

Degradation of Poly(vinyl Chloride) to Small Molecules

ULRICH SCHWENK, FRANZ LÖMKER, INGE KÖNIG, and HORST STREITBERGER, *Department of Research, Hoechst AG, 6230 Frankfurt/Main 80, Werk Gendorf, West Germany*

Synopsis

By treatment with alkali in 2-methoxyethanol, poly(vinyl chloride) is converted to an insoluble network structure. On subsequent oxidation with 65% HNO_3 , a water-soluble mixture of acids is obtained. Per 1000 carbon atoms of the original polymer chain, approximately 4 moles succinic acid, 2 moles glutaric acid, and 1 mole adipic acid are found. In spite of the fact that the occurrence of succinic acid is in the same order as tail-to-tail polymerization in PVC, it must be assumed that unexpected aggregation of more than two CH_2 groups is due to rearrangement during the alkali treatment or the oxidation procedure.

INTRODUCTION

Numerous papers relating to the irregularities of the fine structure of poly(vinyl chloride) have been published.¹ The main objective of these investigations is to discover the reason for the unexpected low thermal instability of PVC. One approach which could provide new insight into the nature of the PVC macromolecule would be to degrade the PVC to totally water-soluble molecules. Shindo² reported that a PVC which is treated for 5 hr at 7°C with alkali in tetrahydrofuran (THF) is transformed to water-soluble compounds. With bulk PVC, treatment with alkali for a longer time leads to a water-insoluble network. In 1939 Marvel³ described a method to eliminate 98% of the original chlorine content of PVC by treatment with KOH in 2-methoxyethanol. Partial oxidation of the network should maintain soluble fragments with the same structural elements present in the original PVC.

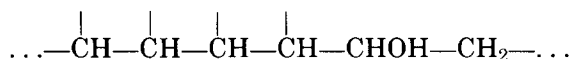
EXPERIMENTAL

Dehydrohalogenation of Bulk PVC with KOH in 2-Methoxyethanol

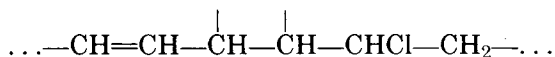
According to the method of Marvel,³ 100 g bulk PVC (Hostalit M 3070, size approximately 100 μ , M_w 96,000, M_n 49,000) in 1000 ml of a 5% KOH solution in 2-methoxyethanol (99.9%) was refluxed for 30 hr with stirring (118°C). After filtration, this procedure was repeated twice using fresh KOH–2-methoxyethanol solutions. The filtered PVC product was washed with dilute HCl to remove the alkali, thereafter washed with water until free of traces of chloride, and subsequently dried for 24 hr at 50°C under vacuum. Fifty grams of crosslinked PVC were obtained; the brown powder had a decomposition temperature of > 300°C.

ANAL. Calcd for $\text{C}_{102}\text{H}_{135}\text{O}_{16}\text{Cl}$: C, 74.2%; H, 8.2%; O, 15.5%; Cl, 2.1%; ash = 0%. Found: C, 74.5%; H, 7.1%; O, 15.3%; Cl, 2.1%; ash = 0%.

The resulting structural formula is approximately 16 units of



mixed randomly with a unit of the following structure:



Determination of Unsaturation in Dehydrohalogenated PVC

Four grams of the dehydrohalogenated PVC was treated for 24 hr with gaseous chlorine, at normal pressure, causing discoloration due to exothermic reaction.

The comparison of the elemental analysis (C, H, O, Cl) before and after the chlorination gives approximately one double bond per 20 carbon atoms.

Oxidation of the Dehydrohalogenated PVC with Concentrated Nitric Acid

Five grams of the crosslinked degradation product was treated with 100 ml nitric acid (65%) for 2 days on a steam bath with occasional stirring. The substance dissolved completely. The transparent reddish-brown liquid was evaporated on the steam bath and subsequently dried for 24 hr under vacuum at 50°C, yielding 4.5 g of a mixture of organic acids (52.7% yield of theory).

ANAL. Found: C, 43.7%; H, 3.0%; O, 48.2%; N, 3.4%; Cl, 0.8%.

The molecular weight (cryoscopic method in methanol) was 274. The acid equivalent weight was 92.6. The iodine number was 12.7 g iodine/100 g of substance.

In a blank test, 5 g of untreated bulk PVC (Hostalit M 3070) was treated similarly with nitric acid for 14 days on a steam bath. The PVC was recovered unchanged.

Quantitative Preparation of Methyl Esters from the Raw Acid Mixture

Esterification of the raw acid mixture with a 50-fold surplus of methanol without any catalyst⁴ and subsequent distillation by the cold finger method (up to 310°C, 0.1 torr) yielded 45% distillate. One hundred milligrams of this distillate was dissolved in 1 ml methanol and diluted with 2 ml diethyl ether. Diazomethane was introduced by means of a diazomethane-saturated nitrogen flow until a yellow color occurred.

Using malonic acid as an internal standard for vapor phase chromatography, 30 moles oxalic acid, 4 moles succinic acid, 2 moles of glutaric acid, and 1 mole adipic acid were found as the main compounds per 1000 C atoms of the original PVC.

Identification of the Raw Acid Mixture by Combined Vapor-Phase Chromatography and Mass Spectrometry

For identification of compounds in minor amounts in the original raw acid mixture, the mixture was esterified in the described manner with diazomethane and identified through a combination of vapor-phase chromatography and mass spectrometry.

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 resulting mixture was separated on a temperature-programmed column (3% OV-1/Chr., WHP 1.5 m) and the E-I and C-I spectra were evaluated. The interpretations were confirmed with authentic samples or by mass spectra published in the literature. The five compounds in minor amounts were present in less than 1 mole per 2000 C atoms in the original PVC (Table I).

RESULTS AND DISCUSSION

The results confirmed the unexpected presence of glutaric and adipic acids. The presence of glutaric and adipic acids could be due to the presence of suspension aids or catalysts used in the polymerization. Hence a bulk PVC free of suspension aids was tested, and similar results were obtained after extraction with methanol.

The possibility of glutaric acid being formed by CH₂ insertion in succinic acid during esterification with diazomethane was negated through a blank experiment. Finally, it was proved by analysis that in the solvent 2-methoxyethanol no substances were present which could lead to succinic acid on oxidation.

The missing link, malonic acid, in the series of oxalic, succinic, glutaric, and adipic acid may be explained as follows: while malonic acid is completely destroyed by treatment with a 20-fold excess of nitric acid (65%) for 20 hr, oxalic acid can still be isolated in 50% yield; succinic acid, adipic acid, and glutaric acid are recovered quantitatively.

The formation of oxalic acid is self-explanatory, since one expects oxidation of secondary C atoms, obtained by the alkaline treatment, to carboxylic groupings. The simplest case is shown in the following scheme:

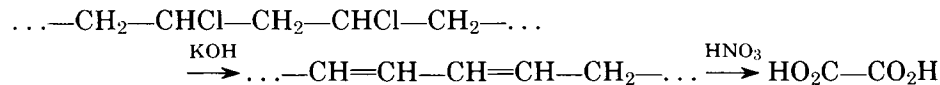
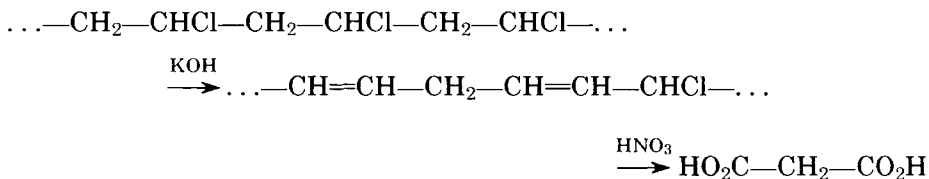


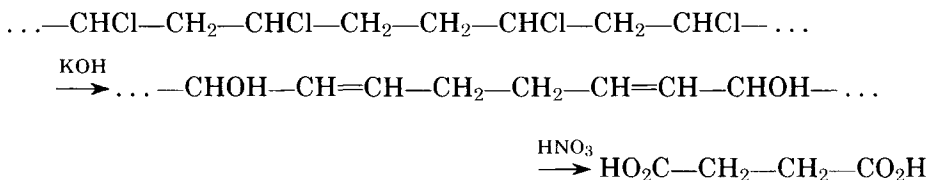
TABLE I
Components Identified in the Methylene Esters of the Raw Acid Mixture

| Elution temperature, °C | Molecular weight | Interpretation |
|-------------------------|------------------|---|
| 56 | 128 | oxalic acid dimethyl ester |
| 71 | 146 | succinic acid dimethyl ester |
| 76 | 136 | benzoic acid methyl ester |
| 81 | 160 | glutaric acid dimethyl ester |
| 94 | 174 | adipic acid dimethyl ester |
| 105 | 188 | pimelic acid dimethyl ester |
| 119-126 | 194 | phthalic acid dimethyl ester |
| 163, 167, 168 | 252 | trimellitic acid trimethyl ester |
| 203, 206, 209 | 310 | pyromellitic acid tetramethyl ester |
| 220 | 368 | benzenepentacarboxylic acid pentamethyl ester |

Similarly, the formation of malonic acid is explained as follows:

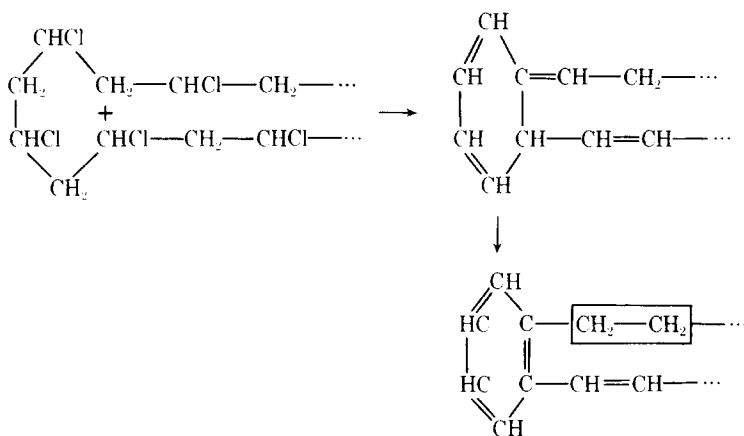


The existence of succinic acid could be easily explained by formation through oxidation of a dehydrochlorinated tail-to-tail polymerization product:



The amount of 4 moles of succinic acid isolated per 1000 C atoms is in the same order as the tail-to-tail elements in a PVC polymer chain published by Rigo⁵ with 10 of 1000 C atoms. The appearance of glutaric, adipic, and even pimelic acids presumes the presence of $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$, or even $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ groups in the PVC polymer chain. This supposes a migration of chlorine during the polymerization which is not in agreement with the conventional theory on polymerization mechanism.

Because of the high probability that the accumulation of CH_2- groups is an artifact, caused by side reactions under quite rigorous conditions of the alkaline treatment or nitric acid oxidation, one is forced to find an explanation such as the benzene ring formation from a PVC chain by transfer of H atoms.



As described above, a multiple formation of aromatic ring systems could be responsible for the structural elements with three and four CH_2- groups. The

References

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