Isolation and Structural Characterization of Tetrameric Oligomers of Vinyl Chloride

John V. Dawkins,* Christopher J. Moody, and David Price

Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire, LE11 3TU, U.K.

Laurence Castle

Food Science Laboratory, Ministry of Agriculture Fisheries and Food, Norwich Research Park, Colney, Norwich NR4 7UQ, U.K.

Oliver W. Howarth

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, U.K.

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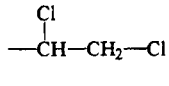
Introduction

The isolation and characterization of oligomers in a polymer may provide important structural and mechanistic information. For addition polymers, an example is the synthesis of polystyrene (PS) of low molecular weight by anionic chain reaction polymerization. Such PS samples may be separated into their constituent oligomers by gel permeation chromatography (GPC)[1] and each oligomer may then be characterized by nuclear magnetic resonance (NMR) spectroscopy.[2] For condensation polymers, cyclic and linear oligomers in poly(ethylene terephthalate) have been characterized.[3] For epoxy resin prepolymers oligomer species may be separated, depending on the chromatographic technique, and structures for some of these oligomers have been postulated.[4]

Much research work[5,6] has been carried out to investigate why the stability of poly(vinyl chloride) (PVC) is lower than would be expected on the basis of its ideal structure $-(CH_2CHCl)_n-$. Van den Heuvel[7] obtained a low molecular weight fraction of PVC by fractional precipitation of a PVC sample produced by suspension polymerization. From ^1H NMR spectroscopy he postulated end groups of the type shown in structures **1** and **2**.



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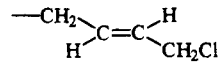

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Hjertberg and Sörvik[8] also indicated the presence of these groups in a range of PVC samples of differing molecular weights. These end groups were postulated following studies by ^1H NMR spectroscopy on modified PVC after phenolysis and bromination. More recently, Starnes *et al.*[9] have confirmed the presence of structures **1** and **2** in a bulk-polymerized sample of PVC by using ^{13}C NMR spectroscopy. The formation of chain structures **1** and **2** was postulated by a mechanism involving chain transfer reactions.

With all this work aimed at trying to elucidate the structure of PVC, it is surprising there have not been reports on the isolation of individual oligomer species followed by detailed structural characterization. Since some structural features of long-chain PVC should be present to the same extent in a low molecular weight fraction, it should be possible to explain structural defects in PVC by the isolation of individual oligomer species and subsequent characterization. Literature reports on the separation of vinyl chloride oligomers have come from Gilbert *et al.*[10–13] Gilbert used a method based on Soxhlet extraction followed by various chromatographic techniques to obtain a very small quantity of oligomer species. A partial characterization of an oligomer fraction was then attempted on the basis of ^1H NMR and mass spectroscopy.

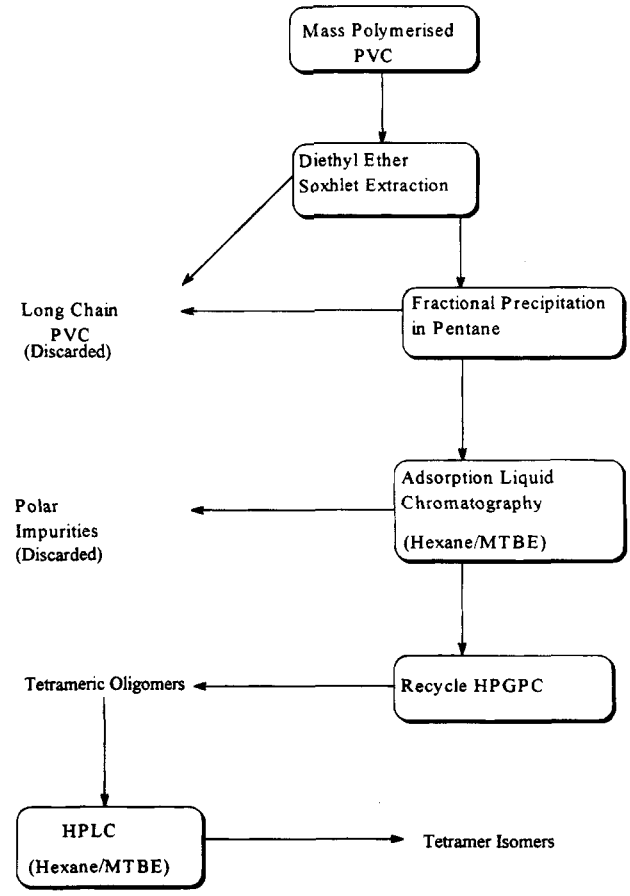

Figure 1. Isolation scheme for tetramer isomers.

Dawkins *et al.*[14] have reported a procedure for the separation of oligomers from a low molecular weight extract of PVC, using a recycle high-performance gel permeation chromatography (HPGPC) system. This system was capable of resolving oligomers in the range pentamer to decamer; however, no structural determinations were made. Here, this technique is incorporated into a separation scheme directed to the isolation of tetrameric oligomers.

Experimental Section

All ^1H and ^{13}C NMR spectra were recorded using a Bruker ACP-400 spectrometer. The mass spectra were recorded on a VG Analytical ZAB-E instrument. All solvents used were HPLC grade (supplied from Fisons, Loughborough) and used without further purification.

The PVC used throughout this investigation was a mass-polymerized sample (Lucovyl RB8010, *K* value 56) supplied by Atochem, Thatcham, U.K. The weight-average molecular weight of this sample was found to be 76 000 using the method described by Dawkins *et al.*[15]

The tetramer was isolated according to Figure 1.

PVC (300 g) was extracted using diethyl ether in a modified large-volume Soxhlet[16] apparatus for 8 h. After extraction,

* To whom correspondence should be addressed.

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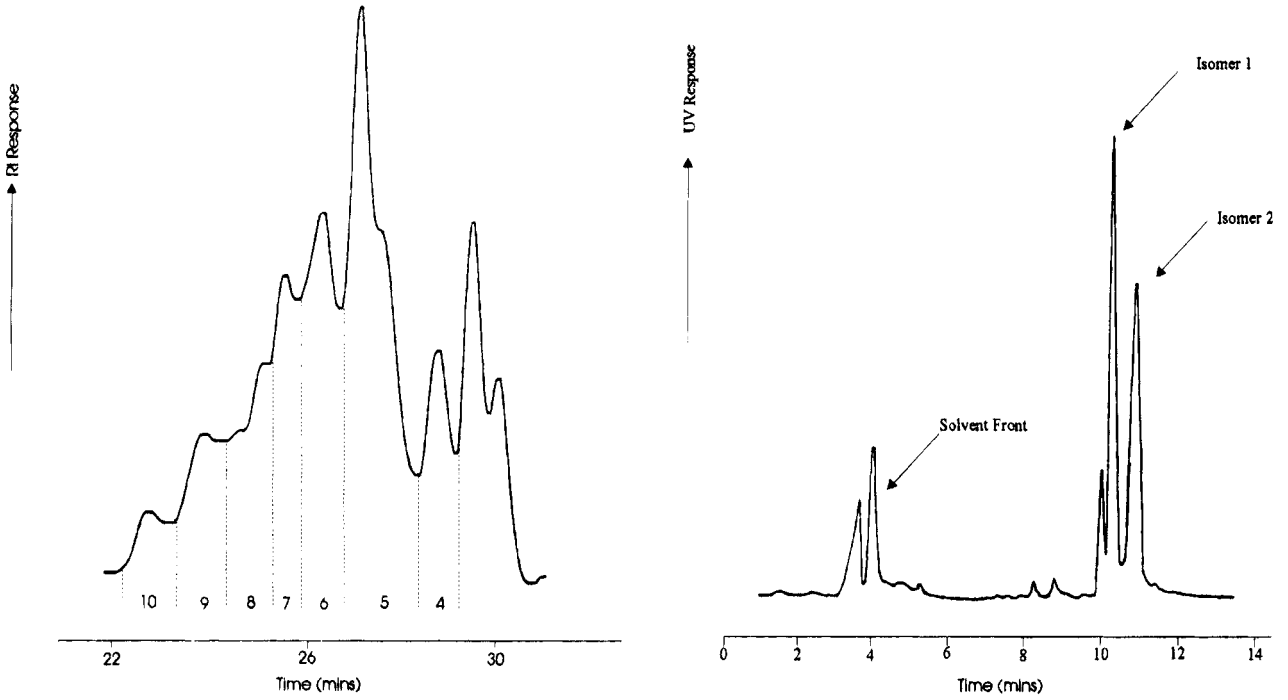


Figure 2. (a, Left) HPGPC separation of PVC low molecular weight fraction (4 = tetramer to 10 = decamer). (b, Right) HPLC separation of VC tetramers.

the volume of diethyl ether was reduced to *ca* 20 mL under reduced pressure. Pentane (300 mL) was added to the residue, and the solution was left to stand for 20 min. Subsequently, the mixture was filtered to remove the high molecular weight fraction. The pentane was then removed under reduced pressure to give a low molecular weight fraction.

The low molecular weight fraction was passed through a preparative adsorption column (Merck Lobar, size B, containing LichroPrep Si 60 (40–63 μm)) to remove any polar impurities. An ICI instruments Model LC 1110 pump was used in conjunction with a Dupont 8800 Spectro series UV detector and a Rheodyne Model 7125 injection valve, fitted with a 200 μL loop. Aliquots of the low molecular weight fraction (100 mg in total) were loaded onto the column with the flow rate of *n*-hexane and MTBE (95:5) set at 3 mL min^{-1}. The fraction eluting between 0 and 300 mL was collected.

Separations by HPGPC incorporating an alternate pumping recycle system as described by Henry[17] was used to isolate the tetramer isomers. The system was based on four 30 cm × 7.5 mm i.d. columns containing 5 μm, 50 Å PL gel (Polymer Laboratories). The columns were used in conjunction with an ICI Instruments Model LC 1110 pump and a Knauer differential refractometer. A recycle system was set up with a Rheodyne 7000 switching valve and a Rheodyne 7125 injection valve. Dichloromethane was used as the eluent at a flow rate of 1 mL min^{-1}. The separation of the tetramer was accomplished by loading 10 mg of sample on the column and passing it, with recycling, through 240 cm of gel bed (Figure 2a, peak 4). The tetramer peak was collected manually and the solvent removed under reduced pressure. This procedure was repeated many times to accumulate enough material to allow characterization of the tetramer to be performed.

The tetramer isomers were then separated by normal phase HPLC. The system used comprised a Knauer 64 HPLC pump, a Pye Unicam PU 4025 detector operating at 200 nm, and a 25 cm × 4.6 mm i.d. column containing Spherisorb S5W silica packing. The mobile phase used was a mixture of *n*-hexane and methyl *tert*-butyl ether (MTBE, 99.5:0.5) at a flow rate of 1 mL min^{-1} (Figure 2b). Under these conditions, 0.5 mg of the tetramer isomers was injected *via* a Rheodyne 7125 valve and a 20 μL injection loop. The individual isomer fractions were collected manually and the solvent removed under reduced pressure.

Results and Discussion

^{1}H NMR data for isomer 1: δ_H (400 MHz, $CDCl_3$) 5.78 (2H, m, J 13, H_{ab}), 4.40 (1H, m, H_c), 4.23 (1H, m, H_d), 4.05 (2H, d, J 6.4, $H_{ee'}$), 3.82 (1H, dd, J 12, 4, H_f), 3.67 (1H, dd, J 12, 4, H_g), 2.57 (2H, m, H_{hi}), 2.26 (1H, m, H_j), 2.00 (1H, m, H_k).

^{13}C NMR data for isomer 1: δ_C (100 MHz, $CDCl_3$) 129.91, 129.75, 58.32, 57.96, 48.12, 44.42, 43.32, 40.89.

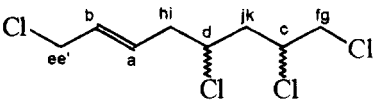
Mass spectral data for isomer 1: found, M^+ 247.9693 ($C_8H_{12}{}^{35}Cl_4$ requires 247.9693), 212 $(M - Cl)^+$, 177 $(M - 2Cl)^+$, 141 $(M - 3Cl)^+$.

^{1}H NMR data for isomer 2: δ_H (400 MHz, $CDCl_3$) 5.80 (2H, m, J 13, H_{ab}), 4.26 (1H, m, H_c), 4.10 (1H, m, H_d), 4.05 (2H, d, J 6.2, $H_{ee'}$), 3.83 (1H, dd, J 12, 4, H_f), 3.77 (1H, dd, J 12, 4, H_g), 2.61 (2H, m, H_{hi}), 2.43 (1H, m, H_j), 2.22 (1H, m, H_k).

^{13}C NMR data for isomer 2: δ_C (100 MHz, $CDCl_3$) 130.16, 129.37, 57.41, 56.85, 47.70, 44.39, 42.61, 39.66.

Mass spectral data for isomer 2: found, $(M - HCl)^+$ 211.9926 ($C_8H_{11}{}^{35}Cl_3$ requires 211.9926), 177 $(M - 2Cl)^+$, 141 $(M - 3Cl)^+$.

The ^{1}H and ^{13}C NMR spectra of the two isomers clearly indicate that the structure of the VC tetramer isomers are two diastereomers of the structure shown as structure **3**.



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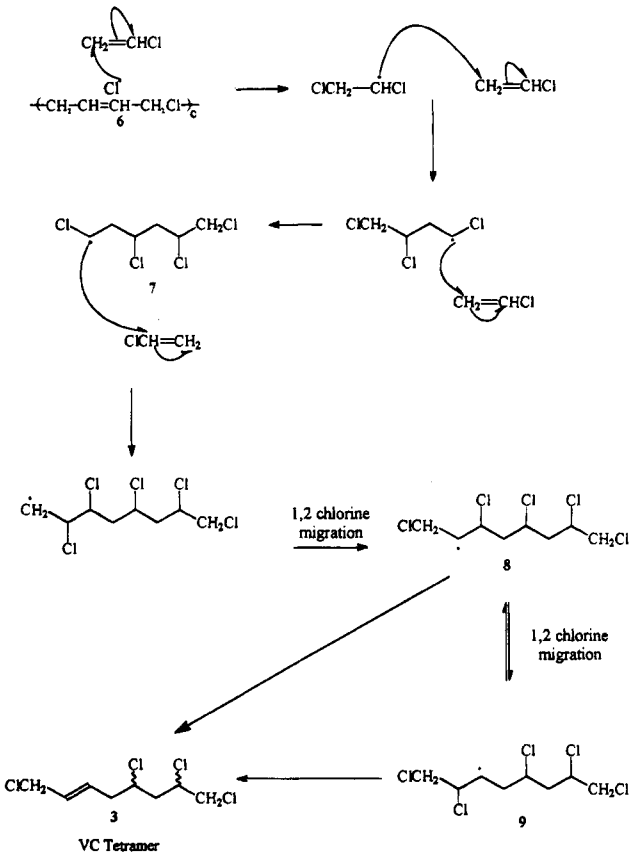
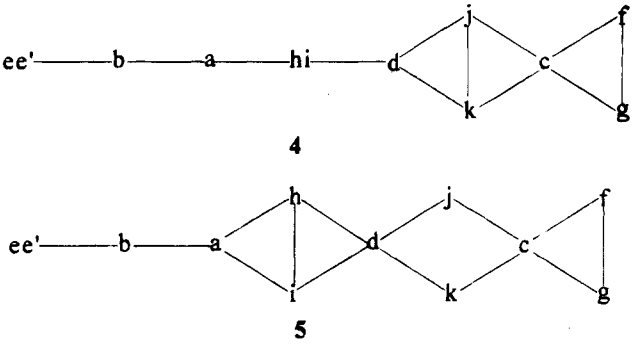
Structure of VC tetramer

The main differences in the spectra occur at the asymmetric carbons. In one isomer, protons c and d occur as two well-defined multiplets separated from the doublet of protons ee′. However, in the other isomer, proton d overlaps with the doublet of protons ee′. The other main difference between the two spectra is the

Scheme 1. Formation of VC Tetramer



coupling pattern observed. From COSY-45 spectra the coupling patterns for the two isomers are shown in structures **4** and **5**.



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Protons f and g as expected show an AB quartet in both structures **4** and **5** and in both cases each proton couples to proton c. The double-bond protons (a and b) are *trans* to each other as shown by the high coupling constant of 13 Hz.

Structure **5** clearly shows a coupling between h and i, which then couple separately to protons a and d. The carbon NMR spectra of the two compounds are also very similar, with structure **5** showing several γ gauche shifts. This is indicative of this isomer being the "m" type by analogy with PVC.

One possible mechanism for the formation of the tetrameric oligomers is shown in Scheme 1. Starnes and Wojciechowski[18] have shown that chlorine radicals as such are not involved in the polymerization of VC. Instead a chlorine atom is transferred directly to the monomer without becoming kinetically free. This is represented in Scheme 1 by structure **6** using the nomenclature of subscript c to denote a cage type structure as proposed by Starnes and Wojciechowski.[18] This cage structure transfers chlorine directly to VC monomer to initiate the reaction. This is then followed by two head-to-tail additions, to give structure **7**.

This assembles the right-hand side of the VC tetramer (structure **7** in Scheme 1), which was found by Starnes *et al.*[9] to be the principal saturated long-chain end in PVC. The mechanism postulated by Starnes for the formation of this chain end was one of chain transfer to monomer and is in agreement with our suggested Scheme 1.

To assemble the left-hand side of the VC tetramer molecule, a head-to-head addition must follow, followed by 1,2 chlorine migration to give structure **8**. The tetramer with structure **3** may then be formed by the loss of a chlorine radical directly or as shown by Starnes and Wojciechowski,[18] a further 1,2 chlorine migration is possible to give structure **9**, which can then lose a chlorine radical to form the VC tetramer **3**. Conclusive evidence for the existence of this part of the molecule was also demonstrated by Starnes *et al.*[9] whose postulated mechanism is also in agreement with Scheme 1.

It may be seen from structure **3** that the tetrameric oligomers do not share the RCH=CHCl structural feature of vinyl chloride monomer. By analogy and by reference to reaction Scheme 1, it may be anticipated that this will be true also for the other PVC oligomers (n = 3, 5, 6, *etc.*).

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