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# POLYVINYL CHLORIDE STABILIZATION

*Jerzy Wypych*

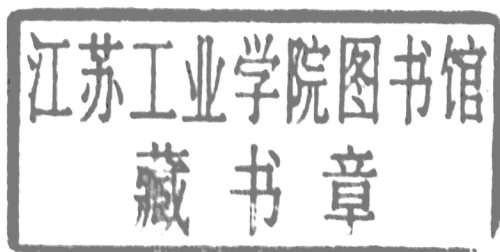
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**ELSEVIER**

Amsterdam — Oxford — New York — Tokyo 1986

ELSEVIER SCIENCE PUBLISHERS B.V.  
Sara Burgerhartstraat 25  
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

*Distributors for the United States and Canada*

ELSEVIER SCIENCE PUBLISHING COMPANY INC.  
52, Vanderbilt Avenue  
New York, N.Y. 10017

ISBN 0-444-42638-8 (Vol. 4)  
ISBN 0-444-41832-6 (Series)

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Printed in The Netherlands

*Polymer Science Library 4*

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# *Polymer Science Library*

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- 4 *J. Wypych, Polyvinyl Chloride Stabilization*

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## INTRODUCTION

For several decades, the position of poly(vinyl chloride) has been established in the processing industry and in everyday use. Nonetheless, many difficulties are still observed so far as its stability is concerned. One might evaluate the present situation from at least two perspectives, e.g, a theoretical understanding of the thermal and photolytic processes polymer may undergo, and the technical ability to process polymer economically and efficiently.

The situation in PVC stabilization is not unusual, as in most technological processes presently in use, practice is far ahead of theory; this is why the scientific approach is sometimes even neglected, which is, of course, wrong. It is well known that the effect of experimental variables on the course of chemical reactions cannot properly be estimated and understood unless the mechanism of reaction is known, and the mechanism of reaction, in turn, cannot be studied if reaction products are not identified. Thus, we cannot expect to choose the proper stabilization formula unless the kinetics of the chemical processes occurring in the course of reactions are determined exactly. Because of the development of new experimental techniques, many optimum solutions have been found, but further development can be expected only if scientific conclusions are reached.

The present monograph is meant to summarize technological achievement in polymer stabilization from the point of view of practical application, although theoretical findings will also be included. Taking into consideration the technical level of the present industry, one can view it as being more advanced at the moment than research laboratories were just a few decades ago; therefore, the data needed for application are not far different from those used by research scientists. Thus, on the following pages one may expect to find the proven facts, which facilitate understanding of the mechanisms of chemical changes occurring at various stages of processing and the further use of the

products.

Poly(vinyl chloride) stability is usually studied in connection with chemical reactions tending to change the initial structure of the polymer when heat is applied during processing, but this is insufficient if one is interested in the further history of the material, which under normal circumstances is exposed to conditions of corrosive atmosphere and photolytic attack. Therefore, such influences must be predicted in the course of process formulation.

Polymer stability in this sense includes any separate or combined action of physical, chemical, and biological means that can contribute to product changes. Starting from processing, we can see that the rheological characteristics of polymer compositions are directly related to heat generation during processing, and thus the lubrication of systems is as important for thermal stability as is the inclusion of thermal stabilizers. Another connection can be seen between polymer thermal degradation in the course of processing and oxidation and photolysis of the product as various instability centers are introduced. On the other hand, only at the stage of processing are we able to protect materials against these changes, which means that proper anticipation of conditions of product use should be achieved in the early stages of material production, sometimes even at the polymerization stage. The important factors to be considered can be concluded from the interaction of components in both processing and use. Finally, product stability can even be affected by the corrosive nature of biodeteriogens, which in their own ways can contribute to material instability and may even modify material to such an extent that it becomes vulnerable to further degradation by outdoor conditions. All those factors related to polymer stability are equally important and call for adequate attention if PVC stability is to be viewed with sufficient thoroughness.

As the stabilization of PVC is the main subject of this book, rather than attempt a complete survey of the literature, the reasons for PVC thermal instability will be discussed only briefly, and the main stress will be placed on the probability of the introduction of particular changes in the structure of the material.

## CHAPTER ONE.

### THE CAUSES OF PVC INSTABILITY.

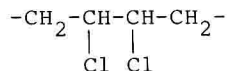
#### 1.1. Irregularities in the PVC chain.

From Staudinger's time it has been known that PVC has a lower thermal stability than that of a comparable low-molecular weight compound such as 1,3,5-trichlorohexane (1). Since then it has been established in many publications (2-5) that PVC undergoes chemical change if the temperature exceeds 373K, which is at least 100K less than should be expected if one looks for an analogy with low-molecular weight substances of similar structure such as 1,4,7-trichloroheptane, 2,4-dichloropentadecane, and so on. It was, therefore, quite natural that, from the beginning of studies on PVC thermal stability, irregularities in the polymer chain have been taken into consideration. Due to the complicated nature of the polymerization reaction mechanism numerous structural defects might be expected and it is also necessary to consider the influence of various additives.

##### 1.1.1. Head-to-head structures.

It is thought that the PVC chain consists mainly of a head-to-tail arrangement of monomer units. The first studies of structures different from these were conducted by Canterino (6), Bailey (7), and Murayama (8), who obtained head-to-head PVC by chlorination of 1,4-polybutadiene. The reaction leading to the synthesis of head-to-head PVC was later studied by several researchers (9-13).

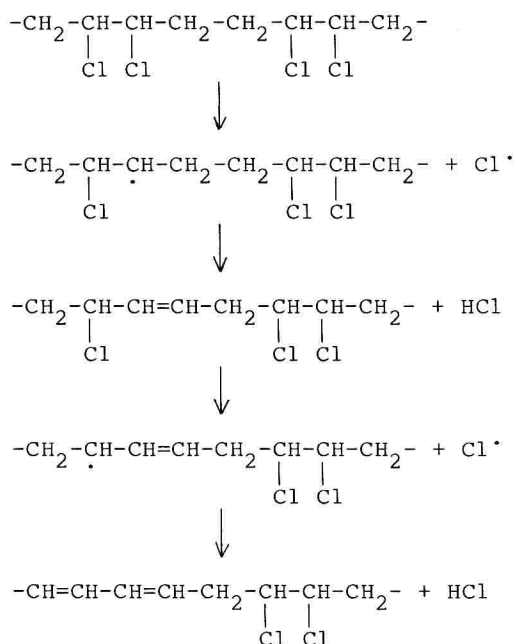
Mitani (14) found that PVC might contain six to seven head-to-head structures per 1,000 monomer units; Schwenk (15) suggested that such structures will account for 8 per 1,000 monomer units. Head-to-head structures, as below,



are thought to form as a result of recombination of macroradicals (16).

Murayama (8) showed that head-to-head PVC degrades at a lower temperature, but the rate of dehydrochlorination is higher for the head-to-tail form, which was also confirmed by Crawley (13), although the differences between the two forms are not great.

Crawley (13) proposed the following mechanism of degradation:



One should say that final conclusions have yet to be reached. It seems, first of all, to be far more important to study the effect of head-to-head structures on the termination mechanism in the formation of polyene sequences than to investigate the effect of these structures on the initiation mechanism. Conversely, comparison of head-to-head and head-to-tail structures has little validity as the polymers that have these structures are of entirely different kinds. For example, Crawley (13) compared

head-to-head PVC obtained from polybutadiene of number-average molecular-weight of 40,800 with a purified industrial PVC, Breon 113. Thus, it seems valuable for future work to concentrate on determining the concentration of these forms in commercially available polymers.

#### 1.1.2. Total and internal double bonds.

The presence of internal double bonds in PVC has been studied by the most sophisticated methods presently available, such as UV and Raman spectrophotometry,  $^{13}\text{C}$  NMR,  $^1\text{H}$  NMR, and degradative methods. It is important for these studies to evaluate the quantity of the double bonds present in various polymer types, but it is also expected that single internal double bonds, sequences of conjugated double bonds, double bonds in conjugation with oxygen-containing groups, and double bonds at chain ends can separately be determined.

Investigations have revealed that emulsion PVC contains more double bonds than does suspension polymer, and the latter has still more than does mass polymerizate (18-20). Using resonance Raman spectroscopy, Peitscher (21) detected long sequences of double bonds, and Kohn (22), using the UV method, found that the concentration of tetrads is  $4 \times 10^{-4}$ /1,000 monomer units. The number of internal and total double bonds was estimated by various authors in the following wide range:

The number of double bonds  
per 1,000 monomer units.

Abbās (23)	4 (internal)
Zilberman (18, 19)	1.4-3.4 (total)
Minsker (24)	0.09-0.27 (internal)
Michel (25)	0.05 (internal)
Boissel (26)	1.5-3 (total)
Starnes (27)	1 (total)
Minsker (16)	>5 (total)

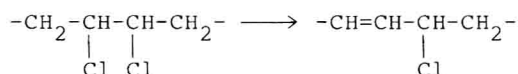
Double bonds are formed due to the presence of admixtures, dehydrochlorination of polymer during production and storage, macroradical recombination, chain termination, and so on. Minsker (16) claims that unsaturation at the chain ends has no effect on polymer thermal stability. There is common agreement



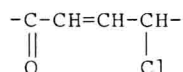
that internal double bonds due to the presence of chloroallyl groups can serve as active initiation centers of dehydrochlorination.

### 1.1.3. Chloroallyl and carbonyl-chloroallyl groups.

The presence of unsaturation alone does not produce any direct danger, but the charge distribution along the chain is severely affected, which is why it attracts the attention of many scientists in the field. Interest in this area was developed early when the first research was done by Baum (28) and Frye (29). Later, Murayama (8) suggested a mechanism for the degradation of head-to-head structures in which chloroallyl groups are also formed:



The possibility of the initiation of the dehydrochlorination process by chloroallyl groups was questioned by Minsker (16, 30-32), who proposed that chloroallyl groups are rapidly oxidized into carbonyl-chloroallyl structures:



which are responsible for initiation of the dehydrochlorination process. The content of these groups depends on monomer purity, the presence of oxygen, and the temperature of the vinyl chloride polymerization process.

It seems possible that such groups may serve as initiation centers, but exclusion of the influence of chloroallyl groups on the initiation rate cannot be viewed along the lines proposed by Minsker (30-32). It is possible that C=O is in conjugation with the other double bonds with a resulting decrease in the activation energy needed to split off the neighboring chlorine.