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# Multi-step procedure for the separation of vinyl chloride oligomers

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## ABSTRACT

A multi-stage scheme was developed for the separation of vinyl chloride (VC) oligomers. A low-molar-mass fraction was isolated from poly(vinyl chloride) by Soxhlet extraction with diethyl ether followed by fractional precipitation with pentane. The presence of VC oligomers up to the decamer was demonstrated by high-performance size-exclusion chromatography (HPSEC). Removal of polar impurities was effected by preparative adsorption liquid chromatography of the low-molar-mass fraction. Recycle HPSEC with repeated injections permitted the accumulation of fractions of VC trimer, tetramer and pentamer oligomers. Separations of isomers of VC tetramer and pentamer oligomers were performed by high-performance liquid 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 $(CH_2CHCl)_x$. 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 the radical polymerization of vinyl chloride monomer (VC) [2,3]. Much information can be obtained from investigations of fractions of low molar mass 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-molar-mass fraction of PVC (including addi-

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tives 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-molar-mass 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 $\mu$m) having exclusion limits below 500 Å. Analysis of these low-molar-mass fractions by gas chromatography–mass spectrometry (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. A separation scheme was devised [9] in which, by routine high-performance liquid chromatographic (HPLC) fractionation, 0.5 mg of a VC tetramer was isolated from a PVC polymer for $^1$H NMR analysis. A partial structural characterization of the VC tetramer was achieved by this technique [10], the principle limitation being the small mass of oligomer available. A greater amount of each species had to be isolated if successful structural studies were to be performed using NMR. To this end, an alternate pumping recycle HPSEC technique [11] was used, which was capable of separating the VC oligomer species up to decamer present in a low-molar-mass fraction of PVC [12].

The object of this work was to improve and extend the separation scheme so that it would be possible to attempt a full structural characterization of each VC oligomer. Because of the requirements of NMR, the preferred separation scheme would be one that permitted the efficient collection of high-purity oligomer species. Another consideration was the inherent thermal instability of VC oligomers and so only chromatographic techniques that functioned at ambient temperatures were utilized and low-boiling-point solvents were used as eluents. The methods described in this paper are directed to VC oligomers up to the decamer with most emphasis on isolating those up to and including the pentamer.

## EXPERIMENTAL

### *PVC polymer*

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

### *Reagents*

Diethyl ether (standard laboratory reagent grade), tetrahydrofuran (analytical-reagent grade), dichloromethane, hexane (95% *n*-hexane) and pentane (75% *n*-pentane) (all HPLC grade) were supplied by Fisons (Loughborough, UK). Methyl *tert.*-butyl ether (MTBE) (HPLC grade) was supplied by Fluka (Glossop, UK).

*Low-molar-mass fractions of PVC*

Low-molar-mass 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 $cm^3$ in a rotary evaporator. A small portion of this mixture was dried in a vacuum oven at room temperature and then characterized by SEC with a 60 cm × 7.5 mm I.D. PL mixed gel (10-$\mu$m) column (Polymer Labs., Church Stretton, UK) in a Model 501 chromatograph (Waters Assoc. Hartford, UK) having a refractive index detector with tetrahydrofuran as mobile phase at a flow-rate of 1 $cm^3$ $min^{-1}$. The reduced extract was then added to 350 $cm^3$ of 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-molar-mass PVC in solution. The dry low-molar-mass fraction was obtained by utilizing first a rotary evaporator and then a vacuum oven at room temperature.

*Preparative adsorption liquid chromatography*

The low-molar-mass 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 $\mu$m) packing, supplied by Merck (Darmstadt, Germany). A Model 64 HPLC pump (Knauer, Berlin, Germany) was used in conjunction with a PU 4025 UV detector (Pye Unicam, Cambridge, UK) and a Rheodyne Model 7125 injection valve fitted with a 200-$\mu$l loop supplied by HPLC Technology (Macclesfield, UK). Aliquots (150 mg) of the low-molar-mass fraction were injected into the chromatograph and the fraction within the elution volume range 0–420 $cm^3$ was collected.

*HPSEC*

Individual oligomer species were separated from the low-molar-mass PVC fraction using an HPSEC system based on two 60 cm × 7.5 mm I.D. columns containing 5-$\mu$m, 50-Å PL gel (Polymer Labs.). The columns were used in conjunction with a Knauer Model 64 pump and a Knauer differential refractometer. An alternate pumping recycle system [12] was set up using a Rheodyne Model 7000 switching valve and the injection valve was a Rheodyne Model 7125, both supplied by HPLC Technology. The mobile phase dichloromethane was delivered at a rate of 1 $cm^3$ $min^{-1}$. A separation was performed by injecting a 10-mg sample and passing it with recycling through 480 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 HPSEC were separated into their isomeric forms by normal-phase HPLC. The chromatograph consisted of a Waters Model 6000A pump, a Pye Unicam PU 4025 detector operated at 200 nm and a 25 cm × 4.6 mm I.D. column containing Spherisorb S5W silica packing supplied by Phase Separations (Queensferry, UK). The mobile phase employed was hexane containing MTBE modifier (1.0–0.25%, depending on the oligomer being separated) at a flow-rate of 1 $cm^3$ $min^{-1}$. Routine fractionation of oligomers was carried out by injecting 2-mg aliquots

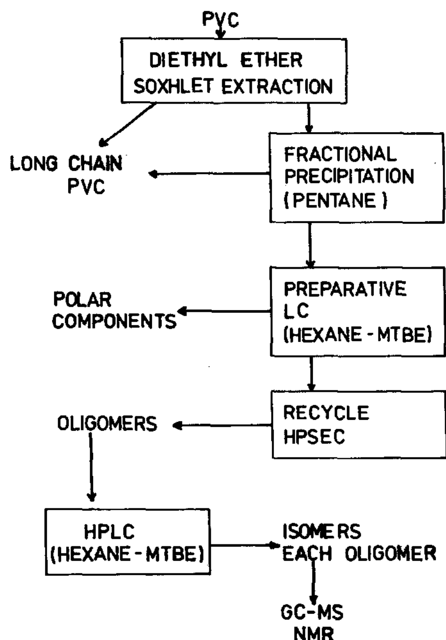



Fig. 1. Separation scheme.

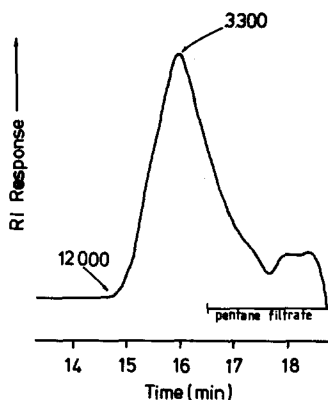
and the fractions blown to dryness using nitrogen. A schematic illustration of the multi-stage procedure for the separation of VC oligomers from a PVC polymer is shown in Fig. 1.

### *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 [7–10]. In each instance a Chrompack 25 m × 0.2 mm I.D. column coated with a 0.12-$\mu$m layer of CP-Sil 5CB was used. The flow-rate of the carrier gas (helium) was 1 ml min$^{-1}$. 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

Extracting the Lucovyl RB8010 PVC polymer with diethyl ether gave an extract yield of 0.80%. When analysed by SEC this extract gave the molar-mass distribution shown in Fig. 2. The low-molar-mass fraction that was obtained from the filtrate after fractional precipitation of the diethyl ether extract with pentane constituted 25% by weight of the original. An HPSEC chromatogram of this fraction is shown in Fig. 3. The peaks due to VC oligomers have been assigned with regard to chain length, and



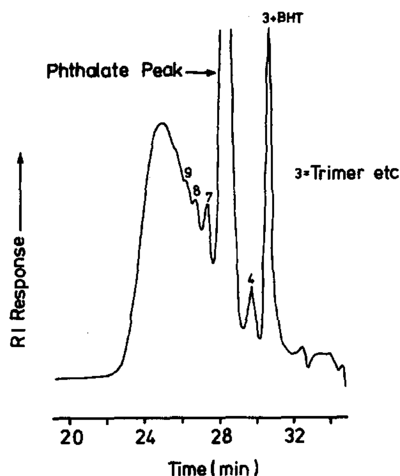




Fig. 2. SEC of diethyl ether Soxhlet extract. Molar mass data (g $mol^{-1}$) with reference to a calibration graph established with polystyrene standards.

Fig. 3. HPSEC of low-molar-mass fraction from pentane filtrate. Column, 120 cm PL gel (5 $\mu$m, 50 Å), eluted with dichloromethane at 1 ml $min^{-1}$.

peaks due to phthalate and 2,6-di-*tert.*-butyl-*p*-cresol (butylated hydroxytoluene; BHT) impurities are also indicated. It was possible to assign the oligomer peaks in Fig. 3 by using VC oligomers as calibrants because the pentamer to decamer oligomers had been prepared and described in a previous paper [12]. The phthalate and BHT impurities had been identified by GC–MS data.

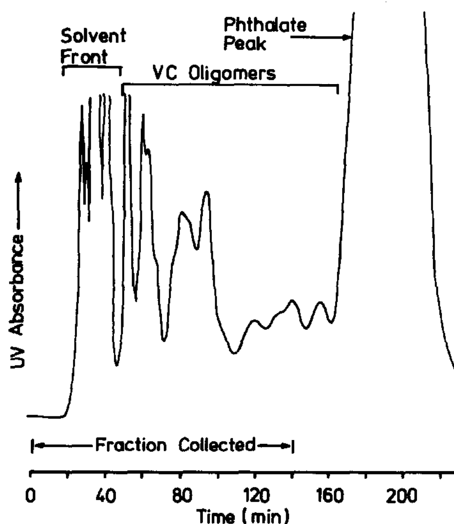



Fig. 4. Adsorption LC of low-molar-mass fraction from pentane filtrate. Mobile phase: hexane–MTBE (95:5) at 3 ml $min^{-1}$

Because some of the oligomer peaks in Fig. 3 were obscured by impurities, a further chromatographic technique was employed to purify the low-molar-mass fraction prior to HPSEC analysis. For this purpose a preparative adsorption liquid chromatographic system was employed. The chromatogram obtained for the low-molar-mass PVC fraction is shown in Fig. 4. It can be seen that the phthalate impurity and the oligomer fraction 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 reasonable times whilst maintaining sufficient oligomer–phthalate resolution. It is clear from Fig. 4 that, in addition to removing more polar impurities, the purification stage also serves to reduce the amount of long-chain PVC in the fraction. The elution volume range designated in Fig. 4 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.*, up to and including the pentamer, were missed. By comparing an HPSEC trace for the purified low-molar-mass PVC fraction (Fig. 5) with Fig. 3, it is possible to see the reduction in the amount of long-chain PVC and the absence of the phthalate peak. The presence of the BHT peak is still evident in Fig. 5 and the failure of the adsorption chromatographic system to separate it from the VC oligomers could be due to its chemical structure, in which the *tert.*-butyl groups in the 2,6-substitution positions shield the hydroxyl group and so inhibit it from interacting with the column packing.

With the alternate pumping recycle technique [12], resolution of the VC oligomers was improved and the chromatogram obtained using 480 cm of gel bed is shown in Fig. 6, where the oligomer species from trimer to pentamer are well separated. These oligomers were of greatest interest because they have the greatest potential for migration from PVC. The absence of any discernible concentration of VC dimer is

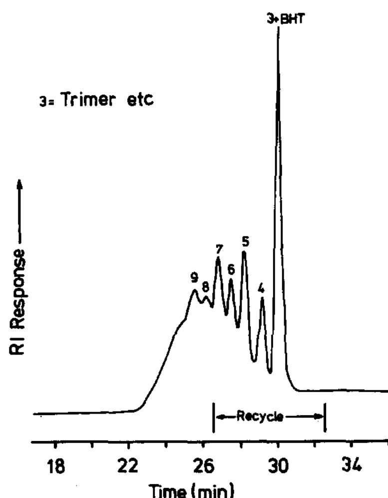



Fig. 5. HPSEC of low-molar-mass fraction from pentane filtrate after preparative adsorption LC. Column, 120 cm PL gel (5 μm, 50 Å), eluted with dichloromethane at 1 ml $min^{-1}$.

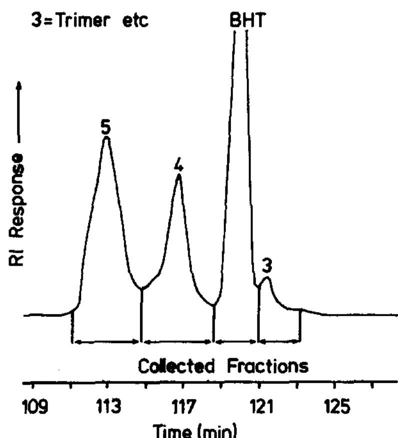



Fig. 6. HPSEC of low-molar-mass fraction from pentane filtrate after preparative adsorption LC. Column, 480 cm by recycle PL gel (5 $\mu$m, 50 Å), eluted with dichloromethane at 1 ml min$^{-1}$.

considered to be due to the monomer stripping process, in which the conditions are severe enough to remove the dimer species also. Amounts of the oligomers from trimer to pentamer were accumulated by fractionating the purified low-molar-mass PVC fraction on the HPSEC system by repeated injections and collecting the fractions designated in Fig. 6. The assignments of the oligomer peaks in Fig. 6, which had initially been performed by use of the VC oligomer standards, were confirmed by analysing each fraction by GC–MS and referring to data that had been published previously [8]. The data obtained confirmed the observation that each VC oligomer species exists as a number of structural isomers, the amount increasing with increasing chain length.

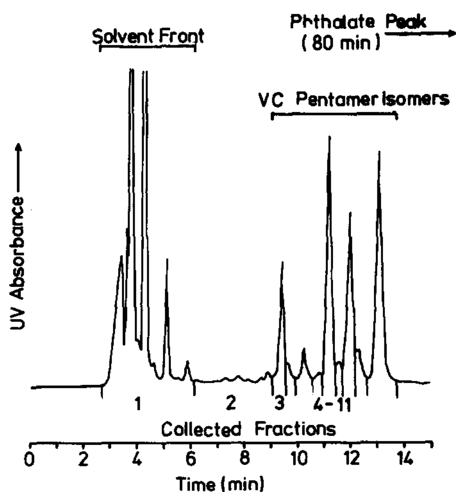



Fig. 7. HPLC of the VC pentamer fraction. Mobile phase: hexane–MTBE (99:1) at 1 ml min$^{-1}$.

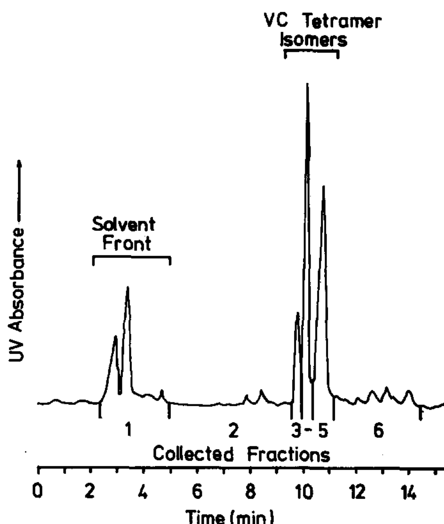



Fig. 8. HPLC of the VC tetramer fraction. Mobile phase: hexane–MTBE (99.75:0.25) at 1 ml $min^{-1}$.

The polyisomeric nature of the VC oligomers necessitated the development of a chromatographic technique for resolving each entity prior to an attempted structural chracterization 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 hexane containing MTBE as a modifier was capable of resolving the isomeric forms of the VC oligomers. The chromatograms obtained for the pentamer and tetramer fractions are shown in Figs. 7 and 8. Only very small amounts of modifier were required to elute the oligomers from the column because of their relatively non-polar nature. Less modifier (0.25%, v/v) was used for the tetramer to optimize the isomer resolution.

The chromatograms were partitioned as shown in Figs. 7 and 8 and the collected fractions were analysed by GC–MS. From the data obtained the peaks within the fraction range 3–11 for the pentamer and 3–5 for the tetramer were found to be isomers of those respective oligomers. Two VC trimer isomers had been found by GC–MS analysis of the trimer HPSEC fraction but it was not possible to differentiate these from the solvent front when this fraction was analysed on the HPLC system. The degree of interaction between the trimers and the silica column is insufficient with the hexane–MTBE eluent. Having established which fractions present in Figs. 7 and 8 represented VC oligomer isomers, HPLC fractionation of the VC pentamer and tetramer fractions from HPSEC was carried out by repeated injections to accumulate a sufficient mass of each isomer for NMR analysis. The results of this spectroscopic study will be reported in a subsequent paper [15].

## 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, a large number of isomeric forms exist. By using this preparation scheme it is possible to accumulate a sufficient amount of each VC oligomer isomer to enable NMR to be employed as a characterization method. This development will enable data that were previously unobtainable to be collected and a clearer view of the structures of these oligomers to be formed.

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