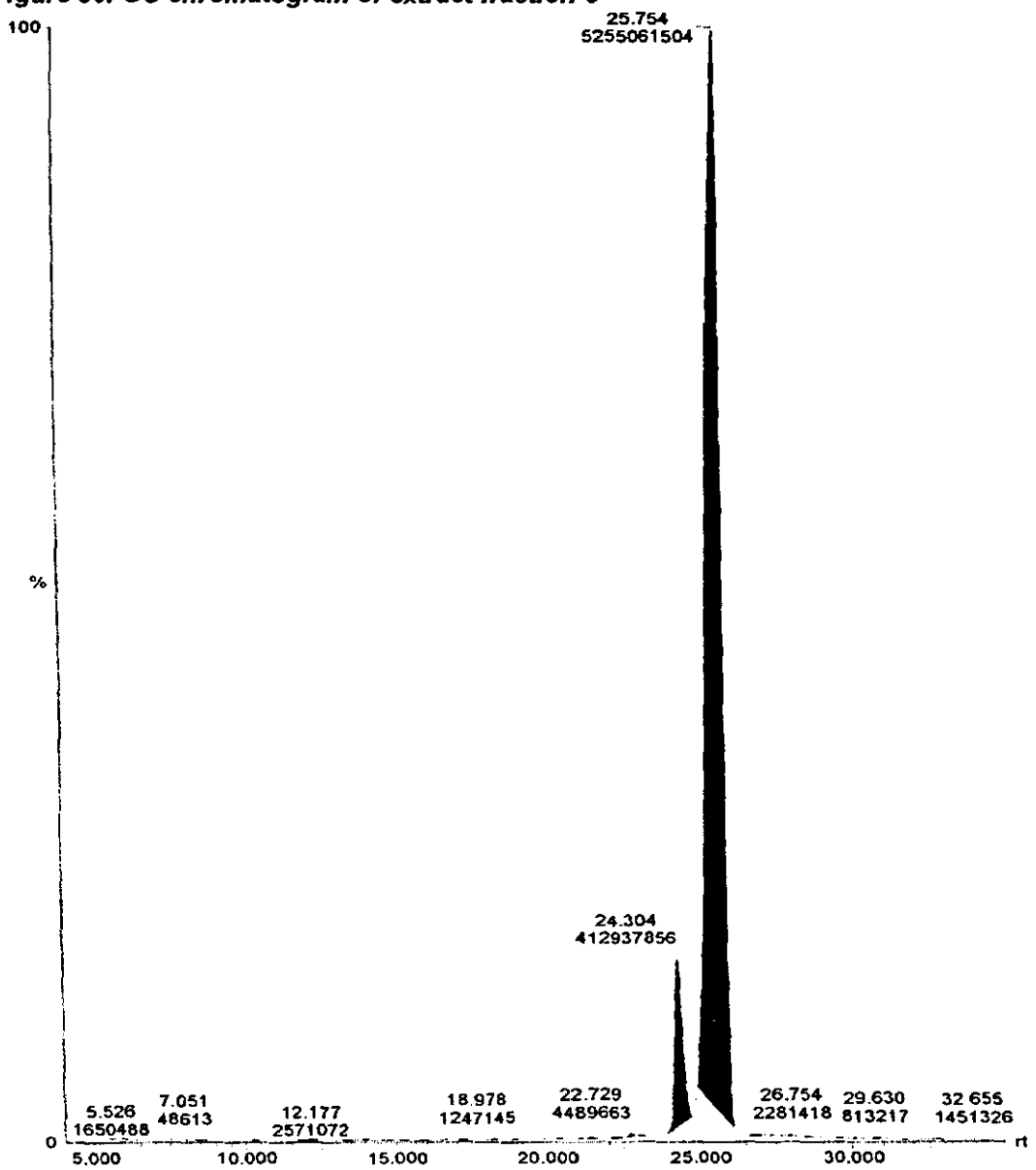
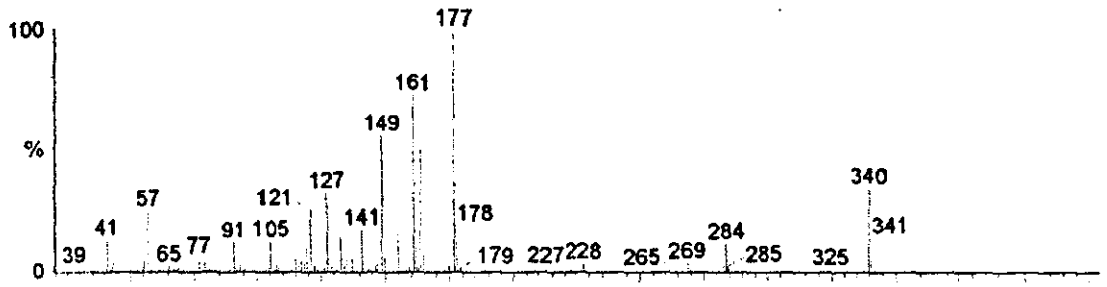


Figure 37. Mass spectra of 2,2-methylenebis (4-methyl-6-tert.butylphenol) (RT 23.304) (phthalate impurity at 25.754 mins)



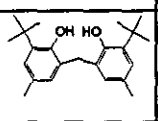
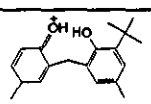
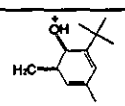
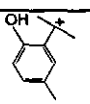
m/z	Structure	m/z	Structure	m/z	Structure	m/z	Structure	m/z	Structure
340		284		177		164		149	

Figure 38. GC chromatogram of extract fraction 6

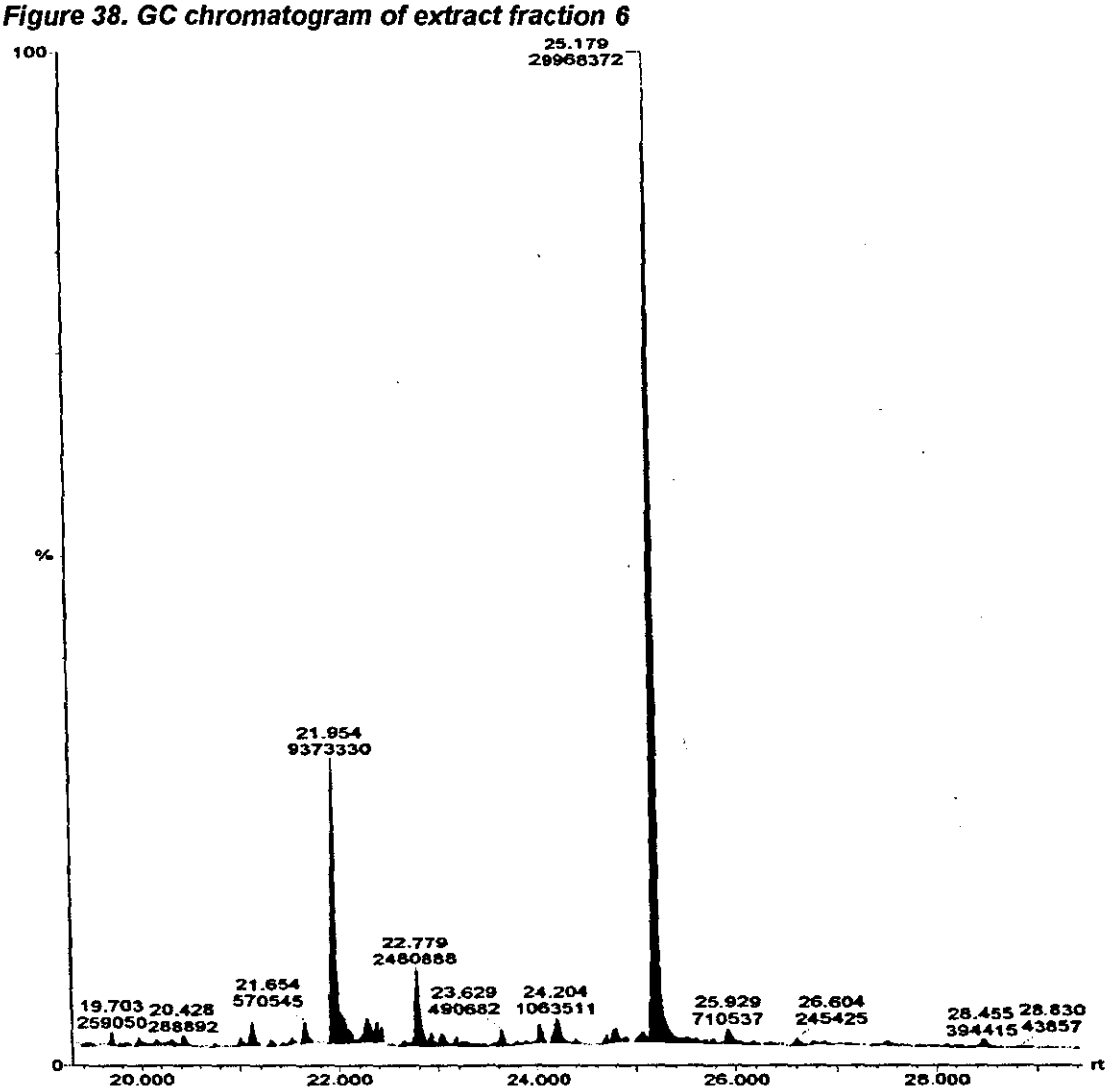
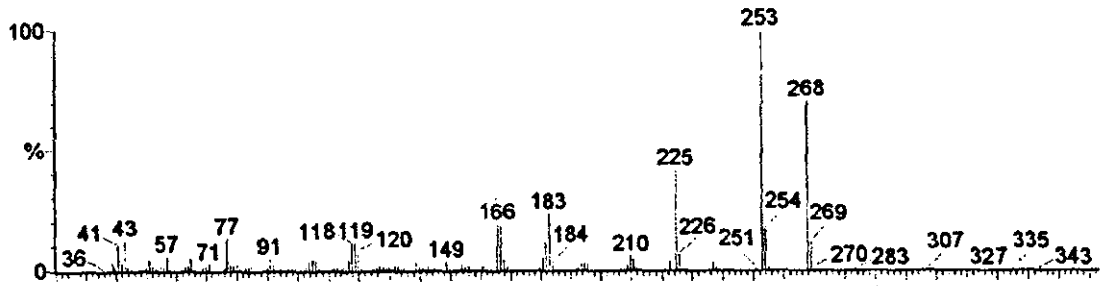


Figure 39. Mass spectra 2-tert.-butyl-4-(dimethylbenzyl)phenol(RT 21.954) (phthalate impurity at 25.179 mins)



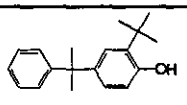
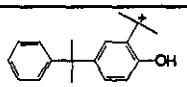
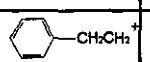
m/z	Structure	m/z	Structure	m/z	Structure
268		119		57	$(CH_3)_3C^+$
253		105			

Figure 40. GC chromatogram of extract fraction 7

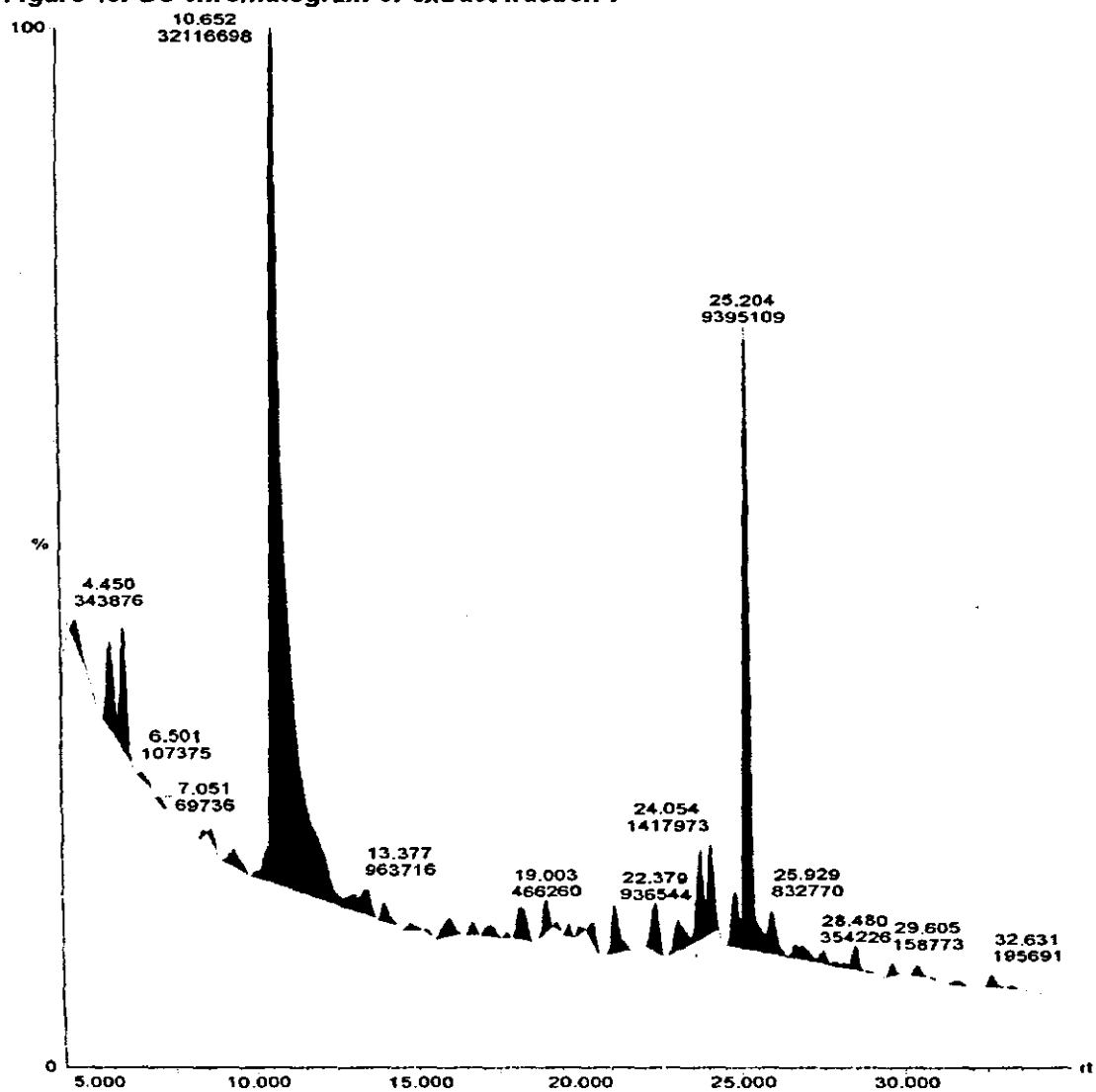
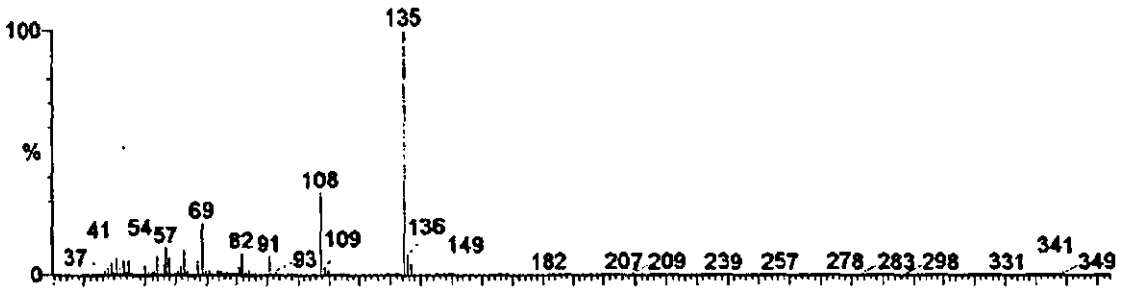


Figure 41. Mass spectra of benzothiazole (RT 10.652) (phthalate impurity at 25.204 mins)



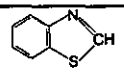
m/z	Structure	m/z	Structure	m/z	Structure
135		108		45	$H\text{-}C{\equiv}S^{+}$

Figure 42. GC chromatogram of extract fraction 8

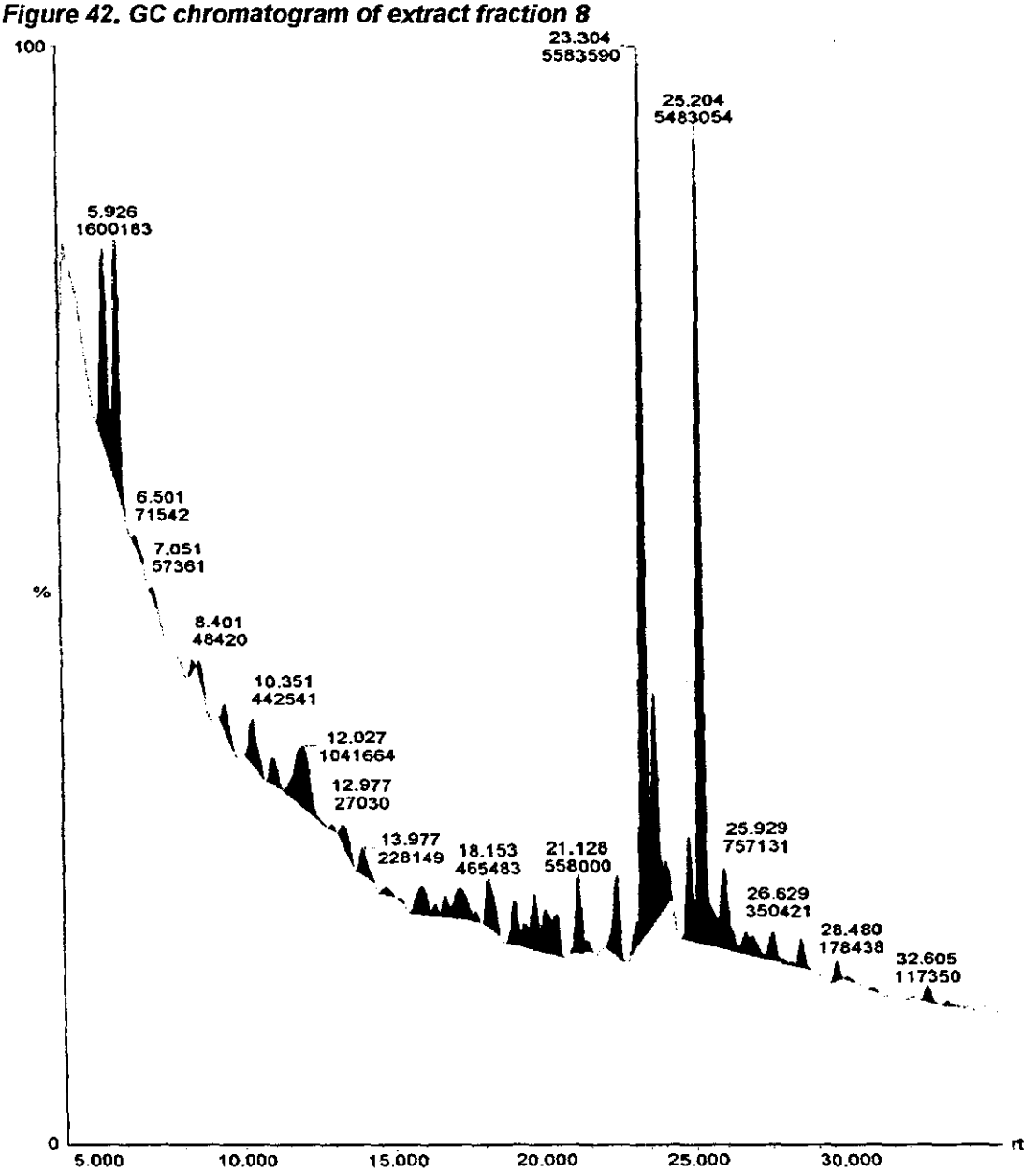
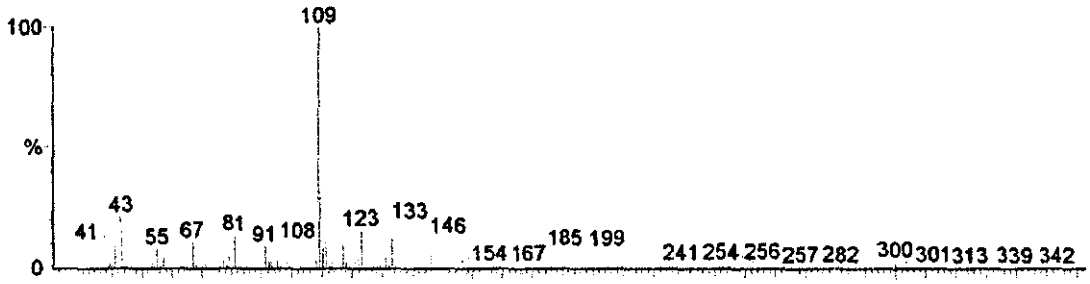


Figure 43. Mass spectra of 2,4-dimethyl 2,4-heptadienal(RT 23.304) (phthalate impurity at 25.204 mins)



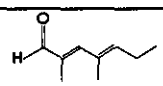
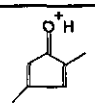
m/z	Structure	m/z	Structure
138		109	

Figure 44. GC chromatogram of extract fraction 9

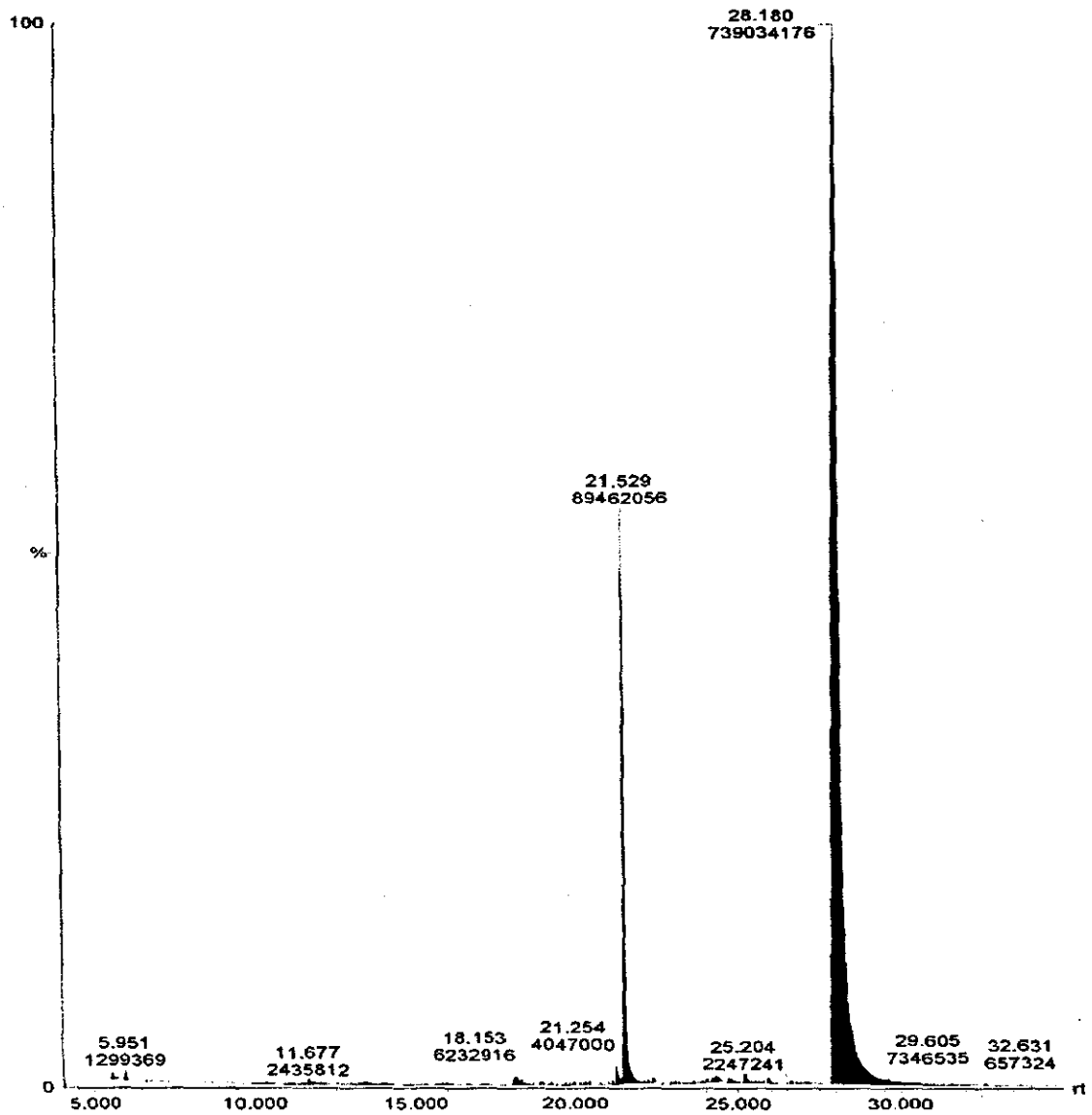
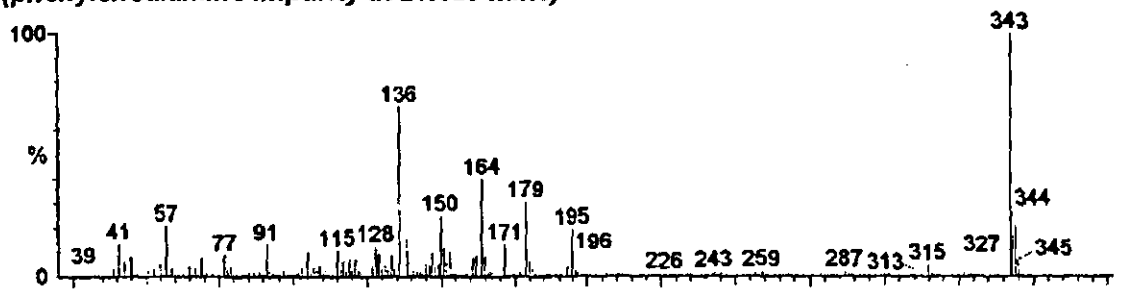


Figure 45. Mass spectra 4,4'-thio-bis-(3-methyl-6-tert.-butylphenol) (RT 28.180) (phenylenediamine impurity at 21.529 mins)



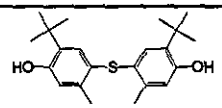
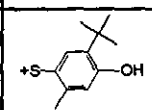
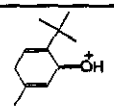
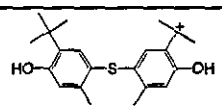
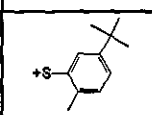
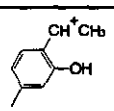
m/z	Structure	m/z	Structure	m/z	Structure
358		195		164	
343		179		136	

Figure 46. GC chromatogram of extract fraction 10

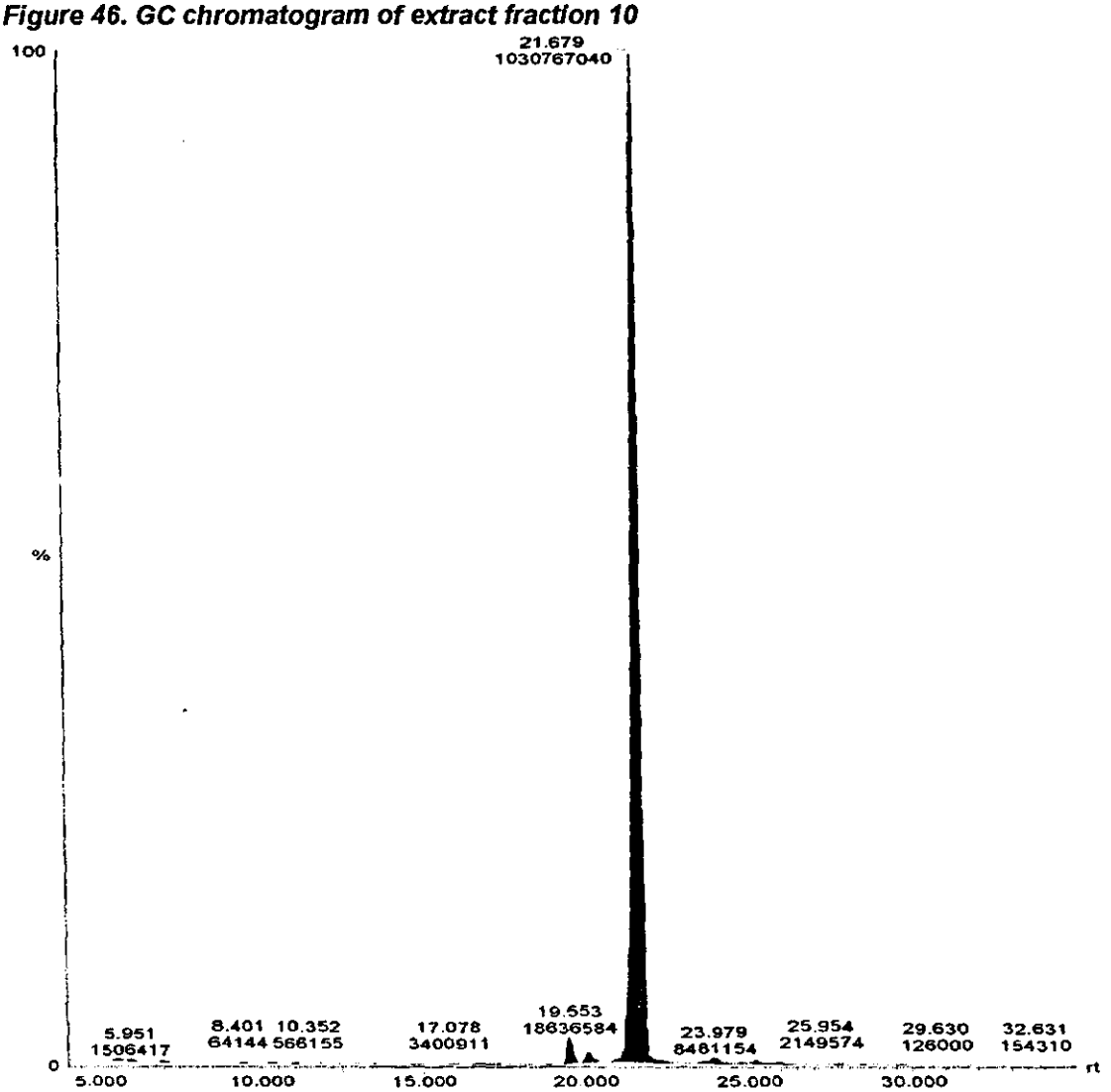
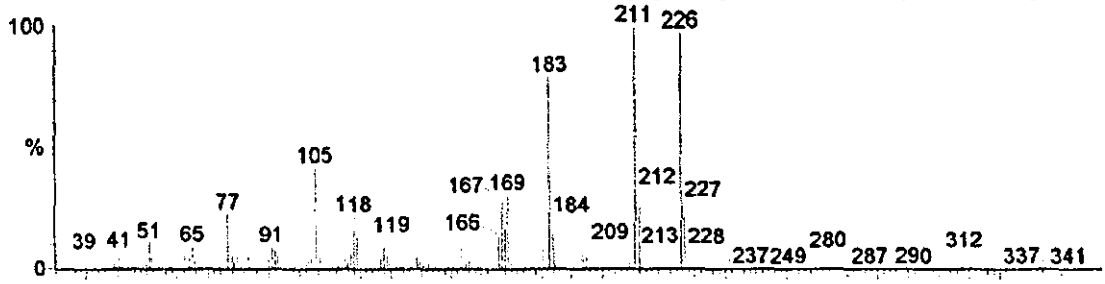


Figure 47. Mass spectra of n-isopropyl-n'-phenyl-p-phenylenediamine (RT 21.679)



m/z	Structure	m/z	Structure	m/z	Structure
226	$CH_3CH(CH_3)NHC_6H_4NHC_6H_5$)	183	$^+NHC_6H_4NHC_6H_5$	168	$C_6H_5N^+C_6H_5$
211	$^+CH(CH_3)NHC_6H_4NHC_6H_5$	169	$C_6H_5NH^+C_6H_5$		

Figure 48. GC chromatogram of extract fraction 11

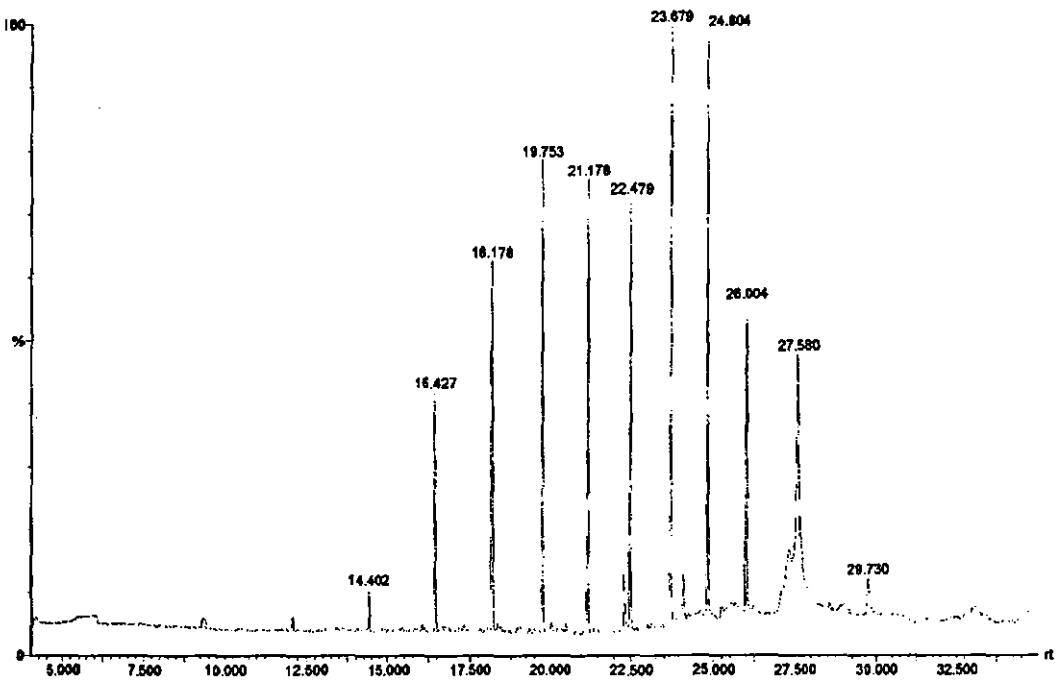


Figure 49. Mass spectra of tetradecamethyl hexasiloxane (RT 16.427)

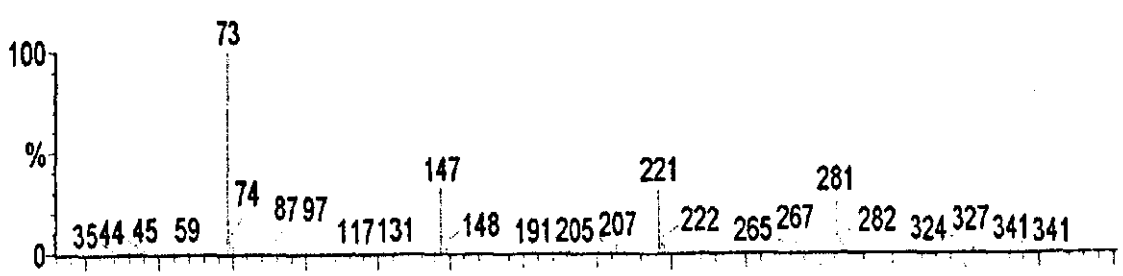


Figure 50. Mass spectra of hexadecamethyl heptasiloxane (RT 18.178)

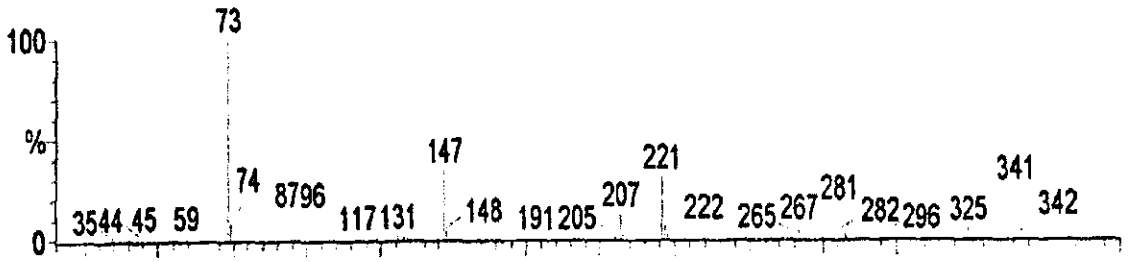
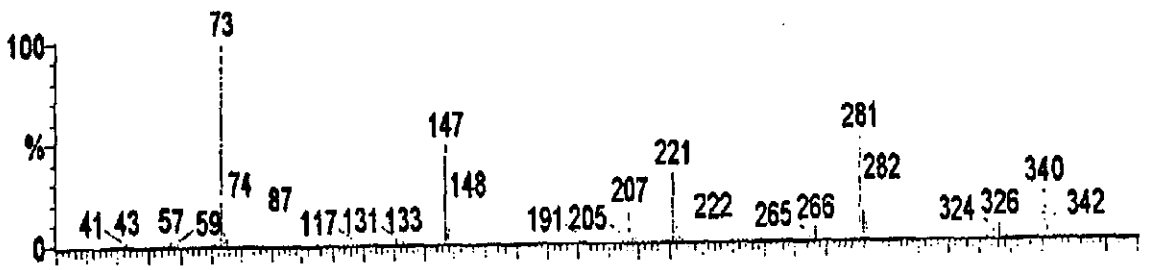


Figure 51. Mass spectra of dodecamethyl pentasiloxane (RT 19.753)



For fractions 11 and 12, unfortunately, it was not possible to give a full characterisation. Fraction 11 could only be partially characterised with respect to 3 compounds. Fraction 12 did not give any valuable spectra.

From the GC-MS analysis and the formulation information provided with NBR (Section 2.2), it was possible to propose the chemical origin of the characterised compounds. It can be seen from Table 15, that a number of compounds extracted from NBR have undergone no chemical change during the curing process. However, it is also apparent that some compounds listed are not featured in the original formulation (Section 2.1.2). These compounds are either a) breakdown products of components during the vulcanisation of NBR, b) impurities incorporated during the formulation process, c) compounds chemically modified by the extraction and chromatographic procedures that were applied to the NBR rubber and low molecular weight extract, or a combination of a, b and c. It is most

likely however, that the detected compounds are the results of a and b. These compounds together with their proposed origin are summarised in Table 16.

Table 16. Identified compounds present in the NBR Soxhlet extract with reference to their proposed chemical origin

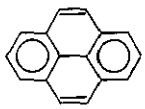
Compound	Origin
Alkanes(mostly tetratetracontane) $CH_3(CH_2)_{42}CH_3$	Astorstag wax (antiozonant)
Pyrene	From carbon black
Butyl hexadecanoate 2-methylpropyl octadecanoic acid	Steric acid/ long-chain aliphatic acid (cure activator)
Di 2-ethylhexylphthalate	Plasticiser
2-tert-butyl-4(dimethylbenzyl)phenol	Santowhite impurity
Benzothiazole	Cure system break-down product
2,2' -methylenebis (4-methyl-6-tert.butylphenol)	Antioxidant (Santowhite)
2,4-dimethyl 2,4-heptadienal	Possibly derived from phenolic antioxidant
4,4'-thio-bis-(3-methyl-6-tert.-butylphenol)	Antioxidant (Santowhite)
N-isopropyl-n'-phenyl-*p*-phenylenediamine	Antiozonant
Various siloxanes	Silicone lubricant used during processing

3.2.6 Proposed chemical origin of identified compounds not specified in the NBR formulation

Alkanes

The presence of these hydrocarbons originate from the Astorstag wax antiozonant which consists of long chain olefins. These hydrocarbons are readily extractable from NBR using hydrocarbon solvents such as *iso*-octane. It is also apparent from the chromatographic analysis that the bulk of this wax is composed of C_{44} hydrocarbons (i.e. tetratetracontane).

Pyrene

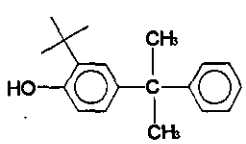
Structure: 

Pyrene is believed to originate from the carbon black reinforcing filler. Carbon blacks are known to contain considerable quantities of aromatic hydrocarbons which are formed during their manufacture by the pyrolysis of gases and oils in limited air.

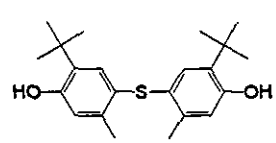
Butyl hexadecanoate and 2-methylpropyl octadecanoic acid

These are components of the stearic acid/long chain aliphatic acid cure activator compound.

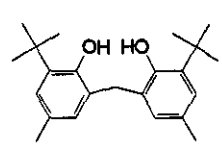
2-tert.-butyl-4(dimethylbenzyl)phenol

Structure: 

2-tert.-butyl-4(dimethylbenzyl)phenol is considered to be an impurity from either 2,2' -methylenebis (4-methyl-6-tert.butylphenol) or 4,4'-thio-bis-(3-methyl-6-tert.-butylphenol).



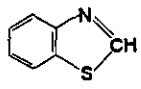
2,2' -methylenebis (4-methyl-6-tert.butylphenol)



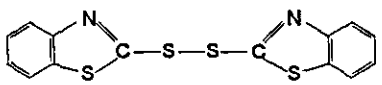
4,4'-thio-bis-(3-methyl-6-tert.-butylphenol)

It was possibly formed by a side reaction during the manufacture of the Santowhite antioxidant rather than during the curing process.

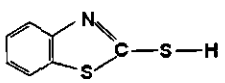
Benzothiazole

Structure: 

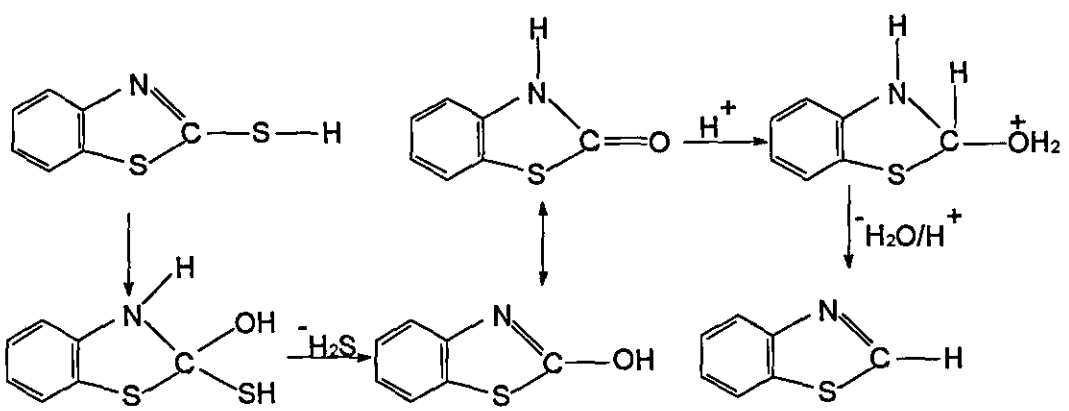
Benzothiazole is formed by the breakdown of 2-mercaptobenzothiazyl disulphide.



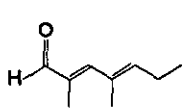
2-mercaptobenzothiazyl disulphide

1) -splitting of disulphide 

2) -formation of benzothiazole by hydrolysis



2,4-dimethyl 2,4-heptadienal

Structure: 

It is not certain of the origin of 2,4-dimethyl 2,4-hepatdienal. It may have been formed by the degradation of a phenol or peroxide impurity.

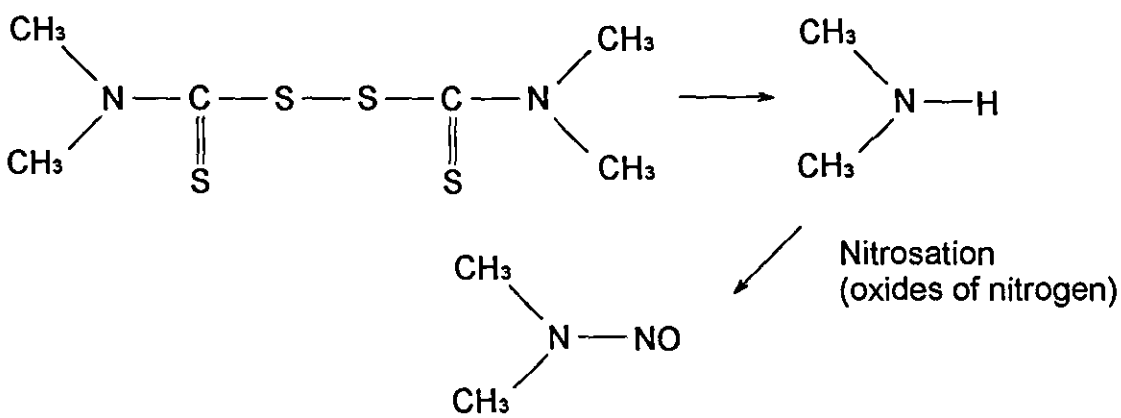
Siloxanes

Although siloxanes are not mentioned in the formulation, their presence is usually associated with silicone oil lubricants used during processing. They

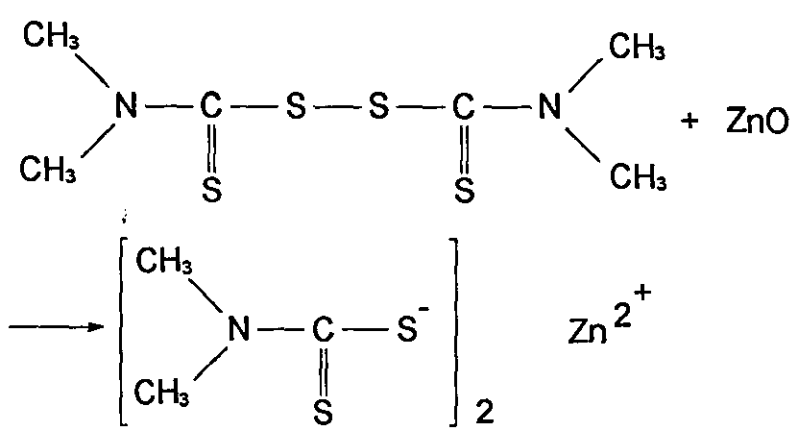
are readily absorbed by NBR and hence feature in the extraction. Incidentally, no siloxanes were detected in initial analysis of the bulk extract by GC-MS.

It has also been reported[216], that a number of additional compounds which were not detected in the analysis of the NBR *iso*-octane Soxhlet extract, may feature in Soxhlet extractions utilising more polar extractants such as ethanol and water. These compounds are known to be formed by the breakdown of the TMTD curative and the reaction of various nucleophiles with the acrylonitile monomer. They will be briefly described below.

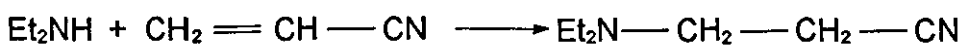
1. Formation of nitrosodimethylamine from TMTD.



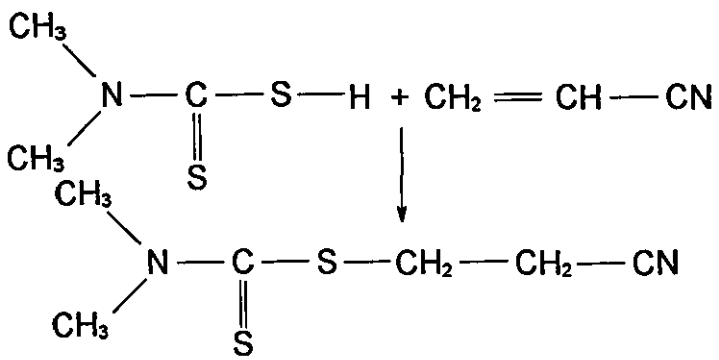
2. Formation of zinc dimethyldithiocarbamate from TMTD



3. Formation of 3-diethylaminopropanonitrile from reaction of monomer acrylonitrile susceptible to nucleophilic substitution.



4. Formation of 2-cyanothyl dimethyldithiocarbamate



Note: Diethyl amine is often an impurity associated with TMTD.

3.2.7 Quantitative analysis of four target compounds extracted from NBR

Quantitative analysis was performed on 4 target compounds[217]. These compounds are believed to have food safety implications. They are *iso*-octane extractable and have been determined by normal phase HPLC using the method in Section 2.2.14. It was required to quantify each target compound present in the *iso*-octane extract and determine the quantity of each material that was extracted from NBR. The following compounds were determined:

Di-2 ethyl hexyl phthalate (D2EHP)

Tetratetracontane $CH_3(CH_2)_{42}CH_3$

Benzothiazole

N-isopropyl-N'-phenyl-*p*-phenylenediamine (IPPD)

3.2.7.1 Cailbration

Calibrants were obtained by fractionating the desired compound identified by GC-MS in the extract by HPLC. Six point calibration curves for each target compound were then constructed and quantitative data were obtained using the Caliber HPLC software. The quantification method was similar for all four target compounds. It will be illustrated using di-2 ethyl hexyl phthalate as an example. A set of six standards was run using an external calibration method. The concentrations of D2EHP in each sample were as follows:

Table 17. Calibration standards used for the quantification of D2EHP in the NBR Soxhlet extract.

Sample Number	Concentration g/l
1	0.3
2	0.25
3	0.2
4	0.15
5	0.1
6	0.05

The response factors (RF) for these calibration samples were calculated using a peak height method by the Caliber software where

$$RF = \frac{\text{Peak height}}{\text{Concentration}}$$

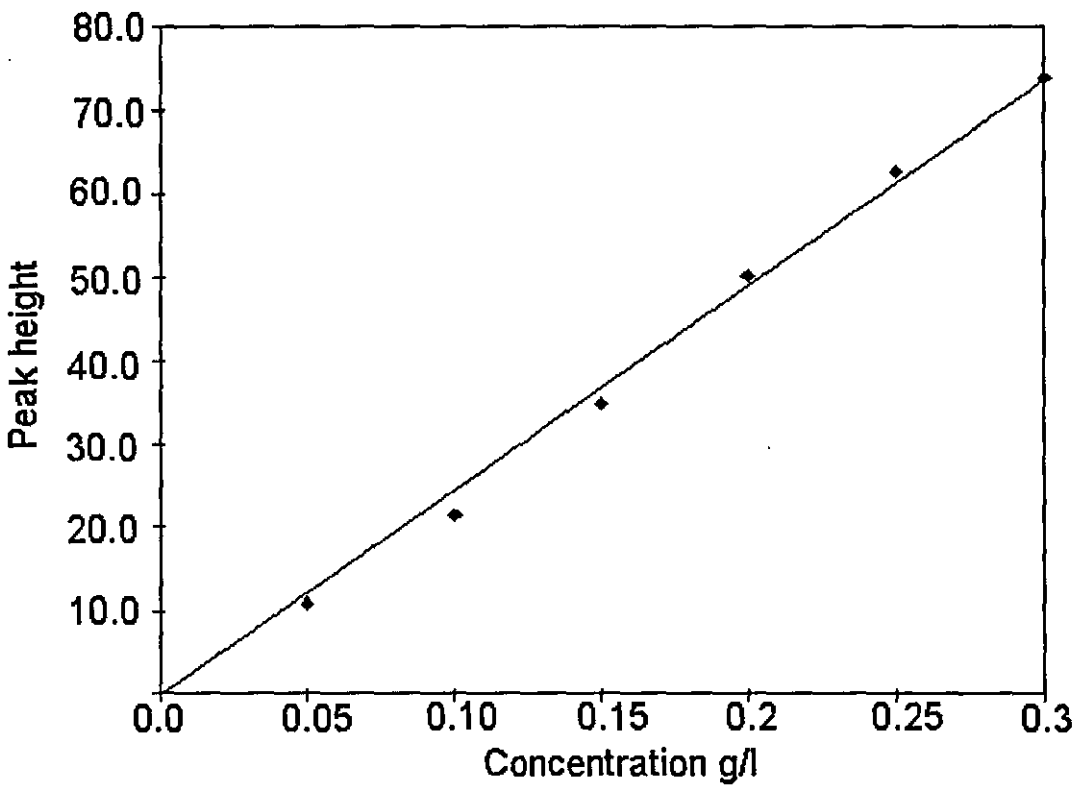
To allow for both linear and non-linear peak response, this term was generalised to

$$\text{Height} = RF2 \times C^2 + RF\,1 \times C + RF0$$

where C is the peak concentration, RF2 and RF1 are the response factors, and RF0 is the intercept.

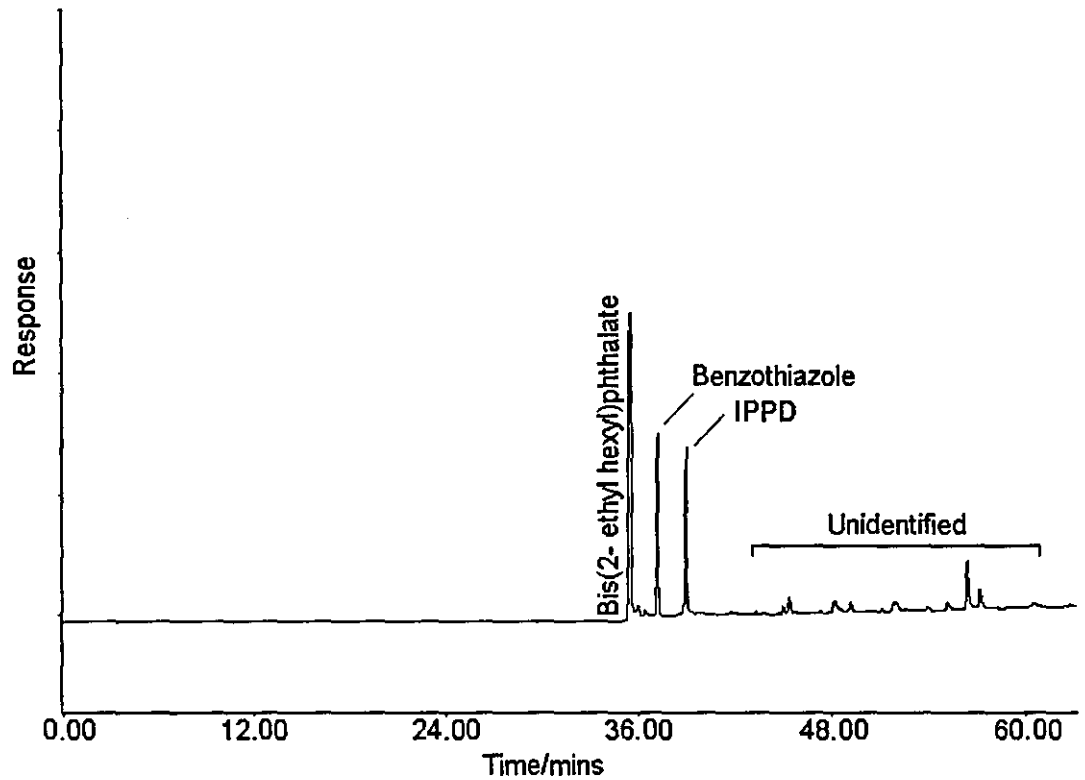
The following calibration plot shown in Figure 52 was obtained for di-2 ethyl hexyl phthalate.

Figure 52. Calibration plot for di-2 ethyl hexyl phthalate



It can be seen from the graph that the calibration is linear. Calibration plots for the other target compounds also produced linear plots. The unknown sample was then run against this calibration file and the following chromatogram (Figure 53) was obtained.

Figure 53. Quantitative analysis of NBR extract using HPLC



(Injection concentrations of the NBR extract for the determination of the four target compounds were as follows: 1% w/v D2EHP, 1% w/v IPPD, 5% w/v benzothiazole, 5%w/v tetratetracontane).

The Caliber software compared the D2EHP peak height (55.063) in Figure 53 with the calibration which corresponded to a concentration of 0.225 g/l.

The concentration of D2EHP present in the NBR extract was determined as follows. From a 1 mg injection, the results indicated that 0.225mg were attributable to D2EHP. Therefore, it was possible to postulate that the NBR extract contains 22.5% D2EHP. It was also required to determine how much D2EHP had been removed from the NBR sample during extraction. (Conditions: 30 g NBR, 200 ml *iso*-octane, temperature 100°C,

extraction time 12 hours). A 30 g sample yielded 4.5 g of extract. It was also known that the D2EHP content in the unextracted sample was at a 5.8% (1.74 g).

The percentage of D2EHP extracted from the NBR could be calculated as follows:

Mass of D2EHP in extract / mass of D2EHP in NBR x 100

$$1.01/1.74 \times 100 = 58\%$$

Therefore, 58% of the D2EHP present in the NBR sample was removed by Soxhlet extraction using *iso*-octane as the extractant. The above procedure was followed for the other three target compounds. The results of these findings are tabulated below in Table 18.

Table 18. Quantitative analysis of the target compounds

Target Compound	% Compound present in NBR extract	% Compound present in NBR formulation	% Compound extracted from NBR
Di-2 ethyl hexyl phthalate	22.5	5.8	58.4
Tetratetracontane	0.098	1.15	1.28
Benzo-thiazole	0.025	0.58	14.4
IPPD	3.78×10^{-3}	0.58	2.17

3.3 Ethylene-propylene-diene monomer elastomer

3.3.1 Large scale extraction of EPDM

Large scale Soxhlet extractions were performed on EPDM using methods described in Section (2.3.11). The extraction results are shown in Table 19.

Table 19. Large scale extraction results of EPDM.

Sample (30g)	Solvent	B.P./°C	Extract/ %	Extract Colour
EPDM	iso-propanol	82	5.06	Yellow

3.3.1.1 Iso-propanol extractables

The total amount of material Soxhlet extracted with iso-propanol from finely shredded EPDM was 5.06% (duplicate values of 5.03% and 5.09%). The theoretical extract based on the level of additive addition is 7.2%. This indicates that much of the process oil present in the formulation has not been extracted.

3.3.2 Molecular weight determination of EPDM Soxhlet extracts

The EPDM Soxhlet extract was characterised using the method described in Section 2.3.13. Molecular weight data (polystyrene equivalent) for the *iso*-propanol Soxhlet extract are given in Table 20.

Table 20. Molecular weight data for the *iso*-propanol Soxhlet extracts.

Sample	Extraction Solvent	Mn	Mw	Mp
EPDM	*iso*-propanol	440	535	405

It was known[218] that the process oil additive was composed of aliphatic hydrocarbons greater than 1000 molecular weight. It is apparent from the molecular weight data that none of this high molecular weight oil is present in the extract. It must also be noted however, that the column was calibrated between 580 and 2100000 using polystyrene standards. The molecular weight data obtained for the EPDM extract was just outside the calibration limit of the column. The results obtained must therefore be considered to be approximate estimates of the molecular weight.

3.3.3 GC-MS analysis of EPDM low molecular weight extract

GC-MS analysis was performed upon the EPDM Soxhlet extract using the method described in Section 2.3.14. The chromatogram and identified mass spectra obtained for the major components in the extract are given in Figures 54-58. A summary of this information is given in Table 21. The main mass fragmentations associated with the mass spectra have also been assigned.

Table 21. Identified components present in *iso*-octane Soxhlet extract of EPDM by GC-MS.

Retention Time	Assignment
12.227	2-(4-isopropylphenyl)-2-propanol
13.227	1-4-(tert.-butyl)phenylethanone
14.002	1,1'-(1,4-phenylene)bis-ethanone
14.777	1-(3-isopropylphenyl)-2-methyl ethanol

Figure 54. GC of EPDM low molecular weight extract

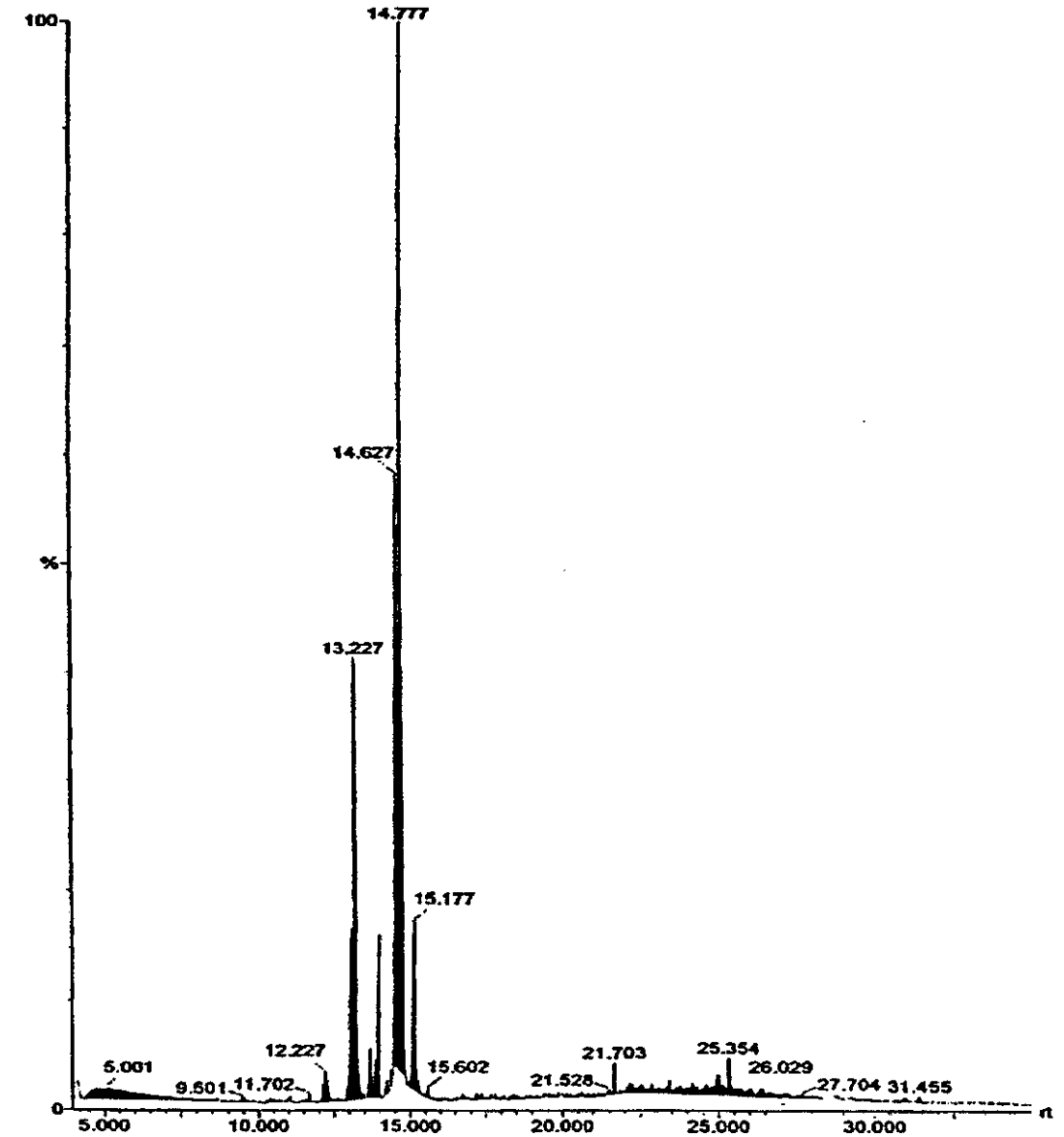
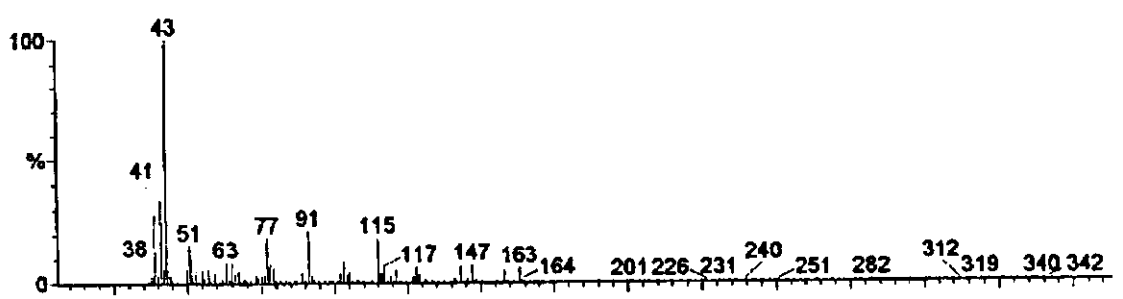


Figure 55. Mass spectra of 2-(4-isopropylphenyl)-2-propanol (RT 12.227)



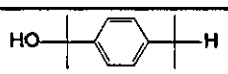
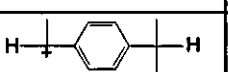
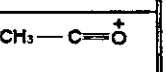
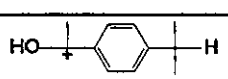
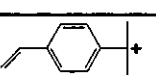
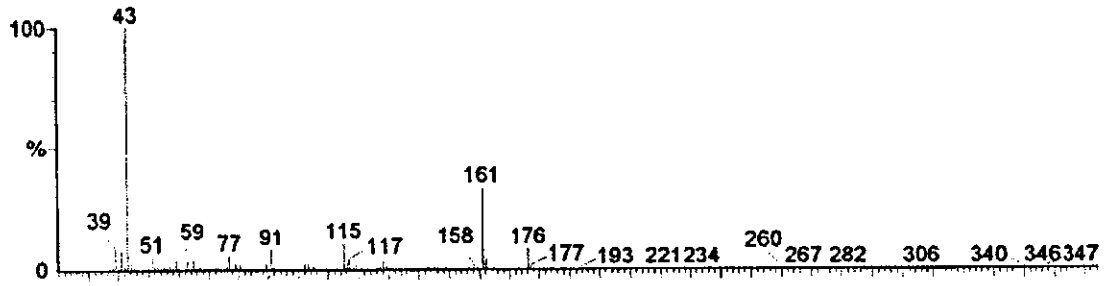
m/z	Structure	m/z	Structure	m/z	Structure
178		147		43	
163		145			

Figure 56. Mass spectra of 1-4-(tert.-butyl)phenyl ethanone (RT13.227)



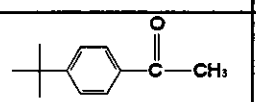
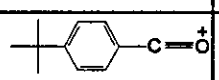
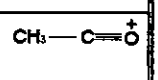
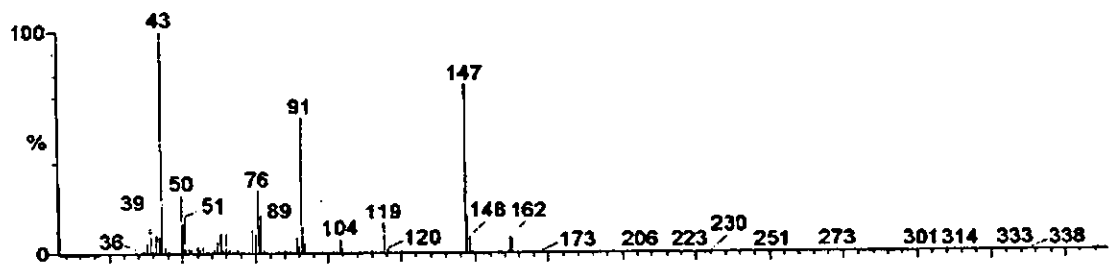
m/z	Structure	m/z	Structure	m/z	Structure
176		161		43	

Figure 57. Mass spectra of 1,1'-(1,4-phenylene)bis-ethanone (RT 14.002)



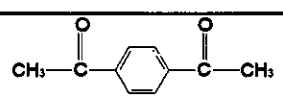
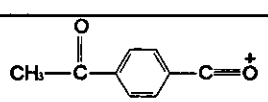
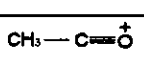
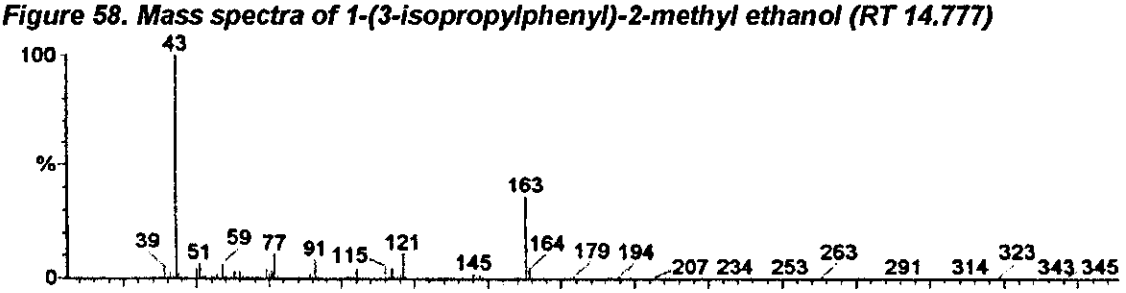
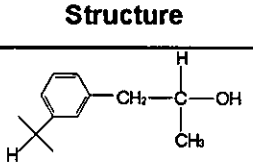
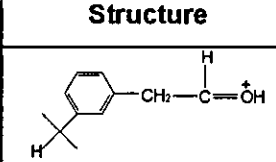
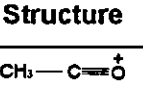
m/z	Structure	m/z	Structure
162		91	
147		43	

Figure 58. Mass spectra of 1-(3-isopropylphenyl)-2-methyl ethanol (RT 14.777)



m/z	Structure	m/z	Structure	m/z	Structure
178		163		43	

It can be seen from the chromatogram in Figure 58 that the peak corresponding to 1-(3-isopropylphenyl)-2-methyl ethanol has the largest response.

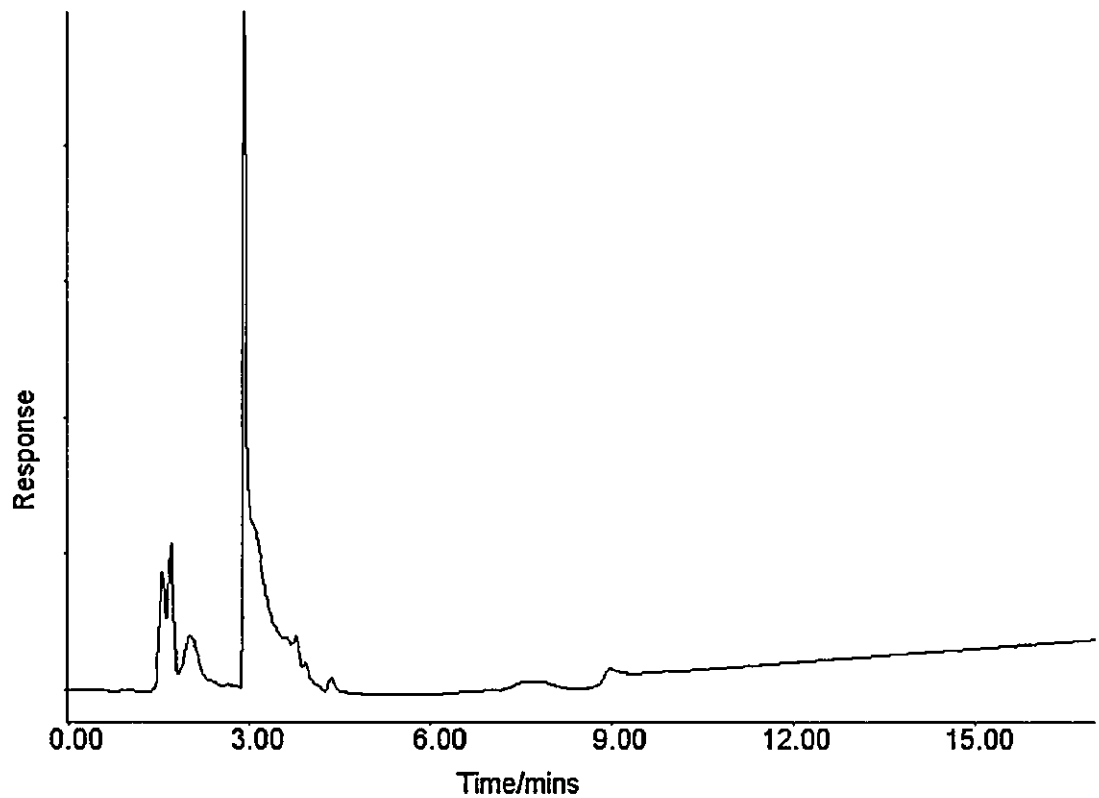
3.3.4 Analysis of EPDM low molecular weight Soxhlet extractables by HPLC

GC-MS analysis carried out on the extract had shown the presence of 4 major peaks that could be identified and a number of smaller peaks that could not be identified due to their low concentration. To aid analysis by mass spectroscopy, HPLC was performed to fractionate and pre-concentrate the extract to give adequate quantities of each species. These fractions then underwent further GC-MS analysis. Compared to the results for NBR in Section 3.2.5, the low number of extracted species is attributable to the solvent resistance of EPDM and the fewer potential extractables in its formulation. It is well known that EPDM has high resistance to polar and non-polar solvents which resulted in a low extract yield obtained from the *iso*-propanol Soxhlet extraction (5.06%).

Utilising the experience gained from the HPLC analysis of NBR, normal phase chromatography was considered the most likely technique to achieve a separation of the EPDM Soxhlet extract. However, reversed phase separations were initially investigated. Reversed phase studies were performed with a HPLC cartridge column (15 cm x 3.9 mm) Nova-pak C_{18} 60 Å 4 μm supplied by Waters Millipore Corporation, (USA). These separations were performed isocratically and in gradient mode. A series of experiments were carried out and optimum separation conditions were found to consist of a water: THF gradient (98% water-70% water in 30

minutes) at 1 ml/min with UV detection at 254 nm with 1% w/v aliquots injected onto the system.

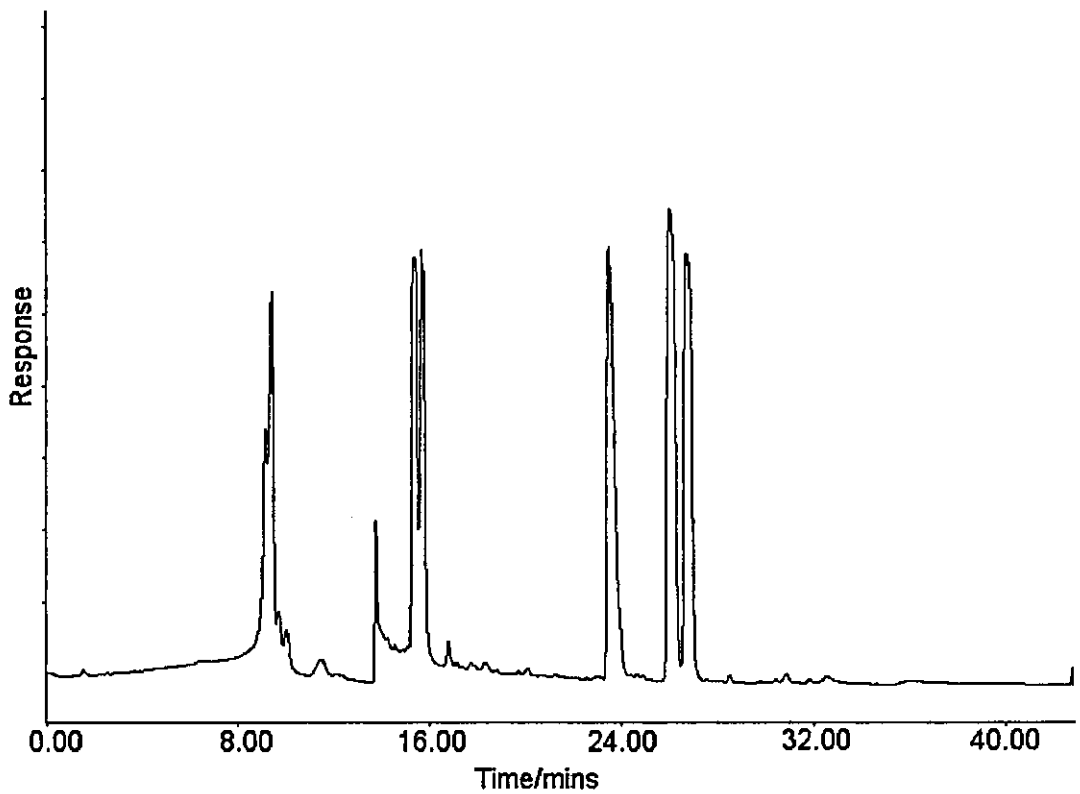
Figure 59. HPLC of EPDM extract using an C_{18} column with a water : THF gradient (98-70% water in 30 mins) at 1 ml/min with UV detection set at 254nm with 1% w/v aliquots injected onto the system



It can be seen in Figure 59 that the optimum separation conditions could only produce a poorly resolved chromatogram.

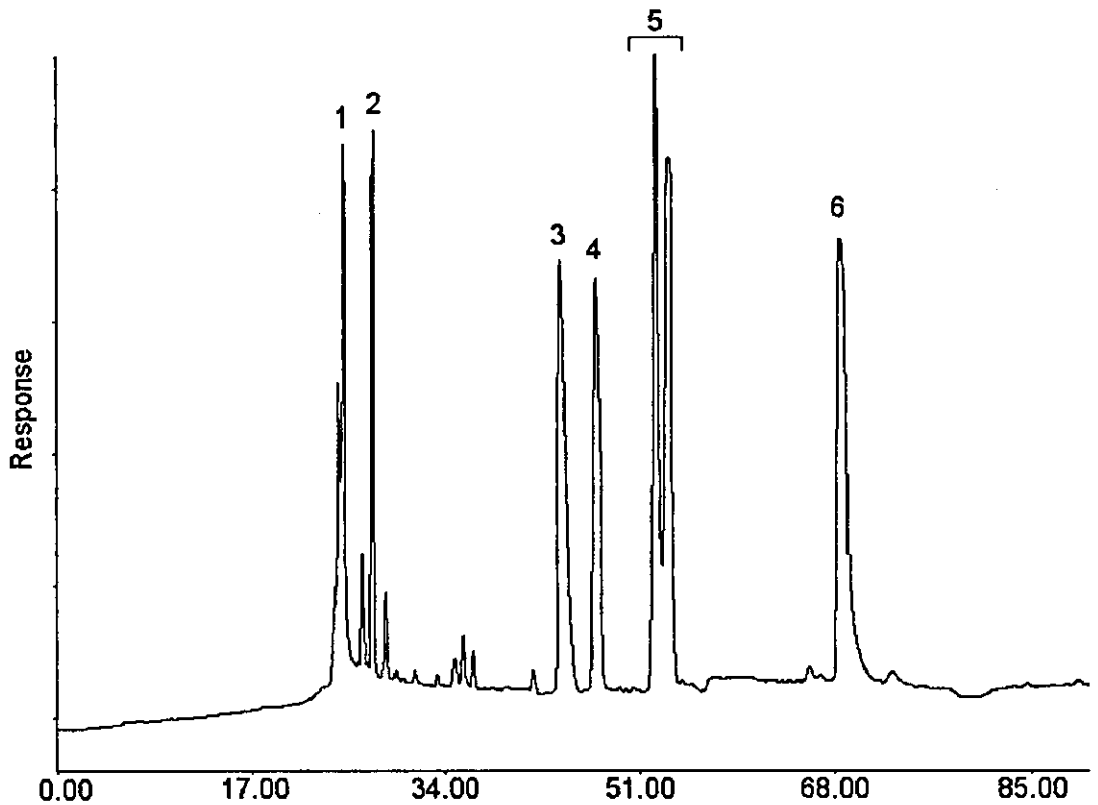
Normal phase studies were then performed with an analytical HPLC column (25 cm x 4.6 mm) containing Spherisorb S5W. These separations were performed isocratically and in gradient mode. A series of experiments were carried out and optimum separation conditions were found to consist of *n*-hexane : *iso*-propanol (97:03) mobile phase at 1 ml/min with UV detection at 254 nm with 2% w/v aliquots injected onto the system.

Figure 60. Separation of EPDM extract by a S5W column (25 cm x 4.6 mm) with a n-hexane : iso-propanol (97:03) mobile phase at 1 ml/min with UV detection at 254 nm with 2% w/v aliquots injected onto the system



The efficiency of the separation method was improved yet further by the incorporation of a semi-preparative column (30 cm x 7.8 mm) containing a S5W packing into the system with a 2 ml injection loop. The optimum conditions consisted of a *n*-hexane : *iso*-propanol (95:05) mobile phase at 1 ml/min with UV detection at 254 nm with 10% w/v aliquots injected onto the system. The chromatographic system was connected to a Frac-100 fraction collector. Aliquots (10% w/v) were injected and the fractions indicated on the chromatogram were then dried in a vacuum oven at room temperature. This procedure was repeated 15 times. These fractions were then subjected to GC-analysis with mass spectroscopic detection in a attempt to identify the collected fractions.

Figure 61. Separation of EPDM extract by a S5W column (30 cm x 7.8 mm) with a n-hexane : iso-propanol (95:05) mobile phase at 2 ml/min with UV detection at 254 nm with 10% w/v aliquots injected onto the system



3.3.5 EPDM extract fraction identification from HPLC by GC-MS

The HPLC chromatogram (Figure 61) was fractionated as described above. The collected fractions then underwent GC-MS analysis with the conditions described in Section 2.3.15. The chromatogram and identified mass spectra obtained for the major components in the extract are given in Figures 62-70. The main mass fragmentations associated with the mass spectra have also been assigned. Unfortunately, fractions 1 and 2 did not give any valuable spectra. A summary of this information is given in Table 22.

Table 22. Proposed structures present in the EPDM Soxhlet extract

Fraction	Identification By GC-MS
1	Unidentified
2	Unidentified
3	1-Isopropyl-3-tert-butylbenzene
4	1,1'-(1,4-phenylene)bis-ethanone
5	2-Methyl-3-phenyl-2-propenal Didodecylphthalate
6	1-(3-isopropylphenyl)-2-methyl ethanol

Figure 62. GC chromatogram of extract fraction 3

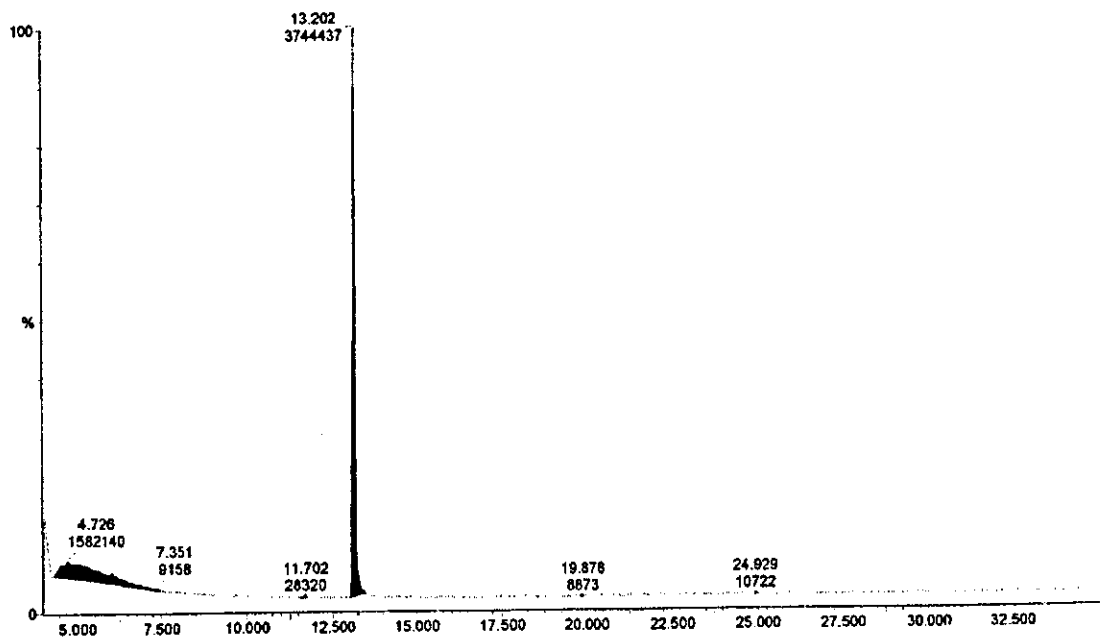
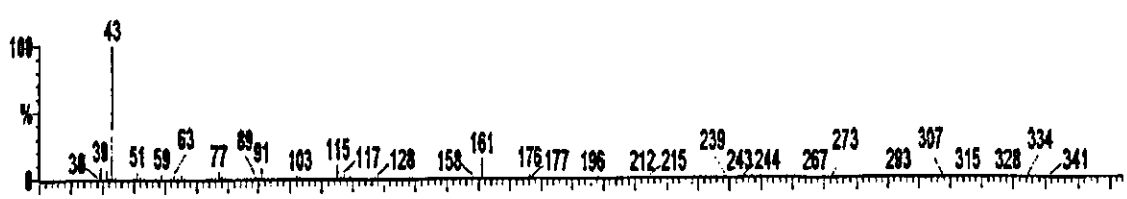


Figure 63. Mass spectra of 1-isopropyl-3-tert-butylbenzene (RT 13.202)



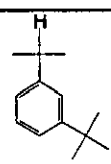
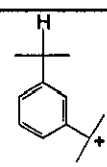
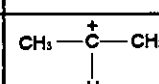
m/z	Structure	m/z	Structure	m/z	Structure	m/z	Structure
176		161		91		43	

Figure 64. GC chromatogram of extract fraction 4

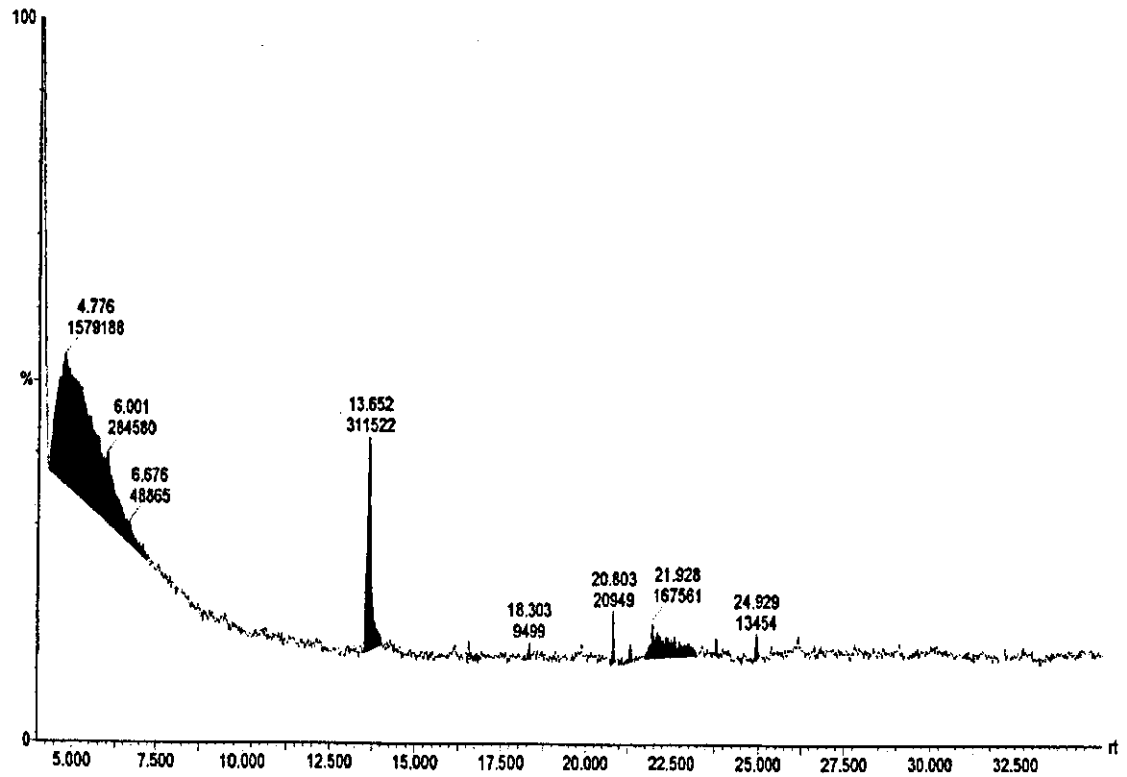


Figure 65. Mass spectra of 1,1'-(1,4-phenylene)bis-ethanone (RT 13.652)

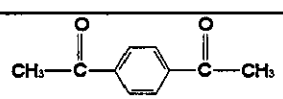
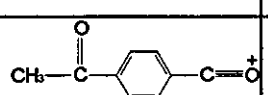
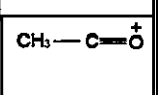
m/z	Structure	m/z	Structure	m/z	Structure	m/z	Structure
162		147		91		43	

Figure 66. GC chromatogram of extract fraction 5

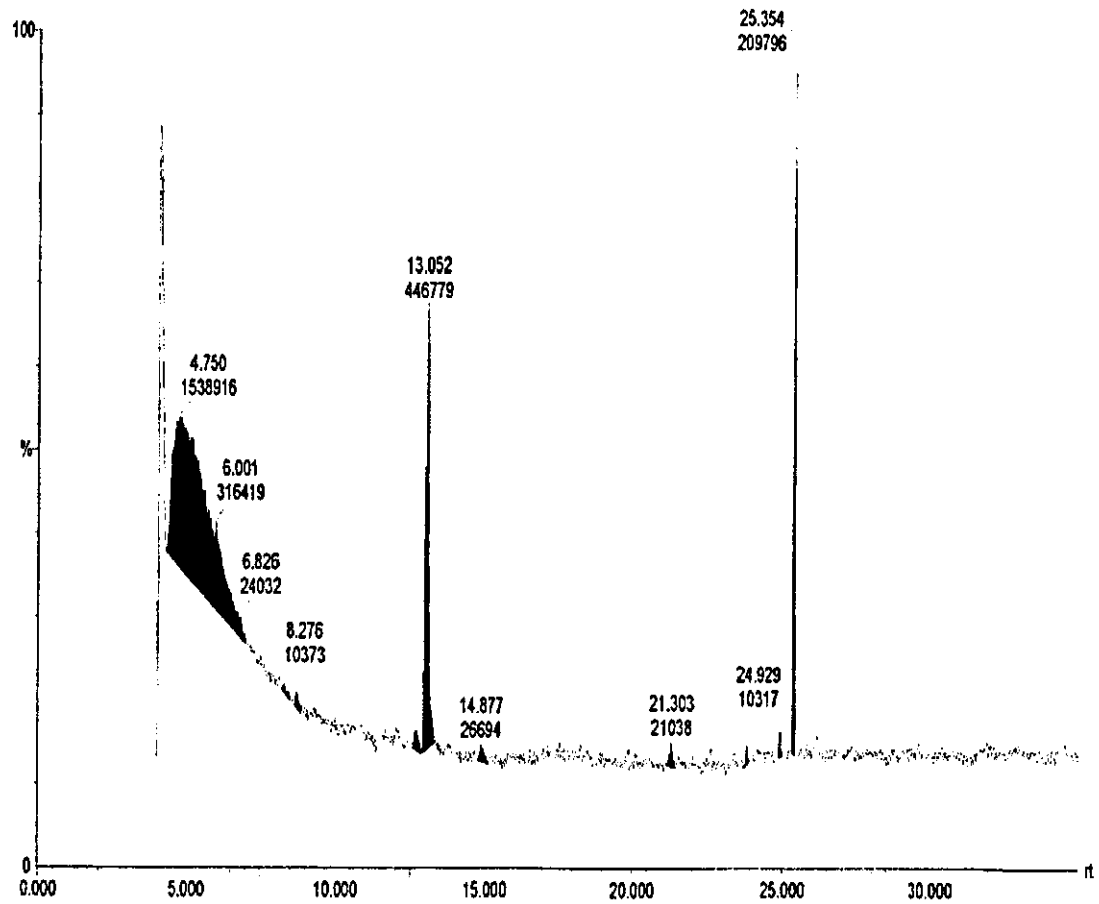
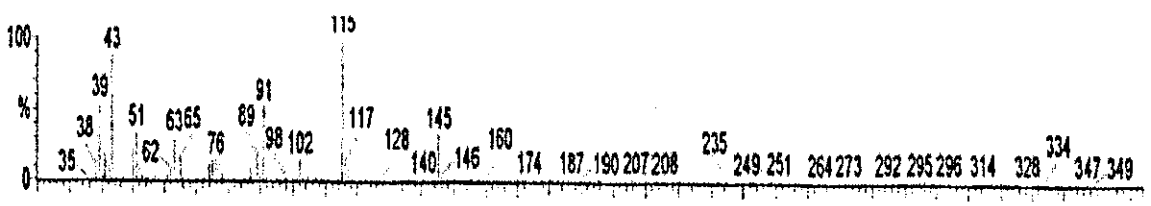


Figure 67. Mass spectra of 2-methyl-3-phenyl-propenal (RT 13.052)



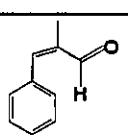
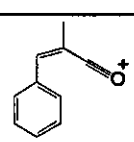
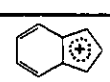
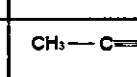
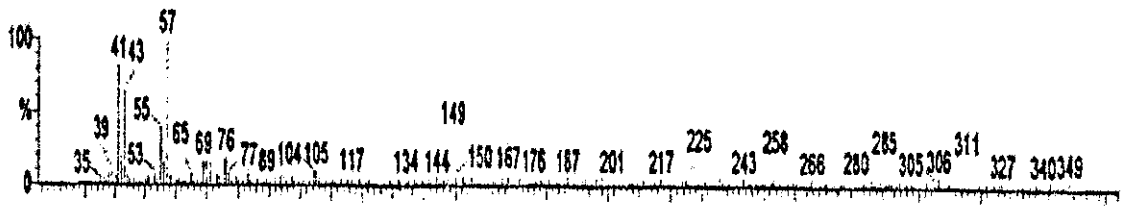
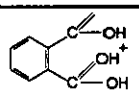
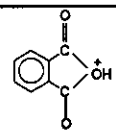
m/z	Structure	m/z	Structure	m/z	Structure	m/z	Structure	m/z	Structure
146		145		115		91		43	

Figure 68. Mass spectra of didodecylphtalate (RT 25.354)



m/z	Structure	m/z	Structure
167		149	

From the spectra, the fragmentation pattern seems to suggest a high molecular weight phthalate. The MS software has identified the spectrum as belonging to didodecylphthalate which would have a molecular ion peak at 502 m/z .

Figure 69. GC chromatogram of extract fraction 6

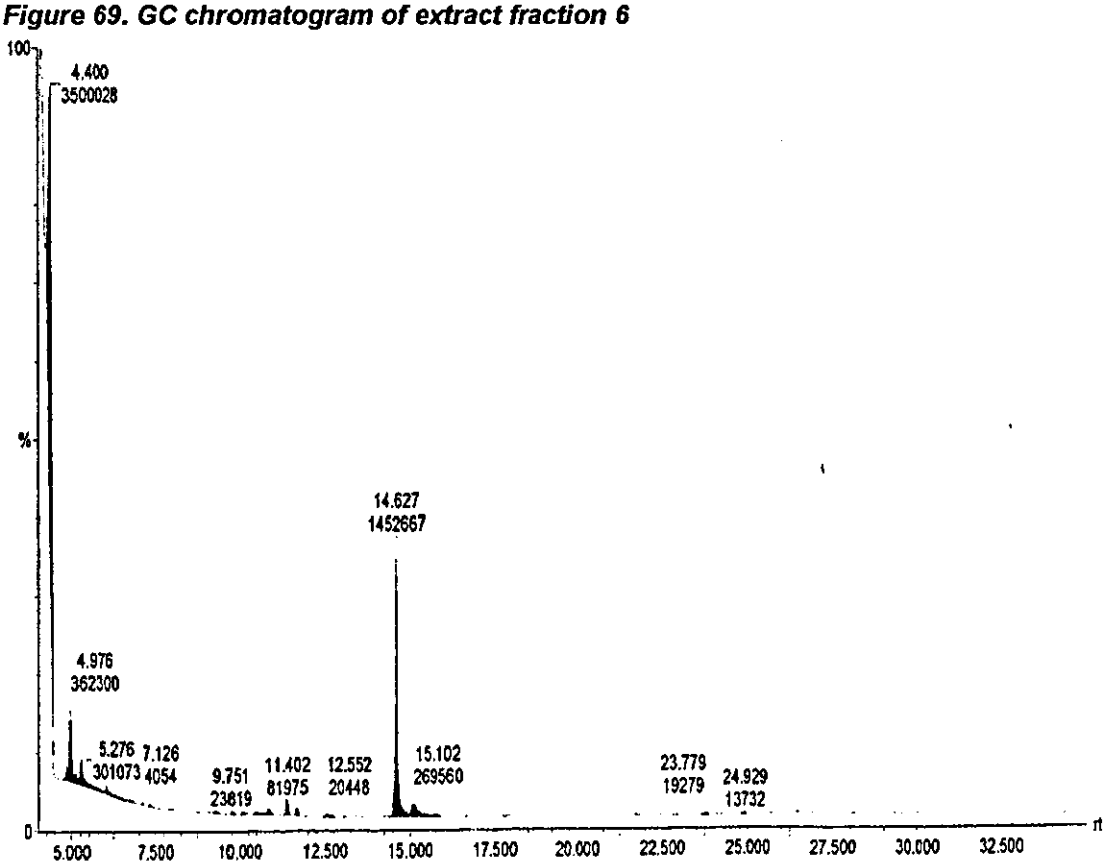
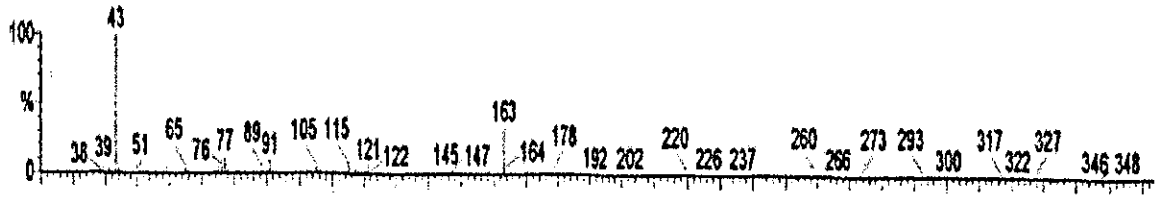
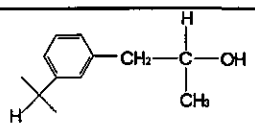
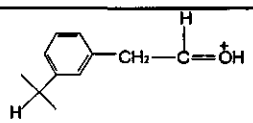
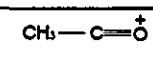


Figure 70. Mass spectra of 1-(3-isopropylphenyl)-2-methyl ethanol (RT 14.627)

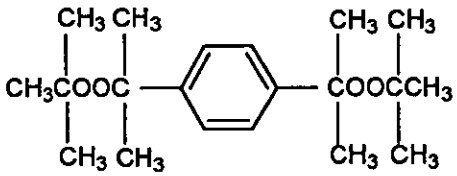


m/z	Structure	m/z	Structure	m/z	Structure
178		163		43	

From the GC-MS analysis, it was possible to ascertain, apart from didodecylphthalate, that all the detected products in the EPDM low molecular weight fraction relate to peroxide breakdown products. Didodecylphthalate is usually used as a plasticiser; however, it does not feature in the formulation given in Section 2.3. It is thought that its presence is a result of contamination during the manufacture of EPDM.

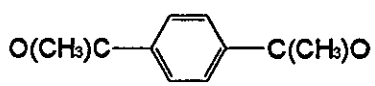
3.3.6 EPDM peroxide curative and associated fragments

In peroxide curing, apart from cross-linking, other reactions occur which do not give rise to cross-linkage, such as chain scission, radical destruction by bimolecular disproportionation, etc. The decomposition of peroxides depends greatly on the stability of the peroxy group which is determined by the nature of the carbon atoms to which it is bound; and other substances present during curing. Primary and secondary carbon atoms give peroxides with a very short half-life time and their decomposition point is generally above room temperature. The decomposition of the tertiary peroxide 1,3 bis-(tert butyl-peroxy-isopropyl)benzene (Perkadox 1440) is mainly homolytic, unless heterolytic decomposition is induced.

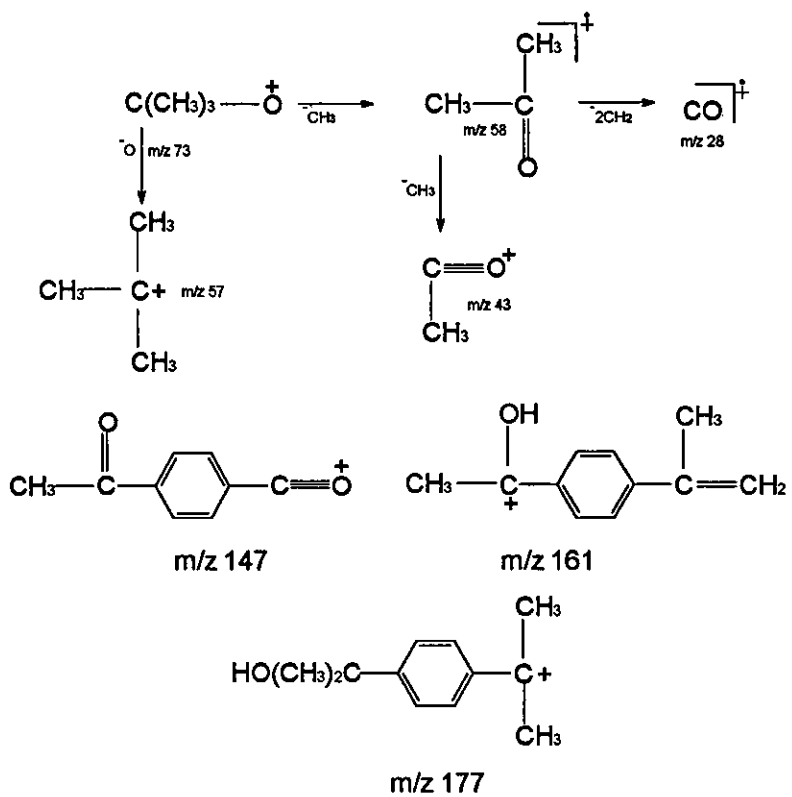


1,3 bis-(tert butyl-peroxy-isopropyl)benzene (Perkadox 1440)

The radicals which form are saturated mainly through dehydrogenation of certain hydrocarbons which are available, e.g. in the polymer chains. Primary degradation in Perkadox 1440 is presumed to occur by C —O and O —O units, occur producing various fragments and regrouping of ions. An example of one such fragment is 1,1'-(1,4-phenylene)bis-ethanone.



Additionally, the following structures are often observed in mass spectra :



Chumicheva[219] examined the products of thermal decomposition of the peroxide used in the EPDM compound. Mass spectral data is presented on the peroxide breakdown products observed

Articles produced with Perkadox 1440 have a strong and offensive smell due to the formation of the above ketones and related compounds. In order to minimise this unpleasant side effect of the curing process, these decomposition products are evaporated in the course of post-vulcanisation in hot air at a high temperature. Often it is necessary to remove the decomposition products by post-curing in order to improve the ageing characteristics of EPDM.

3.4 Silicone rubber

3.4.1 Large scale extraction of silicone rubber

Large scale Soxhlet extractions were performed on silicone rubber using methods described in Section (2.4.11). The extraction results are shown in Table 23.

Table 23. Large scale extraction results of silicone.

Sample (30 g)	Solvent	B.P./°C	Extract/ %	Extract Colour
Silicone	*n*-hexane	68	1.76	Colourless

3.4.1.1 Hexane extractables

The total amount of material Soxhlet extracted with *n*-hexane from finely shredded silicone was 1.76% (duplicate values of 1.70% and 1.82%).

3.4.2 GC-MS analysis of silicone low molecular weight extract

GC-MS analysis was performed upon the silicone Soxhlet extract using the method described in Section 2.4.15. It is apparent from the chromatogram and associated mass spectra, that the majority of the species present in the extract are either cyclic or linear oligomers. The similarity of the mass spectra and the absence of the molecular ion (off-scale due to its high m/z value) made identification very difficult. The results therefore in this section rely upon the MS software interpretation of the spectra. As a consequence, only tentative assignments have been

made. The chromatogram and mass spectra are given in Figures 71-78. A summary of this information is given in Table 24.

Table 24. Proposed structures present in the silicone rubber Soxhlet extract.

Retention Time/Mins	Assignment
5.103	Octamethyl cyclotetrasiloxane
9.053	Decamethyl cyclopentasiloxane
11.854	Dodecamethyl cyclohexasiloxane
22.206	Linear siloxane oligomers
23.406	Linear siloxane oligomers
24.531	Linear siloxane oligomers
25.656	Tetradecamethyl hexasiloxane
27.106	Undentified siloxane oligomer
29.081	Undentified siloxane oligomer
31.857	Undentified siloxane oligomer

Figure 71. GC of silicone low molecular weight extract

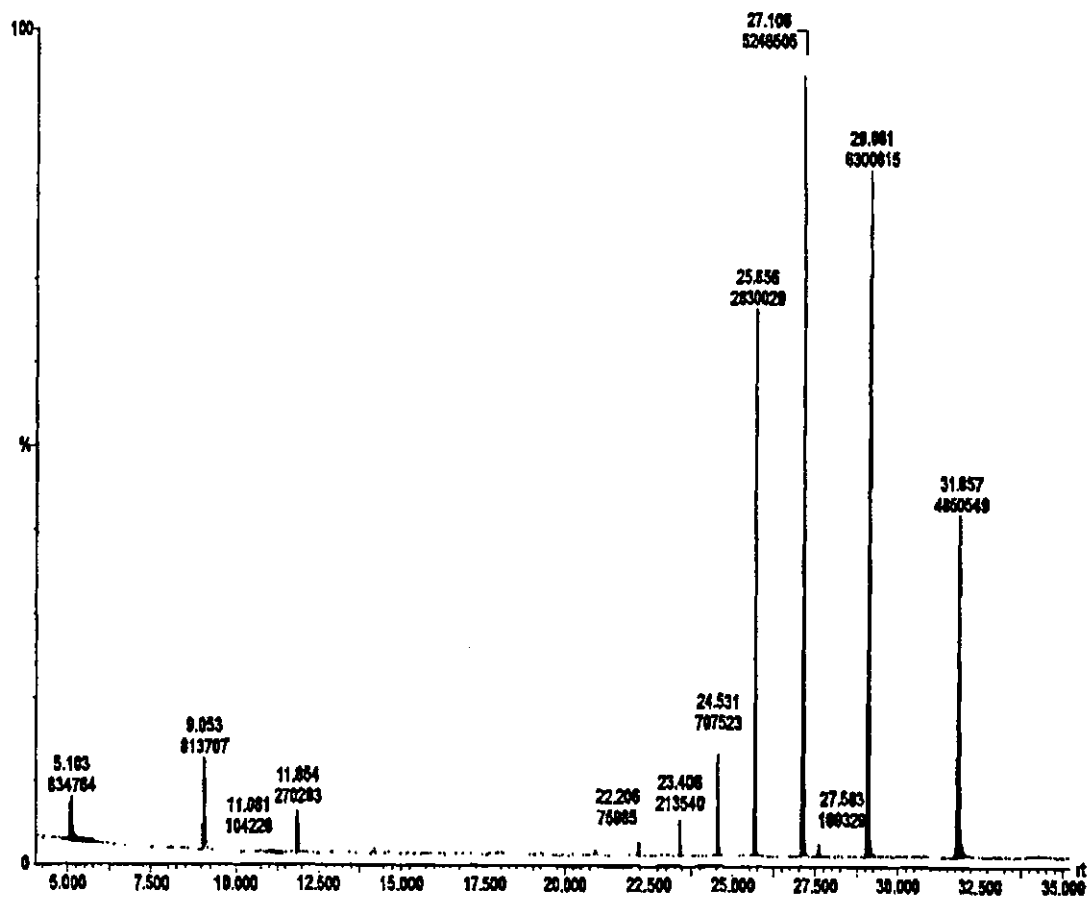


Figure 72. Mass spectra of octamethyl cyclotetrasiloxane (RT 5.103)

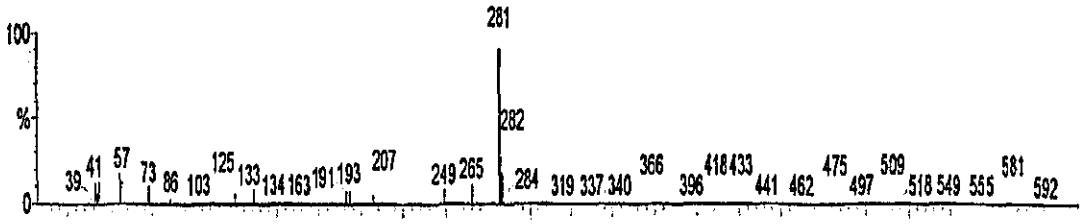


Figure 73. Mass spectra of decamethyl cyclopentasiloxane (RT 9.053)

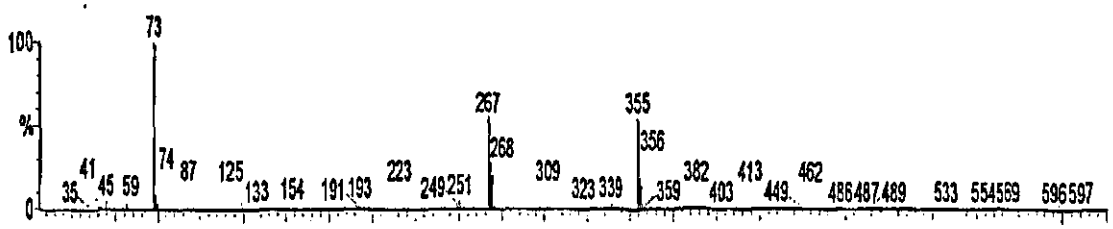


Figure 74. Mass spectra of dodecamethyl cyclohexasiloxane (RT 11.854)

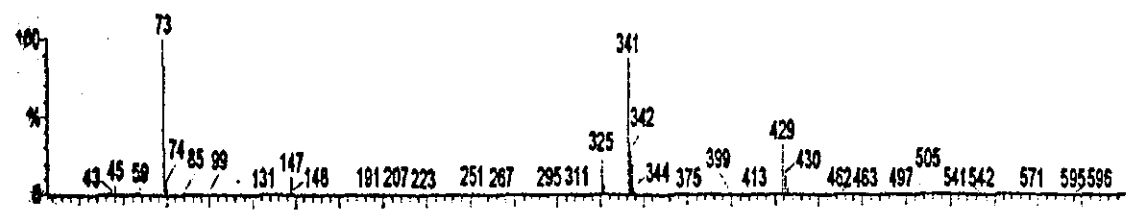


Figure 75. Mass spectra of linear siloxane oiligomers (RT 22.206)

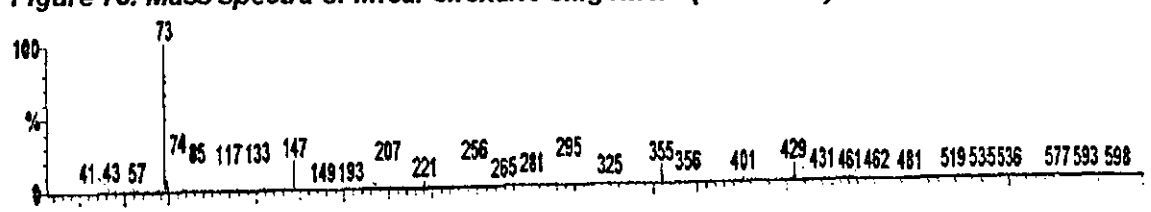


Figure 76. Mass spectra of linear siloxane oiligomers (RT 23.406)

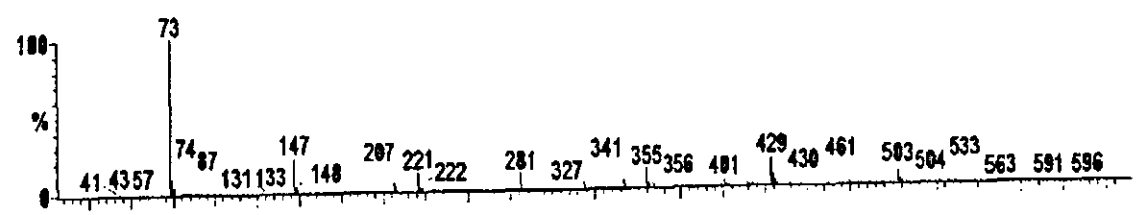


Figure 77. Mass spectra of linear siloxane oiligomers (RT 24.531)

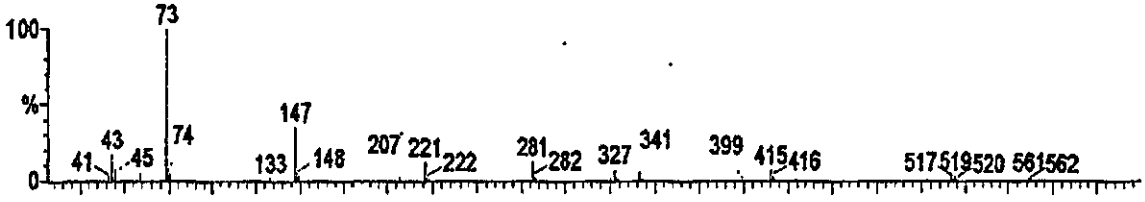
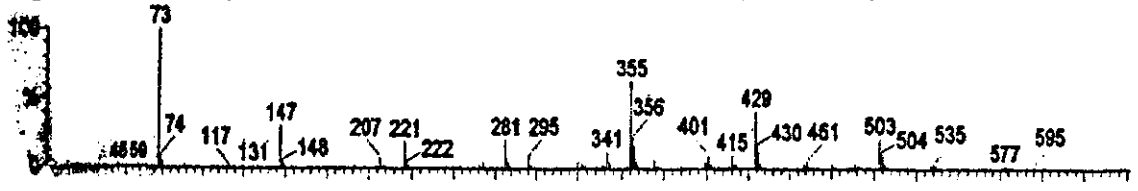
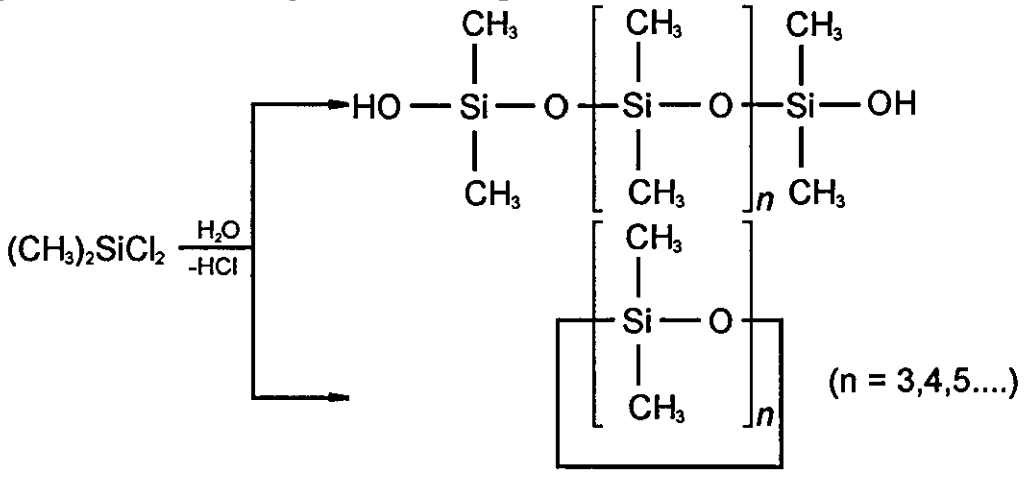


Figure 78. Mass spectra of tetradecamethyl hexasiloxane (RT 25.656)



It can be seen from Table 24 that a number of cyclic siloxanes were detected by GC-MS analysis. Their presence can be attributed to the hydrolysis of dichlorosilanes[55] during manufacture of the silicone rubber. Normally the hydrolysis of dimethyldichlorosilane leads to a mixture of linear and cyclic polymers as illustrated in Figure 79.

Figure 79. Formation of cyclic silicone oligomers

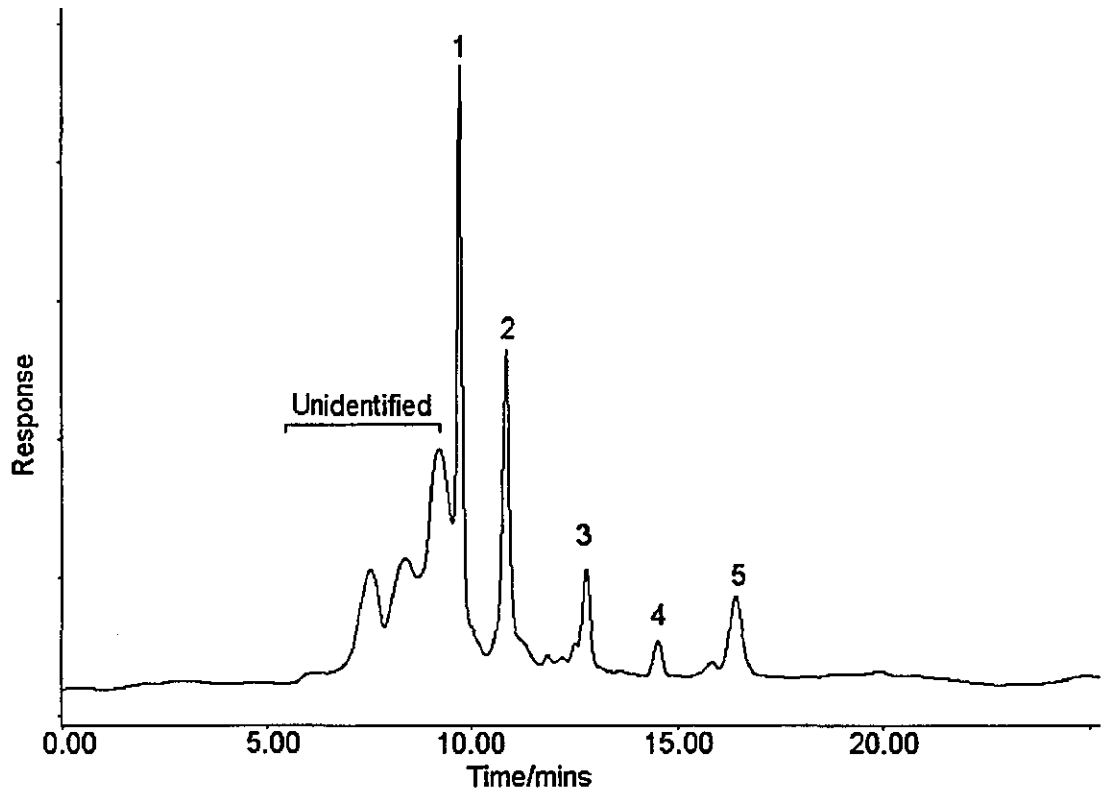


The ratios of cyclic and linear polymers are determined by the reaction conditions; however, the cyclic tetramer forms the main part of the cyclic fraction.

3.4.3 Analysis of silicone low molecular weight Soxhlet extractables by HPLC

As mentioned in Section 3.2.3 the peak height ratioing performed by the GC-MS computer software had the effect of increasing the signal to noise ratio of the scan. It was therefore possible that species of a non-silicone origin at low concentrations may be present in the extract but were undetectable in the base-line noise. It was known that the absence of chromophores in silicone did not lend itself to UV detection. Refractive index detection could not be used in most cases because of gradient elution requirements. The extract was therefore fractionated using HPLC with UV detection set between 203 and 254 nm which could reveal any non-silicone species such as peroxide breakdown products or processing aids present in the extract. Normal phase studies were performed initially with an analytical HPLC column (25 cm x 4.6 mm) containing Spherisorb S5W and then scaled up to incorporate a semi-preparative column (30 cm x 7.8 mm) also containing Spherisorb S5W. These separations were performed isocratically and in gradient mode. A series of experiments were carried out and optimum separation conditions were found to consist of a *n*-hexane : THF (90:10) mobile phase at 2 ml/min, a 2 ml injection loop, UV detection at 203 nm with 10% w/v aliquots injected onto the system. The chromatographic system was connected to a Frac-100 fraction collector. The collected fractions were then dried in a vacuum oven at room temperature. These fractions were then subject to GC-analysis with mass spectrographic detection in a attempt to identify the collected fractions.

Figure 80. Separation of the silicone extract by a S5W column (30 cm x 7.8 mm) with a n-hexane : THF (90:10) mobile phase at 2 ml/min with UV detection at 203 nm with 10% w/v aliquots injected onto the system



3.4.4 Silicone extract fraction identification from HPLC by GC-MS

Unfortunately, the GC-MS analysis of the fractions obtained from HPLC analysis of the silicone extract revealed only silicone oligomer species present. No other compounds were identified.

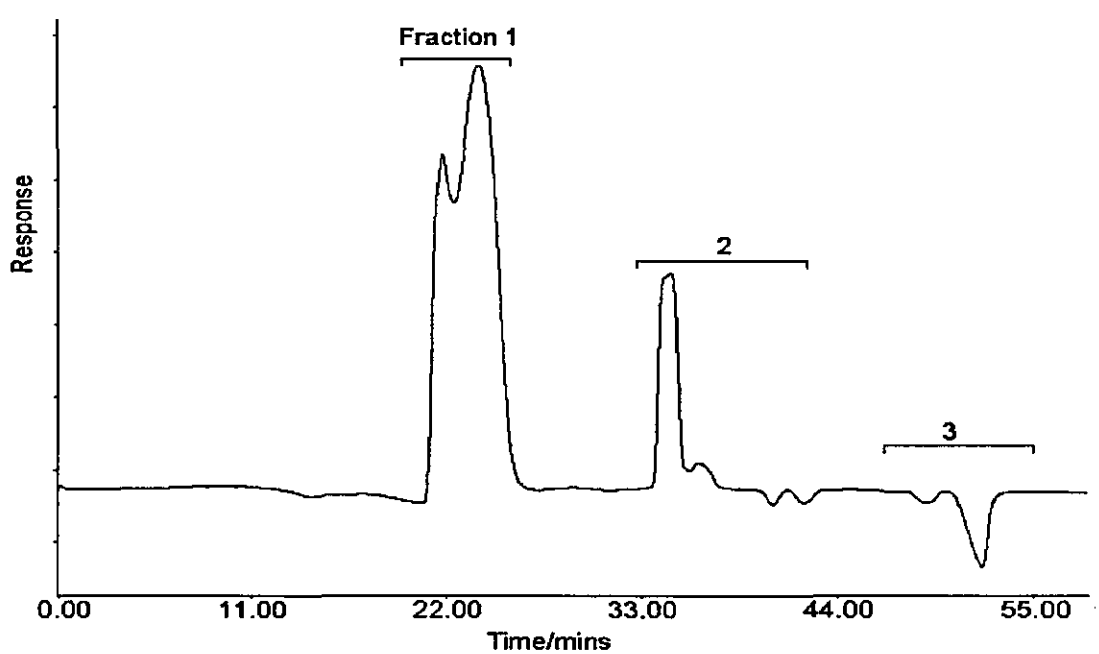
Table 25. Silicone rubber extract fraction identification from HPLC by GC-MS

Fraction	Assignment
1	Tetradecamethyl hexasiloxane (Tentative assignment)
2	Hexadecamethyl heptasiloxane (Tentative assignment)
3	Linear siloxane oligomers
4	Linear siloxane oligomers
5	Linear siloxane oligomers

3.4.5 Analysis of silicone low molecular weight Soxhlet extractables by SEC

HPLC analysis had not provided any information about potential non-silicone species present in the extract. If indeed, any non-silicone compounds were present, it was possible that they may have co-eluted with the silicone oligomers. The mechanisms in SEC involve size exclusion rather than adsorption phenomena. The co-elution that may have been experienced with the HPLC separations could be avoided therefore enabling non-silicone fractions to be collected with silicone interference. An SEC system was developed based on four (30 cm x 7.5 mm) columns containing 5 μm, 50 Å PL gel. The columns were used in conjunction with an RI detector and a Rheodyne 7125 injection valve fitted with a 200 μl loop. The chromatographic system was connected to a Frac-100 fraction collector. Toluene, the mobile phase, was delivered at a rate of 1.0 ml/min. 5% w/v aliquots were injected onto the system.

Figure 81. Separation of the silicone extract by 4 (30 cm x 7.5 mm) columns containing 5 μm, 50 Å PL , a toluene mobile phase delivered at 1 ml/min and RI detection. 5% w/v aliquots injected onto the system



It can be seen from the chromatogram in Figure 81 that there are three main groups of peaks. Unfortunately, due to technical problems associated with the rotor seals in the switching valves, it was not possible to utilise the recycle technique mentioned in Section 3.1 to improve the resolution the chromatogram. Fraction 3 exhibited a negative detector response. This can be attributed to these separated species in solution having a lower refractive index than that of toluene, the mobile phase. The three fractions indicated on the chromatogram were collected and dried at room temperature in a vacuum oven.

3.4.6 Silicone extract fraction identification from SEC by GC-MS

The SEC chromatogram (Figure 81) was fractionated as described in Section 3.4.5. The collected fractions then underwent GC-MS analysis with the conditions described in Section 2.4.15. A summary of this information is given in Table 26.

Table 26. Silicone extract fraction identification from SEC by GC-MS

Fraction From Sec	Compound / Retention Time/ Mins
1	Linear siloxanes
2	Linear siloxanes
3	Benzoyl chloride (7.700) 2-phenyl-1,2-bis(trimethylsilyloxy)propane (7.775) Decamethyl cyclopentasiloxane (9.201) 1-(2,4,6-trimethylphenyl)ethanone (13.454)

Figure 82. GC chromatograms of extract fraction 1

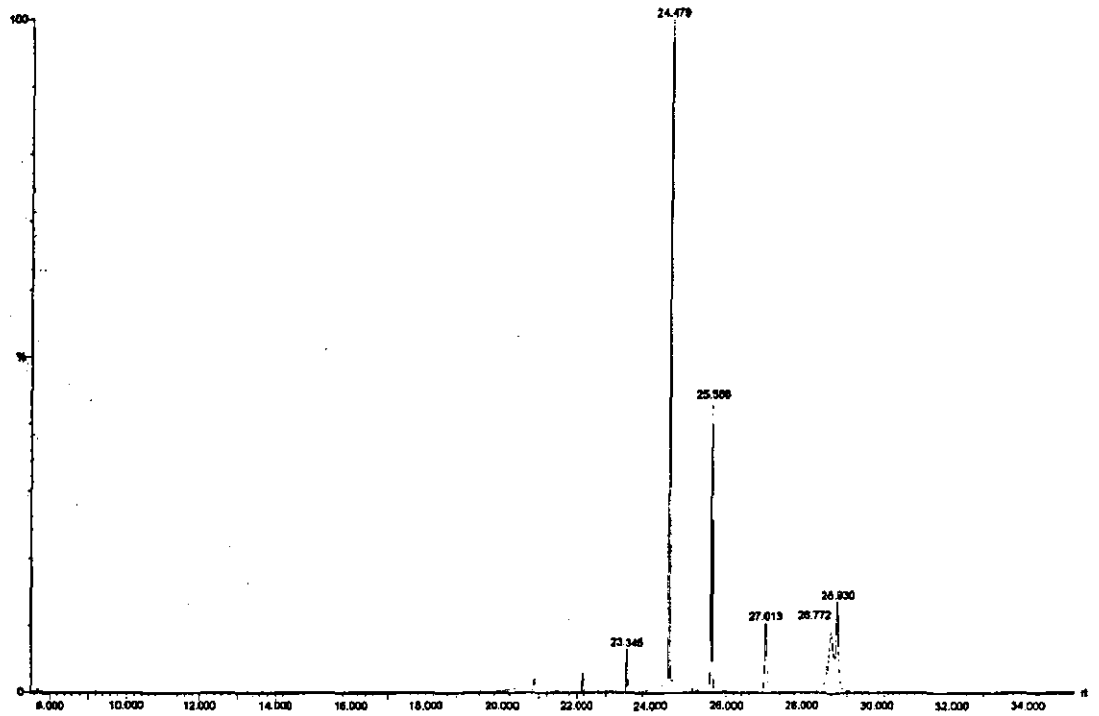


Figure 83. GC chromatograms of extract fraction 2

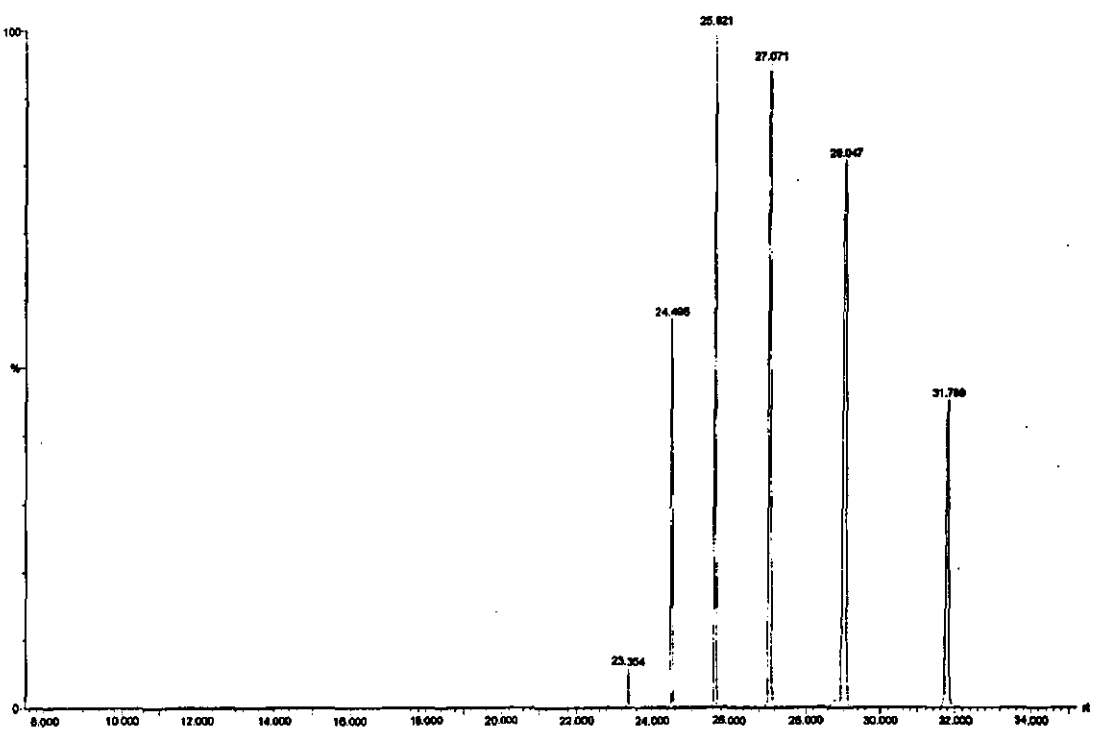


Figure 84. GC chromatograms of extract fraction 3

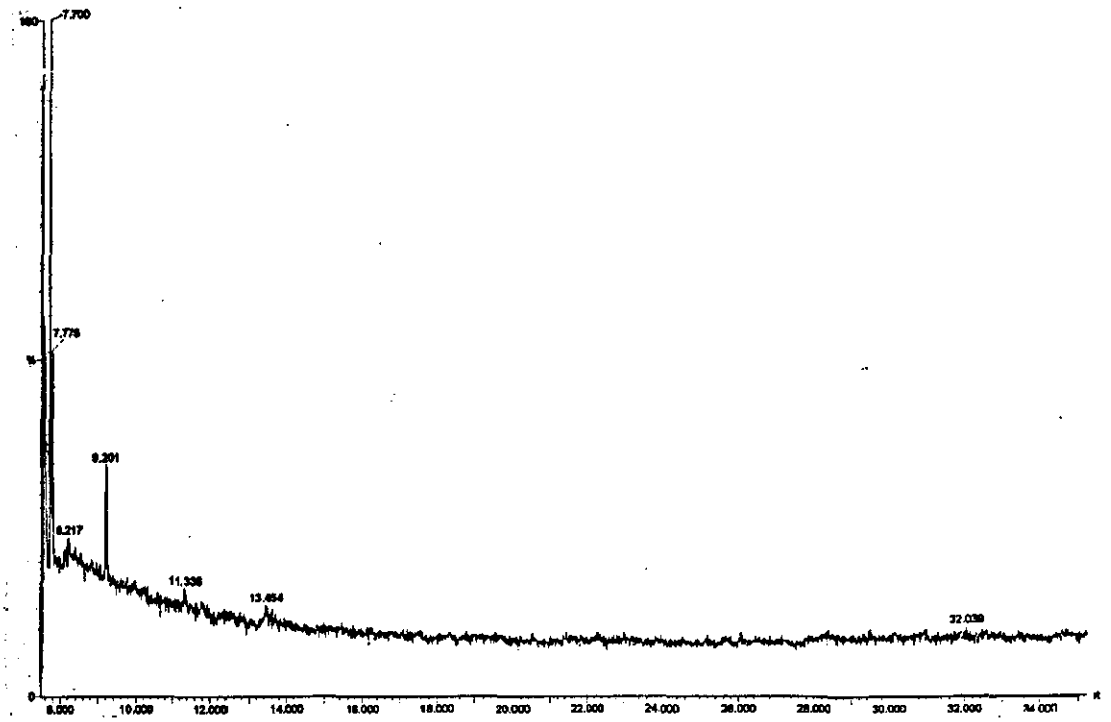


Figure 85. Mass spectra of benzoyl chloride (7.700)

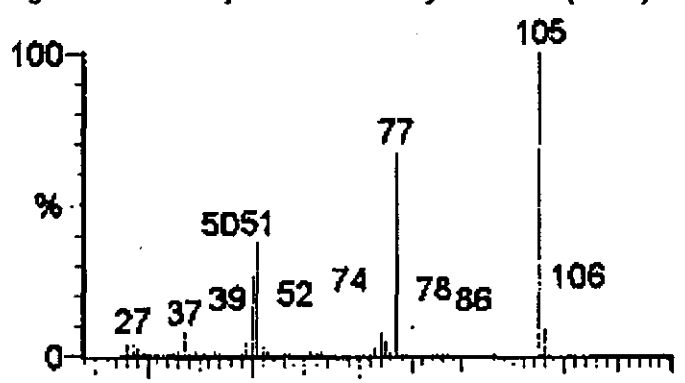


Figure 86. Mass spectra of 2-phenyl-1,2-bis(trimethylsilyloxy)propane (RT 7.775)

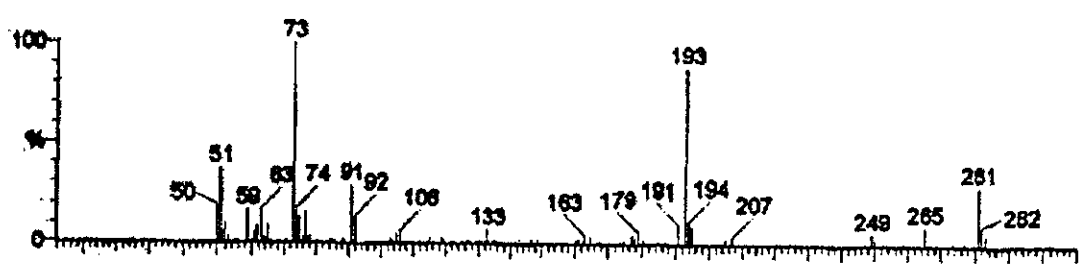


Figure 87. Mass spectra of decamethyl cyclopentasiloxane (RT 9.192)

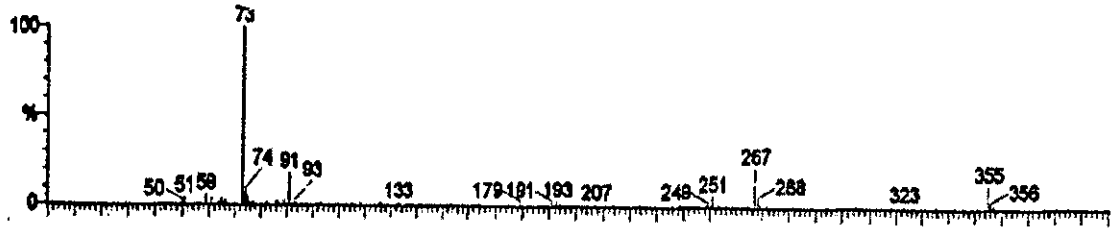
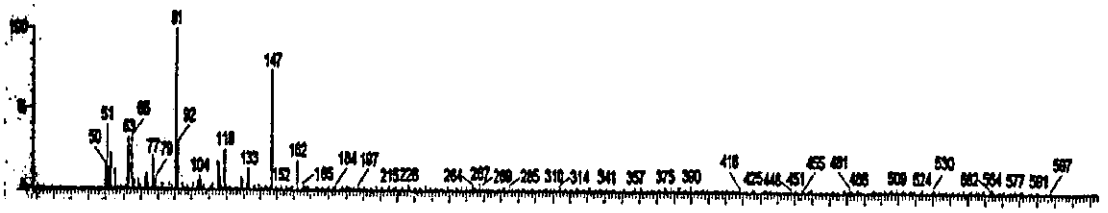
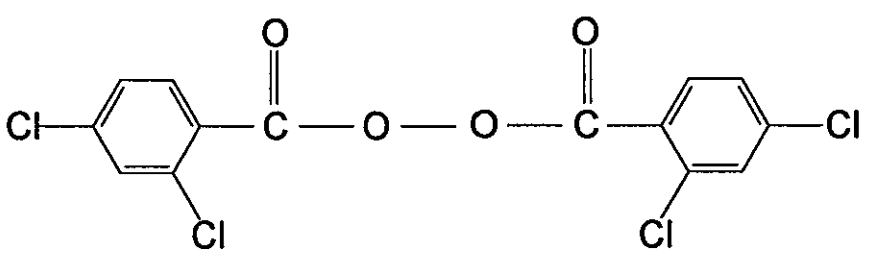


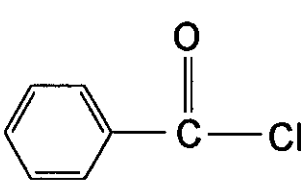
Figure 88. Mass spectra of 1-(2,4,6-trimethylphenyl) ethanone (RT 13.045)



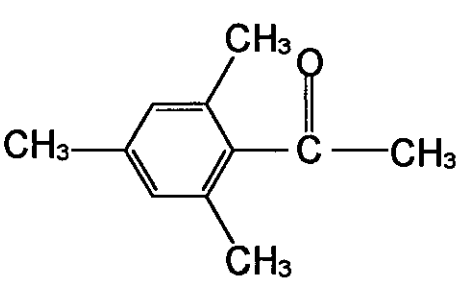
It can be seen from Table 26 that fraction 3 contained benzoyl chloride and 1-(2,4,6-trimethylphenyl) ethanone. It was originaly considered that these two compounds may have been formed by the breakdown of the cross-linking agent bis (2,4-dichlorobenzoyl) peroxide.



Bis (2,4-dichlorobenzoyl) peroxide



Benzoyl chloride



1-(2,4,6-trimethylphenyl) ethanone

However, by examining their structures, it must be concluded that it is unlikely that benzoyl chloride and 1-(2,4,6-trimethylphenyl) ethanone were formed by the decomposition of bis (2,4-dichlorobenzoyl) peroxide. In

addition, it must also be noted that no breakdown products of the peroxide curative were detected. The possible origin of these two compounds may be attributable to the proprietary additives used in the silicone formulation. Unfortunately, it was not possible to obtain any information about these compounds from the manufacturer.

4. Conclusions and suggestions for further work

4.1 General conclusions

During this investigation, new methods have been developed which characterise and quantify additives, oligomers and breakdown products associated with a variety of food contact polymers. The data obtained from these studies have highlighted the complex nature and range of possible migrating species, particularly those relating to elastomeric materials. It is hoped that these techniques will assist in the development of possible methodologies to obtain validated data for the migration, under appropriate conditions, of species present in food contact polymers.

The nature of migrating material is dependent on the extraction solvent/food simulant type. For example, an acidic simulant such as 3% acetic acid readily extracts phenylene diamine antiozonants and reacts with inorganic oxides and carbonates to form soluble acetates. Major products of the thiazole and peroxide cure systems examined are particularly water soluble. Di 2-ethylhexylphthalate, relative to other potential migrants has only limited solubility in aqueous simulants however has higher solubility in non-polar simulants such as *iso*-octane. During this investigation however, the choice of extractants were determined by MAFF.

4.2 Poly(vinyl chloride)

One of the major aims of this investigation was to ascertain whether coupled column chromatography would be a viable technique for the separation of potential migrants, such as additives and oligomers found in

polymers used in food contact applications. The major benefit of a coupled system is the possibility to select only those fractions of analytical interest from a chromatogram and perform further chromatography upon them bypassing the need for any additional sample handling. This has the effect of increasing the efficiency of the analysis by eliminating sample waste and speeding up run times. In order to achieve this objective, it was necessary to identify a polymer system which had been well characterised[207]. Lucovyl RB8010 was chosen as an appropriate PVC system which possessed sufficient quantities of low molecular weight compounds that, under certain conditions, could migrate into food.

Initial studies were aimed at duplicating the extraction and chromatographic techniques performed on the Lucovyl RB8010 system in an attempt to repeat the separations obtained in previous investigations[207]. It was then intended to improve the efficiency of the extraction techniques and apply coupled column methodologies to the same separations and duplicate the results once again. Direct comparison of the chromatograms was used to confirm that coupled column chromatography had successfully duplicated the separations obtained using non-coupled techniques.

4.2.1 Soxhlet extraction of PVC

This work has optimised the process of obtaining low molecular weight Soxhlet extracts from a PVC base resin, with respect to three important areas: extract yield, contamination and degradation.

4.2.2 Acquiring a low molecular weight PVC fraction from the diethyl ether Soxhlet extract

Impurities in the low molecular weight fraction were known to hinder detection and separation of the VC oligomers by SEC. These impurities were removed by fractional precipitation and adsorption liquid chromatography. It was possible to efficiently prepare reasonably pure low molecular weight fractions from Soxhlet extracts of PVC.

4.2.3 Separation of VC oligomers

The polyisomeric nature of the VC oligomers necessitated the development of a chromatographic technique capable of resolving each entity prior to any attempted structural characterisation by NMR. An SEC system based on columns containing 5 μm, 50 Å PL gel packing was found to be capable of separating the VC oligomers from tetramer to decamer from a low molecular weight PVC fraction. The data confirmed the observation that each VC oligomer species exists as a number of structural isomers, the amount increasing with increasing chain length. To investigate this further, the pentamer was accumulated by fractionating the purified low molecular weight fraction.

4.2.4 Separation of the VC pentamer fraction

The analysis of the pentamer fraction revealed at least four isomeric forms. The analysis was accomplished by an HPLC system based on a S5W silica column and a mobile phase of *n*-hexane containing 1% v/v MTBE modifier. The principle limitation of this method however, was the small amount of VC pentamer available and the requirement for repeated fraction collection to obtain sufficient mass if successful structural studies were to be performed using NMR.

4.2.5 Separation of VC pentamer, hexamer and heptamer oligomers by coupled column chromatography

It was attempted to improve and extend the separation scheme so that it would be possible to achieve a full structural characterisation of VC oligomers from the pentamer isomer. Due to the requirements of NMR, the existing separation scheme was modified to incorporate a coupled column system where fractions from the SEC system were directed via a switching valve on-line into the HPLC. By eliminating sample waste, the efficiency of the analysis increased reducing the need for multiple fraction collection. Efforts were directed at duplicating the results obtained for the pentamer fraction. It was evident by comparing the pentamer isomer chromatograms that there was good agreement between the coupled column and the off-line technique.

The coupled column technique was then applied to the hexamer and heptamer oligomer fractions and were resolved successfully into their constituent isomers. This data confirmed the observation that each VC oligomer species exists as a number of structural isomers, the amount increasing with increasing chain length.

4.2.6 Structural characterisation of the VC oligomers

The limited quantity of each isomer available hampered structural characterisation of the VC oligomers. Even with the implementation of the coupled column procedure, considerable fractionation was still required in order to obtain sufficient sample for NMR and mass spectroscopic studies to be performed.

4.2.7 Suggestions for further work

The amount of structural information that could be obtained on each VC oligomer was limited due to the very small quantities available. The isomer preparation programme must be further modified in order to facilitate the accumulation of much larger quantities of each species. The efficiency of the coupled column work could be further improved should preparative columns be utilised instead of the analytical type. The optimisation of material transfer from one column system to another must be optimised and the application of a universal mobile phase for both column systems.

4.3 Nitrile Rubber

4.3.1 Soxhlet extraction

Soxhlet extractions were performed with *n*-hexane and *iso*-octane. The mass of the theoretical extract based on the level of additive addition and assuming that all of the sulphur is present in the polymer network was less than the experimental extract yield for both extractants. This suggested that solubles associated with the polymer were also extracted.

4.3.2 Analysis of Soxhlet extract

GC-MS analysis revealed that the extract contained di-2 ethyl hexyl phthalate plasticiser, antiozonant and compounds associated with the antioxidant. Normal phase HPLC utilising a *n*-hexane : THF gradient was then performed on the extract in an attempt to fractionate these compounds and others that were present in the extract but not positively identified by GC-MS because of their low residual concentration. GC-MS analysis of these collected fractions revealed the presence of a number of compounds

previously unidentified during the analysis of the bulk extract. These compounds were believed to originate from cure system break-down products, carbon black, silicone lubricants and components of the antiozonant.

Although the GC-MS analysis was routine, a limitation was experienced with the mass spectrometer. The mass spectrometer range was unfortunately restricted to under 600 m/z. Although this did not pose a problem for the identification of low molecular weight compounds, high molecular weight hydrocarbons and silicone oligomers could not be fully identified. Ideally, these compounds would have undergone NMR analysis; however, this was not possible due to the low concentration of these analytes in the collected fractions.

4.3.3 Quantitative analysis of four target compounds extracted from NBR

Quantitative analysis was performed on 4 target compounds which were considered to have food contact implications. These compounds were *iso*-octane extractables and were determined by normal phase HPLC. The concentrations of the 4 specified components present in the *iso*-octane extract were determined as was the quantity of each material that was extracted from NBR as follows: di-2 ethyl hexyl phthalate, tetratetracontane, benzothiazole and N-isopropyl-N'-phenyl-*p*-phenylene diamine.

4.3.4 Suggestions for further work

The amount of structural information that could be obtained for each fraction was limited due to the very small quantities of analyte available. It

is therefore necessary to improve the efficiency of the extraction procedure in order to increase the quantity of extracted species. This could be achieved by increasing the surface area of the sample undergoing extraction and utilising more aggressive solvents. The efficiency of fraction collection could also be improved by utilising larger scale chromatographic columns. In addition to NMR studies, it will be also useful to submit fractions for mass spectroscopy utilising a more powerful spectrometer with a greater m/z range.

4.4 Ethylene-propylene-diene monomer elastomer

4.4.1 Soxhlet extraction

Soxhlet extractions were performed with *iso*-propanol. The mass of the theoretical extract based on the level of additive addition was greater than the experimental extract yield. This result indicated that much of the process oil has not been extracted. The low extract yield is attributable to the solvent resistance of EPDM. It is well known that EPDM has a high resistance to polar and non-polar solvents.

4.4.2 Analysis of Soxhlet extract

From SEC analysis, the molecular weight of the extract was found to be less than 600. It was known that the process oil additive was composed of aliphatic hydrocarbons greater than 1000 molecular weight. It is apparent from the molecular weight data that none of this high molecular weight oil or high molecular weight compounds originating from the precured polymer are present in the extract.

GC-MS analysis in conjunction with HPLC revealed that apart from didodecylphthalate, all the detected products in the EPDM low molecular weight fraction related to peroxide breakdown products.

4.4.3 Suggestions for further work

Analysis of the EPDM sample proved difficult because of its inherent chemical inertness and its resistance to solvents resulting in low extract yields. Unlike NBR with its multi-component formulation, the EPDM formulation is relatively simple with only few potentially extractable additives and break-down products associated with its cure chemistry. It is necessary to improve the efficiency of the extraction procedure in order to increase the quantity of extracted species. This could be achieved by increasing the surface area of the sample. The efficiency of fraction collection could also be improved by utilising larger scale chromatographic columns. It would also be desirable to perform NMR studies on the collected fractions and submit fractions for mass spectroscopy utilising a more powerful spectrometer with a greater m/z range.

4.5 Silicone Rubber

4.5.1 Soxhlet extraction

The silicone rubber underwent Soxhlet extraction utilising *n*-hexane as the extractant. It gave the lowest extraction yield of all the elastomers in this investigation (1.76%).

4.5.2 Analysis of Soxhlet extract

Unfortunately, it was not possible to perform SEC molecular weight analysis on the extract. This was due to the fact that an appropriate mixed gel system with a toluene mobile phase was not available. GC-MS analysis was performed upon the Soxhlet extract which revealed the presence of cyclic and linear silicone oligomers. The similarity of the mass spectra of the linear oligomers and the absence of the molecular ion (-off scale due to its high m/z value) made identification very difficult. The results therefore relied upon the MS software interpretation of the spectra. As a consequence, only tentative assignments were made. After a series of chromatographic experiments utilising various chromatographic procedures, SEC was used to fractionate the extract. These fractions underwent GC-MS analysis and a number of non-silicone compounds were identified which were thought to originate from the process additives incorporated during manufacture.

4.5.3 Suggestions for further work

As with the PVC, NBR and EPDM, the major problems are the low concentrations of individual species present in the silicone extract which limit the choice of spectroscopic analysis that can be performed and necessitate lengthy repeat fractionation procedures. It is therefore necessary to optimise fractionation to increase the quantity of individual species using techniques described in the previous sections to facilitate analysis by techniques such as NMR and high resolution mass spectroscopy.

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6. Appendix

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Separation of Oligomers from Poly(vinyl chloride) by Coupled Column Chromatography

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A multistage scheme was developed for the separation of vinyl chloride (VC) oligomers. A low-molecular-weight fraction was isolated from poly(vinyl chloride) by Soxhlet extraction with diethyl ether followed by fractional precipitation with *n*-pentane. The presence of VC oligomers up to decamer was demonstrated by high-performance gel permeation chromatography (HPGPC). Removal of polar impurities was accomplished by preparative adsorption liquid chromatography of the low-molecular-weight fraction. Recycle HPGPC with repeated injections permitted the accumulation of fractions of VC pentamer oligomers which were resolved into their isomers by high-performance liquid chromatography (HPLC) off-line. These results were duplicated utilizing a coupled column system comprising of recycle HPGPC connected on-line to HPLC. This coupled technique was then applied to the hexamer and heptamer oligomers which were resolved into their constituent isomers.

Keywords: Vinyl chloride oligomers, coupled column chromatography, high-performance liquid chromatography, high-performance gel permeation chromatography

INTRODUCTION

The chemical and molecular structure of poly(vinyl chloride) (PVC) has been investigated in some detail because the thermal stability of the polymer is lower than expected on the basis of its ideal structure $(CH^2CHCl)_x$.

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Work indicating the presence of anomalous structures such as branching, head-to-head addition, unsaturation and "labile chlorine" in PVC has been reviewed [1]. Explanations for these structural defects have been considered in terms of possible mechanisms occurring during radical polymerisation of vinyl chloride monomer (VC) [2,3]. Much information can be obtained from investigations of low-molecular-weight species in order to identify and quantify end groups and structural defects at branch points [4,5]. In addition, studies have been directed to the low-molecular-weight fraction of PVC (including additives and oligomers) because these components are potential migrants in plastics packaging [6].

It follows that efficient separation methods are required to isolate VC oligomers. Gilbert *et al.* [7] obtained low-molecular-weight fractions of PVC by Soxhlet extraction followed by fractional gel filtration. The size distribution of components in these fractions was assessed by high-performance gel permeation chromatography (HPGPC) using cross-linked polystyrene gels (particle size 10 μm) having exclusion limits below 500 Å. Analysis of these low-molecular-weight fractions by gas chromatography-mass spectroscopy (GC-MS) [8] enabled the oligomer species from trimer to hexamer to be separated, with some evidence of the heptamer and octamer. From MS data obtained from hydrogenation studies on samples, each oligomeric species was postulated to exist in saturated and unsaturated forms, with each form itself occurring as a number of structural isomers. The total population of isomers was found to increase with increasing chain length. For any given oligomer the mass spectra of its isomers were very similar and no detailed structural information could be elucidated. It was apparent that other analytical techniques, such as nuclear magnetic resonance spectroscopy (NMR), would need to be employed to obtain these data. Continued from previous work [9], a separation scheme was devised [10] in which an alternate pumping recycle HPGPC technique [11], followed by routine high-performance liquid chromatographic (HPLC) fractionation, was capable of resolving the VC pentamer fraction present in a low-molecular-weight fraction into its constituent isomers. With this method, it was possible to isolate 0.5 mg of VC pentamer from a PVC polymer for proton NMR analysis. The principle limitation was the small amount of VC oligomer available and the requirement for repeated fraction collection to obtain sufficient mass if successful structural studies were to be performed using NMR. These limitations can be minimized by the application of a coupled-column system where

the HPGPC was coupled directly on-line to the HPLC chromatograph bypassing the need for any additional sample handling. By eliminating sample waste, the efficiency of the analysis increased reducing the need for multiple fraction collection.

The object of this work is to improve and extend the separation scheme so that it would be possible to attempt a full structural characterisation of VC oligomers from pentamer to heptamer. Because of the requirements of NMR, the existing separation scheme [10] was modified to incorporate a coupled-column system. The methods described in this paper are directed at duplicating the results obtained for the pentamer fraction by the use of a coupled-column system and then applying this coupled technique to the hexamer and heptamer fractions of the low molecular weight extract.

EXPERIMENTAL

PVC Polymer

The PVC polymer used was Lucovyl RB8010 with a K value (solution viscosity parameter used by PVC manufactures) of 56. This was a mass-polymerised sample kindly provided by Atochem (UK).

Reagents

Diethyl ether, tetrahydrofuran, dichloromethane, *n*-hexane, *n*-pentane, methyl *tert* butyl ether (MTBE) and *iso*-propanol (all HPLC grade) were supplied by Fisons (UK).

Low-Molecular-Weight Fractions of PVC

Low-molecular-weight fractions were obtained from the PVC polymer by a two-stage process. Initially, the polymer (250 g) was extracted in a Soxhlet apparatus with diethyl ether for 20 h. At the end of an extraction, the extract was filtered and then reduced to ca. 20 mL in a rotary evaporator. A small portion of this mixture was dried in a vacuum oven at room temperature and then characterized by GPC with a 60 cm × 7.5 mm i.d. PL mixed-gel (10 μm) column (Polymer Laboratories, UK) in a Model 501

chromatograph (Waters Assoc., UK) having a refractive index detector with tetrahydrofuran as a mobile phase at a flow-rate of 1.0 mL/min. The reduced extract was then added to 350 mL of *n*-pentane at room temperature. The mixture was left for 20 min 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 utilizing first a rotary evaporator and then a vacuum oven at room temperature.

Preparative Adsorption Liquid Chromatography

The low-molecular-weight PVC fraction was purified and further fractionated on a Merck Lobar size B column (31 cm × 25 mm i.d.) containing LiChroprep Si 60 (40–63 μm) packing, supplied by Merck (Germany). A Model 64 HPLC pump (Knauer, Germany) was used in conjunction with a PU 4025 UV detector (Pye Unicam, UK) and a Rheodyne Model 7125 injection valve fitted with a 200-μL loop supplied by HPLC Technology (UK).

The mobile phase employed was *n*-hexane containing MTBE modifier (5.0%) at a flow rate of 3.0 mL/min. Aliquots (75% w/v) of the low-molecular-weight fraction were injected into the chromatograph and the fraction within the elution volume range 0–420 mL was collected.

High-Performance Gel Permeation Chromatography

Individual oligomer species were separated from the low-molecular-weight PVC fraction using a GPC system based on two 60 cm × 7.5 mm i.d. columns containing 5-μm, 50 Å PL gel (Polymer Laboratories). The columns were used in conjunction with a Knauer Model 64 pump and a Knauer differential refractometer. An alternate pumping recycle system [10] was set up using a Rheodyne Model 7000 switching valve and a Rheodyne Model 7125 injection valve fitted with a 200-μL loop, all supplied by HPLC Technology (UK). Dichloromethane, the mobile phase, was delivered at a rate of 1.0 mL/min. A separation was performed by injecting an aliquot (5% w/v) and passing it with recycling (1½ recycles) through 300 cm of gel bed. Oligomers corresponding to resolved oligomer peaks were collected manually and the dry oligomer fractions were obtained using a vacuum oven at room temperature.

HPLC

Oligomers prepared by recycle HPGPC were separated into their isomeric forms by normal-phase HPLC. The chromatography consisted of a Waters 600A pump, a 25 cm × 4.6 mm i.d. column containing Spherisorb S5W silica packing supplied by Phase Separations, (UK), a Pye Unicam PU 4025 detector operated at 200 nm and a Rheodyne Model 7125 injection valve fitted with a 200-μL loop supplied by HPLC Technology (UK). The mobile phase employed was *n*-hexane containing MTBE modifier (1.0%) at a flow rate of 1.0 mL/min. Routine fractionation was carried out by injecting aliquots (1% w/v) and the fractions blown to dryness using nitrogen. A schematic illustration of the muti-stage procedure for the separation of VC oligomers from a PVC polymer is shown in Figure 1.

Coupled-Column Chromatography

The coupled-column chromatograph comprised of two dimensions. GPC, the first dimension, consisted of a Model 64 pump, a Model 98 refractive index detector (both Knauer, Germany), a Model 7125 injection valve (Rheodyne, USA) and four PL gel 5-μm, 50Å (30 cm × 7 mm) columns (Polymer Laboratories, UK) with a Model 7000 recycle valve (Rheodyne, USA). HPGPC was used to fractionate the PVC extract into its constituent oligomeric and additive portions with the aid of a recycle technique (1½ recycles). HPLC, the second dimension consisted of a Model 64 pump (Knauer, Germany) a S5W silica HPLC column (25 cm × 4.6 mm) (Spherisorb, UK) and a Model 8800 variable UV detector (Dupont, UK) set at 200 nm. The two dimensions were connected via a Model 7010 switching valve (Rheodyne, USA). As the desired oligomer fraction eluted from the GPC chromatograph, the switching valve was rotated diverting the eluting peak into the HPLC system. Once this was accomplished, the switching valve was rotated back. Aliquots (15% w/v) of the low-molecular extract in HPLC grade dichloromethane were injected via a 200-μL injection loop onto the first chromatographic system (GPC). The mobile phase in the first column system was dichloromethane at a flow rate of 1.0 mL/min. The second system (HPLC) employed a *n*-hexane mobile phase containing *iso*-propanol modifier (2.0–4.0% v/v). The flow rate varied between 0.6 and 1.0 mL/min. Both detectors were connected to a Caliber data station (Polymer Laboratories, UK) which displayed the chromatograms in "real-time".

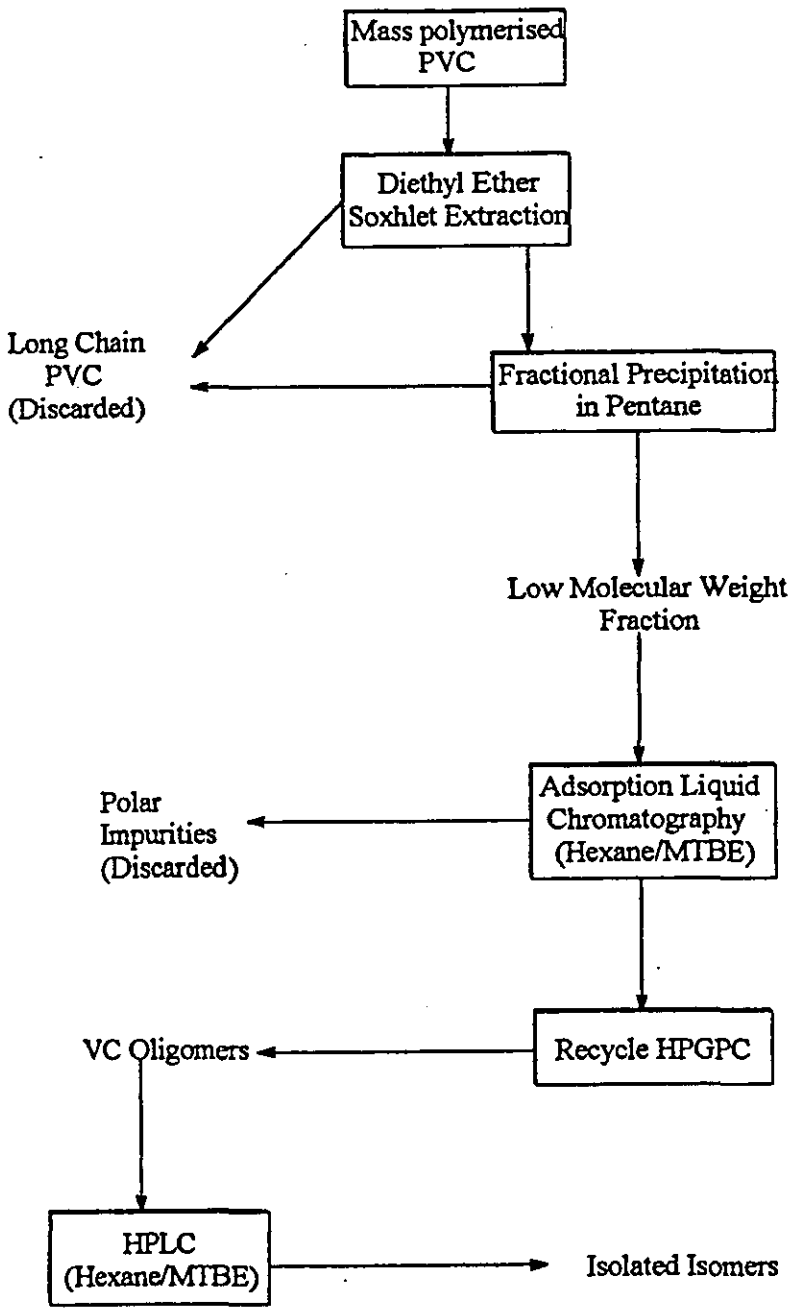

FIGURE 1 Separation scheme.

GC-MS

GC-MS analysis of the various VC oligomer fractions was carried out using either a Carlo Erba Model 4160 gas chromatograph coupled to a VG Mass Labs Quadrupole 15-250 mass spectrometer or a gas chromatograph of the same type connected to a VG Mass Labs 7070 EQ mass spectrometer [7–9]. In each instance, a Chrompack 25 m × 0.2 mm I.D. column coated with a 0.12 μm layer of CP-Sil 5CB was used. The flow rate of the carrier gas (helium) was 1.0 mL/min. Separations were carried out under both isothermal and temperature programmed conditions and the data obtained were processed using an LVG 11-250 data system.

RESULTS AND DISCUSSION

Lucovyl RB 8010 PVC polymer gave an extract yield of 0.80%. When analyzed by GPC, this extract gave a molecular weight of 578. The low-molecular-weight fraction that was obtained from the filtrate after fractional precipitation of the diethyl ether extract with *n*-pentane constituted 25% by weight of the original. The fractions due to VC oligomers have been previously assigned with regard to chain length, as have the peaks due to phthalate and 2,6-di-*tert*-butyl-p-cresol (butylated hydroxytoluene; BHT) impurities [12]. The absence of any discernible concentration of VC dimer is considered to be due to the monomer stripping process, in which the conditions are severe enough to remove the dimer species also. It was possible to assign the oligomeric peaks by using VC oligomers as calibrants because the pentamer to decamer oligomers had been prepared and described in a previous paper [10]. The phthalate and BHT impurities had been identified by GC-MS data.

Because some of the oligomer peaks were obscured by impurities, a further chromatographic technique was employed to purify the low-molecular-weight extract prior to GPC analysis. For this purpose a preparative adsorption liquid chromatographic system was employed. The chromatogram obtained for the low-molecular-weight PVC fraction is shown in Figure 2. It can be seen that the phthalate impurity and oligomer fractions collected are well separated owing to the greater polarity, and hence longer retention time of the phthalate. The amount of MTBE modifier in the mobile phase was set at 5% (v/v). To enable separations to be carried out in

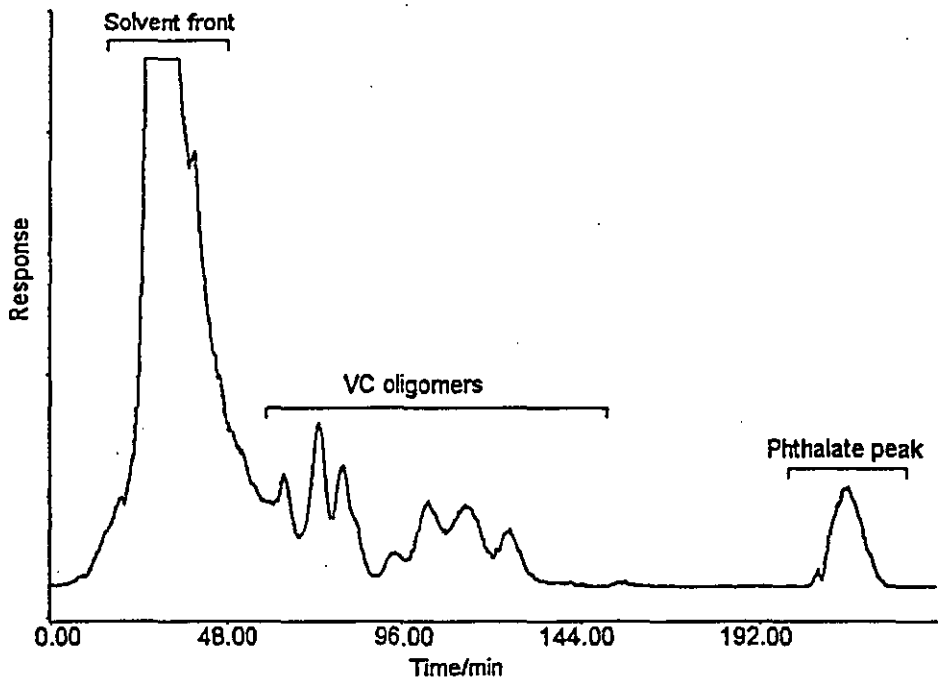

FIGURE 2 Preparative adsorption liquid chromatography of low-molecular-weight fraction from *n*-pentane filtrate. Mobile phase: *n*-hexane-MTBE (95:5) at 3.0 mL/min.

reasonable times while maintaining sufficient oligomer-phthalate resolution. The elution volume range designated in Figure 2 for collection was derived by determining the volume required for all of the VC decamer isomers to elute from the column. As elution time is proportional to oligomer chain length, this ensured that none of the isomers of the oligomers of greatest interest, that is, pentamer, hexamer and heptamer were missed.

With an alternate pumping recycle technique [11], resolution of the VC oligomers was improved and the chromatogram obtained using 300 cm (1½ recycles) of gel bed is shown in Figure 3, where the oligomer species from trimer to decamer are well separated.

The assignments of the oligomer peaks in Figure 3, which had initially been performed by use of the VC oligomer standards, were confirmed by referring to data that had been published previously [8]. The data confirmed the observation that each VC oligomer species exists as a number of structural isomers, the amount increasing with increasing chain length. To investigate this further, the pentamer fraction was accumulated by fraction-

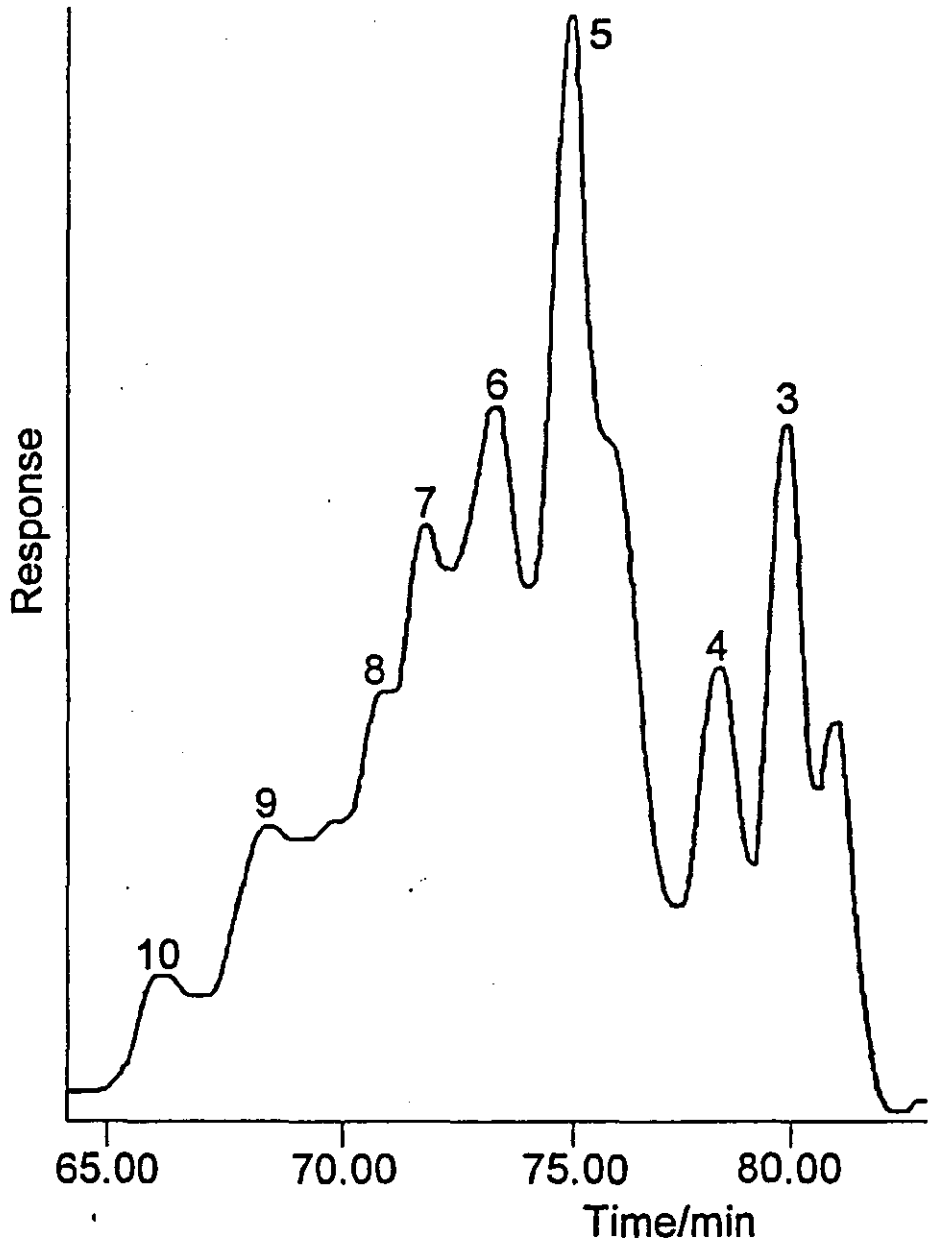

FIGURE 3 GPC of low-molecular-weight fraction from *n*-pentane after preparative adsorption liquid chromatography. Column, 300-cm PL gel (5 μm, 50 Å), eluted with dichloromethane at 1.0 mL/min. The peak numbers refer to the degree of polymerization.

ating the purified low-molecular-weight fraction designated in Figure 3. The polyisomeric nature of the VC oligomers necessitated the development of a chromatographic technique for resolving each entity prior to an attempted structural characterization by NMR. Such a combination of HPLC and ^{13}C NMR analysis has been reported for 2-vinylpyridine oligomers [13]. Liquid-solid chromatography has been used for isomer separation [14] and it was found that a normal-phase HPLC system based on a Spherisorb S5W silica column and a mobile phase consisting of *n*-hexane containing MTBE as a modifier was capable of resolving the isomeric forms of the VC pentamer is shown in Figure 4. Only very small amounts of modifier were required to elute the oligomers from the column because of their relatively nonpolar nature.

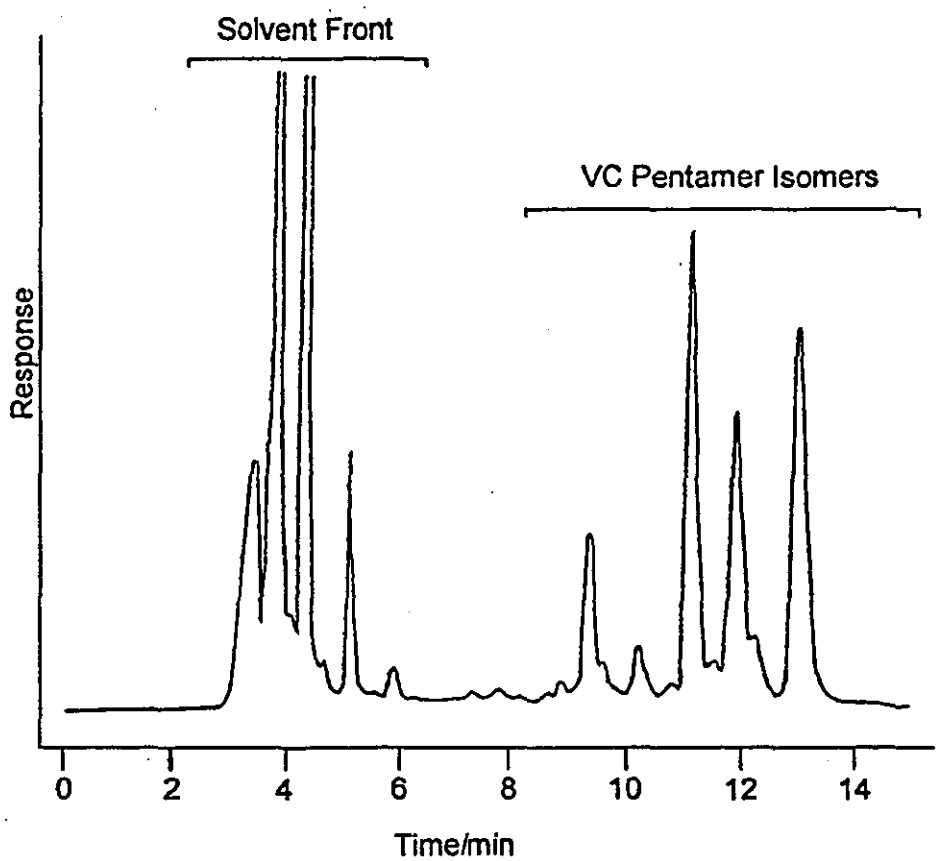

FIGURE 4 HPLC of the VC pentamer fraction. Mobile phase: *n*-hexane-MTBE (99:1) at 1.0 mL/min.

The chromatograms in Figure 4 showed four well-resolved peaks. These peaks were fractionated and analyzed by GC-MS. HPLC fractionation of the VC pentamer from HPGPC was carried out by repeated injections to accumulate a sufficient mass of each isomer for NMR analysis. This method proved to be very time consuming because of the large number of steps involved, the considerable sample handling, and the small mass of oligomer available. Another consideration was the inherent thermal instability of VC oligomers and so only chromatographic techniques that functioned at ambient temperatures could be utilized. These difficulties were minimized by the application of a coupled-column system where fractions from the HPGPC system where directed on-line into the HPLC. Low-molecular fractions isolated from Lucovyl RB 8010 base resin by diethyl ether Soxhlet extraction followed by fractional precipitation were analyzed by recycle HPGPC, as shown in Figure 5. As the pentamer fraction eluted from the HPGPC chromatograph, the switching valve that connected the HPGPC to the HPLC was rotated diverting the eluting peak into the HPLC

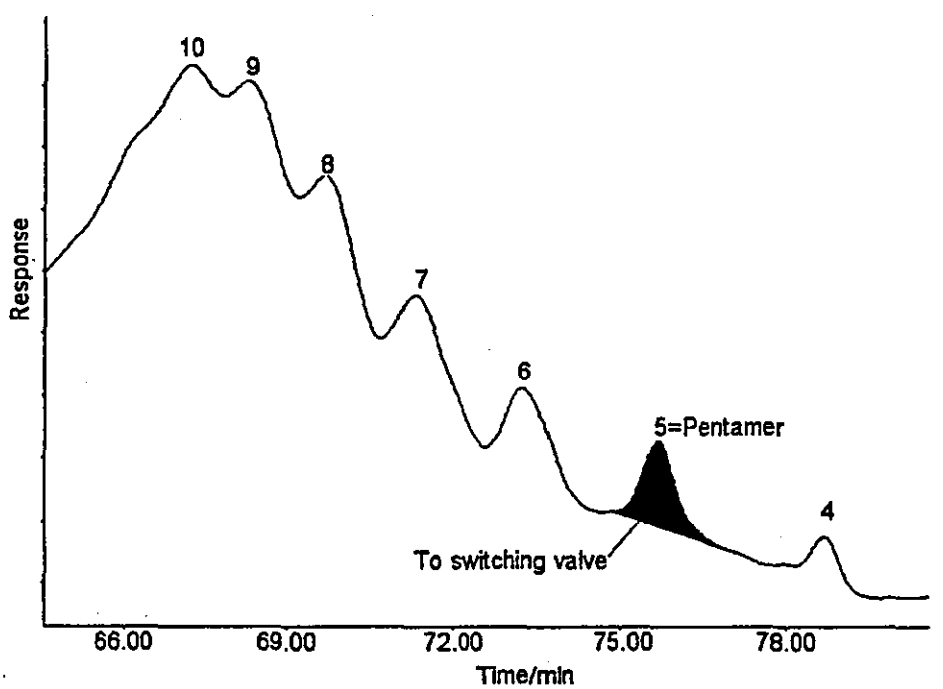

FIGURE 5 GPC of low-molecular-weight fraction from *n*-pentane filtrate utilizing the coupled-column technique. Column, 120-cm PL gel (5 µm, 50 Å), eluted with dichloromethane at 1.0 mL/min. The peak number refer to the degree of polymerization.

system. Once this was accomplished, the switching valve was rotated back. The chromatogram obtained for the pentamer isomers is shown in Figure 6.

It is evident by comparing Figures 3 and 4 with Figures 5 and 6 that there is good agreement between the two techniques. The slight increase in retention times of the isomers in Figure 6 compared to Figure 4 can be attributed to the participation of dichloromethane, the eluent from the HPGPC system, the use of *iso*-propanol (4.0%) as the modifier rather than MTBE and differences in the void volumes of the two systems. These results indicate that the choice of *iso*-propanol as a modifier for the coupled-column system provided comparable resolution to MTBE. Therefore, isomer fractions may be collected for NMR analysis.

The coupled-column technique was then applied to the hexamer and heptamer oligomer fractions. Preliminary studies indicate the presence of isomeric species, as shown by the chromatograms in Figures 7 and 8.

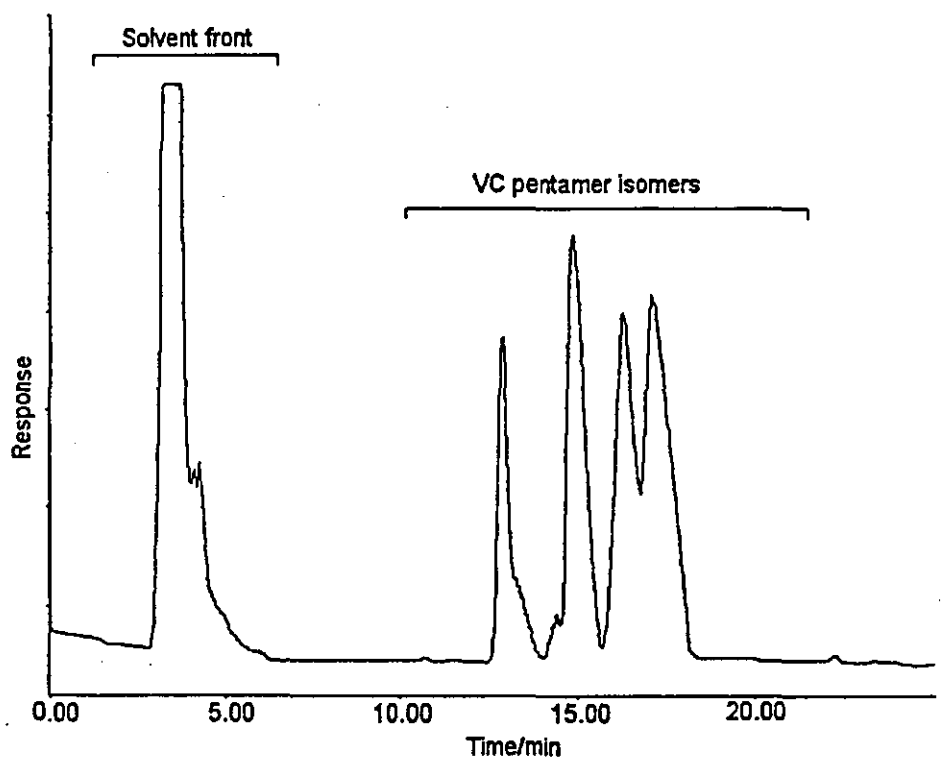

FIGURE 6 HPLC of the VC pentamer fraction obtained by the coupled-column technique. Mobile phase: *n*-hexane-*iso*-propanol (96:4) at 0.9 mL/min.

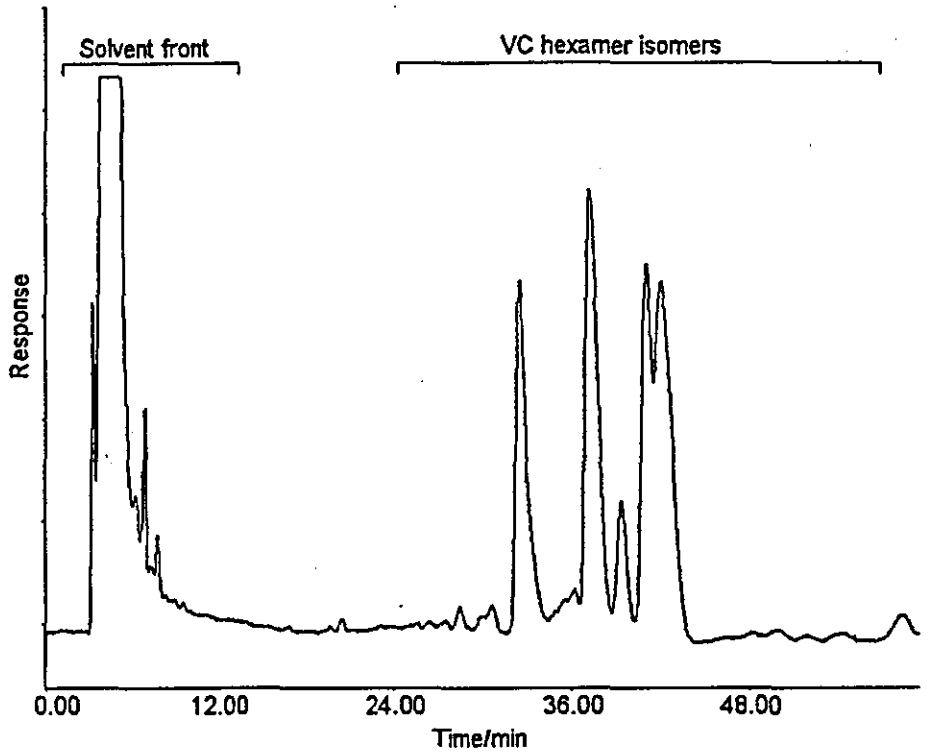

FIGURE 7 HPLC of the VC hexamer fraction obtained by the coupled-column technique. Mobile phase: *n*-hexane-*iso*-propanol (98:2) at 0.6 mL/min.

CONCLUSIONS

It has been demonstrated how, by a series of fractionation procedures utilizing a number of chromatographic techniques, relatively pure VC oligomer isomers can be isolated from a PVC polymer. The results show that, even for the VC oligomer pentamer, at least four isomeric forms exist. By using this preparation scheme, it is possible to accumulate a sufficient amount of each VC oligomer to enable NMR to be employed as a characterization method. This work has also shown that coupled-column chromatographic techniques are feasible and could be used for the analysis of targeted species within complex samples. PVC oligomers from pentamer to heptamer have been resolved successfully into their constituent isomers. Further work is planned to characterise these isomers fully.

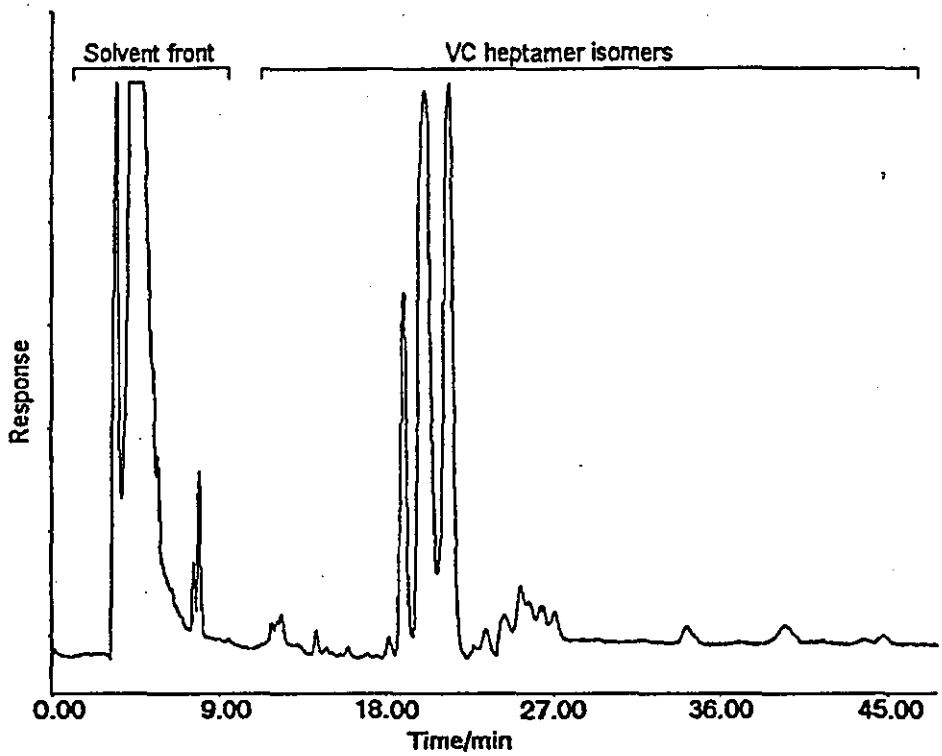

FIGURE 8 HPLC of the VC heptamer fraction obtained by the coupled column technique. Mobile phase: *n*-hexane-*iso*-propanol (96:4) at 1.0 mL/min.

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