

Elucidation of the Fine Structure of Poly(vinyl Chloride) by Hydrogenation and ^{13}C -NMR Analysis of Low Molecular Weight Fractions

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Synopsis

The following experiment was performed based on the assumption that the characteristic structural features of high molecular weight poly(vinyl chloride) (PVC) should be present to the same extent in its low molecular weight fractions. Two PVC fractions of molecular weight, 1500 and 800, respectively, (0.14% of total polymer) were isolated from bulk PVC (M_n 32,000) by extraction with methanol. This extract was transformed into paraffins by a new hydrogenation method using an excess of Raney nickel in order to facilitate identification. ^{13}C -NMR spectral data of the paraffins showed that almost 2 out of 1000 carbon atoms were linked to a side chain with more than five carbon atoms, and 5 out of 1000 carbon atoms were methyl branched. Gas chromatography-mass spectrometry (GC-MS) analyses confirmed that the low molecular weight paraffins consisted of a sequence of even-numbered homologs. These findings suggest indirectly that the surprisingly low degradation temperature of PVC is due to the arrangement of the chlorine atoms rather than to the branching of the alkyl chain.

INTRODUCTION

Numerous investigations have been carried out to determine the fine structure of PVC. Recent papers¹⁻⁵ deal with the question: why does PVC split off HCl at a temperature as low as 100°C? In order to find the weak places in PVC, Braun⁶ and Batzer⁷ reduced PVC with LiAlH_4 . This method has the disadvantage that a chlorine content of 10% remains unconverted, and the new double bonds that are formed make the identification of the dehalogenated product more difficult.

Since low molecular weight PVC has better solubility and lower viscosity than high molecular weight PVC, analyses, especially NMR, should be easier on such fractions. Furthermore, low molecular weight material should be accessible to GC analysis, thus providing another method for determining the fine structure. A low molecular weight PVC isolated by methanol extraction was therefore chosen for these studies.

It was assumed that the structural features of low molecular weight PVC are comparable to those of the high molecular weight base material. Finally, the choice of the original PVC was based on the assumption that bulk PVC is preferable for these investigations since it does not contain suspension aids which might blur results.

For the initiation of the bulk polymerization of vinylchloride, only 200 ppm peroxide was used, no water was added, and less than 1 ppm HCl was released.

Consequently, this indicates that (1) there is a 15-fold transfer; (2) as a result of the transfer, each macromolecule should possess one double bond or the corresponding amount of cycloparaffin.

EXPERIMENTAL

Isolation of Solid PVC of Molecular Weight 1500

PVC (Hostalit M 3057, M_w 61,000, M_n 32,000), 700 g was placed in a 0.7-liter Soxhlet and extracted with methanol for 50 hr at a throughput of approximately 1 l/hr (e.g., 50 liters methanol total). The methanol was initially concentrated to 150 ml at atmospheric pressure followed by further concentration to 50 ml at 30°C and 50 mbar. On standing overnight, a precipitate of 500 mg (0.07%) of solid PVC was obtained which was separated by suction.

The molecular weight in methanol was 1500, determined by osmometry; the chlorine content was 56.1% (calculated 56.8%). The chlorine value shows that the PVC of molecular weight 1500 might contain a "non-PVC fraction" of 1.3% at the most.

Isolation of "Soft" PVC of Molecular Weight 800

The mother liquor of the preceding experiment was concentrated to 10 ml at 50 mbar vacuum, after which 500 mg (0.07%) of a rubberlike product precipitated with a chlorine content of 52.0% (calculated 56.8%) and a molecular weight of 800. The investigations were predominantly carried out with the PVC of molecular weight 1500, since the PVC of molecular weight 800 was not as pure.

Determination of Unsaturation in Low Molecular Weight PVC by "Mild" Hydrogenation

Ionic chlorine was not eliminated in the determination of the double bond level by mild hydrogenation using glacial acetic acid and palladium charcoal at 20°C and 1 bar. For each mole of PVC of molecular weight 1500, 1.5 double bonds was found. This result indicates that no alicyclic structures are present in the molecule.

Dechlorination of Low Molecular Weight PVC by "Hard" Hydrogenation

Three grams PVC of molecular weight 1500, 10 g sodium acetate (anhydrous), 100 ml tetrahydrofuran (THF), and 100 g Raney nickel, rinsed with THF, were hydrogenated for 75 hr at 100°C and 200 bar. The content of the autoclave was separated by suction using filtering aids, rinsed with 200 ml THF and precipitated with water. The paraffin precipitate was filtered, redissolved in CH_2Cl_2 , and evaporated. The yield equalled 1 g; the chlorine content was 10%. Finally, 1.5 g hydrogenated PVC (chlorine content 10%) was collected from several runs and hydrogenated for a second time for 75 hr with 100 g Raney nickel and 10 g sodium acetate yielding 0.7 g paraffin on similar work-up (chlorine content 3.1%). This material was used for ^{13}C -NMR analysis.

Hydrogenation of 10 g of the "soft" low molecular weight PVC (molecular weight 800) with 100 g Raney nickel yielded 4.3 g paraffin (chlorine content 9.3%, molecular weight 560). Sixty percent of this product could be distilled, and the forerun (7.5%) collected at $200^{\circ}_{0.1}$ was the base material for the GC analysis.

RESULTS AND DISCUSSION

^{13}C -NMR Analysis

The NMR analysis of the 3.1% chlorine-containing two-fold hydrogenated paraffin of molecular weight 800 (after the hydrogenation) without solvent at 70°C gave the results shown in Figure 1.

Methyl Endgroups

Based on the position and height of the peaks of the diagram shown in Figure 1 at 14.2, 22.9, 32.2, and 30.0 ppm, it could be calculated that CH_3 endgroups of long chains are attached to 3.3% of all C atoms. Calculated on the molecular weight of 800 and based on the assumption that the structure represents a straight chain, the number of C atoms with CH_3 endgroups, in reference to the total number of C atoms, is 3.5%. This is in very good agreement with the ^{13}C -NMR analysis.

Short-Chain Methyl Branching

According to Rigo, Palma, and Talamini,⁸ PVC is assumed to contain methyl branches. The position and the height of the peaks at 19.9, 33.2, 37.5, 27.5, and 30.0 ppm shows that 5 out of every 1000 C atoms of the paraffin chain have methyl branches. On the premise that the loss of yield on twofold hydrogenation does not lead to a shift in composition, one can assume that the number of methyl

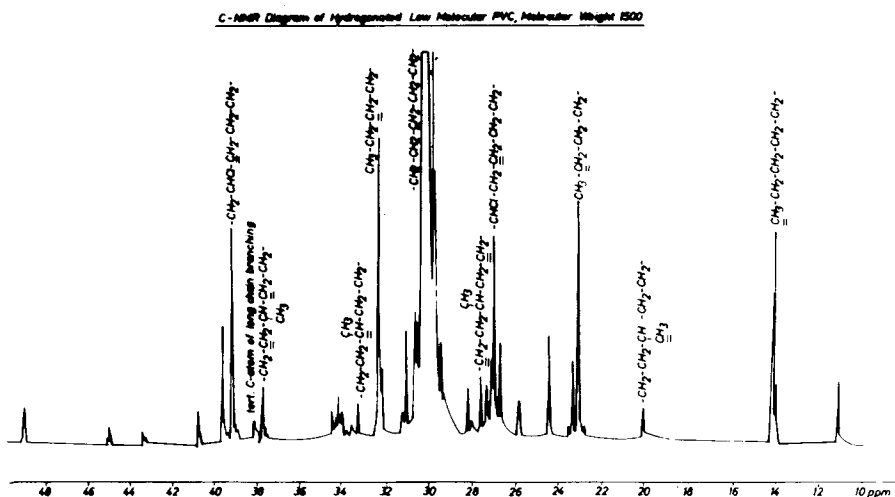


Fig. 1. ^{13}C -NMR diagram of hydrogenated PVC of molecular weight 1500. Molecular weight after hydrogenation was 800. XL-100-15 Varian, tetramethylsilane as reference; lock signal C_6D_6 .

branches in the macromolecule is in good agreement with Abbas⁹ who reported three methyl groups per 1000 C atoms in PVC.

Ethyl Branching

According to Randall,¹⁰ the peaks at 11.2 and 26.7 ppm could be the signal of an ethyl branch, but the methyl C at 39.7 ppm and the α - and β -C atoms at 34.1 and 27.3, respectively, are not in the correct relationship to the first peaks (11.2 and 26.7 ppm). Further investigation is planned to clarify these findings.

Long-Chain Branching

A peak at 38.1 ppm intensity 0.2% may be attributed to the tertiary C atoms of a long-chain branching (with more than five C atoms). A maximum of two branching sites could fall into every 1000 C atoms provided that the analytical result with molecular weight 1500 can be extrapolated to the molecular weight 30,000. Abbas⁹ found one branching site for every 1000 C atoms.

Residual Chlorine Content

The sites of —CHCl— structural elements in hydrogenated PVC of molecular weight 1500 were identified (using 4-chlorododecane as model compound) by position and height of the peaks at 26.8, 39.1, 63.8, and 30.0 ppm. This indicates that one —CHCl— group exists for every 75 C atoms. This is in very good agreement with classical elemental analysis in which one —CHCl— group exists for every 81 C atoms.

Combined GC-Mass-Spectrometric Analysis

The GC was a Packard Instruments Model 7400, detection T.I.C. (total ionic current). The mass spectrometer was an MS 12 Kratos AEI 20 and 70 eV.

The GC diagram shown in Figure 2 was obtained on a column of 10% UCCW

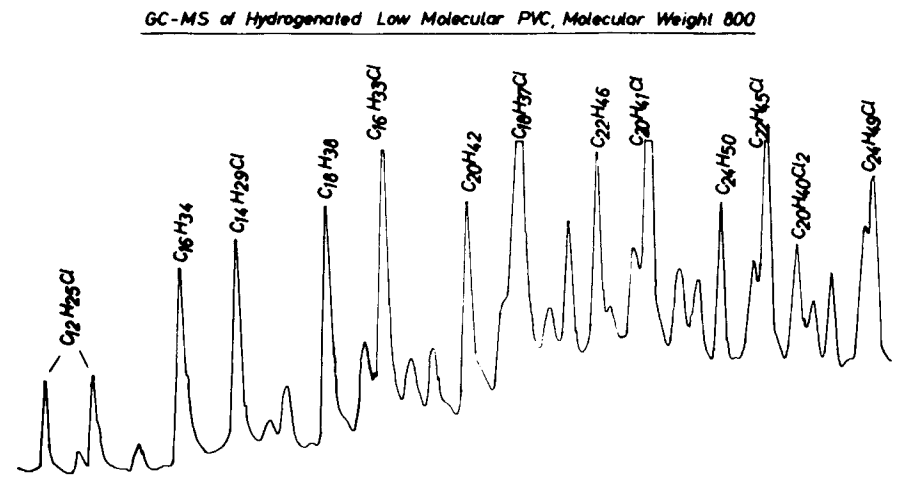


Fig. 2. GC analysis of hydrogenated PVC of molecular weight 800. Molecular weight after hydrogenation was 560.

982 on Chromosorb WAW-DMCS. For this analysis the forerun of the hydrogenated "soft" PVC was used (which had a molecular weight of 560 after hydrogenation). While containing 2 C atoms fewer than the corresponding paraffins, the monochloroparaffins have about the same elution time (Fig. 2). In mass spectrometry the chloroparaffins are indicated by a parent peak representing the mass of the corresponding olefins formed by elimination of HCl. It can be established that only even-numbered species are detected, as expected, and branched paraffins cannot be detected. It should be noted that the limit of analytical detection is in the order of 5%.

CONCLUSIONS

As expected, low molecular weight PVC contains at least one double bond per molecule. It can be hydrogenated to the point that it is almost free of chlorine; and, provided that no structural change occurs in this reaction, 1 in every 200 carbon atoms constitutes a methyl branching and, at most, one in every 500 carbons is the starting point for long-chain branching. It is possible that this finding, which has been observed with low molecular weight PVC, is also applicable to higher molecular weights.

The irregularities of PVC can more easily be explained in relation to the position of the chlorine atoms rather than the negligible chain branching.

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