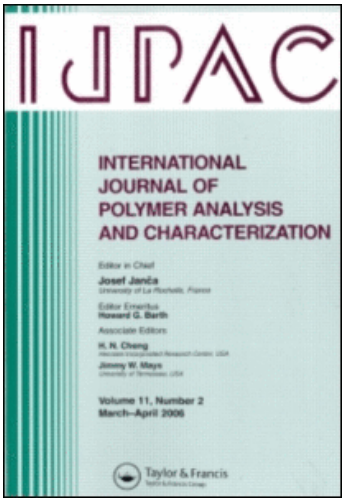

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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

Alexander H. Celik[a]; John V. Dawkins[a]; David Price[a]; Martin J. Forrest[b]
[a] Department of Chemistry, Loughborough University, Loughborough, Leicestershire [b] Rapra Technology Limited, Shrewsbury, Shropshire, UK

To cite this Article Celik, Alexander H. , Dawkins, John V. , Price, David and Forrest, Martin J.(1998) 'Separation of Oligomers from Poly(vinyl chloride) by Coupled Column Chromatography', International Journal of Polymer Analysis and Characterization, 4: 3, 189 — 203
To link to this Article: DOI: 10.1080/10236669808009709
URL: http://dx.doi.org/10.1080/10236669808009709

Int. J. Polym. Anal. Charact.,
1997 Vol. 4, pp. 189–203
Reprints available directly from the publisher
Photocopying permitted by license only

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

ALEXANDER H. CELIK[a], JOHN V. DAWKINS[a,*], DAVID PRICE[a] and MARTIN J. FORREST[b]

[a]*Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU and* [b]*Rapra Technology Limited, Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK*

(Received 31 January 1997; In final form 03 March 1997)

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 $(CH_2CHCl)_x$.

*Corresponding author.

Presented at the 9th International Symposium on Polymer Analysis and Characterization (ISPAC-9) held at Oxford, U.K., July 1–3, 1996.

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 characterization 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".

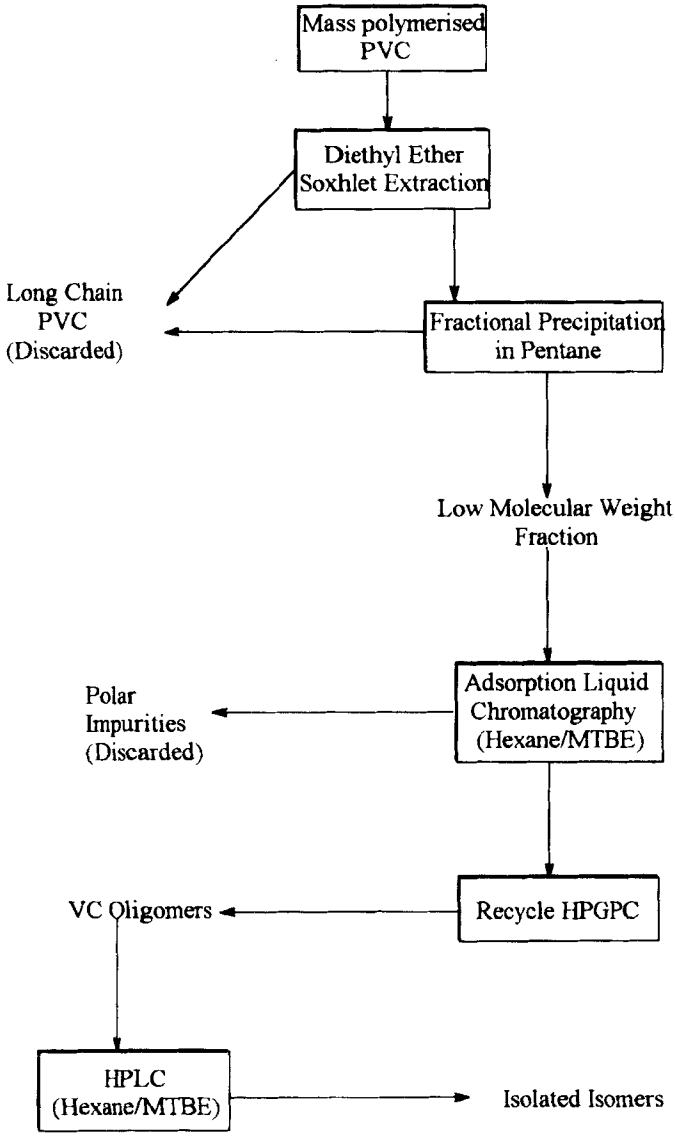

FIGURE 1 Separation scheme.

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

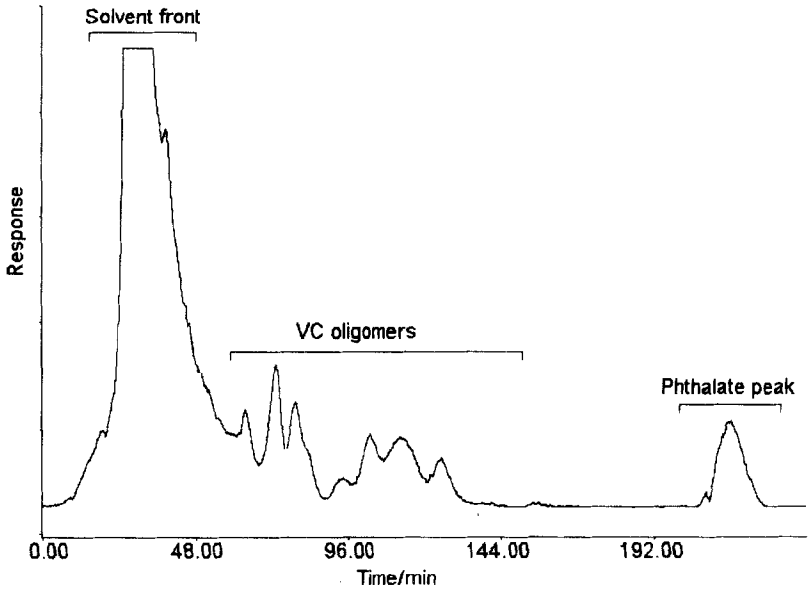

FIGURE 2 Preparative adsorption liquid chromatography of low-molecular-weight fraction from *n*-pentane filtrate. Mobile phase: *n*-hexane-MTBE (95:5) at 3.0 mL/min.

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-

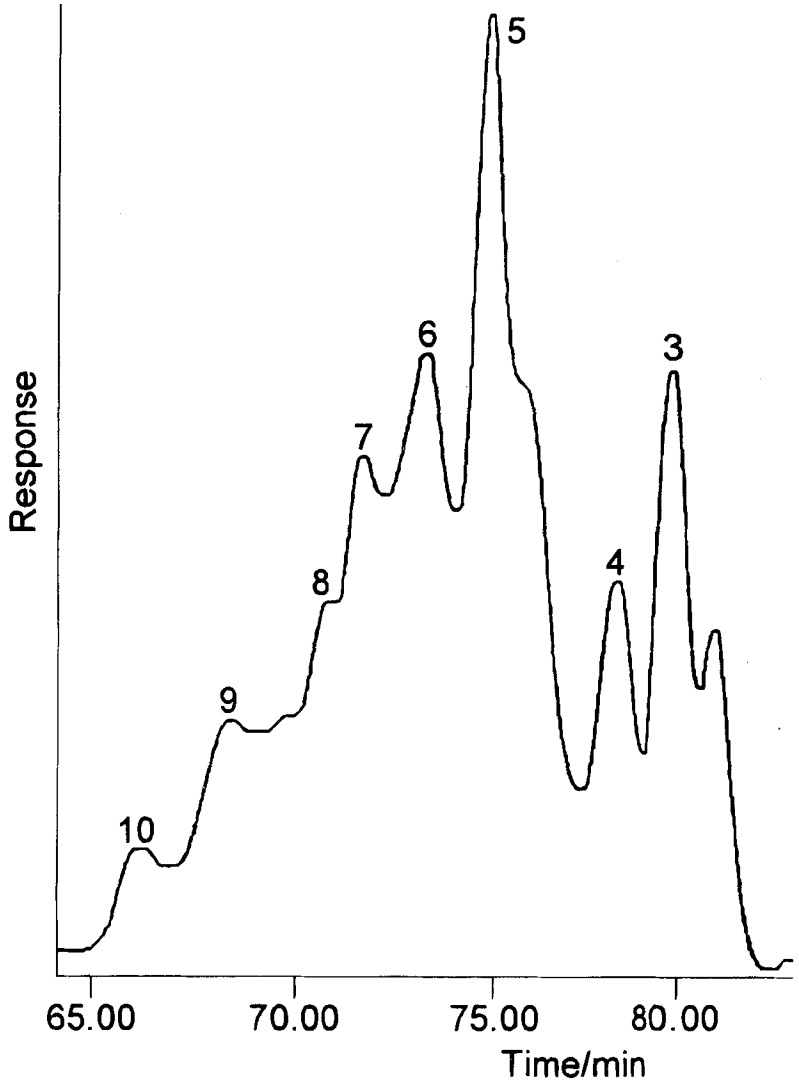

FIGURE 3 GPC of low-molecular-weight fraction from *n*-pentane after preparative adsorption liquid chromatography. Column, 300-cm PL gel (5 μm, 50 Å), eluted with dichloromethane at 1.0 mL/min. The peak numbers refer to the degree of polymerization.

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.

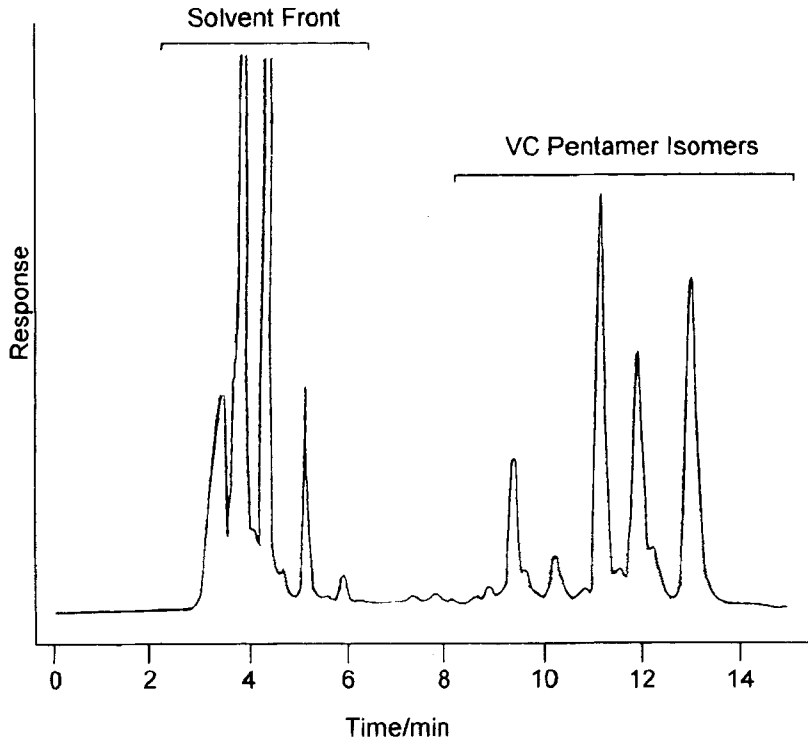

FIGURE 4 HPLC of the VC pentamer fraction. Mobile phase: *n*-hexane-MTBE (99:1) at 1.0 mL/min.

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

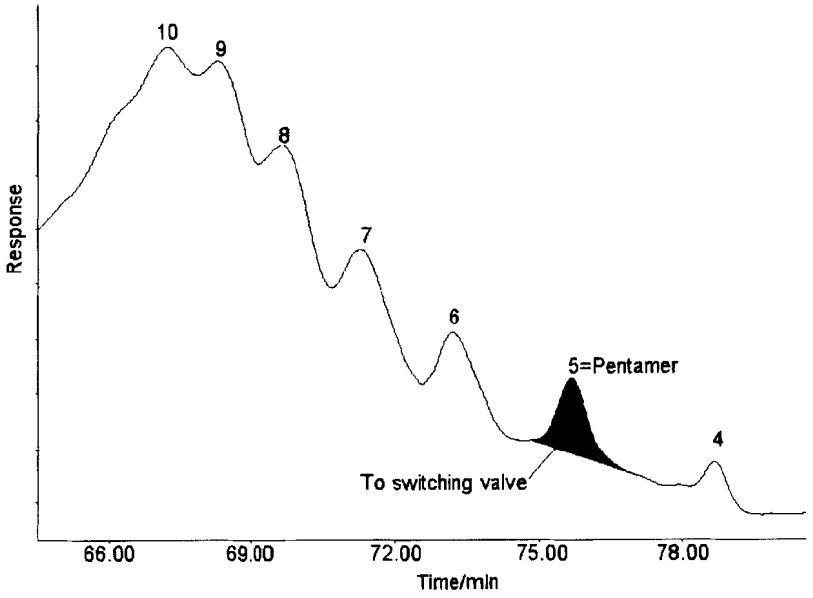

FIGURE 5 GPC of low-molecular-weight fraction from *n*-pentane filtrate utilizing the coupled-column technique. Column, 120-cm PL gel (5 μm, 50 Å), eluted with dichloromethane at 1.0 mL/min. The peak number refer to the degree of polymerization.

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.

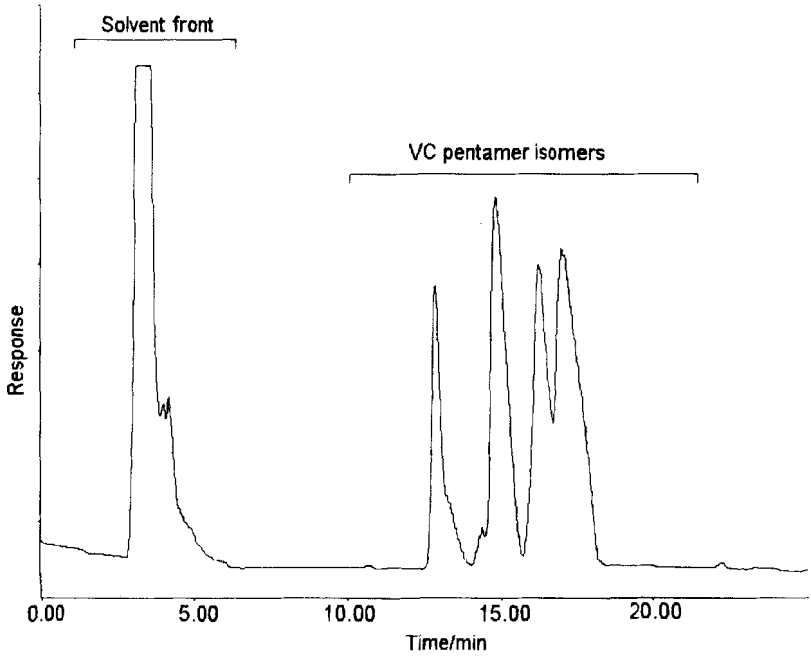

FIGURE 6 HPLC of the VC pentamer fraction obtained by the coupled-column technique. Mobile phase: *n*-hexane-*iso*-propanol (96:4) at 0.9 mL/min.

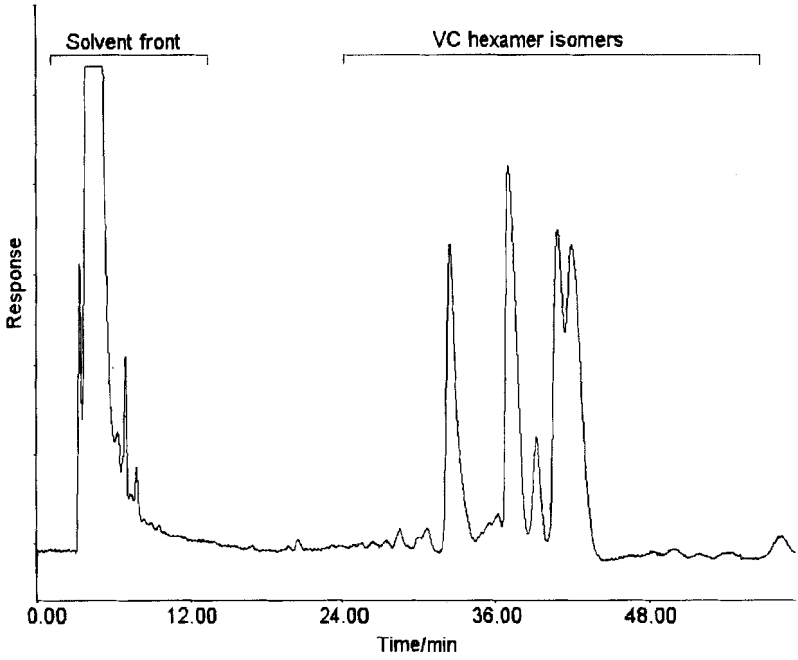

FIGURE 7 HPLC of the VC hexamer fraction obtained by the coupled-column technique. Mobile phase: *n*-hexane-*iso*-propanol (98 : 2) at 0.6 mL/min.

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.

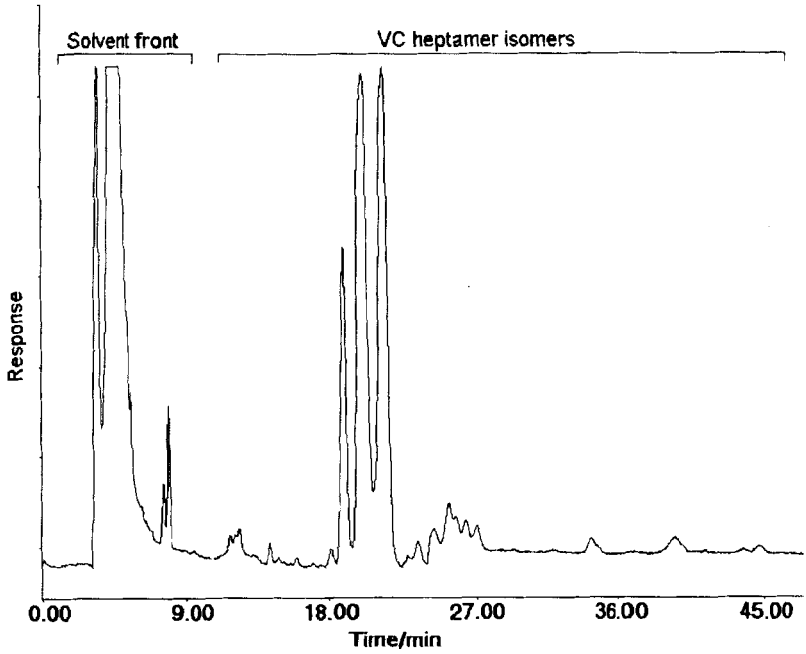

FIGURE 8 HPLC of the VC heptamer fraction obtained by the coupled column technique. Mobile phase: *n*-hexane-*iso*-propanol (96:4) at 1.0 mL/min.

Acknowledgements

The authors wish to express their thanks to the Ministry of Agriculture, Fisheries and Food for their support in this work and to Dr. L. Castle and Mr. S. Pugh for helpful discussions.

References

[1] Caraculacu, A. A. (1981). *Pure Appl. Chem.*, **53**, 385.
[2] Hjertberg, T. and Sorvik, E. M. (1982). *J. Macromol. Sci. Chem.*, **A17**, 983.
[3] Darricades-Llauro, M. F. Michel, A., Guyot, A., Waton, H., Petiaud, R. and Pham, Q. T. (1986). *J. Macromol. Sci. Chem.*, **A23**, 221.
[4] Schwenk, U., Cavagna, F., Lomker, F., Konig, I. and Strietberger, H. (1979). *J. Appl. Polym. Sci.*, **23**, 1589.
[5] van den Heuvel, C. J. M. and Weber, A. J. M. (1983). *Macromol. Chem.*, **184**, 2261.
[6] Shepherd, M. J. (1982). *Food Chem.*, **8**, 129.
[7] Gilbert, J., Shepherd, M. J. and Wallwork, M. A. (1980). *J. Chromatogr.*, **193**, 235.
[8] Gilbert, J., Shepherd, M. J., Startin, J. R. and Wallwork, M. A. (1982). *J. Chromatogr.*, **237**, 249.

[9] Gilbert, J., Shepherd, M. J. and Wallwork, M. A. (1985). *J. Chromatogr.*, **320**, 361.
[10] Dawkins, J. V., Forrest, M. J. and Shepherd, M. J. (1990). *J. Liq. Chromatogr.*, **13**, 3001.
[11] Henry, R. A., Bryne, S. H. and Hudson, D. R. (1974). *Chromatogr. Sci.*, **12**, 197.
[12] Dawkins, J. V., Forrest, M. J. and Shepherd, M. J. (1991). *J. Chromatogr.*, **550**, 539.
[13] Huang, S. S. and Hogen-Esch, T. E. (1985). *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 1203.
[14] Snyder, L. R. and Kirkland, J. J. (1978). *Introduction to Modern Liquid Chromatography*; 2nd ed., (Wiley-Interscience, New York) p 356.