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DETERMINATION OF OLIGOMERS IN VINYL CHLORIDE POLYMERS BY STERIC EXCLUSION CHROMATOGRAPHY

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SUMMARY

Low-molecular-weight materials were isolated from poly(vinyl chloride) resins by diethyl ether soxhlet extraction and these were subsequently fractionated on a combination of steric exclusion columns. Estimations of oligomer levels in the isolated molecular weight fractions were made on the basis of gravimetric measurements and micro chlorine determinations.

The presence in each fraction of a large number of species was demonstrated by high-performance steric exclusion chromatography and mass spectrometry was employed for attempted characterisation.

INTRODUCTION

It has become increasingly important in recent years to be able to quantify minor constituents present in plastic food packaging materials, as they may have a potential for migration into foodstuffs. Although attention has centred mainly on measuring levels of residual monomers in plastics (for example vinyl chloride (VC)[1-4], acrylonitrile[5,6], vinylidene chloride[7,8] and styrene[9]) interest has also extended to additives such as heat stabilisers[10,11] which might be incorporated by the fabricator during the course of manufacture of the finished article. Residues of ingredients from the polymerisation process and oligomers provide additional sources of minor constituents in the polymer which are not often considered as potential migrants. In this paper we report our studies on the solvent extractable material isolated from poly-(vinyl chloride) (PVC) base resins, and the application of steric exclusion fractionation for estimations of oligomer content on the basis of micro chlorine determinations.

There are no published reports to date of studies on VC oligomers although other oligomers [*e.g.* styrene and poly (ethylene terephthalate) (PET)] of plastics of commercial food packaging significance have been widely examined both because of their technical importance to the polymer chemist and as useful model compounds for demonstrating separation techniques. Styrene oligomers have been separated by steric exclusion chromatography (StEC)[12-14] with identification of the trapped com-

ponents by ^{1}H nuclear magnetic resonance (NMR) spectrometry[14], and by gradient-elution high-performance liquid chromatography (HPLC)[15,16] with identification by infrared spectroscopy[16]. The formation of oligomers in the thermal copolymerisation of styrene with acrylonitrile has been demonstrated by gas chromatography–mass spectrometry (GC–MS)[17]. In a recent paper early work on PET oligomers was reviewed[18] and two methods were described for their preparative isolation, thin-layer and HPLC systems being employed for the separation of individual species of five separate series of PET oligomers[18].

However, despite the analytical data available it is only recently that interest in these oligomers (styrene and PET) as species capable of migration from plastics into food has become evident[19]. In a preliminary report[19] are described, firstly the synthesis of ^{14}C-labelled polymer from the labelled monomer, and secondly incorporation of an individual species of ^{14}C-labelled oligomer into inactive polymer.

Neither of these approaches is suitable for the study of VC oligomers because the information on the identity and quantity of individual species in commercial polymers is not available. VC oligomers present additional analytical problems in that firstly differences in the polymerisation process will leave significantly lower levels of oligomer in the polymer. Secondly the absence of a suitable chromophore in VC oligomers will make detection by HPLC at high sensitivity more difficult. Finally the polyhalogenated long chain hydrocarbons are known generally to undergo thermal degradation and it may be expected that a similar instability in VC oligomers during GC and MS analysis would make data interpretation unusually difficult.

In this paper the results are reported of the first stage of a continuing programme of work aimed at measuring the potential for VC oligomer migration into foods. We report evidence for the occurrence of VC oligomers in low-molecular-weight fractions isolated from solvent extracts of PVC resins. On the basis of chlorine determinations and assuming a simplified oligomer structure (without initiator end groups) estimations are made of the possible levels present in three commercially available grades of PVC, one of which is commonly employed for the manufacture of bottles intended for food applications.

EXPERIMENTAL

Materials

Glass columns with adjustable end pieces (SR 25/45 and SR 10/50J) and gel packing (Sephadex LH-60) were obtained from Pharmacia (Uppsala, Sweden) and Bio-Beads S-X3 from Bio-Rad Labs. (Richmond, CA, U.S.A.). Calibration standards for StEC were from the following: alkanes (Sigma, St. Louis, MO, U.S.A.), Monopol polystyrene 600 (Chrompack, Middelburg, The Netherlands) and ethylene glycol oligomers (BDH, Poole, Great Britain). PVC resins, weight-average mol.wt. 100,000 and 200,000 with respective K values of 87 and 125, were obtained from BDH and Corvic S57/116, a bottle blowing grade of weight-average mol.wt. between 75,000 and 100,000 with a K value of 56–57, from ICI Plastics Division (Welwyn Garden City, Great Britain). Tris(nonylphenyl)phosphite (TNPP, "Phosclere P315") was from Akzo Chemie (Liverpool, Great Britain) and *p*-nonylphenol from Pfaltz and Bauer (Stamford, CT, U.S.A.).

Methods

Solvent extraction of base polymer. Base polymer (20 g) contained in pre-extracted thimbles was soxhlet extracted with purified re-distilled diethyl ether for 8 h. After solvent removal on a rotary evaporator and vacuum drying at 40° the weighed residues were stored at −15° until required.

Steric exclusion chromatography. "Sephadex LH-60" columns were prepared and used as described in an earlier paper[20]. Column lengths were 33 ± 1 cm and two fractions were routinely collected, standardised at 0–90 ml (S1) and 90–190 ml (S2), the former containing high-molecular-weight material. Total ether extracts were fractionated in 160–180-mg aliquots dissolved in re-distilled tetrahydrofuran (THF) (2 ml), the collected fractions being weighed after solvent removal by blowing down under nitrogen.

"Bio-Beads S-X3" gels were prepared by a slurry technique in THF using Pharmacia SR10/50J columns to give a gel bed of 47 × 1.0 cm. Aliquots (40 mg) of fraction S2 from the Sephadex column in THF (0.2 ml) were syringed onto a filter disc at the front of the column and chromatographed in the normal manner. Elution profiles were generated by collecting 0.5-ml fractions (Gilson microcol TDC 80 fraction collector) in pre-conditioned, pre-weighed 10-ml tubes. After blowing to dryness under nitrogen, the tubes were heated for 30 min at 40° in a vacuum oven, allowed to recondition for 2 h and reweighed. Calibration with individual *n*-alkanes showed typical peak widths of 2–3 ml.

High-performance steric exclusion chromatography (HPStEC) was carried out with a Waters Assoc. 6000A pump using an Altex (Model 210) sample injector and detection with an Optilab Multiref 902 refractive index detector which was thermo-stated at 30° with a water bath. Exclusion chromatography was carried out on a series of four crosslinked polystyrene columns (30 × 7.7 cm) connected in the sequence shown in Table I which also includes the technical data for the columns. Freshly re-distilled THF was employed as the solvent in all experiments operated at a flow-rate of 1 ml/min at *ca.* 1000 p.s.i. pressure.

TABLE I

TECHNICAL DETAILS OF HPLC COLUMNS

No.	Name	Average pore size (Å)	Approx. exclusion limit
1	PL gel (10 μm)	50	10^3
2	PL gel (10 μm)	100	2×10^3
3	PL gel (10 μm)	500	2×10^4
4	Waters Assoc. μStyragel (10 μm)	100	7×10^2

Elemental analysis. Elemental microanalysis for chlorine was performed by Butterworth Labs. (Teddington, Great Britain). All samples collected from StEC columns were heated at 40 °C in a vacuum oven to constant weight and amounts of not less than 10 mg per determination were sent for analysis.

Phosphorus determinations. Weighed samples were diluted with THF (S2 to 50 ml and B2 to 100 ml), aliquots (1 ml) were blown to dryness and oxidised using sulphuric acid and "AnalaR" 30% hydrogen peroxide. Phosphorus in the digests was estimated by the method of Morrison[21], using calibration curves obtained with TNPP.

Nonylphenol determinations. Nonylphenol was estimated in extracts by GC after formation of the trimethylsilyl derivative. Fractions were transferred to a volumetric flask (5 ml) with THF, blown to dryness and dry diethyl ether (100 μl), bis-(trimethylsilyl)trifluoroacetamide (100 μl) (Regis, Morton Grove, IL, U.S.A.) and pyridine (100 μl) were added and the reaction mixture allowed to stand overnight. The solution was then made to volume with diethyl ether and nonylphenol estimated by GC. A 5 ft. $\times$ $^1/_4$ in. glass column was employed packed with 3% OV-1 on Gas-Chrom Q operated at a carrier gas flow of 60 ml/min and isothermally at 235 °C. Although at lower GC temperatures isomers of nonylphenol (identifications confirmed by GC–MS) were evident both in TNPP extracts and in the reference standard, by operation at higher temperatures the mixture could be estimated as a single component.

RESULTS AND DISCUSSION

Although it would be possible to use StEC as the primary method of separating oligomers from PVC (as well as for their subsequent fractionation), solvent extraction was preferred because its capacity for handling large amounts of material facilitates subsequent gravimetric and micro elemental examination. Solvent extraction however has the disadvantage of possibly being selective and incomplete. Hence data obtained for oligomer concentrations will be the minimum levels likely to be present in the base resins.

The total ether extracts accounted for approximately 0.8% of the Corvic resin, and 0.32 and 0.24% for the other resins in order of increasing molecular weight. As expected the greatest amount of extractable material was found in the polymer with the lowest nominal molecular weight.

Initial separations performed on Sephadex LH-60 produced fractions S2 containing all material of molecular weight less than about 2000. The limit is not precise because exclusion is a function of molecular size rather than weight and also because there are few well characterised standards available in the molecular weight range 1000–3000. However it is evident from the data in Table II that in terms of migration of oligomers approximately 70% of the ether extracts can be eliminated from consideration, on the grounds of molecular weight.

HPStEC of S2 fractions yielded profiles as shown in Fig. 1. The presence of large concentrations of two discrete components in the Corvic polymer were attributed to TNPP and its decomposition product nonylphenol. Standard samples of TNPP and nonylphenol chromatographed with identical elution volumes to these components of the S2 fraction. TNPP acts as a "pre-stabiliser" during the drying stages of polymer production. Gravimetric fractionation of the Corvic S2 fraction was carried out on Bio-Beads S-X3; the elution profiles are shown in Fig. 2. The profiles in Figs. 1 (c) and 2 can be seen to be essentially similar. Differences between the replicate chromatograms (Fig. 2) are largely due to two factors, *viz*, unavoidable variations in the cut-off point between S1 and S2 on LH-60 fractionation leading to differences in the mass of high-molecular-weight material present and changes in the degree of decomposition of TNPP altering the relative proportions of TNPP and nonylphenol. Calibration of the Bio-Beads column against individual *n*-alkanes produced the curve shown in Fig. 3 with typical peak widths of 2–3 ml (determined by GC) per

TABLE II

LOW-MOLECULAR-WEIGHT COMPONENTS OF PVC RESINS

Polymer	Fraction	Molecular weight (MW)*	Concentrations (ppm) in base resin				
			Total non-volatiles	Oligomers	TNPP	Nonyl-phenol	Un-identified**
Corvic S57/116	S1	>2000	4900				
	S2	<2000	3200	1500	800		
	B1	2000>MW>600	1250	900	15	—	350
	B2	600>MW>400	1450	400	800	—	250
	B3	< 400	500	110	10	200	190
PVC (MW ca. 2·10⁵)	S2	<2000	1100	766	—	—	334
PVC (MW ca. 1·10⁵)	S2	<2000	1500	1180	—	—	320

* Approximate values (see text).
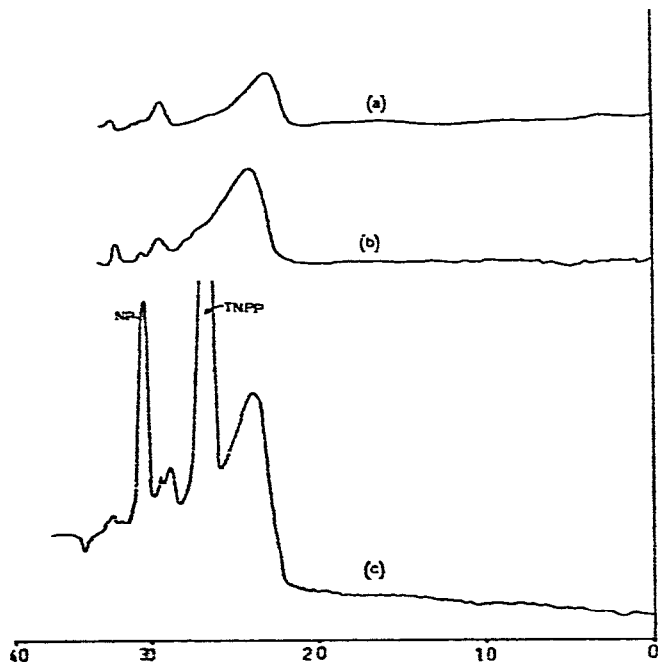** Neglecting TNPP values for fractions B1 and B3.

Fig. 1. High-performance exclusion chromatograms of (a) S2 fraction from PVC (mol.wt. ca. 2·10⁵), (b) S2 fraction from PVC (mol.wt. ca. 10⁵), (c) S2 fraction from Corvic S57/116 polymer. TNPP = tris(nonylphenyl)phosphite, NP = nonylphenol. Columns: Total of 4 (30 cm × 7.7 mm I.D.), details in Table I. Solvent, THF; flow-rate, 1.0 ml/min; Detection, refractive index. Horizontal axis: time (min); vertical axis: recorder response.

alkane. The material separated on the Bio-Beads column was collected as three fractions designated B1, B2 and B3 in order of decreasing average molecular weight; the volumes are indicated in Fig. 2.
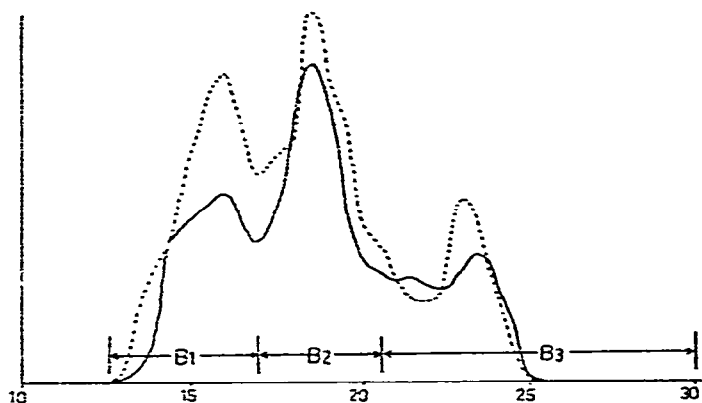
Fig. 2. Gravimetric StEC elution profiles (duplicates) of fractions S2 from Corvic S57/116 polymer on Bio-Beads S-X3 column. Horizontal axis: elution volume (ml); vertical axis: solute mass.
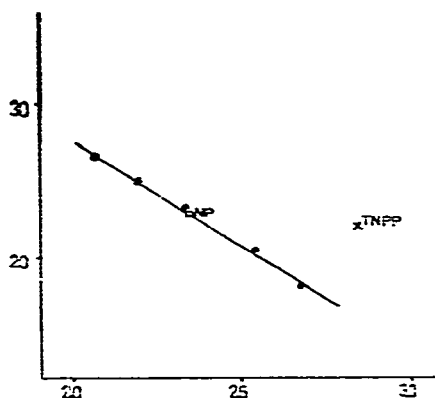

Fig. 3. StEC calibration curve on Bio-Beads S-X3 for a series of n-alkanes (C_6–C_{36}). TNPP–tris(nonyl-phenyl) phosphite (mol.wt. 691); NP = nonylphenol (mol.wt. 220). Horizontal axis: $\log_{10}$ (molecular weight); vertical axis: elution volume (ml).

The decomposition of TNPP is known to result in the formation of nonyl-phenol. Using authentic compounds it was shown that TNPP is eluted in fraction B2 and nonylphenol in B3. The latter is volatile and was analysed by GC but TNPP is non-volatile and was estimated by wet oxidation and measurement of phosphorus. The results given in Table II are based on the assumption that the phosphorus was present as TNPP. In fact comparison of the IR spectrum of B2 with those of triphenyl phosphite and triphenyl phosphate indicated that the material actually present in B2 is probably the phosphate analogue of TNPP; this is probably an artefact formed during the analysis by oxidation of TNPP by the peroxides which are readily formed in unstabilised THF. The materials in fractions B1 and B3 are not identified but in B3 there is probably a phosphorus containing acid.

The elemental micro chlorine results for the various fractions are shown in Table III. From this data the oligomer levels given in Table II were thereby calculated on the assumption that oligomers have the same empirical formula as does PVC itself.

$$\text{``Oligomers''} = \text{total non-volatiles} \times \frac{\%\ \text{chlorine in fraction}}{56.73}$$

TABLE III

ELEMENTAL MICROCHLORINE DETERMINATION ON StEC FRACTIONS

Polymer	Fraction	Chlorine (%)
Corvic S57/116	S2	27.4
(mol.wt. between 75,000 and 100,000)	B1	40.4
	B2	15.8, 16.0
	B3	12.9
PVC (mol.wt. ca. 200,000)	S2	39.2
PVC (mol.wt. ca. 100,000)	S2	44.5

This equation underestimates the oligomer content where molecules contain non-chlorinated initiator or terminator residues but because of the importance of chain transfer in the polymerisation reaction[22] only a small proportion of PVC molecules will contain such residues. Consequently, even large end groups, such as those derived from lauryl perixode (which is frequently used as an initiator), will give rise to only small errors in the values shown in Table II. Discounting any such adjustments, oligomers of molecular weight less than about 600 account for a minimum of 500 ppm in the bottle-blowing grade of PVC examined and therefore represent a significant potential of polychlorinated species for migration. Similarly 760 ppm and 1180 ppm of oligomers were estimated as being present in the other high- and low-molecular-weight grades of PVC.

Calibration curves for the HPStEC system are shown in Fig. 4. As discussed
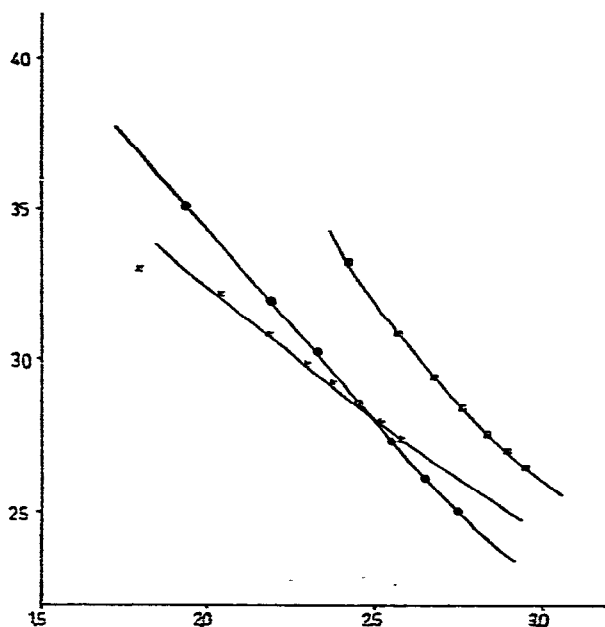

Fig. 4. Calibration curves for HPStEC system. ■, Series of oligostyrenes; ●, series of n-alkanes; ×, series of ethylene glycol oligomers. Horizontal axis: $\log_{10}$ (molecular weight); vertical axis: elution volume (ml).

for the LH-60 column, estimations of molecular weight ranges for the "unknown" oligomers were again based on extrapolation and on experience of the behaviour of a variety of standards of differing molecular size. The system had an exclusion limit of molecular weight approximately 2000 and was shown capable of baseline separation of species with molecular weight differences of approximately 15%.

However for the three PVC resins smooth curves with wide molecular weight distributions were obtained by HPStEC indicating that no individual species was predominant and suggesting a complexity of both linear and branched chains both with and without lauryl end group terminations. Further work is in progress attempting to employ reversed-phase HPLC for resolving these complex mixtures. Attempts to trap small fractions from the HPStEC system and characterise by direct insertion probe MS has produced spectra containing evidence of chlorine isotopic patterns and molecular ions of approximately the molecular weights anticipated from StEC. Interpretation has proved difficult and identification of compounds will be published elsewhere at a later stage.

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