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IDENTIFICATION BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY OF VINYL CHLORIDE OLIGOMERS AND OTHER LOW-MOLECULAR-WEIGHT COMPONENTS IN POLY(VINYL CHLORIDE) RESINS FOR FOOD PACKAGING APPLICATIONS

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SUMMARY

Material of molecular weight less than approximately 400–500 was isolated from food grade poly(vinyl chloride) resins by initial soxhlet diethyl ether extraction and subsequent size-exclusion fractionation. Analysis by packed-column gas chromatography using Hall electrolytic conductivity detection showed the presence of a series of chlorinated components which by subsequent gas chromatography–mass spectrometry were tentatively identified as vinyl chloride oligomers. The chlorinated constituents in the extracts were selectively isolated from other low-molecular-weight components by silica gel chromatography. From low-resolution capillary gas chromatography–mass spectrometry data (together with evidence from hydrogenated extracts) the structures of these oligomers were postulated as being a complete series ranging from trimer to hexamer (and probably to the octamer), each oligomer being represented by species containing a ring or a double bond and each occurring as a number of structural isomers. Other non-chlorinated compounds identified in the resins included mixed phthalates, alkanes, nonylphenol, and undecyl dodecanoate, the latter being derived from the polymerisation initiator lauryl peroxide.

INTRODUCTION

There have been many studies on the oligomers of styrene both because of their widespread use as calibration standards in size-exclusion chromatography (SEC)[1,2] and because they enable an insight into the mechanisms of polymer initiation and propagation reactions[3–5]. Poly(ethylene terephthalate) (PET) oligomers have also been characterised and have been shown to have undesirable effects in certain technical applications[6,7]. Despite the extent of analytical data available both on the separation of these oligomers from one another[8] and from the polymer[9], and on their structural elucidation[10,11], it is only recently that there has been any interest in them as species capable of migration from plastics into foods[12].

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In marked contrast there has been no published work whatever on the isolation and identification of oligomers from vinyl chloride (VC) polymers, although VC monomer itself has received considerable attention both in terms of residual levels in the plastic[13,14] and as a consequent contaminant in foods[15,16]. In the course of our research programme on plastic packaging materials for food, we have taken a particular interest in the low-molecular-weight components present in poly(vinyl chloride) (PVC) resins, as these represent a considerable potential source for migration. We have previously reported the occurrence of 1,1,1-trichloroethane in PVC resins and bottles used for food packaging[17,18], and more recently have determined on the basis of molecular weight fractionation and micro chlorine estimations, the overall minimum concentrations of VC oligomers in food grade PVC resins[19]. These results did not distinguish between individual oligomer species and it was originally anticipated that the analytical difficulties (particularly thermal instability) which apply to chlorinated paraffins[20,21] would by analogy cause problems in the separation and identification of VC oligomers. However using glass capillary columns and an all-glass coupling line to the mass spectrometer it has now proved possible both to separate and tentatively assign structural identification to the individual oligomers below molecular weight *ca.* 500 which were found to range from trimers to hexamers. Other evidence indicated the presence of heptamers and octamers. In this paper we report this gas chromatography–mass spectrometry (GC–MS) evidence for the occurrence of these previously unidentified species in PVC resins, together with the silica gel column chromatographic "clean-up" of the extracts, and the GC–MS results for the hydrogenated material. Further evidence from chemical ionisation MS and accurate mass measurements (from GC–MS) substantiated the initially postulated oligomer structures.

EXPERIMENTAL

Materials

Six PVC resins (designated A to F) were obtained from a number of European polymer manufacturers as being representative of a wide range of the types of materials used for PVC food packaging. Tris(nonylphenyl) phosphite (TNPP, "Phosclere P315") was obtained from Akzo Chemie (Liverpool, Great Britain), *p*-nonylphenol from Pfaltz and Bauer (Stamford, CT, U.S.A.) and undecyl dodecanoate was synthesized in the laboratory by sulphuric acid catalysed esterification of *n*-dodecanoic acid with *n*-undecanol.

Methods

Solvent extraction of base polymer. Base polymer (20 g) contained in preextracted thimbles was soxhlet extracted with re-distilled diethyl ether for 16 h. After solvent removal on a rotary evaporator and vacuum drying at 40°C the weighed residues were stored at −15° until required.

Size-exclusion chromatography. "Sephadex LH-60" columns were prepared and used as previously described[22]. Column lengths were 33 ± 1 cm and two fractions were routinely collected, standardised at 0–90 ml and 90–190 ml, containing respectively high-molecular-weight and low-molecular-weight material. Total ether extracts were fractionated in 160–180 mg aliquots dissolved in redistilled tetrahydro-

furan (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 SR25/45 columns to give a gel bed of 32 ± 2.5 cm. Aliquots (up to 250 mg) of the low-molecular-weight fraction from the Sephadex column in THF (2.0 ml) were subjected to chromatography in the normal manner[22]. Elution profiles were generated by collecting 2.5-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°C in a vacuum oven, allowed to re-condition for 2 h and re-weighed.

Fractions intended for subsequent GC analysis were simply blown to dryness under nitrogen without further heating. From calibration of the column the fraction (53–90 ml) nominally containing material of molecular weight 0 to 500 was routinely collected (designated B3 fraction).

Elemental analysis. Elemental microanalysis for chlorine was performed by Butterworth Labs. (Teddington, Great Britain). All samples collected from SEC 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.

Purification of oligomer fractions

Silica gel column chromatographic purification of B3 oligomer fractions was carried out using a 10 × 1 cm I.D. bed of silica gel (Merck 7734, 70–230 mesh) packed in *n*-hexane. After the sample (up to 0.08 g B3 in 2 ml hexane) was loaded onto the column, it was washed with *n*-hexane (100 ml) to remove alkanes and the oligomers eluted with toluene (50 ml). The solvent was removed on a rotary evaporator under vacuum at 60°C prior to GC analysis.

Hydrogenation of oligomer fractions

The purified oligomer fraction B3 (up to 0.1 g) dissolved in dry methanol (20 ml) was shaken for 5 min with palladium chloride (0.01 g) under hydrogen (1.5 atm) at ambient temperature. After filtration of the supernatant through a 0.45-μm PTFE filter (Millipore), the methanol was removed on a rotary evaporator under vacuum and the sample blown to dryness under nitrogen prior to GC analysis.

The hydrogenation procedure was tested to show complete saturation of double bonds by converting 2,4-hexadiene to hexane, but was shown to be sufficiently mild to avoid displacing chlorine by leaving dichlorononane unchanged after an identical treatment.

Gas chromatography

Packed-column chromatography was performed with a Pye Series 104 chromatograph using the following columns and conditions:

(a) 2.7 m × 2 mm I.D. glass column packed with 3% OV-1 on Diatomite CLQ (100–120 mesh). Nitrogen carrier gas was used at 25 ml/min. On-column injections were made with the column oven held at 130°C for 2 min and then programmed at 8°/min to 300°C.

(b) 1.5 m × 2 mm I.D. glass column packed with 3% Dexsil 300 on Supelcoport (100–120 mesh). Nitrogen carrier gas was used at 25 ml/min. On-column

injections were made with the column oven at 150°C, immediately programmed at 8°/min to 400°C.

The effluent was split between a flame ionisation detector (FID) (30%) operated at 350° (OV-1) or 450°C (Dexsil 300), and a Tracor model 700 Hall electrolytic conductivity detector (70%) with an interface temperature of 350° (OV-1) or 450°C (Dexsil 300); furnace temperature 850°C; hydrogen make-up gas flow 50 ml/min; and isopropanol–water flow-rate 0.8 ml/min. The conductivity setting was × 100.

Capillary column chromatography used a Carlo Erba model 4160 chromatograph fitted with a 20 m × 0.3 mm borosilicate glass column coated with 0.2-μm OV-101. The carrier gas velocity was 25 cm/sec measured at 200°C. Splitless injections using THF as solvent were made with the injector at 250°C. The split valve was opened to provide an injector purge 20 sec after injection. The column oven was held at 75° for 2 min and then programmed to 240°C at 5°/min. The FID was held at 270°C.

Gas chromatography–mass spectrometry

Capillary column GC–MS was performed with a Carlo Erba 4160 chromatograph operated as above, and connected to a VG7070H mass spectrometer via an all-glass direct coupling interface. The transfer line was held at 250°C. The MS was operated at a source temperature of 200°C with 70 eV electron energy and a 200 μA trap current. Nominal mass spectra were obtained at 1000 resolution (10% valley) scanning from *m/z* 500–25 at 0.7 sec/decade. Accurate masses were obtained using C_2I_4 as internal reference at 2000 resolution and 1.5 sec/decade. All spectra were processed with a VG2000 data system.

RESULTS AND DISCUSSION

Six different samples of PVC resins intended for food contact applications were obtained from a number of European manufacturers. Resins A, B and F were bottle blowing–rigid foil grades whilst resins C, D and E were designated as film grades. Average molecular weights of resins for films (M_n *ca.* $65 \cdot 10^3$) are generally substantially higher than those of resins for bottle blowing (M_n *ca.* $37–45 \cdot 10^3$). When each of the polymers was soxhlet extracted with diethyl ether and fractionated by SEC the total amount of material obtained with a molecular weight of less than 400–500 (*i.e.* B3 fractions) varied from 500 to 1150 mg/kg, as shown in Table I.

Using elemental chlorine data obtained on these fractions and assuming an empirical formula for all oligomers identical to that of vinyl chloride, it is possible to estimate oligomer concentrations as discussed in an earlier paper[19]. Data generated in this manner requires a number of other assumptions, not least that all the available chlorine is present as oligomers rather than as any alternative chlorinated organic compounds. Nevertheless, these results do indicate that PVC resins probably contain substantial amounts of low-molecular-weight oligomers.

When GC–FID analysis of the B3 fractions of the PVC resins was carried out using packed columns, complex chromatograms were obtained with significantly different profiles from one polymer to another. However using dual detection with the effluent split to a Hall electrolytic conductivity detector operated in a halogen specific mode, the Hall detector showed similar chromatograms for all the resins (Fig. 1).

TABLE I

ESTIMATED TOTAL CONCENTRATIONS OF MATERIAL IN LOW-MOLECULAR-WEIGHT FRACTIONS AND CONCENTRATIONS OF INDIVIDUAL IDENTIFIED COMPONENTS

Polymer	*Concentration (ppm) in base resin*					
	Total non-volatiles mol. wt. 400–500*	*Chlorine** containing mol. wt. 400–500*	C_{22} *Hydrocarbon*** n-docosane*	*Undecyl-dodecanoate****	*Nonyl-phenol****	*Mixed phthalates****
A	500	110	30–40	15–20	200	10
B	840	240	30–40	15–20	<1	<1
C	680	160	<1	<1	<1	40
D	720	250	70	20	<1	<1
E	510	180	<1	<1	<1	<1
F	1150	350	110	30	<1	<1

* Estimated gravimetrically from SEC fraction (B3).
** Estimated by micro-chlorine assuming oligomers of PVC empirical formula.
*** Estimated by gas chromatography using response factor of standard compounds.

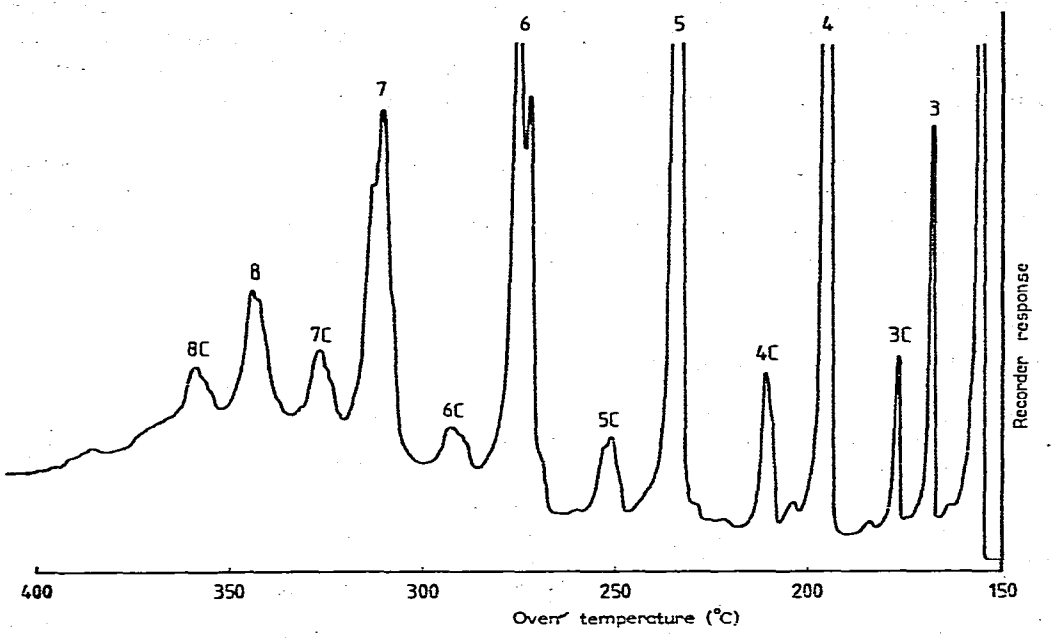


Fig. 1. Hall electrolytic conductivity chromatogram of a B3 fraction from resin A. Dexsil column. For other conditions, see *Methods* section.

Hence the B3 extracts contain essentially the same chlorinated compounds in very similar amounts, but differ from one another only in the presence of other low-molecular-weight non-halogenated components. Glass capillary column GC–MS analysis of the B3 fractions led to the identification of a number of these non-halogenated components, although several still remain unidentified. Alkanes in the range C_{13}–C_{22} at low levels occur widely and in four of the six resins C_{22} is present in

significant amounts (see Table I). Undecyl dodecanoate was unequivocably identified both by comparison of its mass spectrum with the authentic synthesized compound and by agreement of retention indices, and was found in significant amounts in the same resins containing the C_{22} alkane. Both these compounds can be formed by decarboxylation of lauryl peroxide[23–25] and are probably derived from the initiator either during polymerisation or subsequently. A characteristic group of isomeric compounds identified as nonylphenols were found in resin A. These are probably derived from the use of tris(nonylphenyl) phosphite as a pre-stabiliser during polymer drying. Similar but unidentified phenolic mixtures found in resins B and F are thought to be derived from 2,6-di-*tert.*-butyl-*p*-cresol (BHT) or other related phenolic antioxidants. In two of the resins (A and C) complex mixtures of C_8 phthalates were identified and it is possible that these derived from their use as solvents, for example for incorporation of minor additives or in some other aspect of the manufacturing process.

Although good mass spectral evidence is presented here for the establishment of the empirical formulae of the VC oligomers, it has not yet proved possible to make a complete structural elucidation. For clarity, the oligomers referred to in this paper have been numbered using the following system. Oligomers 3, 4, *n* are respectively trimer, tetramer and *n*-mer. This corresponds to $(CH_2CHCl)_n$ *i.e.* vinyl chloride oligomers containing one double bond. A suffix letter C refers to a second oligomer series but in this case cyclic. Thus 3C designates a trimer of the same empirical formula as 3 but where the hydrogen deficiency is thought to be due to a cyclic structure.

The molecular weights, retention indices, empirical formulae (and number of isomers observed by capillary GC–MS) for the oligomers in PVC resin A are given in Table II. A reconstructed total ion chromatogram of a B3 extract from resin C is shown in Fig. 2 in which peaks due to oligomers are marked by arrows. Because of a

TABLE II

PHYSICAL DATA FOR VINYL CHLORIDE OLIGOMERS FROM PVC RESIN A

Oligomer	*Number of isomers observed by capillary GC–MS*	*Empirical formula*	*Mol. wt. (based on ^{35}Cl)*	*Retention index range**
3	1	$C_6H_9Cl_3$	186**	1250
3C	1	$C_6H_9Cl_3$	186**	1360
4	3	$C_8H_{12}Cl_4$	248**	1600–1620
4C	2	$C_8H_{12}Cl_4$	248**	1770
5	4	$C_{10}H_{15}Cl_5$	310	1990–2010
5C	4	$C_{10}H_{15}Cl_5$	310	2140–2170
6	2	$C_{12}H_{18}Cl_6$	372	2350–2410
6C	—	$C_{12}H_{18}Cl_6$	372	2500–2520
7	—	$C_{14}H_{21}Cl_7$	434	*ca.* 2740
7C	—	$C_{14}H_{21}Cl_7$	434	*ca.* 2920
8	—	$C_{16}H_{24}Cl_8$	496	*ca.* 3090
8C	—	$C_{16}H_{24}Cl_8$	496	—

* Retention indices were generated by co-chromatography of B3 fractions with a series of *n*-alkanes.
** Molecular ion observed on mass spectra.

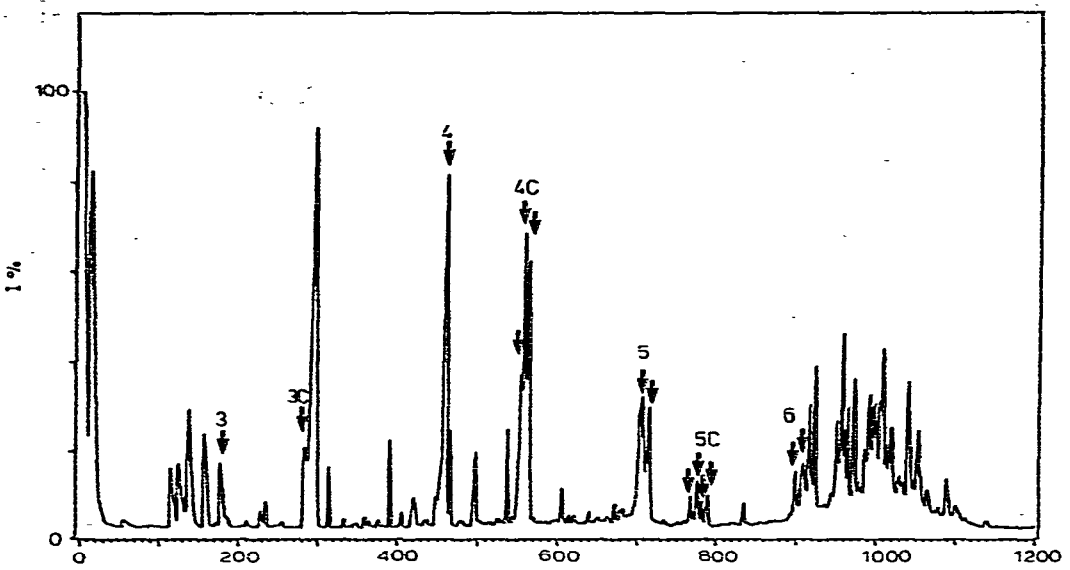


Fig. 2. Reconstructed total-ion capillary GC–MS chromatogram of a B3 fraction from resin C. Isomeric clusters of oligomers are indicated.

temperature limit of 250°C on the GC–MS interface we were unable to obtain spectra for oligomers eluting after the hexamer. In future, however, with improved heating to the GC–MS transfer line, this restriction will not apply.

Some typical oligomer mass spectra are shown in Fig. 3 and the MS evidence of identification is summarised in Table III which shows the assignment of the characteristic fragment ions for the oligomers, except for 6, where the spectra were both mixed and of low absolute intensity. Measurements of "accurate" mass gave good agreement ($\pm$ 5 m.m.u.) with calculated values for most of the more intense high mass fragments. At lower masses the technique was found to be unreliable by analysis of reference compounds giving known fragments.

Molecular ions were either not observed or were of low relative intensity (1–6%). Chemical ionisation (CI) using either isobutane or ammonia failed to give any enhancement, either of oligomers or standard chloroalkanes. Negative-ion CI gave only chlorine ions of great intensity at m/z 35 and 37. This behaviour is consistent with the interpretation that the oligomers are chlorinated aliphatic alkanes as typified by dichlorononane. Standard chloroalkenes could not be obtained.

The most striking features of the oligomer spectra are the clusters of ions due to ^{35}Cl–^{37}Cl combinations, in some instances further complicated by overlapping patterns caused by losses of either Cl or HCl from the same precursor ion. For example, for the tetramer (mol. wt. 248) two fragments at 212 and 213 are produced and these give rise to isotope peaks at 214, 216 and 218 and also 215, 217 and 219 with the overall effect of producing a characteristic cluster of ions at every mass from 212 to 219. It was observed that further fragmentation of such cluster by loss of Cl or HCl frequently occurs in such a fashion that the primary products were due to M $-$ HCl_2 with only a small contribution from M $-$ H_2Cl_2.

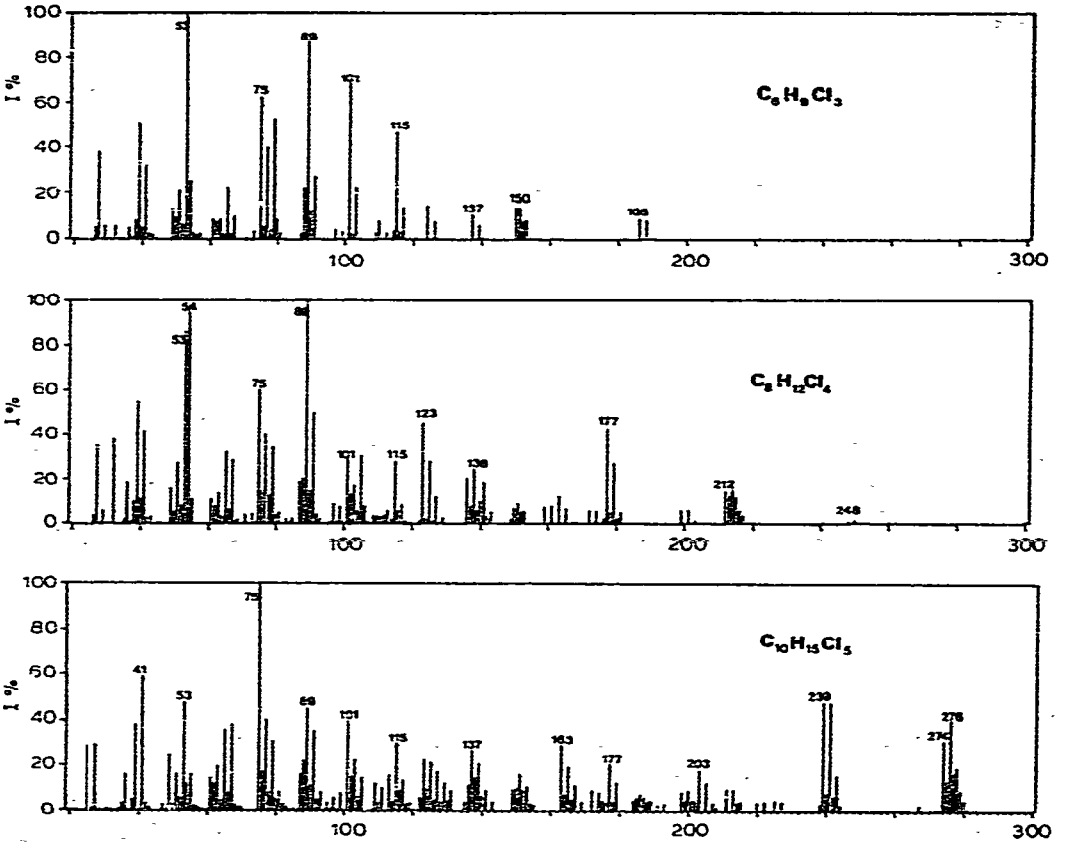
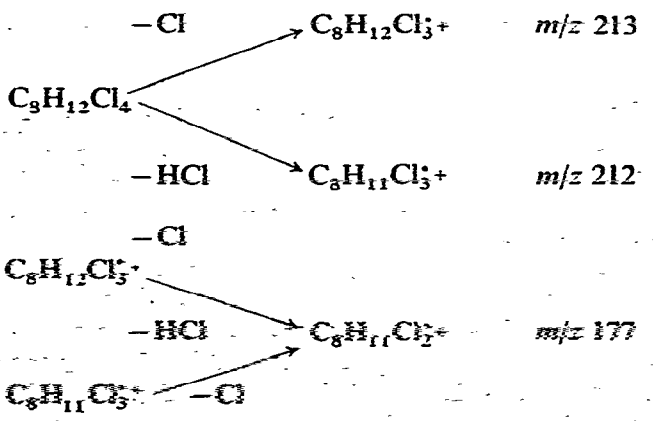


Fig. 3. Typical mass spectra for oligomers 3 ($C_5H_9Cl_3$), 4 ($C_8H_{12}Cl_4$) and 5C ($C_{10}H_{15}Cl_5$).



Several regions of the chromatogram showed partially resolved groups of peaks where the spectra of the individual member peaks were virtually indistinguishable (Fig. 2). It is likely that these groups are due to isomeric families of oligomers arising

TABLE III

CHARACTERISTIC IONS FROM 70 eV FRAGMENTATION OF VINYL CHLORIDE OLIGOMERS

m/z	*Assignment**	*VC oligomers % intensity*					
		3	*3C*	*4*	*4C*	*5*	*5C*
53	C_4H_5	100	34	75	40	35	55
54	C_4H_6	32	5	100	8	10	8
75	$C_3H_4\ ^{35}Cl$	95	100	61	100	61	100
89	$C_3H_6\ ^{35}Cl$	73	48	84	41	29	49
91	—	24	15	31	18	100	37
101	$C_5H_6\ ^{35}Cl$	61	53	33	36	32	46
115	$C_6H_8\ ^{35}Cl$	32	75	28	35	17	29
123	—	0	16	49	18	29	29
127	—	0	3	10	8	62	22
137	$C_5H_7\ ^{35}Cl_2$	11	74	10	27	21	29
150	$C_6H_8\ ^{35}Cl_2$	10	55	6	7	0	15
163	—	0	0	12	28	55	31
177	—	0	0	37	51	16	17
186	$C_6H_9\ ^{35}Cl_3$	(m^+) 6	(m^+) 6	1	2	0	12
199	—			6	0	22	0
212	$C_8H_{11}\ ^{35}Cl_3$			13	22	0	0
239	$C_{10}H_{14}\ ^{35}Cl_3$			0	0	19	42
248	$C_8H_{12}\ ^{35}Cl_4$			(m^+) 1	(m^+) 5	0	0
274	$C_{10}H_{14}\ ^{35}Cl_4$					13	44
275	$C_{10}H_{15}\ ^{35}Cl_4$					0	14

* In all cases ions from ^{35}Cl isotopes only are shown.

from different chlorine substituent position patterns since oligomers which differ in branching would give rise to member peaks more widely separated.

The components designated 3C and 4C give spectra similar to those of 3 and 4 but with some differences in the relative abundancies of certain fragment ions. For example, lower intensities were observed for *m/z* 53 and 54 for 3C and 4C compared with 3 and 4 and conversely, higher intensities for *m/z* 75. In addition the relative intensities of the M − Cl and M − HCl fragments were significantly higher for the C series oligomers. Molecular ions are not observed for either 5 or 5C. In the spectrum ascribed to 5C this was immediately apparent from the presence of overlapping 4 − Cl groups at *m/z* 274 and 275 and although the similar loss from 5 could not be so readily deduced from the pattern of the (less intense) group at *m/z* 274, strong similarities exist between this spectrum and that due to 4. The identification ascribed to 6 was generally consistent with this spectrum but the relative intensities of ions were rather unreliable because of the low absolute intensity of the spectrum and because of the subtractions required due to its elution with a phthalate ester as a partially mixed peak.

On the basis of mass spectral evidence empirical formulae could be obtained for oligomers 3, 4, 5 and 6 and also 3C, 4C and 5C. When the electrolytic conductivity chromatogram of a B3 fraction (Fig. 1) is inspected the regularity of the pattern of peaks immediately suggests the presence of two homologous series of oligomers.

Consequently the tentative assignations of oligomer structures 7 and 8 and also 6C, 7C and 8C have been associated with the later-eluting peaks of this chromatogram. The molecular weights of both 8 and 8C are 496 (all ^{35}Cl) and thus the lack of higher oligomers as evidenced in Fig. 1 is entirely consistent with the estimated molecular weight cut-off point for the B3 fraction of 400–500. It might be expected that considerably greater amounts of 8 and 8C would be found in the B2 fraction.

In further support of this identification of the higher oligomers, it was found that the non-cyclic oligomeric species were absent from a chromatogram of a hydrogenated purified B3 fraction (Fig. 4), being replaced by another, later-eluting, series of peaks of similar relative intensities. This makes it unlikely that the original peak spacings of the non-cyclic oligomer series were fortuitous. Further GC–MS studies with a high temperature interface should settle this point.

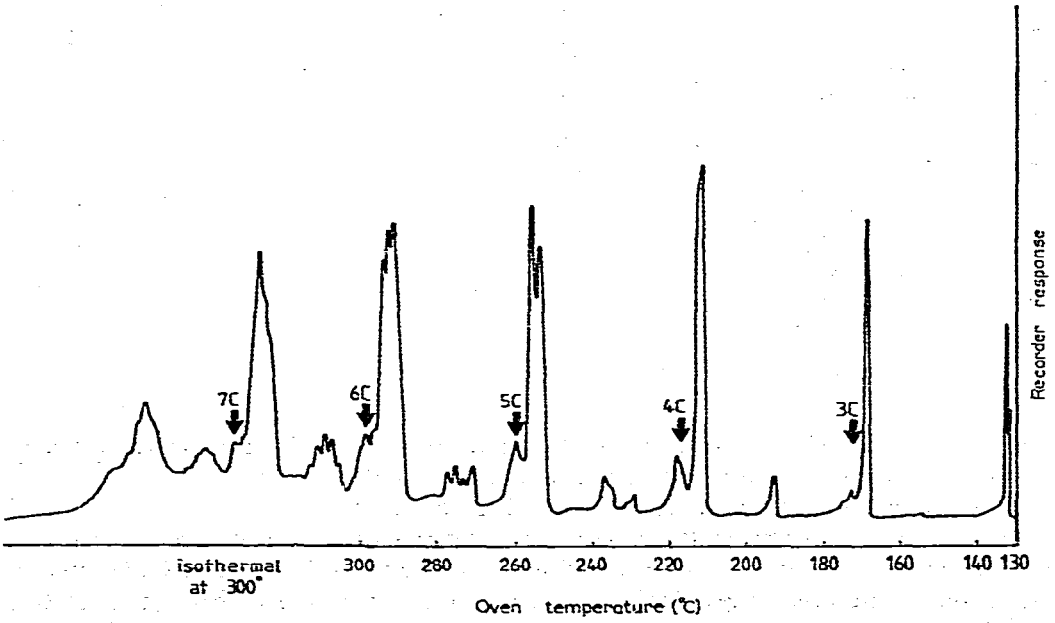


Fig. 4. Hall electrolytic conductivity chromatogram of a hydrogenated purified B3 fraction from resin A. OV-1 column. For other conditions, see *Methods* section.

The major evidence for cyclic structures for the C series also came from hydrogenation studies as 3C, 4C and 5C remained the only oligomers unchanged in both retention time and mass spectra. In the electrolytic conductivity chromatogram of a similar hydrogenated fraction (Fig. 4) peaks were found at the predicted retention times of all the series C oligomers.

Although the conditions of hydrogenation were carefully chosen and tested on a model chloroalkane to avoid any hydrogenolysis, hydrogenation of oligomer fractions led to significant changes in the non-cyclic oligomer series, as described above, which did not represent simple saturation of double bonds. While the products were still chlorine-containing, as shown by both the mass spectra and the electrolytic conductivity–GC traces, the spectra were not easily interpretable and it is possible

that rearrangement reactions did take place during hydrogenation. The apparent survival of intact 3C, 4C and 5C suggests otherwise but "scrambling" of the chlorine substituent patterns in these would not have been detected.

In this context it is interesting that Schwenk *et al.*[26] deduced that certain allylic chlorines were replaced by methoxy groups during hydrogenation of low-molecular-weight PVC at 0°C in methanol. Our experiments were carried out at an ambient temperature of around 20°C and thus a similar substitution can be expected to have occurred but even considering this possibility the mass spectra remained uninterpretable. Micro-hydrogenation of trapped GC peaks may be of help in elucidating the changes occurring on hydrogenation.

The origin of the compounds giving electrolytic conductivity peaks intermediate between the series of cyclic oligomer peaks and the next-eluting major peak (Fig. 4) is unknown but may be artifactual or alternatively derived from the hydrogenation of a non-volatile oligomer in the B3 fraction. Although the silica gel clean-up of this fraction was very effective, more polar oligomers might have been co-eluted, as was the case with undecyl dodecanoate.

One factor suggesting that other, more polar, oligomers were present in the B3 fraction is that the quantitative estimate of total oligomer concentrations (Table I) derived from micro-chlorine and gravimetric data[19] is significantly greater than the sum of the individual oligomer concentrations (Table IV). The latter concentrations were estimated by calibration of the electrolytic conductivity detector with a solution of dichlorononane in order to obtain a response factor per unit mass of chlorine. The numbers of chlorines per oligomer were then deduced; for 3–6 and 3C–5C from the mass spectra and for 7 and 8 and 6C–8C by inference. GC analysis of a known mass of B3 fraction completed the determination. The relative distribution of the different oligomers was very similar for all six resins examined. Because of the number of assumptions involved, the extent of experimental error is difficult to assess and is probably quite high but the difference between the two measures of total oligomers is so great that the presence of non-volatile oligomers in the B3 fraction seems likely. Literature reports[26–28] of end-groups detected in low-molecular-weight PVC by nuclear magnetic resonance (NMR) techniques include:

$$-CH_2-CHCl-CH = CH-CH_2\,Cl$$
$$-CHCl-CH_2-CH = CH-CH_2\,Cl$$
$$-CHCl-CH_2\,Cl$$
$$-CH_2-CH_2\,Cl$$

Polar end-groups have not been found to any appreciable extent. Thus some other source of such non-volatile species is required to explain these observations. This might involve artifacts or alternatively, for example, oligomers retaining initiator end groups.

To summarise, although good evidence is presented for the occurrence of a series of vinyl chloride oligomers at mg/kg levels in a number of different commercial PVC resins, further work still needs to be carried out to establish unequivocably the structures of these compounds. This work is necessary in order to assess whether vinyl chloride oligomers represent potential migratory species in food packaging materials and additionally could possibly provide useful information on the sites of unsatura-

TABLE IV

QUANTIFICATION OF VINYL CHLORIDE OLIGOMERS IN PVC RESINS

Oligomer	*Amount of oligomer found (ppm in base resin)*				
	Resin A		*Resin C*		*Resin F**
	Duplicates	*Mean (% of total)*	*Duplicates*	*Mean (% of total)*	*(% of total)*
3	1.0	1.55	2.4	2.7	3.1
	2.1	(3.2)	3.0	(10.5)	(2.8)
3C	0.7	0.85	2.2	1.9	1.2
	1.0	(1.8)	1.6	(7.4)	(1.1)
4	9.7	10.25	5.4	5.4	13.8
	10.8	(21.4)	5.4	(21.1)	(12.5)
4C	1.7	1.7	4.3	3.75	2.5
	1.7	(3.6)	3.2	(14.6)	(2.3)
5	12.1	11.75	3.8	3.8	23.2
	11.4	(24.6)	3.8	(14.8)	(21.0)
5C	3.3	3.15	1.4	1.4	3.4
	3.0	(6.6)	1.4	(5.5)	(3.1)
6	9.8	10.2	3.8	3.5	24.7
	10.4	(21.3)	3.2	(13.7)	(22.4)
6C	1.7	1.7	1.4	1.4	5.4
	1.7	(3.6)	1.4	(5.5)	(4.9)
7	4.7	4.85	0.8	0.8	28.8
	5.0	(10.1)	0.8	(3.1)	(26.1)
7C	1.7	1.7	1.0	1.0	4.2
	1.7	(3.6)	1.0	(3.9)	(3.8)
Total	46.4 48.8	47.8	26.5 24.8	25.6	110.3
Total found by micro-chlorine analysis	110 (43.5)		160 (16.0)		340 (32.4)

* Oligomers 8 (5.1 ppm) and 8C (1.3 ppm) were quantified in Resin F.

tion in PVC. Possible approaches to the structural elucidation of the oligomers under consideration are, isolation of individual species by preparative GC for subsequent NMR analysis and use of microchemical techniques such as epoxidation or ozonolysis in conjunction with GC for location of the double bonds in these unsaturated structures.

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