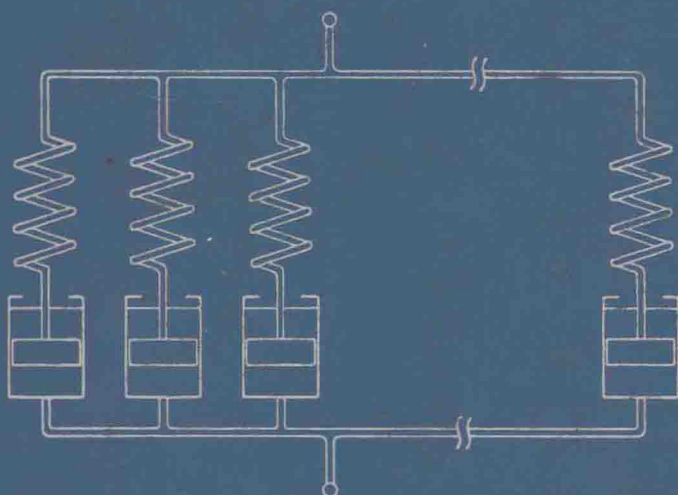


# PRINCIPLES OF **POLYMER ENGINEERING RHEOLOGY**

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JAMES LINDSAY WHITE



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A WILEY-INTERSCIENCE PUBLICATION

John Wiley & Sons, Inc.

NEW YORK / CHICHESTER / BRISBANE / TORONTO / SINGAPORE

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***Library of Congress Cataloging-in-Publication Data:***

White, James Lindsay, 1938–

Principles of polymer engineering rheology.

Bibliography: p.

1. Polymers and polymerization—Rheology. I. Title.

QD381.9.R48W48 1988 668.9 88-33830

ISBN 0-471-85362-3

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

# **PRINCIPLES OF POLYMER ENGINEERING RHEOLOGY**

# PREFACE

The polymer industry is an area of great energy and dynamism. New materials with new combinations of properties continue to come to the marketplace. Engineering parts ranging from sophisticated extrusion profiles and injection moldings to tires are undergoing continuous development. Engineering plastics continue to make rapid headway against metals in aircraft components. The engineer requires a detailed understanding of the flow behavior of these materials in order to design the dies and molds required to form tomorrow's structural components.

The flow or rheological behavior of polymer melt systems is very complex and is still not fully understood. Such systems include not only the traditional pure melts, but solutions and compounds containing anisotropic (fiber or disc) or colloidal particles. Pure polymer melt systems themselves consist not only of flexible chain materials, which include polyolefins, but rigid chain substances that form ordered structures, that is, liquid crystals. New and complex materials continue to reach the market.

It is the purpose of this book to provide the basic background needed by engineers to (1) determine experimentally and interpret the rheological behavior of polymer melts and (2) apply it to analyze flow in processing operations. To accomplish this we must critically treat three different areas or disciplines. We develop the fundamentals of continuum mechanics and show how it may be applied to devise methods for measurement of rheological properties, formulation of three-dimensional stress-deformation relationships, and analysis of flow in processing operations. We also discuss the structure of polymers and interpret the rheological behavior in terms of structure. Finally, we discuss polymer fabrication technology and seek to analyze and design these processes.

The book is divided into three parts. Chapters I–III represent the background in polymer science, continuum mechanics, and polymer technology needed to understand and appreciate the need for rheological characterization. Chapters IV–VI deal with the experimental foundations of modern rheology and rheo-

optics and the interpretation of experimental data. Chapters VII and VIII deal with constitutive equations relating stress to deformation history in non-Newtonian fluids and their applications. Chapter VIII concerns specific applications to polymer processing. Each chapter begins with a critical historical survey of the subject matter and then proceeds to develop the material in a pedagogical manner.

This book is written for first-year graduate students in polymer engineering. It could be used equally well by chemical or mechanical engineering graduate students.

*Arkon, Ohio*  
*January 1990*

JAMES LINDSAY WHITE

# **PRINCIPLES OF POLYMER ENGINEERING RHEOLOGY**

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# BACKGROUND



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# I

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## INTRODUCTION TO POLYMERS

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### A. INTRODUCTION

Rheology treats the deformation and flow of materials. To properly design and utilize instruments, the rheologist must know the material with which he or she deals, whether the material is homogeneous or multiphase, and its operating temperatures and chemical stability. Often the rheologist must use his/her talents to interpret experiments in terms of structure.

In this chapter we discuss the nature of polymer materials, the various classes of possible structural variation, and the nature and states of matter of the major polymer of commercial interest.

## B. COMMERCIAL POLYMERS AND DEVELOPMENT OF THE MACROMOLECULAR HYPOTHESIS

Polymers have been used in the service of mankind since the beginning of recorded history. Leather, wood, wool, linen, and cotton are polymeric substances of plant and animal origin. Textile structures are polymeric composites and the textile industry is a polymer industry, though they are rarely considered as such. It was only in the period after 1820, with the development of a rubber industry based upon coagulated rubber latex from South America (38, 42, 95, 96), that concern was exhibited over the structure of polymeric substances. Early entrepreneurs such as Thomas Hancock (42, 95, 96) and Charles Goodyear (38) exhibited concern over the composition and molecular structure of their products. Perhaps the first careful study of a polymer was made at the behest of Hancock by Michael Faraday (31, 42), who carried out an analysis of the chemical composition of natural rubber and its latex.

In the half century stretching roughly from 1838 to 1890, entrepreneurs discovered they could chemically modify many industrial substances which we now consider as polymeric to produce more useful products. Nathaniel Hayward (44), Goodyear (37, 38), Hancock (41, 42), and Alexander Parkes (42, 67) developed procedures for modifying (vulcanizing) rubber with sulfur and heat. Christian Schonbein (76) shortly thereafter nitrated cellulose and in succeeding years the acetates (45) and xanthates (9, 29, 45) of cellulose were developed. These developments, coupled with the discovery and application of gutta percha, led to the plastics industry. Charles Hancock (40) and others developed gutta percha, which we describe today as a 'plastic'. From about 1845, it was widely used as electrical insulation. Largely through the efforts of Alexander Parkes (50, 68) and the Hyatt brothers, John Wesley and Isaiah Smith (47, 48, 97), in the period 1865–1880, cellulose nitrate was developed as a plastic. As *celluloid* it became very widely used. In the decade 1884–1894, a man-made fiber industry based on cellulose nitrate came into being largely through the efforts of Chardonnet (27, 45). This later led to regenerated cellulose or rayon fibers based on cellulose xanthate (9, 29, 45).

The realization of the polymeric nature of rubber and the cellulose awaited the development of quantitative measurements of molecular weight for substances that could not be vaporized. This came with the development of colligative property measurements in the 1880s and 1890s. In 1889, Gladstone and Hibbert (35) found, using freezing-point depression, that rubber had a molecular weight of 12,000. Amylodextrin formed in the hydrolytic degradation of starch was noted by Brown and Morris (12) at about the same time to have a molecular weight of about 30,000. In 1914 Caspari (24), extrapolating osmotic pressure data to infinite dilution, determined molecular weights of 100,000 for rubber and 40,000 for gutta percha. Most contemporary chemists refused to accept these high molecular weights and argued that they were due to associations of small molecules. Polymers were confused with colloidal suspensions. In some cases, it was argued that these materials were ring structures associated together (70).

A new era in polymer science came in 1920 when Hermann Staudinger (81) clearly elucidated the modern theory of the structure of polymers, arguing that materials such as rubber and polystyrene were linear long chains with repeating units, indeed the same repeating units we accept today. During the next decade and more, Staudinger (81–85) carried on a heroic struggle to establish this macromolecular hypothesis. Through extensive molecular weight measurements and critical investigations of chain structure, he gradually won over his opponents or forced them to retire from the field. He showed that if rubber is hydrogenated or converted to other derivatives, it always maintained its “colloidal” characteristics. He clearly showed the distinction between polymers and associated colloids whose characteristics depend on the suspending medium. Staudinger’s efforts climaxed with his 1932 monograph *Die hochmolekularen organischen Verbindungen* (83).

In the late 1920s and 1930s, a younger generation of convinced adherents of Staudinger began the rational synthesis of new macromolecules. The most spectacular, carefully documented effort of this type was carried out by Wallace H. Carothers (1, 18–22) in the period 1929–1936. This led to polychloroprene, aliphatic polyamides (nylons), aliphatic polyesters, and other polymers (10, 22).

Commercial development of truly synthetic polymers dates to the beginning of the century, more than a decade before Staudinger’s efforts and a generation before their acceptance. Leo Baekeland (6, 26) commercialized phenol-formaldehyde resins in about 1909. The first commercial developments of synthetic rubber were carried out at about the same time at Farbenfabriken Bayer in Germany under the leadership of Fritz Hofmann (39, 88, 92, 94). The 1920s saw the commercialization of polystyrene and polyvinyl chloride by the German I. G. Farbenindustrie a combine of Farbenfabriken Bayer, BASF and Farbwerke Hoechst (50). The same firm developed butadiene–styrene copolymer (Buna-S) and butadiene–acrylonitrile (Buna-N) synthetic rubber (88). The efforts of Carothers and his coworkers led to the commercialization of polychloroprene synthetic rubber (22, 28) and nylon synthetic fiber (10, 19) by E. I. duPont de Nemours in the United States.

By 1940, the development of polymer science and the polymer industry was well under way. The activities of scientists and industry during World War II accelerated it into the modern era, with the contributions of the Rubber Reserve Program (93) in the United States being most significant. The I. G. Farbenindustrie developed nylon-6 and polyurethanes in the same period. Kurashiki Rayon (Kuraray) developed polyvinyl alcohol in Japan in the same period and applied it to fibers.

## C. POLYMER STRUCTURE

### 1. General Remarks

Polymers are in general high-molecular-weight, long-chain molecules. In the simplest case, a polymer consists of a single repeating unit:



Many of the most important polymers are of this type.

The most important type of linear polymers are vinyl polymers, with the repeating structure unit (32)



They include polyethylene ( $\text{R} = \text{H}$ ), polypropylene ( $\text{R} = -\text{CH}_3$ ), polystyrene ( $\text{R} = \text{phenyl}$ ,  $\bigcirc$ ), polyvinyl chloride ( $\text{R} = \text{Cl}$ ). They have been shown to possess primarily head-to-tail structures, as indicated in Figure 1-C-1.

The carbon atom with the asterisk is asymmetric, thus leading to the possibility of geometric or stereoisomerism. Such polymers were first synthesized and characterized by Natta and his coworkers (62–66) in the mid-1950s. If all the asymmetric carbons possess the same configuration, the polymer is said to be *isotactic* (62, 64, 66). If the configurations of the asymmetric carbons alternate, the polymer is said to be *syndiotactic*. If there is not regular order, the term *atactic* is used (Figure 1-C-1). One may quantify the intermediate level of tactic structures, but such a development would be out of place here.

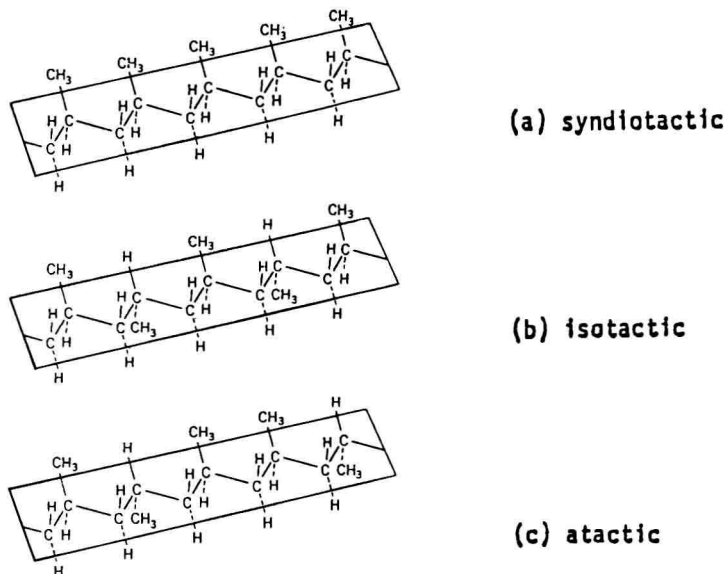


FIGURE 1-C-1. Tacticity in polypropylene.

Related to the vinyl polymers are structures of the form



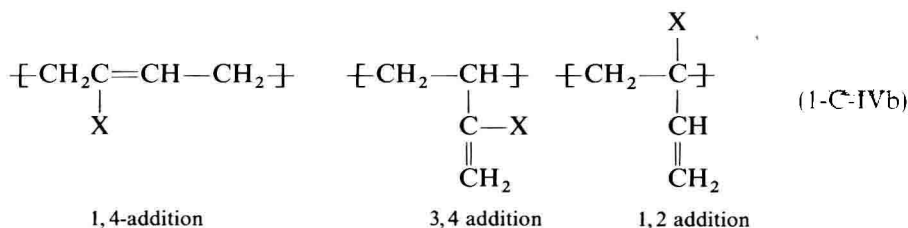
When  $\text{R}_1$  and  $\text{R}_2$  are the same, the polymer is referred to as *vinylidene*. When  $\text{R}_1 = \text{R}_2 = \text{Cl}$ , we have polyvinylidene chloride. There are no tacticity distinctions in vinylidene polymers. However, when  $\text{R}_1$  is not the same as  $\text{R}_2$ , the situation is the same as in vinyl polymers. Generally polymers with the structure of formula (1-C-III) are also tied together in a head-to-tail manner.

Regularities in geometric configurations allow a polymer to crystallize. Commercial polypropylene is primarily isotactic, while commercial polystyrene is atactic. Thus polypropylene readily crystallizes, while polystyrene cannot crystallize and vitrifies to form a glass. Vinyl polymers are used commercially primarily as plastics, though some polypropylene is melt spun to form fiber.

Another important class of polymers is the *polydienes*, which are formed from the monomer

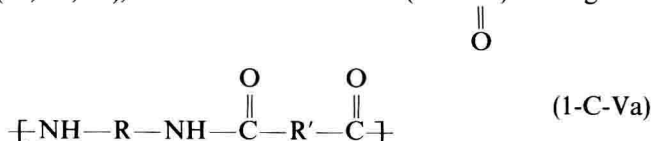


and generally consist of a mixture of the structural units

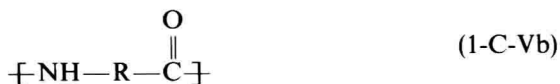
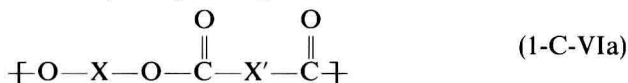


The double bond may be *cis* or *trans*. The commercial dienes are used as elastomers and generally have a predominantly 1,4 addition form (88, 93). Isotactic and syndiotactic structures for 1,2 and 3,4 addition polydienes are possible.

Mention should also be made of condensation polymers (18, 32), including, notably, polyamides (19, 21, 52), which have the amide  $-\text{NHC}(=\text{O})-$  linkage



or

and polyesters, which have the  $(-\text{OC}-)$  linkage:

or



Both polyamides and polyesters are important as synthetic fibers, fibers, and plastics. When R in formula 1-C-Vb is an aliphatic polymer chain, the material is called a nylon; when R is  $(-\text{CH}_2)_5$ , the material is called nylon-6. A similar distinction exists for formula 1-C-Va where one speaks of nylon-*mn* polymers. If R is  $(-\text{CH}_2)_6$  and R' is  $(-\text{CH}_2)_4$ , we have nylon-66. Other important polycondensates are polycarbonates



and polysulfides

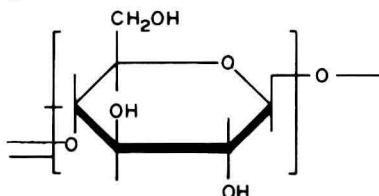


Certain natural products should be cited also, notably polypeptides, which are a special class of polyamides:



which include the proteins. The substituents R vary considerably. In silk, an important protein material, R is largely H and  $\text{CH}_3$ . Other proteins have more complex distributions of substituents. Synthetic polypeptides, especially poly( $\gamma$ -benzyl glutamate) have been widely studied.

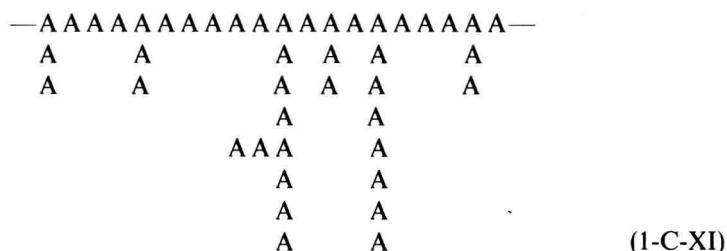
A second important biological macromolecule is cellulose, whose structural unit is a saccharide ring:





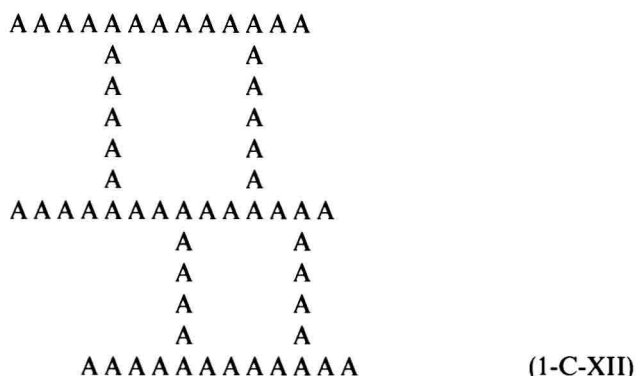
Cellulose esters and ethers are important commercial products.

Polymer chains may be branched as well as linear, that is, they may possess structures of the form



The branches may be either short or long and may themselves have branches.

In addition, polymer chains may be cross-linked into three-dimensional structures:



This causes the polymer system to be unable to flow under the action of stresses and to respond as a solid rather than a fluid. *Thermosetting* resins and vulcanized rubber are three-dimensional network structures.

Another class of polymers is *copolymers*, which contain more than one structural unit. The arrangement of the units in a copolymer chain may vary considerably. The units may be arranged in random



alternating



or block structures such as

