Hans Ulrich

# Introduction to Industrial Polymers

HANSER
PUBLISHERS

Henri Ulrich

# Introduction to Industrial Polymers

Distributed in the United States of America by
Macmillan Publishing Co., Inc., New York

Collie

HANSER
PUBLISHERS

Ulrich · **Industrial Polymers**

Henri Ulrich
Director,
Donald S. Gilmore Laboratories
The Upjohn Company
North Haven, CT.

Distributed in USA by
Scientific and Technical Books
Macmillan Publishing Co., Inc.
866 Third Avenue, New York, N.Y. 10022

Distributed in Canada by
Collier Macmillan Canada Distribution Center,
539 Collier Macmillan Drive, Cambridge, Ontario

Distributed in all other countries by
Carl Hanser Verlag
Kolbergerstr. 22
D-8000 München 80

CIP-Kurztitelaufnahme der Deutschen Bibliothek

**Ulrich, Henri:**
Introduction to Industrial Polymers/
by Henri Ulrich. – München; Wien: Hanser 1982
ISBN 3-446-13561-8
ISBN 0-02-949790-6 Macmillan Publishing Co., Inc., New York

Library of Congress Catalog Card Number 81-85878

Cover design: C. A. Loipersberger

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or by any information storage and retrieval system, without permission in writing from the Publisher.

Copyright © Carl Hanser Verlag München Wien 1982
Printed in Germany by Erich Spandel, Nürnberg

此为试读,需要完整PDF请访问: www.ertongbook.com

# Foreword

The Society of Plastics Engineers is pleased to sponsor and endorse this volume on "Industrial Polymers". A number of current books on plastics materials treat the subject from the academic viewpoint. This volume, however, is among the first to consider the commercial significance and utilization of available materials.

This also marks the first time that SPE has cooperated with the distinguished German publisher, Carl Hanser Verlag. Hopefully, it marks the beginning of a long relationship between the two organizations.

SPE, through its Technical Volumes Committee, has long sponsored books on various aspects of plastics and polymers. Its involvement has ranged from identification of needed volumes to recruitment of authors. An ever-present ingredient, however, is review of the final manuscript to insure accuracy of the technical content.

This technical competence prevades all SPE activities, not only in publication of books but also in other activities such as technical conferences, educational seminars and periodicals. The resource of some 24,000 practicing plastics engineers has made SPE the largest organization of its type in plastics worldwide. Further information is available from the Society at 14 Fairfield Drive, Brookfield Center, Connecticut 06805.

Again, we are delighted to inaugurate the SPE-Hanser series with this volume.

*Robert D. Forger*
Executive Director
Society of Plastics Engineers

**Technical Volumes Committee**

James L. Throne, Chairman
Lee L. Blyler, Jr.
A. Wayne Cagle
Jerome L. Dunn
Tom W. Haas
John L. Kardos
Richard R. Kraybill
Timothy Lim
Eldridge M. Mount, III
Nikolaos A. Peppas
B. J. Sexton

# Preface

In early 1979 I taught a mini-course on industrial polymers at Wesleyan University in Middletown, Connecticut. My attempts to find a suitable textbook met with complete failure. Most textbooks in polymer science deal with principles and are slanted toward materials science rather than chemistry. I felt that it was essential to indicate to the students the polymers that are used extensively in today's world, their significance and social impact, and future trends in the development of useful macromolecules.

Polymer science is still a young discipline. Hermann Staudinger, the first Nobel Prize winner in this field, did his pioneering work on the "existence" of macromolecules in the 1920s. Nevertheless, we are now in the plastics age. Plastics production, on a volume basis, surpassed steel production in the United States in 1979. Total plastics consumption is currently about 20 million tons and will triple by the year 2000. Recent years have seen the emergence of functional polymers, especially in the design of new drug delivery systems, polymeric catalysts, and polymeric reagents.

This text is divided into four parts---Part I provides an overview of the industry, and Parts II through IV deal with addition polymers, condensation polymers, and special polymers. Classification of the polymers according to polymerization technique and monomer composition provides an orderly approach, whereas classification based on polymer uses, that is, plastics, rubber materials (elastomers), fibers and coatings, would result in too much overlap. For example, polyamides are used mainly as synthetic fibers, but they have also found uses as thermoplastic molding compounds and as powder coatings. Polypropylene is not only used as a thermoplastic molding compound; it has also found uses as a fiber-forming material.

The vinyl compounds are all based on the homopolymerization of an olefin monomer. To differentiate them, the various types of olefin homopolymers are classified by the substituents attached to one carbon atom of the double bond. If the substituent is hydrogen (as in polyethylene) or an alkyl or aryl group, the products are listed under polyolefins. If the substituent is a nitrile, a carboxylic acid, or a carboxylic acid ester, we are dealing with derivatives of acrylic acid, and the derived polymers are listed under acrylics. A third group of olefin homopolymers with substituents bonded to the double bond through an oxygen or nitrogen atom are described under polyvinyl compounds.

The use of trade names has been avoided whenever possible. However, many trade names have become household words (nylon, formica, lycra, etc.), and they are used to identify the more common products.

Plastics serve a range of needs never anticipated by early polymer chemists. Future trends will include merger of the high volume materials to create new multipolymers or hybrids. Regulatory restrictions in the industrial countries dictate this development because it will become exceedingly difficult to get governmental approval for the manufacture of new products. Recycling of the volume plastics will become a reality,

and the marketplace will experience increasingly cannibalistic competition among the thermoplastics: growth at the expense of each other, rather than replacement of traditional materials. However, supply and demand of the major materials will be in balance for the rest of this century, and the availability of fossil-based raw materials will not be a determining factor in plastics growth. In spite of many prophets of doom, it is clear that plastics are here to stay and that their potential impact on society grows ever larger.

Guilford, Connecticut *Henri Ulrich*

# Contents

## Part I: General Introduction



## Part II: Addition Polymers

## Part III: Condensation Polymers

## Part IV: Special Polymers



此为试读,需要完整PDF请访问: www.ertongbook.com

# Part I General Introduction

# 1. Historical Overview of Industrial Polymers

On a volume basis, U.S. plastics production in 1979 surpassed U.S. steel production, heralding the arrival of the plastics age in the United States. Plastics are still evolving, still changing and improving as the 21st century approaches. Their potential impact on society appears greater than ever. We have all seen their increasing use in everyday life: in apparel, home furnishings, housewares, construction materials, tanks and pipes, insulation, storage, transportation, packaging, medical uses, recreational activities, communications, electronics, aerospace, and many other applications.

Natural polymeric products have been used widely throughout the ages, but synthetic polymers are of fairly recent vintage. Before today's sophistication in plastics could be achieved the chemists of the last century had first to develop an understanding of natural polymers. The first hypothesis of the existence of macromolecules was advanced by Kekulé in 1877 when he proposed that natural organic substances consist of very long chains of molecules from which they derive their special properties. Interestingly, in 1868 John Wesley Hyatt had already manufactured the first synthetic plastic in the United States, producing celluloid by treating cotton with nitric acid and camphor. This development was prompted by a shortage of ivory which led Hyatt to seek a synthetic material for the production of billiard balls. Celluloid was later used as a base for the first films used in still photography and in the early motion pictures. In 1893 Emil Fisher proposed a structure for natural cellulose. He considered cellulose to contain a chain of glucose units. He also postulated that polypeptides are long-chain polyamino acids. In 1909 another American scientist, Leo Hendrik Baekeland, invented phenol formaldehyde resins. These materials, which became known as Bakelite, were used widely in the manufacture of molded parts, including the first mass-produced telephones.

The step from the idea of macromolecules to the reality of producing them at will was still not made, because both Hyatt and Baekeland invented their plastics by trial and error. It needed the genius of Hermann Staudinger, who in 1924 proposed linear structures for polystyrene and natural rubber. Later Staudinger received the Nobel Prize in chemistry for his pioneering work in macromolecular chemistry. After the recognition of the fact that macromolecules really are linear polymers, it did not take long for other materials to emerge. In 1927 cellulose acetate and polyvinyl chloride (PVC) were developed, and 1929 saw the production of urea formaldehyde resins. In 1930 the U.S. production of the new industrial materials called plastics was only 23,000 metric tons, mostly phenolics and celluloid.

Again it needed a scientist with a broad vision to provide a new concept for the development of synthetic polymers. This man was Wallace H. Carothers, who pioneered linear condensation polymers, such as polyesters and polyamides. Carothers joined DuPont's central research laboratory in Wilmington in 1928, coming from Harvard University. He chose as his project to study long-chain molecules made from difunctional monomers. One member of his group, Paul Flory, received the Nobel Prize in chemistry in 1974. The basic research efforts of the Carothers team led to the development of neoprene, polyesters, and polyamides. DuPont's nylon production started in 1938, and nylon-6 (perlon) production by I. G. Farben began in 1939. In Germany, P. Schlack had developed the caprolactam route to nylon, which was the first example of a ring-opening polymerization. Today, 40 years later, over 3 million tons of nylon are produced worldwide.

The years prior to World War II saw the rapid development of many important plastics such as acrylics and polyvinyl acetate in 1936, polystyrene in 1938, melamine formaldehyde (formica) in 1939, and polyester and polyethylene in 1941.

The amazing scope of wartime applications led to the development of scratch-resistant, heat-stable, weatherproof, transparent plastics for aircrafts, buildings, and containers; lightweight, waterproof, nonflammable, noncreasing synthetic fibers for garments, carpets, upholstery, and draperies; cellular plastic insulation and sandwich construction used in lightweight structural materials for walls, ceilings, and furniture; resins with improved heat resistance and electrical insulation qualities in detection devices for aircraft, ships, and trains; plastic sheeting and fiber-reinforced materials fabricated into large, light, tough structures for cars and appliances; and elastomeric crosslinked copolymers to provide superior performance in wire insulation, weather-stripping, rainwear, hospital accessories, chemical-resistant coatings, and structural adhesives.

After the war, the development of new polymeric materials accelerated at an even faster pace. In 1947 epoxies were developed; in 1948 acrylonitrile-butadiene-styrene terpolymer, ABS. The polyurethanes, which were produced in Germany in the 1930s, were rapidly developed in the United States as German technology became available after the war. By 1949 the annual production of plastics in the United States reached 570,000 tons.

Again the input of a brilliant scientist stimulated polymer science, and this person was Karl Ziegler at the Max Planck Institute in Mühlheim, Ruhr, West Germany. Ziegler was involved in synthetic organometallic chemistry. Exposure of ethylene to some aluminum alkyl compounds led very rapidly to polymerization of the ethylene. Fifty years earlier an investigator would have discarded such an intractable material, but the time was right for macromolecules, and Ziegler recognized the importance of his finding. He and Giulio Natta extended the work to other olefins. Both chemists received the Nobel Prize in 1963 for their discovery of stereospecific polymerization.

The 1950s saw the emergence of linear polyethylene, polypropylene, acetal, polyethylene terephthalate, polycarbonate, and a host of new copolymers. The U.S.

plastics production in 1959 was 2,730,000 tons. The next decade saw the development of an incredible number of processing techniques accompanying the surge of plastics to a significant position as materials of construction. Also more highly temperature-resistant materials such as polyimides, polyarylsulfones, and polyarylamides were introduced. Automotive consumption of plastics reached several hundred pounds per car, and by 1978 the annual production of plastics in the United States exceeded 19 million tons. Significant new plastics launched in the 1970s include polyphenylene sulfide and polybutylene terephthalate. The highlights of the short history of industrial polymers are listed in Table 1.

Table 1. Historical Development of Industrial Polymers*

| Date | Event |
|---|---|
| 1868 | J. W. Hyatt invented cellulose nitrate and the injection-molding machine |
| 1877 | A. Kekulé postulated that natural products are long-chain molecules |
| 1893 | E. Fischer verified that the structure of cellulose is indeed a macromolecule |
| 1909 | L. H. Baekeland invented PF resins (Bakelite). |
| 1924 | H. Staudinger proposed the linear chain structure for polystyrene. |
| 1927 | Introduction of cellulose acetate and PVC. |
| 1928 | O. Röhm commercialized polymethyl methacrylate (PMMA). |
| 1929 | Introduction of UF resins. |
| 1930 | First production of polystyrene (PS). |
| 1935 | W. H. Carothers first synthesized nylon-6,6. |
| 1936 | Introduction of PAN, SAN, and polyvinyl acetate |
| 1937 | O. Bayer invented polyurethanes. |
| 1938 | P. Schlack invented nylon-6 and epoxy resins. R. J. Plunkett discovered the polymerization of tetrafluoroethylene. High-pressure polymerization of ethylene was introduced. |
| 1940 | G. E. Rochow invented the direct process for the manufacture of chlorosilanes, the raw materials for silicone resins. |
| 1941 | J. R. Whinfield and J. T. Dickinson invented polyethylene terephthalate (PET). |
| 1942 | Commercial introduction of PAN fibers (Orlon®). |
| 1948 | Introduction of ABS. |
| 1952 | K. Ziegler developed catalysts for the low-pressure polymerization of ethylene. |
| 1953 | G. Natta used Ziegler catalysts to synthesize stereoregular polypropylene (PP). H. Schnell invented polycarbonate. |
| 1956 | A. S. Hay discovered polyphenylene oxide (PPO). |
| 1958 | Commercial introduction of polyacetal. |

* A list of abbreviations for industrial polymers is given at the end of the book.

The social and economic challenges of the 1980s have added a new dimension to macromolecules. Petrochemicals are the feedstock for plastics. Although less than 1.5% of the oil and natural gas consumed annually in the United States is used in the production of plastics, government allocations of oil-derived products and price escalation have had a major impact on the plastics industry.

Synthetic materials have become essential to the well – being of humans – on this earth. The world population has passed the 4 billion mark and is growing by approximately 200,000 daily. Manufacture of polymers causes less environmental stress than the growing of wool, cotton, and wood, especially since we need to expand agricultural land use for food production. Plastic products are often more energy efficient than alternative materials, and past experience suggests that there are no partical limits to the extent to which synthetic polymers may serve human needs in the next century and beyond.

此为试读,需要完整PDF请访问: www.ertongbook.com