Eur. Polym. J. Vol. 21, No. 6, pp. 555–559, 1985
Printed in Great Britain

0014-3057/85 $3.00 + 0.00
Pergamon Press Ltd

STRUCTURAL STUDIES OF AN OLIGOMER (VINYL CHLORIDE TETRAMER) ISOLATED FROM POLY(VINYL CHLORIDE) RESIN USED FOR FOOD PACKAGING APPLICATIONS

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(*Received* 2 *January* 1985)

Abstract—A presumptive single component previously isolated from PVC base resin and tentatively identified from GC–MS data as a vinyl chloride tetramer (mol. wt = 248) has been the subject of further studies. After hydrogenation, two isomeric compounds were separable by capillary GC. Mass spectra confirmed the earlier assignment of one double bond in the parent compounds. Further evidence for the presence of a pair of isomers in the apparently pure tetramer was obtained by epoxidation where two products giving identical mass spectra were produced. The MS fragmentation pattern suggested that the double bond position was allylic to chlorine; GC–MS analysis of the derived chlorohydrins supported this conclusion. Analysis of the tetramer by NMR gave complex overlapping signals, thought to be due to impurities, which hindered interpretation. Some supportive evidence for an allylic double bond was obtained. The structure of the tetramer thus remains only partially determined; the complexities of isomer purification and the difficulties of assigning chlorine substituent patterns make future unequivocal characterisation unlikely.

INTRODUCTION

Due to the likely structural and thus toxicological analogies between vinyl chloride oligomers and vinyl chloride itself, these compounds have been of interest for some time as potential migrants from PVC packaging materials into foods. Previous characterisation [1, 2] of the low molecular weight fraction of PVC has indicated the presence of two homologous series of oligomers, each ranging in size from trimer to hexamer and with corresponding members having the same empirical formulae. It was considered that the difference between the two series arose from their possession either of a ring system or a double bond. In addition each member occurred as a family of isomers [2]. These isomer groups were found to be present in the PVC at minimum amounts of 1 to 10 mg/kg with both qualitative and quantitative similarities in the pattern of components over a range of commercial food grade resins [2].

In order adequately to assess the significance of these oligomers, it was decided that more detailed structural information was required and that this would necessitate the separation and purification of a single oligomeric species. A multi-stage chromatographic procedure was therefore developed [3], based on sequential size exclusion separations using alternative solvents to achieve differential solvation of the oligomers. The fractionated poduct was monitored by capillary GC with both flame ionisation and specific chlorine detection. Using this procedure, 0.5 mg of non-cyclic tetramer was isolated which by GC was apparently free of impurities. This paper reports the chemical and spectroscopic studies carried out on this material with the objective of further elucidating its structure.

Although there are no published reports on the structure of low molecular weight PVC oligomers, there has been considerable investigation of the fine structure of PVC itself particularly in relation to structural anomalies as sites of thermal instability [4, 5]. One approach has been to enrich the structural defects (and in particular the end-groups) of bulk PVC by preparing low molecular weight material (mol. wt = 1500) and thus enable NMR to be employed [6]. Additionally model chloroalkenes have been synthesised and their NMR characteristics determined to allow identification of terminal structures in PVC [7, 8]. Although the results from the various approaches are not in total agreement, there is considerable evidence supporting $-CH_2-CH=CH-CH_2Cl$ as the main unsaturated structure and $-CHCl-CH_2Cl$ as the principal saturated chain end. It is thought that chain branching is relatively low with methyl side chains occurring on average at 1 in every 200 carbon atoms and longer chain branching at about 1 in every 500 carbon atoms. As the proportion of oligomers with molecular weights low enough (< 500) to be of possible importance as migrants from PVC food packaging would be insignificant in relation to the mass of higher oligomers in the fractions studied, it is not necessarily the case that end groups of the former would follow this pattern. However a consistent mechanism of formation of end groups by such routes as chain transfer to monomer or head to tail

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addition followed by 1,2-Cl migration and Cl· elimination would argue for similarities irrespective of chain length.

The work reported in this paper provides more direct evidence for the structure of an oligomer than has been published elsewhere because it concerns isolated tetramer rather than extrapolation from analysis of complex mixtures of homologues. Nevertheless severe limitations in respect of the amount of material which could be isolated and in the performance of the chromatographic procedures for separating isomers have restricted the outcome of the study to only partial structural characterisation.

EXPERIMENTAL

Materials

PVC base resin intended for film application with weight-average molecular weight of 180,000, K value of 69 and a viscosity number of 120 (ISO R174) was obtained from Norsk-Hydro (Aycliffe, Co. Durham).

Methods

Solvent extraction of the base polymer, preparative size exclusion chromatography, silica gel chromatography and sequential high performance size exclusion chromatography in eluents of different solvating power were as described previously [3].

Hydrogenation

Tetramer as isolated (*ca* 50 μg) was dissolved in dry chloroform (10 ml). Palladium chloride catalyst (0.5 mg) was added and the flask evacuated and then filled with H_2 to a pressure of 0.25 MPa, the process being repeated three times to ensure complete replacement of gas in the headspace. The flask was shaken at ambient temperature for 5 min and the solution filtered through a 0.45 μm PTFE filter (Millipore) prior to analysis.

Epoxidation

Tetramer as isolated (*ca* 10 μg) was dissolved in chloroperbenzoic acid solution (25 μl, 0.05 M in redistilled hexane). The sealed vial was heated to 80° for 30 min. Excess reagent was removed by washing with 5% aqueous sodium metabisulphite (100 μl) followed by sodium bicarbonate (100 μl of a 5% solution) and water. The organic phase was then dried with a few crystals of sodium sulphate. The reaction product was removed by syringe and submitted to GC–MS analysis.

Chlorohydrin formation

After GC–MS analysis, the remaining epoxide solution from the above experiment was evaporated to dryness under a stream of N_2 and treated with a solution of dry HCl in diethyl ether (200 μl) allowing reaction to take place for 30 min at room temperature. After evaporation to dryness, the product was redissolved in diethyl ether and re-evaporated to remove excess HCl. The chlorohydrin was derivatised by treatment with BSTFA (50 μl) and pyridine (50 μl) allowing reaction at room temperature for 1 hr.

GC–MS analysis

GC–MS was carried out using a Carlo Erba 4160 chromatograph directly coupled to a VG 12000 quadrupole mass spectrometer. The GC conditions were as follows: column, 25 m × 0.25 mm fused silica WCOT coated with 0.12 μm CPSIL 5CB. Carrier gas, He at a flowrate of 1 ml/min. Injection, splitless (1 μl) at an injector temperature of 200°. Temperature programming was as follows: 60° for 2 min, then at 40°/min to 130° and at 8°/min to 300° followed by 10 min isothermally. Electron impact spectra were obtained with a source temperature of 200°, electron energy of 70 eV and a trap current of 200 μA. The MS was repetitively scanned from m/z 30 to 600 in 1 sec and the spectra were processed with a VG DS2000 data system.

NMR analysis

^{1}H-NMR spectra were obtained on a Nicolet 200 MHz spectrometer. The samples were dissolved in $CDCl_3$ containing TMS as an internal reference. All spectra are reported in parts per million (ppm).

RESULTS AND DISCUSSION

The tentative identification of the vinyl chloride tetramer from its EI mass spectrum has been discussed previously, based on a molecular ion at m/z 248, isotopic clusters of ions consistent with the presence of four chlorines, and mass spectral eliminations consistent with known chloroalkenes and chloroalkanes. Although previously hydrogenation was carried out on a mixture of oligomers and some conclusions were drawn from the shifts in peak retention times, the mass spectra were not easily interpretable possibly due to substitution of allylic chlorines by methoxy groups during hydrogenation in methanol solvent. In the work reported in this paper, where a different hydrogenation procedure was employed, there was again a shift to an earlier retention time after hydrogenation of the tetramer while an additional barely resolved peak was observed to elute before the major product. Chromatograms obtained before and after hydrogenation are shown in Fig. 1. The mass spectra of the peaks produced by hydrogenation were virtually identical and although in neither case showing molecular ions, they did exhibit shifts of two mass units in many of the fragments compared with the tetramer, as would be expected following the saturation of a double bond. The cluster of ions containing three chlorines at m/z 212 attributed to M-HCl in the VC tetramer was thus shifted to m/z 214 and the cluster at m/z 177 shifted to m/z 179. The mass spectra of the VC tetramer together with that of the major of the two isomeric hydrogenation products is shown in Fig. 2.

There was previously some evidence from its lack of symmetry that the GC peak due to the VC tetramer contained more than one component, although resolution into discrete components could not be achieved even with high performance capillary GC columns and no differences could be observed between spectra obtained at different time intervals through the GC peak. This suggests that the isomers present were very closely related. Saturation of the double bond on hydrogenation however permitted chromatographic resolution of these isomers, although unfortunately it is difficult to derive any structural information from this observation. A similar effect was noted on epoxidation of the tetramer: two easily resolvable components were produced again showing close similarities in their mass spectra. As with other chlorinated compounds molecular ions were not evident in the spectra of the epoxides but the cluster at m/z 229, with an isotope pattern consistent with three chlorines corresponds to the loss of chlorine from the molecular ion. The mass spectra of the epoxide is illustrated in Fig. 3 from which some

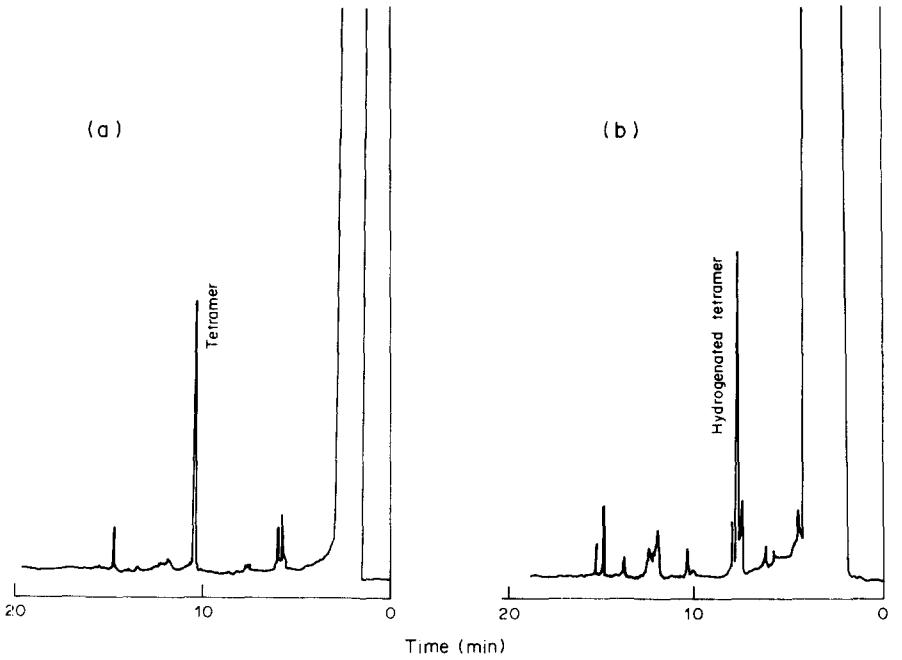

Fig. 1. FID chromatograms of (a) purified VC tetramer and (b) products of hydrogenation. Column, 25 m × 0.25 mm fused silica coated with CPSIL 5CB operated at a H_2 carrier gas flow rate of 1 ml/min. Splitless injection initially with an oven temperature isothermal at 60°, then with temperature programming at 4°/min to 130° followed by 8°/min to 300° and finally isothermally for 10 min.

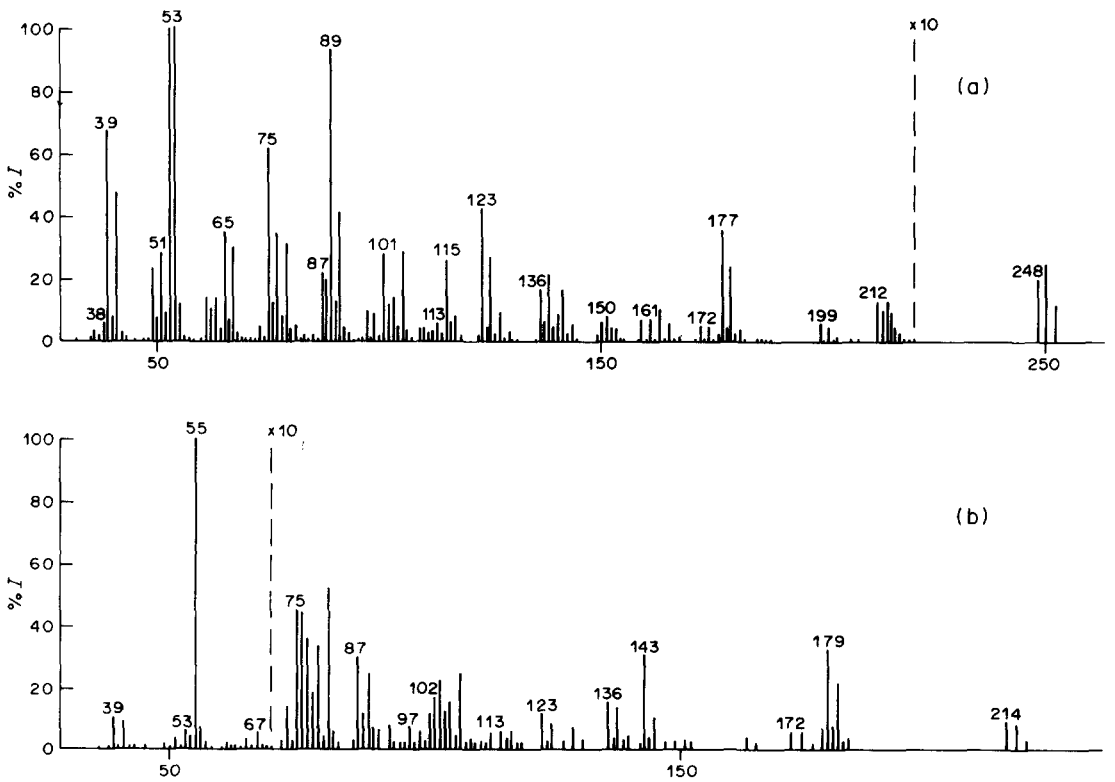

Fig. 2. EI mass spectra of (a) VC tetramer (mol. wt = 248) and (b) hydrogenated product (mol. wt = 250, major component) GC–MS conditions as in "Experimental" section.

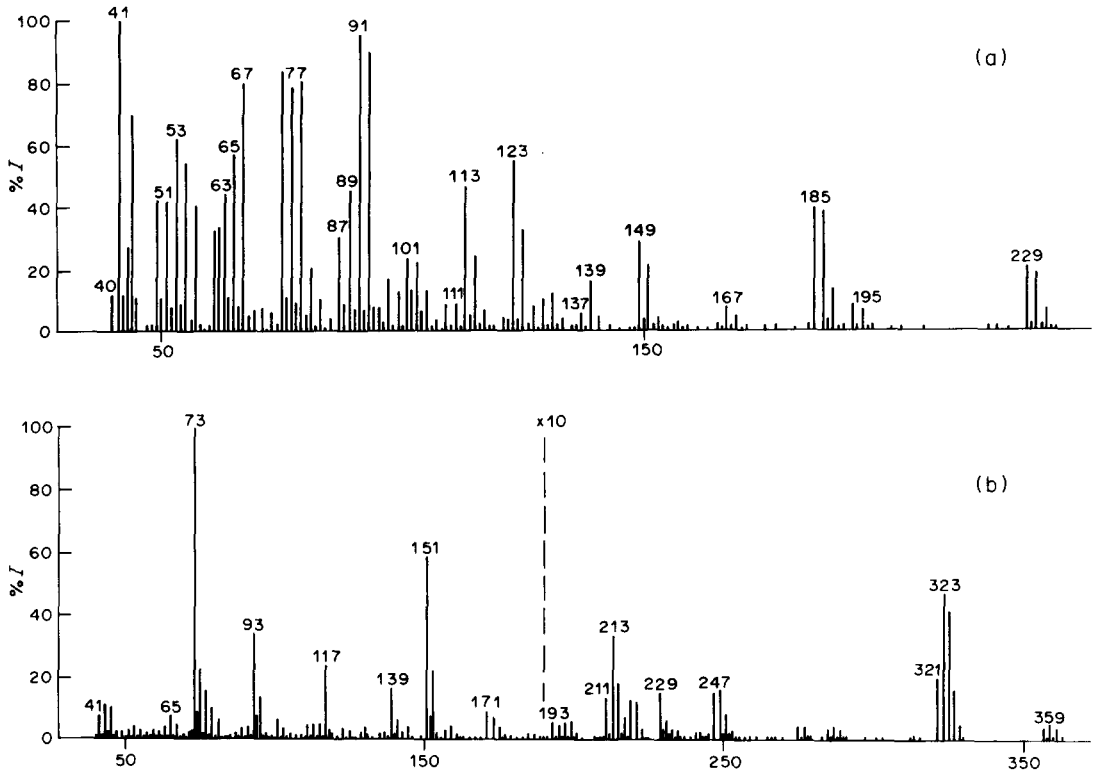

Fig. 3. EI mass spectra of (a) epoxide of VC tetramer, mol. wt = 264. Both isomers gave essentially the same spectrum. (b) Trimethylsilyl derivatised chlorohydrin of VC tetramer, mol. wt = 372. Both isomers gave essentially the same spectrum. GC–MS conditions as in "Experimental" section.

further structural information can be deduced. The major ion at m/z 185 can be postulated as being due to:

$$[CH_2Cl—CHCl—CH_2—CHCl=CH]^+$$

with m/z 91 probably due to:

$$[CH(=O)—CH—CH_2Cl]^+$$

Both fragments support an allylic double bond system although neither gives any further information on the remaining chain structure.

It is unlikely that the two epoxide compounds observed were *cis* and *trans* isomers as, in model compounds, such isomers were inseparable under these GC conditions [9]. It is more probable that the loss of the double bond had caused a sufficient change in structure to allow chromatographic separation of what were, before reaction, inseparable isomers.

In previous work with unsaturated compounds [9], it was noted that, by sequential formation of their epoxides and chlorohydrins and subsequent MS analysis of the TMS derivatives of the latter, it was possible to deduce useful structural information on double bond positions. This was due to the fact that the epoxides normally formed equal amounts of two chlorohydrins (A—CHOH—CHCl—B and A—CHCl—CHOH—B) which on TMS derivatisation and mass spectral fragmentation gave both $[A—CH—O—TMS]^+$ and $[TMS—O—CH—B]^+$ as major ions, thus confirming the position of unsaturation. In the case of the VC tetramer the two TMS-chlorohydrin GC peaks obtained from their respective epoxides gave, as expected, identical mass fragmentation patterns (a representative spectrum is shown in Fig. 3). Consistent with TMS-chlorohydrin MS behaviour, the highest mass ions observed were at m/z 357, corresponding to M-15 (loss of methyl from the TMS group) with the isotopic pattern expected from its five chlorines. Loss of HCl gave rise to the cluster of ions at m/z 321 again consistent with fragmentation behaviour for this type of chlorinated compound. A major ion at m/z 151 could be:

$$(TMSO—CH—CH_2Cl]^+$$

which fits the previous evidence for an allylic double bond, but there was surprisingly no fragment at m/z 213, the expected ion for:

$$[CH_2Cl—CHCl—CH_2—CH(OTMS)]^+$$

Thus the formation of the chlorohydrin in this instance must be directed in some way, possibly sterically, such that only a single chlorohydrin isomer can be formed:

$$CH_2Cl—CH_2—CHCl—CHCl—CH_2—$$
$$CHCl—CH(OH)—CH_2Cl$$

The cumulative evidence from characterisation of these three derivatives is thus for the double bond to

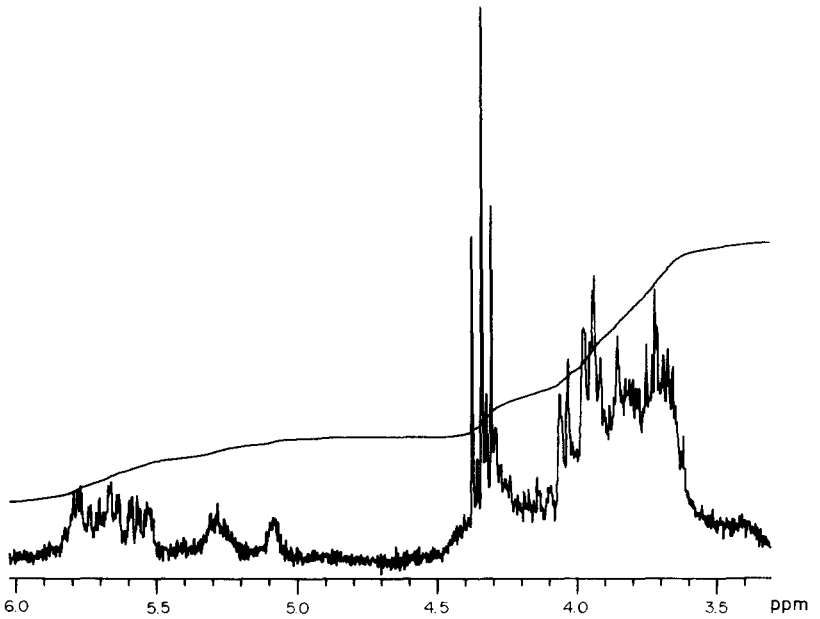

Fig. 4. Portion of ^{1}H-NMR spectrum of VC tetramer in region 3.5–6.0 ppm. Conditions: nicolet 200 MHz spectrometer; sample dissolved in $CDCl_3$ with TMS internal standard at 25°.

be allylic and for there to be slight differences, probably in the arrangement of the chlorines, in the remainder of the chain structure.

A sample of tetramer as isolated (estimated from GC analysis to have a mass of about 0.5 mg) was analysed by proton NMR. A complex spectrum was obtained which was not easily interpretable but indicated from signals at 7.2 ppm and from 0.5 to 2.5 ppm that considerable branched chain phthalate impurity was present. Further signals at <0.1 ppm were assigned to silyl groups thought to be due to silicone oil contamination. Despite these difficulties it was possible to gain some structural information from the spectrum especially from the region 3.5 to 6.0 ppm which is displayed in Fig. 4. The multiplet of peaks in the region 5.5–6.0 ppm is strikingly similar to that reported by Bezdadae *et al.* [7, 8] for alkenic protons of 4-chloropent-1-ene and 3-chloropent-1-ene, and to those found by Hjertberg and Sorvik [5] for the end groups in low molecular weight fractions of PVC. A doublet of similar intensity at 4.05 ppm was assigned to —CH=CH—$\underline{CH_2}$Cl protons. Peaks in the region 3.5–4.0 ppm are due to various —$\underline{CH}$Cl and —$\underline{CH_2}$Cl environments but cannot be used to deduce any specific structural information. The triplet at 4.3 ppm may be indicative of the —CH_2—CH=$\underline{CH}$—CH_2Cl proton.

CONCLUSION

The GC–MS data and formation of various derivatives are consistent with the isolated compound being a vinyl chloride tetramer containing one double bond. Fragmentation both of the epoxide and the derived chlorohydrin indicate an allylic double bond position and this conclusion is supported by partial interpretation of the NMR spectrum. The products of hydrogenation and epoxidation were separable by GC and were shown in both cases to be isomeric, indicating that the tetramer as isolated also consisted of (probably) two isomeric components. The structure of the tetramer thus remains only partially determined but the complexities of elucidating chlorine substituent positions makes unequivocal characterisation unlikely.

Acknowledgement—We thank Norsk-Hydro (Aycliffe, Co. Durham) for the gift of PVC base resin.

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