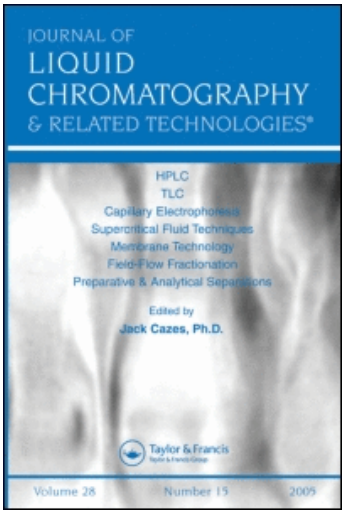

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Separation of Vinyl Chloride Oligomers by Recycle High Performance Size Exclusion Chromatography

J. V. Dawkins[a]; M. J. Forrest[a]; M. J. Shepherd[b]
[a] Department of Chemistry Loughborough, University of Technology Loughborough, Leicestershire, England [b] Ministry of Agriculture, Fisheries and Food Food Science Division, Norwich, England

To cite this Article Dawkins, J. V. , Forrest, M. J. and Shepherd, M. J.(1990) 'Separation of Vinyl Chloride Oligomers by Recycle High Performance Size Exclusion Chromatography', Journal of Liquid Chromatography & Related Technologies, 13: 15, 3001 — 3011
To link to this Article: DOI: 10.1080/01483919008049083
URL: http://dx.doi.org/10.1080/01483919008049083

JOURNAL OF LIQUID CHROMATOGRAPHY, 13(15), 3001-3011 (1990)

SEPARATION OF VINYL CHLORIDE OLIGOMERS BY RECYCLE HIGH PERFORMANCE SIZE EXCLUSION CHROMATOGRAPHY

J. V. DAWKINS[1], M. J. FORREST[1], AND M. J. SHEPHERD[2]

[1]*Department of Chemistry*
Loughborough University of Technology
Loughborough, Leicestershire, LE11 3TU
England

[2]*Ministry of Agriculture, Fisheries and Food*
Food Science Division
Haldin House
Queen Street
Norwich NR2 4SX
England

ABSTRACT

Low molar mass PVC was isolated by Soxhlet extraction followed by gel filtration. Individual oligomer species from pentamer to decamer in this low molar mass fraction have been separated by high performance size exclusion chromatography in an alternate pumping recycle system with high efficiency columns (5 μm, 50Å column packing).

INTRODUCTION

Multi-stage separation methods of isolating vinyl chloride (VC) oligomers from poly(vinyl chloride) (PVC) obtained by

suspension polymerisation have been developed. Gilbert et al. (1) indicated the oligomer levels that can be expected in various food-grade PVC resins. Also, a VC oligomer fraction that had been isolated by a multi-stage chromatographic procedure was shown by gas chromatography-mass spectrometry (GC-MS) analysis to consist of a series of oligomers ranging from trimer to hexamer (2). Each oligomer species was also considered to exist as a number of isomers, both straight chain and cyclic. Because the mass spectra of the VC oligomers did not yield much information regarding their structure, a further multi-stage chromatographic procedure was developed (3), in order to characterise a tetramer species. However, only a partial structural assignment was possible because of insufficient mass of the tetramer species, the possibility of tetramer isomers and the presence of impurities (4).

Size exclusion chromatography (SEC) has been an important technique in the multi-stage separation method (1-4). Improvements in chromatographic techniques are required in order to obtain non-contaminated oligomers. In this paper we show how high resolution separations of oligomers may be achieved by recycle high performance SEC (HPSEC) with high efficiency columns.

EXPERIMENTAL

PVC Extraction

The PVC was a mass-polymerised sample (Lucovyl RB8010, K value 56) obtained from Atochem, Thatcham, U.K. This PVC (250 g) was extracted using diethyl ether in a modified Soxhlet (5) for 20 hrs. After extraction a rotary evaporator was employed to remove most of the solvent. The low molar mass PVC fraction in this extract was obtained after drying in a vacuum oven at room temperature.

Preparative Gel Filtration

Glass gel filtration (GF) columns with adjustable end pieces (SR 25/100) were obtained from Pharmacia, Uppsala, Sweden and Bio-beads S-X8 gel packing from Bio-Rad Laboratories, Richmond, California, U.S.A. Bio-beads S-X8 were swollen overnight in toluene (HPLC grade) obtained from Fisons, Loughborough, U.K. and GF columns were packed by a slurry technique to give a gel bed of 88 x 2.5 cm. The flow rate under gravity after packing was 3.5 cm^3 $min.^{-1}$ The columns were calibrated with a polystyrene 580 standard supplied by Polymer Laboratories, Church Stretton, U.K. Aliquots (200 mg) of diethyl ether extract were injected onto the column and the GF fraction within the elution volume range 200-270 cm^3, assumed to contain oligomers with molar masses up to 578 g mol^{-1} (polystyrene calibration), collected. The dry oligomer fraction was obtained by removing most of the toluene on a vacuum frame and then using a vacuum oven, both processes being conducted at room temperature.

HPSEC

The alternate pumping recycle system described by Henry et al. (6) was employed. Our system comprised a Knauer 64 HPLC pump and Knauer differential refractometer, a Rheodyne 7125 injection valve fitted with a 200 µL loop, a Rheodyne 7000 switching valve, two 60 cm HPSEC columns containing 5 µm, 50 Å PL gel which were obtained from Polymer Laboratories, Church Stretton, U.K. with toluene as solvent at 1 cm^3 min^{-1}. Aliquots (10 mg) of the GF fraction were separated and fractions of VC oligomers corresponding to HPSEC peaks were collected. These HPSEC oligomer fractions were dried in a vacuum oven at room temperature and were then subjected to GC-MS analysis. A Carlo Erba 4200 gas chromatograph, fitted with a 25 m x 0.2 mm

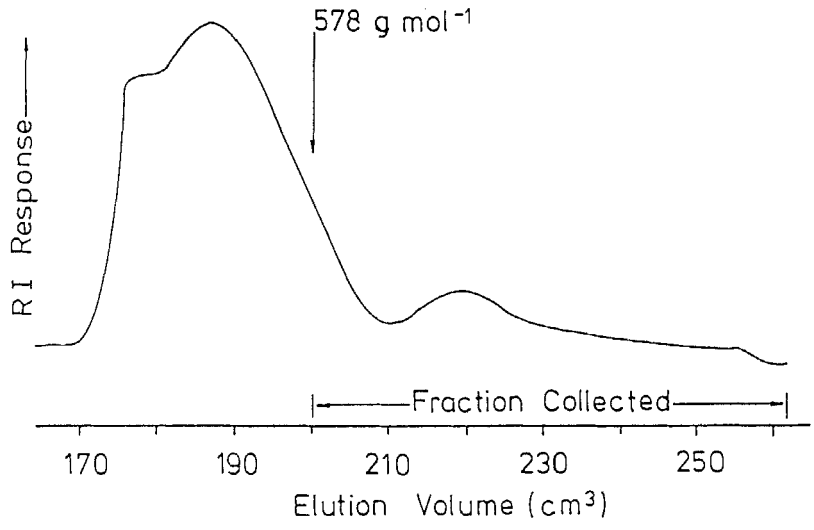

FIGURE 1

Gel filtration chromatogram of diethyl ether extract of PVC.

capillary column coated with BP1, connected to a Kratos MS80 mass spectrometer via an all glass coupling interface was employed.

RESULTS AND DISCUSSION

The GF elution profile obtained from the Soxhlet extract is shown in Figure 1. Collection of the eluent in the elution volume range corresponding to molar masses below 578 g mol^{-1} (polystyrene calibration) yielded a GF fraction (~70 mg of VC oligomers). Analysis of this GF fraction by GC-MS revealed a substantial quantity of phthalate compounds which might contribute to the secondary peak at about 220 cm^3 in Figure 1.

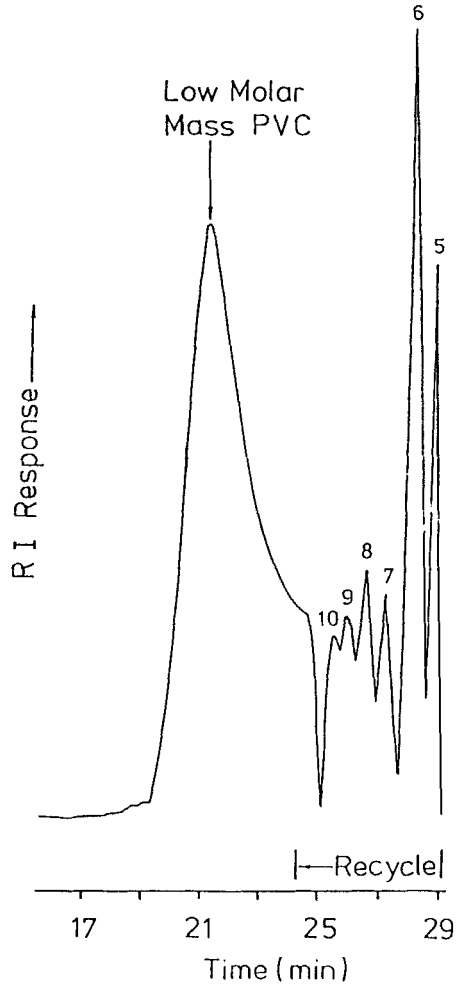

FIGURE 2

HPSEC of GF fraction with gel bed length = 120 cm. 5 = Pentamer to 10 = Decamer.

The presence of phthalate compounds and derivatives of initiators used in VC polymerisations have been identified previously in low molar mass fractions of PVC (2). In agreement with previous work (2), GC-MS analysis revealed that the GF fraction contained a series of VC oligomers ranging from trimer to heptamer. There was no evidence of a VC dimer species which is presumably lost during the stripping of VC monomer from the polymerisation product.

Separation of the GF fraction by HPSEC is shown in Figure 2. This chromatogram indicates a substantial quantity of short chain PVC having a molar mass somewhat greater than 578 g mol^{-1}. This may be explained firstly by the proposal that VC oligomers and styrene oligomers do not follow the same SEC molar mass calibration since it is known that these high polymers have different calibration curves (7), and secondly by the poor resolution of the GF column packing resulting in carry-over of long chain PVC into the GF fraction with molar masses below 578 g mol^{-1} (polystyrene calibration).

Figures 2, 3, 4 and 5 demonstrate clearly that as the length of the gel bed increases by employing the alternate pumping recycle system the separation of the individual oligomer species also increases. These chromatograms demonstrate that a gel bed length of 480 cm is required for adequate resolution of the oligomers. As the gel bed length increases, shoulders become apparent on the oligomer peaks, possibly indicating the presence of isomers for each oligomer.

In order to achieve an unambiguous molar mass characterisation, the species generating each oligomer peak were isolated from fractions collected in the elution volume ranges

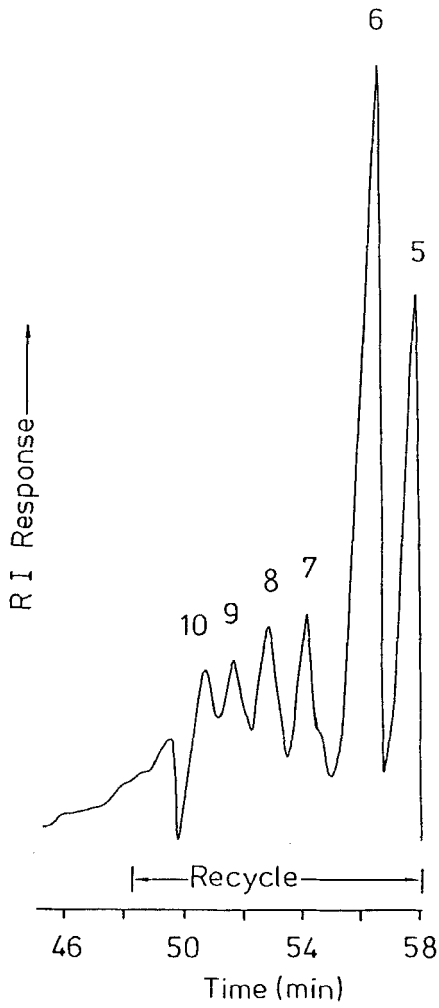

FIGURE 3

HPSEC of GF fraction with gel bed length = 240 cm (1 recycle). 5 = Pentamer to 10 = Decamer.

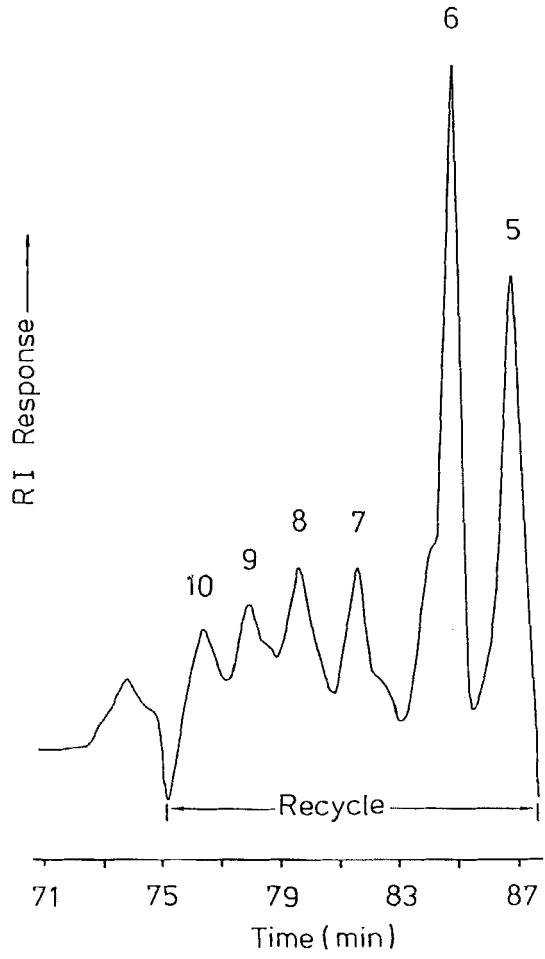

FIGURE 4

HPSEC of GF fraction with gel bed length = 360 cm (2 recycles). 5 = Pentamer to 10 = Decamer.

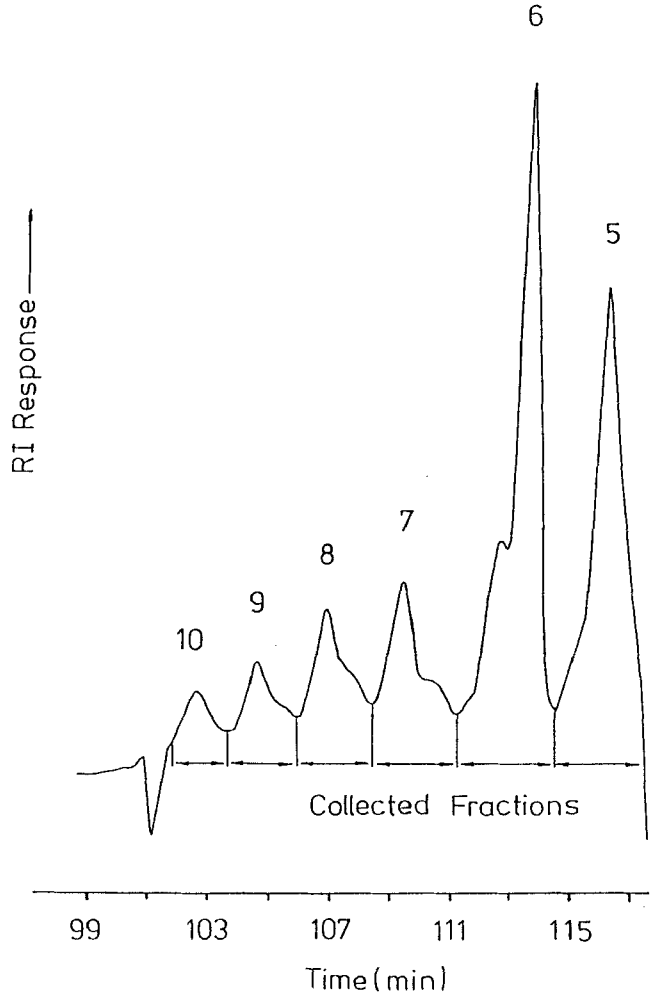

FIGURE 5

HPSEC of GF fraction with gel bed length = 480 cm (3 recycles). 5 = Pentamer to 10 = Decamer. (⟷) fractions collected for GC-MS analysis.

identified in Figure 5 and were then analysed by GC-MS. Tne characteristic mass spectra of VC oligomers up to the heptamer were known (2,8), thus permitting the assignment of the HPSEC peaks from pentamer to decamer. The absence of peaks for tetramer and trimer in Figures 2-5 is presumed to arise partly because of the low refractive index increment of these oligomers in toluene and also because of other low molar mass compounds, e.g. initiator moieties which may be extracted and separated by GF with the oligomers, possibly obscuring the tetramer and trimer peaks by eluting at similar elution volumes.

CONCLUSIONS

This recycle HPSEC system provides high resolution separations of VC oligomers. Routine separations may be performed to isolate sufficient mass of each oligomer for structural identification with analytical techniques.

ACKNOWLEDGEMENTS

We thank Dr J. Gilbert for valuable discussions. The authors at Loughborough University of Technology wish to thank the Ministry of Agriculture, Fisheries and Food for the support of this research with a MAFF research grant.

REFERENCES

1. Gilbert, J., Shepherd, M.J., and Wallwork, M.A., J. Chromatogr., 193, 235, (1980).

2. Gilbert, J., Shepherd, M.J., Startin, J.R., and Wallwork, M.A., J. Chromatogr., 237, 249, (1982).

3. Gilbert, J., Shepherd, M.J. and Wallwork, M.A., J. Chromatogr., 320, 361, (1985).

4. Gilbert, J., Shepherd, M.J., Wallwork, M.A., Crews, C., Startin, J.R., and Mitchell, J.C. Eur. Polym. J., 21, 555, (1985).

5. Forrest, M.J., Ph.D. thesis, Loughborough University of Technology, U.K., 1988.

6. Henry, R.A., Byrne, S.H., and Hudson, D.R., J. Chromatogr. Sci., 12, 197, (1974).

7. Dawkins, J.V., Eur. Polym. J., 13, 837, (1977).

8. Wallwork, M.A., M.Sc. thesis, University of East Anglia, U.K., 1984 .