

POLY(VINYL CHLORIDE)

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POLY(VINYL CHLORIDE)

Polymer Monograph

Edited by HERBERT MORAWETZ, *Polytechnic Institute of Brooklyn*

A new series of short monographs, each dealing with one specific polymer. They are written by experts from leading industrial research laboratories and cover equally basic scientific information on a polymer and information pertinent to its practical utilization.

Volume 1

POLY(1-BUTENE)—ITS PREPARATION AND PROPERTIES

I. D. RUBIN, *Texaco Inc.*

Volume 2

POLYPROPYLENE

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Volume 3

POLY(VINYL CHLORIDE)

J. V. KOLESKE and L. H. WARTMAN, *Union Carbide Corporation*

Additional volumes in preparation

Editor's Preface

We hear much these days about the publication explosion and all of us are haunted by the specter of our inability to keep up with the technical literature. In this situation it becomes increasingly important to persuade competent and dedicated scientists to undertake the exacting task of summarizing the available knowledge on some given subject. Since the labor involved is very considerable, it has become the fashion to publish symposium volumes in which a number of experts contribute chapters on their speciality. However, this procedure leads to the publication of relatively expensive books which are bought almost exclusively by libraries and hardly at all by the individual investigator. This is very obviously a very undesirable state of affairs, since nothing can replace the advantage gained from personally possessing literature which provides a background for our work.

This difficulty may be felt particularly strongly by those active in the polymer field. We have therefore decided to embark on the publication of a series of small books, modest in size and price, each summarizing present knowledge on one specific polymer. We believe that many who would hesitate in acquiring a large volume of some twenty chapters, of which only a few might be in the field of their own activity, will welcome the opportunity to select from the series those small books which will give the requisite background on polymers which specifically interest them.

HERBERT MORAWETZ

Preface

Although poly(vinyl chloride) was one of the earliest synthetic plastic materials to be exploited industrially, it retains a high degree of interest to polymer chemists. It is a versatile thermoplastic; the growth in its usage during the years since its first production are due in large measure to continuing technological developments which have fitted it for applications previously found unsuitable. Also, the physical and chemical behavior of poly(vinyl chloride) is intriguing. For example, the structural basis for crystallinity in the polymer and the unique effects imparted by the crystallites are imperfectly understood. This area, as well as others, requires further elucidation.

As might be expected, the literature on poly(vinyl chloride) is voluminous. In the preparation of a small volume of this type it is necessary to be somewhat selective. Propinquity may have led us to select a disproportionate amount of work done by colleagues from the laboratories of Union Carbide Corporation. Where two or more investigators have covered the same field with similar findings, we have in several instances arbitrarily chosen one for summarizing and cited the others by literature references.

The limit on the size of this volume precludes any extensive discussion of the technology associated with the fabrication, formulation, and use of poly(vinyl chloride). A short discussion which might be considered to be educational material for neophytes in this area is presented in chapter 6. For those desiring a more complete treatment, references are given at the end of chapter 6. Also, the Society of Plastics Engineers is sponsoring a treatise by specialists in various areas on the chemistry and technology of poly(vinyl chloride). It should appear sometime in 1969.

In the preparation and review of the manuscript, we are indebted to many for their help. Dr. F. E. Bailey, Mr. J. H. Field, Dr. R. W. Quarles, and Mr. J. J. Smith made several important corrections and suggestions for improvements. Professor H. Morawetz of the Polytechnic Institute of Brooklyn reviewed the manuscript and offered several pertinent, constructive comments. Thanks are also due to Miss Diane Ainsworth for her typing of the manuscript and to Mrs. Patricia Shahan for preparation of the figures.

J. V. KOLSKIE
L. H. WARTMAN

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CHAPTER 1

Introduction

Only a small number of polymers with a particularly advantageous combination of properties have found a major place in commerce. The topic of this monograph is one of these polymers. Poly(vinyl chloride) production capacity was estimated to be 2.3 billion pounds in 1965 with an additional 0.8 billion pounds under construction¹. This fact alone surely marks poly(vinyl chloride) as a polymer that has found a significant position in today's marketplace. Paradoxically, this polymer is chemically one of the least stable of the common polymers, and its exploitation came about only through the development of proper technology for handling the resin and the discovery of suitable stabilizers.

Poly(vinyl chloride) is a free radical-produced thermoplastic polymer that is essentially noncrystalline or amorphous, unless it is highly oriented or of very low molecular weight. Esters and ketones are the usual solvents. The skeletal structure of the repeating unit in the polymer is $-(CH_2CHCl)_n-$ where n can take large values. Almost implicit in the above structure is the fact that the polymer is prepared from vinyl chloride, a compound that boils at -14°C and freezes at -160°C . Because of its low boiling point, care must be taken in production so that explosions and fires do not occur.

The first observation of the polymerization of vinyl chloride is often attributed to Regnault² for his work done in 1838. However, the polymer actually prepared by Regnault was poly(vinylidene chloride)^{3, 4}. Following this work, Baumann in 1872 studied the polymerization of various vinyl compounds⁵ and the ultraviolet light initiated polymerization of vinyl chloride⁶. Although his idea of a dehalogenated polymer was later disproved, valuable contributions to the understanding of vinyl halide polymerization were

made by Ostromislensky⁷ whose name appears several times in the literature published between 1912 and 1929. Other than this work, the early literature is sprinkled with few references to the polymerization of vinyl chloride. Beginning in 1930, the literature relating to vinyl chloride polymers and to its copolymers becomes voluminous. The Society of Plastics Engineers has published a guide to the literature concerning poly(vinyl chloride)⁸ that contains a multitude of references through 1962 (the first edition has over 6000 references and the second edition has been enlarged from this number). This book can be very helpful to those seriously interested in poly(vinyl chloride)—especially the technological aspects.

It was not until 1927 that the polymer was introduced commercially. By 1936 the annual production rate exceeded one million pounds—a level which may be considered as placing the polymer in a commercially accepted class. Production climbed through the years and reached about 1.7 billion pounds in 1965. Although demand has been growing rapidly, production capacity still leads sales by a sizable margin. Comparison of the production and capacity figures listed above (which are only approximations) indicates the industry is operating at 75 percent of capacity. As would be expected, a situation such as this leads to price attrition. Over the fifteen year period beginning in 1950, the polymer price dropped from 36 to 16c a pound. A recent computer forecast study⁹, shows that poly(vinyl chloride) production had a 15 percent growth rate over the 1960 to 1965 period and will enjoy a 14 percent growth rate over the 1965 to 1970 period. Production was estimated to attain 3.7 billion pounds in 1970 with capacity being almost equal to production. In terms of 1965 dollars, the study indicates that the price will be 9.5c per pound in 1970. From this discussion, it is seen that in about forty years the production of poly(vinyl chloride) has grown from nothing to a level where the polymer plays an important role in the chemical industry.

The ensuing chapters in this book will be concerned with the polymerization of vinyl chloride (methods, initiation, and kinetics), characterization of the polymer (molecular weight determination, spectroscopic studies, physical constants), chemical properties (reactions, degradation, stabilization), and physical properties

(properties in bulk, plasticized polymer, dilute solutions). In addition, technological applications of the polymer will be briefly discussed.

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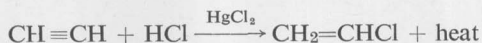
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CHAPTER 2

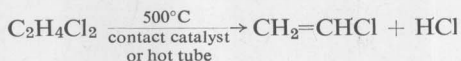
Polymerization

2.1 PREPARATION OF VINYL CHLORIDE

Current commercial processes for production of vinyl chloride can be placed into two classes. The first class involves the gas-phase reaction of acetylene, obtained from either calcium carbide or petrochemical feedstock, with hydrogen chloride using mercuric chloride^{1, 2} or other heavy metal halides³ as a catalyst.



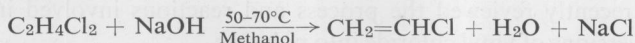
In this process it is essential that the gas streams be dry and free from arsine, phosphine, and sulfur compounds. With the second class of processes, ethylene dichloride is first produced by the reaction of ethylene with chlorine in the vapor phase^{4, 5} or in the liquid phase^{6, 7} or by the oxychlorination of ethylene with hydrogen chloride and air or oxygen with a suitable catalyst^{8, 9}. The ethylene dichloride is then pyrolyzed to yield vinyl chloride and hydrogen chloride¹⁰.



An advantage of the acetylene-based process is that no hydrogen chloride is produced. However, this gas can be recovered in the ethylene-based process and used in a complementary acetylene-based vinyl chloride process. A process flowsheet describing a balanced operation of this type used by a Japanese plant is detailed by Buckley¹¹. Current manufacturing costs for a plant based on the oxychlorination process with utilization of the by-product hydrogen chloride in the acetylene reaction described above are given in *Chemical Week*¹². Fourteen processes which, in general,

fit into these two classes are discussed by Bier¹³. Albright¹⁴ recently reviewed a number of techniques for making vinyl chloride.

Laboratory synthesis of vinyl chloride is often accomplished by the dehydrochlorination of dichloroethane in methanolic caustic solution¹⁵.



This reaction takes place to give a high yield of vinyl chloride which is purified by redistillation.

Vinyl chloride is a gas at normal room conditions and is soluble in ethyl alcohol and in diethyl ether but is essentially insoluble in water. Selected properties of this monomer as reported by Alexander and Cohan¹⁶ are given in table 2.1.

TABLE 2.1
Selected Properties of Vinyl Chloride Monomer

Property	Value
Molecular weight	62.50
Normal boiling point	-13.81°C
Freezing point	-153.77°C
Density, -20°C	0.98343 g/ml
Refractive index, n_D^{15}	1.398
Viscosity, -20°C	0.274 cps
Surface tension, -20°C	22.27 dyn/cm
Volume decrease when polymerized	35%
Dielectric constant, 17.2°C, 10^5 cps	6.26
Flash point, COC	-78°C
Explosive limits in air	4-22% by vol.

2.2 POLYMERIZATION OF VINYL CHLORIDE

Vinyl chloride can be polymerized by bulk, solution, suspension, or emulsion techniques. The latter two techniques are the more important commercial preparative methods. In the United States the suspension process accounts for over three-fourths of homopolymer production and the emulsion process accounts for nearly all the remainder. In Europe there is a more equal balance between production by these two processes. While bulk and solution processes are less important in a tonnage sense, Pechiney-St. Gobain

(France) employs the bulk process and Union Carbide Corporation employs the solution process for a portion of their commercial production. The open literature contains few details of commercial vinyl chloride polymerization processes, but in some instances, general descriptions of certain systems can be found¹⁷⁻¹⁹. Albright²⁰ has recently reviewed the process and reactions involved in the conversions of vinyl chloride into polymer.

2.2.1 Bulk process

For most monomers the monomer acts as a solvent for the initiator and the polymer, and the end product of a bulk polymerization is a solid mass of polymer. However, with vinyl chloride, the process takes place in solution only during the early stages of the polymerization. When the polymer particles reach sufficient size, they precipitate as a fine powder and the polymerization continues in the solid phase²¹. Usually it is necessary to separate the polymer from the slurry before the reaction is 50 percent complete. If this is not done, an extremely rapid reaction takes place because of poor heat transfer and autoacceleration²² of the polymerization in the solid particles. Bulk polymerization of vinyl chloride is usually limited to laboratory preparations. In the laboratory relatively small masses are involved and a uniform temperature is more readily maintained. Pechiney-St. Gobain carries out the bulk polymerization of poly(vinyl chloride) commercially. Although process details are not generally available, there is a patented description²³. In one example, vinyl chloride monomer containing 0.8 percent benzoyl peroxide as an initiator is reacted for 17 hours at 58°C. The polymerization is carried out in a rotating cylinder that contains stainless steel spheres.

2.2.2 Solution process

A solution process differs from a bulk process in that a solvent is added to the polymerization system. The system may be homogeneous with both monomer and polymer soluble, or it may be heterogeneous in which case the monomer is soluble but the polymer is insoluble. Examples of systems employing heterogeneous solvents for the polymerization of vinyl chloride in hexane²⁴, in ethyl acetate²⁵, in butane²⁶, and in cyclohexane²⁷ have been