

Cosmetic Science and Technology Series/Volume 22

Principles of Polymer Science and Technology in Cosmetics and Personal Care

**edited by
E. Desmond Goddard
James V. Gruber**

Principles of Polymer Science and Technology in Cosmetics and Personal Care

COSMETIC SCIENCE AND TECHNOLOGY

Series Editor

ERIC JUNGERMANN

Jungermann Associates, Inc.

Phoenix, Arizona

1. *Cosmetic and Drug Preservation: Principles and Practice*, edited by Jon J. Kabara
2. *The Cosmetic Industry: Scientific and Regulatory Foundations*, edited by Norman F. Estrin
3. *Cosmetic Product Testing: A Modern Psychophysical Approach*, Howard R. Moskowitz
4. *Cosmetic Analysis: Selective Methods and Techniques*, edited by P. Boré
5. *Cosmetic Safety: A Primer for Cosmetic Scientists*, edited by James H. Whittam
6. *Oral Hygiene Products and Practice*, Morton Pader
7. *Antiperspirants and Deodorants*, edited by Karl Laden and Carl B. Felger
8. *Clinical Safety and Efficacy Testing of Cosmetics*, edited by William C. Waggoner
9. *Methods for Cutaneous Investigation*, edited by Robert L. Rietschel and Thomas S. Spencer
10. *Sunscreens: Development, Evaluation, and Regulatory Aspects*, edited by Nicholas J. Lowe and Nadim A. Shaath
11. *Glycerine: A Key Cosmetic Ingredient*, edited by Eric Jungermann and Norman O. V. Sonntag
12. *Handbook of Cosmetic Microbiology*, Donald S. Orth
13. *Rheological Properties of Cosmetics and Toiletries*, edited by Dennis Laba
14. *Consumer Testing and Evaluation of Personal Care Products*, Howard R. Moskowitz
15. *Sunscreens: Development, Evaluation, and Regulatory Aspects. Second Edition, Revised and Expanded*, edited by Nicholas J. Lowe, Nadim A. Shaath, and Madhu A. Pathak
16. *Preservative-Free and Self-Preserving Cosmetics and Drugs: Principles and Practice*, edited by Jon J. Kabara and Donald S. Orth
17. *Hair and Hair Care*, edited by Dale H. Johnson
18. *Cosmetic Claims Substantiation*, edited by Louise B. Aust
19. *Novel Cosmetic Delivery Systems*, edited by Shlomo Magdassi and Elka Touitou
20. *Antiperspirants and Deodorants: Second Edition, Revised and Expanded*, edited by Karl Laden
21. *Conditioning Agents for Hair and Skin*, edited by Randy Schueller and Perry Romanowski
22. *Principles of Polymer Science and Technology in Cosmetics and Personal Care*, edited by E. Desmond Goddard and James V. Gruber

ADDITIONAL VOLUMES IN PREPARATION

Botanicals in Cosmetics, edited by Larry Smith

Principles of Polymer Science and Technology in Cosmetics and Personal Care

**edited by
E. Desmond Goddard**

*Former Corporate Research Fellow
Union Carbide Corporation
Tarrytown, New York*

James V. Gruber

*Amerchol Corporation
Edison, New Jersey*



MARCEL DEKKER, INC.

NEW YORK • BASEL

Transferred to Digital Printing 2005

Library of Congress Cataloging-in-Publication Data

Principles of polymer science and technology in cosmetics and personal care / edited by E. Desmond Goddard and James V. Gruber.

p. cm.—(Cosmetic science and technology : v. 22)

Includes bibliographical references and index.

ISBN 0-8247-1923-9 (alk. paper)

1. Cosmetics. 2. Toilet preparations. 3. Polymers. I. Goddard, E. D. (Errol Desmond). II. Gruber, James V.

III. Series: Cosmetic science and technology series : v. 22.

TP983.P8924 1999

668'.5—dc21

99-17274

CIP

Headquarters

Marcel Dekker, Inc.

270 Madison Avenue, New York, NY 10016

tel: 212-696-9000; fax: 212-685-4540

Eastern Hemisphere Distribution

Marcel Dekker AG

Hutgasse 4, Postfach 812, CH-4001 Basel, Switzerland

tel: 41-61-261-8482; fax: 41-61-261-8896

World Wide Web

<http://www.dekker.com>

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the headquarters address above.

Copyright © 1999 by Marcel Dekker, Inc. All Rights Reserved.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

Current printing (last digit):

10 9 8 7 6

Series Introduction

The Cosmetic Science and Technology series was conceived to permit discussion of a broad range of current knowledge and theories of cosmetic science and technology. The series is made up of books either written by a single author or edited with a number of contributors. Authorities from industry, academia, and the government are participating in writing these books.

The aim of this series is to cover the many facets of cosmetic science and technology. Topics are drawn from a wide spectrum of disciplines ranging from chemistry, physics, biochemistry, analytical and consumer evaluations to safety, efficacy, toxicity, and regulatory questions. Organic, inorganic, physical, and polymer chemistry, as well as emulsion technology, microbiology, dermatology and toxicology all play a role in cosmetic science.

There is little commonality in the scientific methods, processes, or formulations required for the wide variety of cosmetics and toiletries manufactured. Products range from hair care, oral care, and skin care preparations to lipsticks, nail polishes and extenders, deodorants, body powders and aerosols, to over-the-counter products, such as antiperspirants, dandruff treatments, antimicrobial soaps, and acne and sunscreen products.

Cosmetics and toiletries represent a highly diversified field with many subsections of science and "art." Indeed, even in these days of high technology, "art" and intuition continue to play an important part in the development of formulations, their evaluation, and the selection of raw materials. There is a move toward more sophisticated scientific methodologies in the fields of preservative efficacy testing, claim substantiation, safety testing, product evaluation, and chemical analyses.

Emphasis in the Cosmetic Science and Technology series is placed on reporting the current status of cosmetic technology and science in addition to historical reviews. Several of the books have found an international audience and have been translated into Japanese or Chinese. Contributions range from highly sophisticated and scientific treatises to primers, practical applications, and pragmatic presentations. Authors are encouraged to present their own concepts, as well as established theories. Contributors have been asked not to shy away from fields that are still in a state of transition, or to hesitate to present detailed discussions of their own work. Altogether, we intend to develop in this series a collection of critical surveys and ideas covering diverse phases of the cosmetic industry.

Principles of Polymer Science and Technology in Cosmetics and Personal Care is the twenty-second volume published in this series. Polymers are important components in a broad range of cosmetic and personal care products. They fill a multitude of functions too numerous to list. This book covers the many classes of polymers used in almost every type of cosmetic formulation and their wide range of applications, special properties, and sometimes specialized requirements.

I want to thank the editors, E. Desmond Goddard and James V. Gruber, and all the contributors for collaborating in the editing and writing of this book. Special recognition is also due to Sandra Beberman and the editorial staff at Marcel Dekker, Inc. In addition, I would like to thank my wife Eva, without whose constant support and editorial help I would never have undertaken this project.

Eric Jungermann, Ph.D.

Preface

Although synthetic polymers first appeared in the last century, it has been the twentieth century, especially the second half, which has witnessed an explosive growth in the development and use of this category of material. Indeed, it is difficult to think of many industries today that do not employ polymers in some form or another. Such employment, of course, includes that by the cosmetic and personal care industry in which the use of polymeric materials continues to develop rapidly. This trend will continue in the next century.

Polymer science—already starting from a solid foundation with the early recognition that many natural products, including proteins and polysaccharides, are polymeric—has grown apace with these developments. Today some would aver that it has been difficult for many scientists, including those actually involved in research and development work involving polymers, to keep abreast of recent theoretical developments, let alone to retain a working familiarity with what has evolved today as basic polymer science. Be this as it may, a need was identified for a book that could be used not only as a reference source for the polymers currently used in the cosmetics industry, but also as a source of information on the basic physical chemistry of polymers as it applies to the functions they serve in the formulation and use properties of cosmetics. Furthermore, because of both the latter features and the overlapping of technology, it seems that such a text might also be found useful by investigators in related fields such as detergent formulation, pharmaceuticals, textiles, and even the latex paint industry. Bearing in mind the breadth of the field, we invited the participation of several other authors, all recognized as experts in their area(s) of polymer science. We believe the result is a comprehensive coverage of the field designated by the title of the book.

The body of the text consists of 12 self-standing chapters comprising a mix of the fundamental science of polymers, their solution and interfacial properties, their interactions with surfactants, the intrinsic properties of polymers employed in cosmetic formulations, and the properties they confer to treated surfaces. There is also an appendix which lists and groups the polymers used in cosmetics.

Chapter 1 is an introduction to polymer science, covering its history, fundamentals, and recent developments. The reader is introduced to the different types of polymers, their

classification and synthesis, molecular weight definitions, and properties in the solid and semisolid state. There follows an overview of the properties of polymers in solution starting with their thermodynamics, considerations of molecular size and shape, and finally their rheology. It concludes with a list of about 50 definitions used in polymer science, potentially useful to newcomers and seasoned practitioners alike.

Many uses of polymers are concerned with the properties of polymers at interfaces. Chapter 2 presents a summary of theories of polymer adsorption and discusses the properties and state of polymers at interfaces and methods for determining the details of their structure, conformations, and so on. The basic theory of colloid-interaction forces in terms of DLVO theory is presented, together with a discussion of the different basic stabilization mechanisms of colloids.

In Chapter 3, the solution and surface properties of a relatively new class of material, namely, polymeric surfactants, are illustrated in some detail using Flory-Huggins theory and current polymer-adsorption theory. This is followed by a discussion of the phenomenon of steric stabilization of suspended particles and how it is affected by the detailed structure of the stabilizing polymeric species. It concludes with a discussion of the stabilization of emulsions by interfacial and bulk rheological effects, and presents closing comments on “multiple” emulsions.

When polymers are employed in personal care formulations, in many (if not most) cases they occur as cocomponents with surfactants. Recognizing a widespread tendency of such components to interact and affect each other's properties (sometimes in dramatic ways), Chapter 4 outlines a number of methods to investigate and analyze such interaction for the main types of polymers—nonionic, ionic, “hydrophobic,” and proteinaceous. Chapter 5 presents an illustrative selection of polymer/surfactant interactions in applied systems that demonstrates how they can be selected to achieve beneficial performance effects.

Realizing that many practicing formulation chemists and research scientists are seeking more immediate and nontheoretical discussion of the polymers used so frequently in cosmetics and personal care, the next four chapters were written to address, in a more nuts-and-bolts fashion, the most popular and widely used polymers employed in the industry, including synthetic polymers, silicone polymers, polysaccharides, and proteins. However, the intent of the authors of these four chapters was not simply to describe lists of formulations, but instead to try and discuss the basic knowledge of these four polymer groups and to develop insights into 1) how one might better formulate with these materials and 2) what behavioral aspects one might expect in using a particular polymer.

Synthetic polymers are ubiquitous in the personal care industry. Chapter 6 strives to address this rather broad topic in a straightforward and easily readable fashion. The chapter starts with a brief discussion of how synthetic polymers are made and the nomenclature used to describe some of the more basic structural principles of synthetic polymers. It expands to address many of the synthetic polymers used in personal care formulations based principally on their primary mode of operation, including thickening polymers, fixative polymers, conditioning polymers, and encapsulating polymers, the last subject becoming more important as formulators develop more sophisticated topical systems to deliver active materials.

Chapter 7 discusses the phenomenal range and use of silicone polymers that can be found in nearly every branch of personal care and cosmetic development. The chapter discusses how the polymers are made, essentially from sand, and the nomenclature used to describe the many different types of silicone-based polymers found in the industry.

A lengthy discussion follows, covering how the polymers behave in use, the spreading characteristics, and the many beneficial properties silicone polymers offer when delivered to keratinous surfaces. The chapter concludes with a thorough discussion of the safety and environmental impact of silicone-based polymers.

Chapter 8 is a review of the use of polysaccharides, perhaps some of the oldest and most well-known ingredients used in personal care. Because polysaccharides are derived from natural sources, the nature of the monosaccharides that comprise these sugar-based polymers and how nature designs the polysaccharides are addressed first. This discussion is followed by greater details of individual cosmetically important polysaccharides based primarily on the ionic nature of the polysaccharide, that is, anionic, cationic, nonionic, or amphoteric, which can be either naturally developed by the polysaccharide source or manipulated by human intervention and invention. The effects of hydrophobic modification of polysaccharides are also discussed. The chapter concludes with a brief discussion of certain polysaccharides that appear to have physiological effects on the human body when applied topically.

Chapter 9 addresses the important issues and chemistry surrounding the use of proteins in personal care. The chapter begins with a thorough review of the structural properties of proteins, including the basic amino acids of which they are composed, the various sources (both plant and animal) of the beneficial proteins, and how these amino-acid-based polymers develop secondary, tertiary, and quaternary structures as they form. The chapter then addresses how proteins behave in formulations and how their functionality can be interrupted or changed by formulations or modification of the proteins that affect these unique protein-folding structures. It concludes with a timely discussion covering protein contaminants, particularly bovine spongiform encephalopathy (BSE), a human contagion the nature of which has appeared to grip the industry somewhat emotionally.

Polycationic materials are well known and have long been used as conditioning agents for hair and skin. Chapters 10 and 11 discuss methods employed, and results obtained, in measurements of their sorption by these substrates. These model studies show that uptake of polymer can be substantial, vastly exceeding that required for simple "monolayer" coverage. Presumably what is involved is the substantial swelling, and the development of diffusion channels, in these substrates on immersion in water. Although some ionic surfactants, that is, anionic, or especially cationic surfactants, can substantially reduce the uptake, they do not eliminate it.

The last chapter (12) is concerned with evaluation methods of polymer-conditioned hair. The first part deals with single-fiber evaluation and includes contact angle, electrokinetic, fluorimetry, friction, and cuticle-cohesion measurements. The second part deals with hair assemblies and includes measurements of combing, "body," optical properties, and static electrification.

Finally, in the appendix, there is a comprehensive listing—an "encyclopedia"—of the polymers used in the cosmetic industry, together with their INCI designations and a brief description of the polymers. We believe that inclusion of this updated compendium adds substantially to the general utility of the book.

On a personal note, Dr. Goddard wishes to express his appreciation to Union Carbide and Amerchol Corporation for sustained support of his own research work on many of the subjects dealt with in this volume. This work would not have been possible without the cooperation and contributions of many of his former colleagues, including, especially, J. A. Faucher, R. B. Hannan, P. S. Leung, and K. P. Ananthapadmanabhan. In particular he wishes to thank the last-mentioned ("Ananth") for many fruitful discussions during

compilation of Chapter 5. Lastly, he wishes also to express his appreciation to J. V. Gruber who, as coeditor of this book and author of two chapters and in many other ways, played a key role in making this undertaking a reality.

Dr. Gruber would like to recognize the friendship and professional relationship which has developed with E. D. Goddard as a result of this undertaking, and to express his appreciation for being invited to become a part of this project. In addition, he wishes to recognize the help that Freida DeBaro provided in completing the chapters he worked on. Her assistance was invaluable. He would also like to thank Frank J. Freiler and the Amerchol Corporation for giving him the opportunity to work on this volume. Both editors thank Sandra Beberman for her help in making the project move along quickly and professionally. Dr. Gruber is indebted to Lori Riday for her patience and understanding as this project borrowed many weekends of personal quality time. He would like to dedicate his efforts on this book to his family and especially to his brother Steve Gruber.

E. Desmond Goddard
James V. Gruber

Contents

<i>Series Introduction</i>	<i>Eric Jungermann</i>	<i>iii</i>
<i>Preface</i>	<i>E. Desmond Goddard and James V. Gruber</i>	<i>v</i>
<i>Contributors</i>		<i>xi</i>
1 Elements of Polymer Science		1
<i>Françoise M. Winnik</i>		
2 Polymer Adsorption: Fundamentals		51
<i>Timothy M. Obey and Peter C. Griffiths</i>		
3 Polymeric Surfactants: Stabilization of Emulsions and Dispersions		73
<i>Th. F. Tadros</i>		
4 Polymer/Surfactant Interaction: Manifestations, Methods, and Mechanisms		113
<i>E. Desmond Goddard</i>		
5 Polymer/Surfactant Interaction in Applied Systems		181
<i>E. Desmond Goddard</i>		
6 Synthetic Polymers in Cosmetics		217
<i>James V. Gruber</i>		
7 Silicones in Cosmetics		275
<i>Marianne D. Berthiaume</i>		
8 Polysaccharide-Based Polymers in Cosmetics		325
<i>James V. Gruber</i>		
		lx

x	Contents
9 Proteins in Cosmetics	391
<i>Alessandro Teglia and Gianfranco Secchi</i>	
10 Measuring and Interpreting Polycation Adsorption	465
<i>E. Desmond Goddard</i>	
11 The Adsorptivity of Charged and Uncharged Cellulose Ethers	509
<i>E. Desmond Goddard, R. B. Hannan, and J. A. Faucher</i>	
12 Evaluation Methods for Conditioned Hair	525
<i>Hans-Dietrich Weigmann and Yashavanth Kamath</i>	
Appendix: Encyclopedia of Polymers and Thickeners for Cosmetics	571
<i>Robert Y. Lochhead and James V. Gruber</i>	
<i>Index</i>	657

Contributors

Marianne D. Berthiaume, M.Sc. Personal Care–Worldwide, Wacker Silicones Corporation, Adrian, Michigan

E. Desmond Goddard, Ph.D. Former Corporate Research Fellow, Union Carbide Corporation, Tarrytown, New York

Peter C. Griffiths, Ph.D. Department of Chemistry, Cardiff University, Cardiff, Wales

James V. Gruber, Ph.D. Amerchol Corporation, Edison, New Jersey

Yashavanth Kamath, Ph.D. TRI/Princeton, Princeton, New Jersey

Robert Y. Lochhead, Ph.D. Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi

Timothy M. Obey, Ph.D. School of Chemistry, University of Bristol, Bristol, England

Gianfranco Secchi Kelisema Italy, Tavernerio, Italy

Th. F. Tadros, Ph.D. Department of Chemical Engineering, Imperial College, London, England

Alessandro Teglia, Ph.D. Kelisema Italy, Tavernerio, Italy

Hans-Dietrich Weigmann, Ph.D. TRI/Princeton, Princeton, New Jersey

Françoise M. Winnik, Ph.D. Department of Chemistry, McMaster University, Hamilton, Ontario, Canada



Taylor & Francis

Taylor & Francis Group

<http://taylorandfrancis.com>

Principles of Polymer Science and Technology in Cosmetics and Personal Care



Taylor & Francis

Taylor & Francis Group

<http://taylorandfrancis.com>

Elements of Polymer Science

Françoise M. Winnik

McMaster University, Hamilton, Ontario, Canada

I. INTRODUCTION

Polymers are molecules consisting of a large number of identical low molar mass units, named repeat units, that are connected covalently. If -A- is the base unit, then a polymer molecule or macromolecule is represented by:



where n is an integer, called degree of polymerization of this macromolecule. Before 1930, polymer molecules were generally considered as physical aggregates of unchanged monomer molecules $(A)_n$, so-called association colloids. However, already in 1920, Staudinger had postulated that these colloidal particles were composed of a single, very long molecule, a macromolecule. This revolutionary concept paved the way for synthetic organic chemists, in particular Carothers, to start building such macromolecules in a systematic way from known monomers. Since the 1930s, many thousands of polymers have been prepared, but less than 100 of them have reached the phase of large-scale industrial production. For accounts of the history of polymer science and technology, see, for example, Refs. 1 and 1a.

Polymers represent a significant share of raw materials used in the cosmetics industry. They are usually classified according to their use, such as thickening agents, film formers, resinous powders, and humectants. Thickening agents are used to adjust the viscosity of products to make them easy to use and to maintain the product stability. For example, they are used to ensure the stability of milky lotions and liquid foundations by preventing the separation of emulsified particles and powders. Thickening agents polymers are in widespread use for this specific purpose. Natural polymers, gums and resins, have been used in the industry since the early 1940s as water-soluble binders, thickeners, and film-forming agents. In today's products they are added to many cosmetics formulations to fulfill these various functions, but often they are used simply because of the growing consumer demand for "natural products." There are drawbacks, however, to the use of polymers isolated from natural sources: they vary in purity and physical appearance, and they are relatively expensive, compared to common synthetic polymers. Problems securing

stable supplies coupled with variations in viscosity and microbial contamination led to a change to synthetic or semisynthetic substitutes. Synthetic or semisynthetic polymers, which are chemically modified natural polymers, have been developed to match the properties of gums and resins. Today, the industry is driven by a need of improved formulations, attainable through the use of current synthetic methodology and through the understanding of the molecular interactions between the polymers and the other components of a care product.

This chapter covers the chemistry, physical properties, and thermodynamics of polymers. First are discussed various methods of macromolecule preparation. Next are discussed the physical properties of polymers in the bulk, with emphasis on the morphology and rheology of polymeric materials. Finally, several aspects of polymer solutions are discussed, including their thermodynamics and rheological properties, which will be related to molecular parameters such as chain conformation. Current theories that account for the properties of macromolecules in the bulk and in solution are presented briefly. The reader is encouraged to seek further information in specialized texts (2–7), dictionaries (8), and encyclopedia (9–11).

A. Natural and Synthetic Polymers

1. Biopolymers

Proteins, polysaccharides, natural rubber, and gums are all natural polymers. The repeat units in proteins are amino acids. Nucleic acids are composed of nucleotides and polysaccharides consist of sugar units.

a. Proteins and Polypeptides. Amino acids in proteins are linked by an amide linkage between the amino group of one molecule and the carboxyl group of another. This amide bond is often called peptide bond (Fig. 1). There are simple proteins composed only of amino acids, such as albumin, gelatin, casein, collagen, or keratin. Other proteins contain not only amino acid residues, but also other groups such as carbohydrates in glycoproteins, or lipids in lipoproteins. Proteins that possess catalytic activity are known as enzymes.

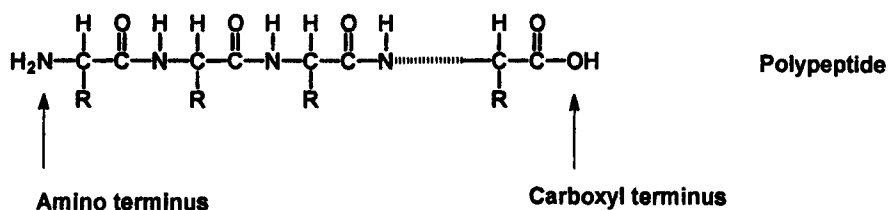
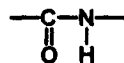
b. Polysaccharides. The repeat units of polysaccharides are simple carbohydrates (sugars) linked to each other by acetal bonds (Fig. 1). Among the important polysaccharides are homopolymers of glucose (starch, glycogen, and cellulose), mannose (guar), or amino-sugars, such as chitosan and hyaluronan. Polysaccharides are important materials of the cosmetics industry. Their chemistry and physical properties are presented in Chapter 8.

2. Synthetic Polymers

Carothers, in 1929, classified synthetic polymers into two classes, according to the method of their preparation, i.e., condensation polymers and addition polymers. In polycondensation, or step-growth polymerization, polymers are obtained by reaction between two polyfunctional molecules and elimination of a small molecule, for example water. Typical condensation polymers are shown in Figure 2. Addition (or chain reaction) polymers are formed from unsaturated monomers in a chain reaction. Examples of addition polymers are shown in Figure 2.

We will conform to Carothers' classification in the sections devoted to the preparation of synthetic polymers. However, when considering the application of polymers it is more useful to consider the following three categories: (1) *plastics*, which include thermosetting resins, such as urea resins, polyesters, or epoxies, and thermoplastic resins, such as poly-

Proteins and Polypeptides:



Polysaccharides

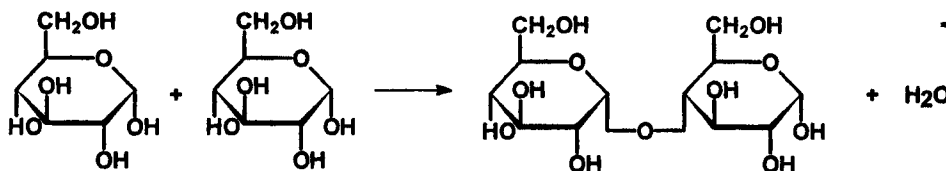
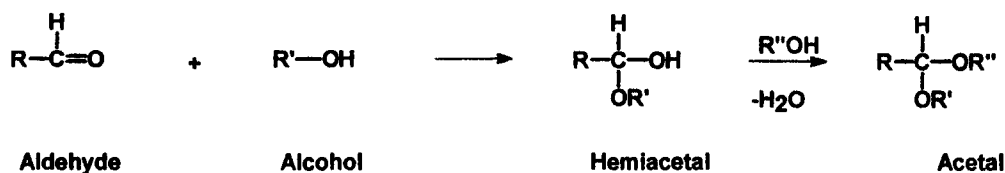
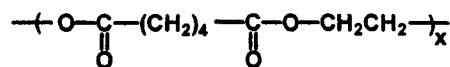
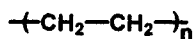
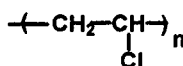
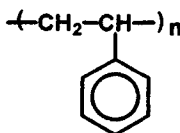
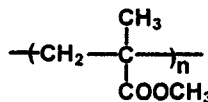


Figure 1 Chemical structures of natural polymers.

Condensation Polymers:**Polyester (fiber)****Polyurethane (fiber)****Polyurea****Addition Polymers****Polyethylene****Poly(vinyl chloride)****Polystyrene****Poly(methyl methacrylate)****Figure 2** Chemical structures of synthetic polymers.

ethylene, polystyrene, or poly(propylene); (2) *fibers*, which include cellulose, such as rayon and acetate, and noncellulosic polymers, such as polyester and nylon; and (3) *rubbers*, for example styrene-butadiene copolymer.

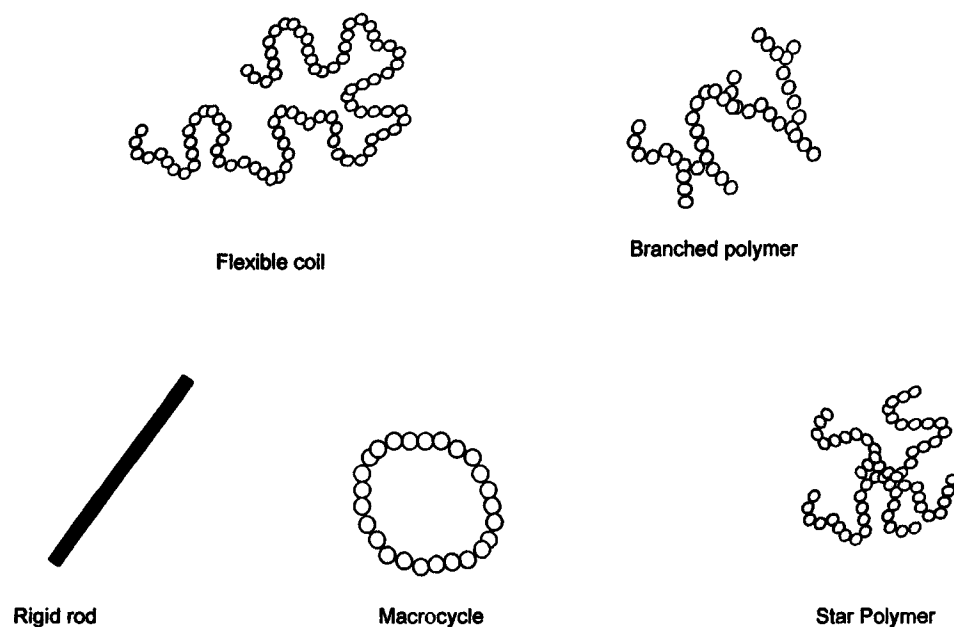
B. Definitions and Nomenclature

Homopolymers are derived from one type of monomer, whereas copolymers require two or more species of monomers. Copolymers are distinguished according to the sequence

Table 1 Sequence of Monomer Units in Various Copolymers

Copolymer type	Schematic composition
Statistical or random	
Alternating	
Diblock	
Triblock	
Graft	

of the various monomer units. They are subdivided into the major classes listed in Table 1. The simplest polymers consist of regular macromolecules, with only one repeat unit in a single sequential arrangement. Examples are poly(acrylic acid), polystyrene, and polyethylene (Fig. 2). The constitutional units form a linear chain. Cyclic polymer molecules result if the two ends of a linear macromolecule are connected. They are called “macro-cycles” (12). Small amounts of cyclic molecules are often formed as by-products during the synthesis of linear chains. Combinations of linear molecules, of linear molecules with cyclic molecules, and of cyclic macromolecules themselves lead to a great variety of molecular architectures (Fig. 3).

**Figure 3** Major macromolecular architectures.

Linear chains may also be arranged at short intervals along a single main chain via trifunctional branch points. These “comb” polymers can be synthesized by polymerization of macromers (a monomer consisting of a polymerizable group linked to a short polymer chain) or by grafting (13). Branched polymers contain branch points (junctions) that connect three or four subchains, which may be side chains or parts of a main chain. Polymers are statistically branched if side chains of different lengths are irregularly distributed along the main chain. These polymers resemble trees. In star polymers (14) three or more branches sprout from a common core. Star polymers with multifunctional ends on the arms can add additional monomers. The resulting polymers, known as dendrimers (15), can be considered as tree polymers with regular sequences of branches or star polymers with subsequent secondary branches.

In cross-linked polymers, all molecules of a sample are interconnected by many bonds, resulting in a single, “infinitely large” molecule. Networks can be generated by intermolecular covalent bond or by physical junctions, such as ion clusters, crystallites, or microphases. Physical (noncovalently bound) networks can *in principle* be dissolved by a solvent, whereas chemical (covalently bound) networks are insoluble in all solvents. The chemical properties of polymer networks depend strongly on the chemical structure of the chemical chain and the type of junction. The mechanical properties are primarily dictated by the cross-link density and by the mobility of the chain segments. Networks may thus be soft, elastic, brittle, or hard. Two independent networks may interpenetrate to form interpenetrating networks (IPN) (16). Nail enamels are examples of physical networks formed upon solvent evaporation, with no chemical cross-linking during drying but only physical interactions among their polymer constituents, primarily nitrocellulose and synthetic resins.

A classification of polymers especially useful in the case of water-soluble polymers is based on the electric charge born by the macromolecule. Electrically neutral water-soluble polymers include various polysaccharides, mostly cellulose ethers, polyacrylamides, and certain polyethers, such as poly(ethylene glycols). Polyelectrolytes are water-soluble polymers with many electrically charged groups per molecule. They form polyions on dissociation. These polyions may be polyanions with negative charges as in dissociated poly(acrylic acid) $\text{—}[\text{CH}_2\text{—CH}(\text{COO}^-)]_n\text{—}$ or polycations as in protonated poly(vinylamine), $\text{—}[\text{CH}_2\text{—CH}(\text{NH}_3^+)]_n\text{—}$. They may also be polysalts, as in the sodium salt of poly(acrylic acid), $\text{—}[\text{CH}_2\text{—CH}(\text{COONa})]_n\text{—}$. Polyions should be distinguished from macroions, which carry only one ionic group, usually at one chain end. Water-insoluble polymers with relatively few ionic groups in the chain are known as ionomers.

II. PREPARATIONS OF MACROMOLECULAR COMPOUNDS

Synthetic polymers are prepared by one of two fundamentally different approaches: (a) polymerization of monomer molecules or (b) modification of existent macromolecules into macromolecules of different constitution, a process known as polymer analog reaction (17–19). Both methods are described briefly in this section, starting with the polymerization reactions, which can proceed via two different processes, condensation reactions in step-growth polymerizations and addition reactions in chain-growth polymerizations.

A. Step-Growth Polymerization

The term “step-growth polymerization” refers to the process in which the polymer molecular weight increases in a slow, step-like manner as reaction time increases. This polymeri-

The polycondensation technique can also be applied to prepare organic-inorganic polymers. The most important such polymers are the polysiloxanes, also known as silicone polymers such as dimethicone, based on the —Si—O— linkage present in glass or sand (see Chapter 7). They are made by polymerization of a low-molecular-weight cyclic analog, such as octamethylcyclotetrasiloxane. When this compound is heated above 100°C with a trace of an acid or base, it polymerizes to form a highly viscous liquid. Although the dimethylsiloxane structure forms the basis of most silicone polymers, other substituents have also been introduced as cosubstituents. These include vinyl, ethyl, phenyl, and *n*-alkyl groups. Polysiloxanes are among the most flexible macromolecules known. They also repel water. Partly because of this property, they are used in protective hand-and-body lotions and creams. They are incorporated also in hair-care formulations to improve luster and sheen.

The melt technique, where an equimolar mixture of two monomers is heated, possibly in the presence of a catalyst. It is an equilibrium process in which the polymer is formed by driving the reaction to completion by removal of the by-products, such as water or hydrochloric acid.

Polyester (Dacron)

$$n \text{ CH}_3\text{CH}_2\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{OCH}_2\text{CH}_3$$

Diethylterephthalate

$$+ n \text{ HOCH}_2\text{CH}_2\text{OH}$$

Ethylene glycol

$$\longrightarrow \cdots \text{CH}_2\text{CH}_2\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{OCH}_2\text{CH}_2\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{OCH}_2\text{CH}_2\text{O} \cdots$$

Nylon 66

$$\text{HO}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})-\text{OH}$$

Adipic Acid

$$+ n \text{ H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$$

Hexamethylene diamine

$$\longrightarrow \cdots \left(\text{NH}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})-\text{NH}(\text{CH}_2)_6 \right)_n \cdots$$

Polycarbonate

$$n \text{ HO}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{OH}$$

Bisphenol A

$$+ n \text{ COCl}_2$$

Phosgene

$$\longrightarrow \cdots \left(\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{C}(=\text{O})-\text{O} \right)_n \cdots$$

Figure 4 Synthetic scheme for the preparation of condensation polymers.

solved in a solvent, which should also be a solvent for the polymer. It is an equilibrium reaction, driven to completion by removal of the by-products, but it has to be carried out at temperatures lower than melt polycondensations.

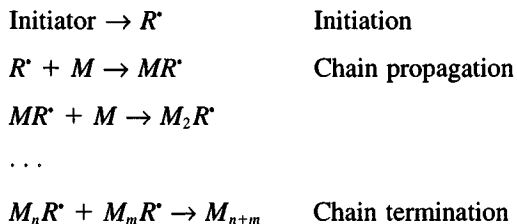
The interfacial technique (20), which is a heterophase process where two fast-reacting reactants are dissolved in a pair of immiscible solvents, one of which is usually water. The aqueous phase contains a diol or a diamine; the organic phase contains a diacid chloride dissolved in a solvent such as dichloromethane, toluene, or diethyl ether. Condensation occurs at the water/organic solvent interface often in the presence of a phase transfer catalyst.

B. Chain-Growth Polymerization

In this process, the only chain-extension reaction is that of attachment of a monomer to a growing “active” chain. The active end group may be a free radical, an anion, or a cation. In contrast to step-growth polymerization, some high-molecular-weight polymer is formed in the early stage of the addition polymerization.

1. Free-Radical Polymerization (21)

The general scheme for free-radical polymerization can be expressed as follows:



where M represents the monomer molecule and R^* a free radical produced in the initial step. Commonly used initiators are peroxides, such as potassium persulfate (soluble in water) or benzoyl peroxide (soluble in organic solvents), and aliphatic azo compounds, such as azobisisobutyronitrile (AIBN).

Various experimental techniques may be used to carry out free radical polymerizations. The choice of method is guided on the one hand by the solubility of the monomers and polymers and on the other hand by the preferred isolation method for the polymer. Common techniques are:

1. Bulk polymerization, where the reaction is carried out without solvent.
2. Solution polymerization, which is done in an inert liquid that dissolves both the monomer and the polymer.
3. Precipitation polymerization, which takes place in an inert liquid that dissolves the monomer, but not the polymer. The polymer is isolated by filtration or decantation.
4. Suspension polymerization, which is used with water-insoluble monomers suspended in water as droplets. Coalescing of the droplets is prevented by use of small amounts of a stabilizer, usually a water-soluble polymer, such as poly(vinyl alcohol). The polymer is isolated in the form of discrete particles 10–1000 nm in diameter.
5. Emulsion polymerization (22), which takes place in a suspension in water of a

water-insoluble monomer in the presence of a surfactant and a water-soluble initiator. Unlike suspension polymerization, this technique produces polymer in the form of a latex, or stable dispersion in water of polymer particles ranging in size from 0.05 to 5 nm.

2. Ionic Polymerization

Ionic polymerizations are initiated by ionic species. The active chain end is an ion, either a carbanion, C^- , in the case of anionic polymerizations (23,24) or a carbocation, C^+ , in the case of cationic polymerizations (25,26). They have to be carried out in organic solvents under strictly anhydrous and oxygen-free conditions. Anionic polymerizations are performed with monomers that contain a double bond substituted with an electron-withdrawing group, such as styrene and various acrylic monomers, and also with oxiranes, such as ethylene oxide, which polymerize by a ring-opening mechanism. Macroanions in solution continue to grow until all initially present monomer molecules are consumed. Addition of new monomer leads to further polymerization. Such polymerizations without internal or external termination reaction are called living polymerizations. They are useful to synthesize homopolymers with narrow-molecular-weight distribution and star or block copolymers.

Cationic polymerizations are started by reaction of electrophilic initiator cations with electron-donating monomer molecules. Catalysts are Lewis acids and Friedel-Crafts catalysts, such as aluminum trichloride ($AlCl_3$), and strong acids, such as sulfuric acid (H_2SO_4). Monomer molecules able to undergo cationic polymerization include electron-rich olefins, such as vinyl aromatics and vinyl ethers, and ring compounds, such as ethylene oxide and tetrahydrofuran.

Other types of chain-growth polymerizations include: (a) insertion polymerizations, such as the Ziegler-Natta process used in the preparation of polyethylene and metathesis polymerizations (27,28), and (b) group transfer polymerizations, a process in which an initiator molecule transfers its active group to a monomer molecule under the action of a catalyst.

C. Polymerization Kinetics

Condensation reactions follow kinetic schemes similar to those of small molecule reactions. They are simple first-order, second-order, etc. reactions. In contrast, the kinetics of chain reactions, such as free-radical polymerization or ionic polymerization, are much more complicated.

1. Condensation Reactions (29)

We will discuss the case of polyesterifications, typical condensation reactions that take place by reaction of a diol (A, $HO-R-OH$) and a diacid (B, $HOOC-R'-COOH$):



The experimental rate of polycondensation polymerization is given by the following expression (Eq. 1), where k is the rate constant:

$$\frac{-d[B]}{dt} = k[B]^2[A] \quad (1)$$

If $[B] = [A] = c$, where c is the monomer concentration at time t , then the rate expression can be written as Eq. 2. Upon integration of the rearranged form (Eq. 3), we obtain Eq.

4, which is conveniently expressed in terms of P , the extent of reaction, defined as the fraction of functional groups that has reacted at time t . The concentration c can be expressed as a function of $1 - P$, the fraction of unreacted A and c_0 , the initial concentration. Substituting c into Eq. 4, we obtain Eq. 5. A plot $1/(1 - P)^2$ versus time should be linear, with a slope of $2c_0^2 k$, from which k can be determined.

$$\frac{-dc}{dt} = kc^3 \quad (2)$$

$$\frac{-dc}{c^3} = kdt \quad (3)$$

$$2kt = \frac{1}{c^2} + \text{constant} \quad (4)$$

$$2c_0^2 kt = \frac{1}{(1 - P)^2} + \text{constant} \quad (5)$$

The number average degree of polymerization, DP_N , for condensation reactions can be expressed as:

$$DP_N = \frac{\text{number of original molecules}}{\text{number of molecules at time } t} = \frac{N_0}{N} = \frac{c_0}{c} = \frac{c_0}{c_0(1 - P)} = \frac{1}{1 - P} \quad (6)$$

For an essentially quantitative synthesis of polyesters, where $P = 0.9999$, the DP_N value calculated from Eq. 6 is equal to 10,000.

2. Free-Radical polymerizations

Free-radical polymerizations involve the simultaneous generation and disappearance of initiator radicals, monomer radicals, and macroradicals. After a few seconds the total concentration of all radicals becomes constant. This steady state or stationary state is obtained at very small monomer conversions. In terms of kinetics, the total free-radical concentration becomes stationary when the rate of radical formation equals the rate of radical disappearance (Eq. 7).

$$R_d = \frac{-d[I]}{dt} = k_d[I] \quad (7)$$

Initiators I dissociate with a rate R_d giving two initiator radicals I' ; therefore, the rate of radical formation R_r is double the rate of initiator decomposition:

$$R_r = \frac{d[I']}{dt} = 2k_d[I] = 2R_d \quad (8)$$

However, since the initiator molecule dissociates in a "cage" surrounding monomer and solvent molecules, some of the newly formed radicals recombine immediately. Due to this cage effect, only a fraction f of initiator radicals I' react with monomer in the start reaction: $I' + M \rightarrow IM'$ (st). The rate of radical formation is thus $R_r = 2fk_d[I]$. Monomer radicals are generated with a rate R_{st} , which is much greater than the rate R_d of initiator decomposition:

$$R_{st} = \frac{-d[I']}{dt} = k_{st}[I'][M] \quad (9)$$

Initiator radicals are consumed as fast as they are generated. The rate-determining step is thus the initiator decomposition. Overall, the instantaneous concentration of initiator radicals and the rate of the start reaction are given by Eq. 10 and 11, respectively:

$$\frac{d[I^*]}{dt} = 2fk_d[I] - k_{st}[I^*][M] = 0 \quad (10)$$

$$R_{st} = k_{st}[I^*][M] = 2fk_d[I] \quad (11)$$

Per initiator radical, only one monomer is consumed in the start of the reaction, but many hundreds in the subsequent propagation reaction. Monomers are thus practically only consumed by propagation. Their consumption by start, termination, and transfer to monomer is negligible. For irreversible reactions, the gross rate of polymerization, R_{gross} , thus approximates R_p (Eq. 12):

$$R_{gross} = \frac{-d[M]}{dt} \approx R_p = k_p[P^*][M] \quad (12)$$

The following assumptions underlie the ideal polymerization kinetics:

1. Only initiator decomposition and start, propagation and termination reactions are considered.
2. All reactions are irreversible.
3. The effective concentration of initiator radicals is steady.
4. The concentration of macroradicals is stationary.
5. Termination occurs only by mutual deactivation of two macroradicals; hence:

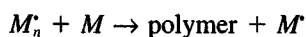
$$R_{gross} \approx \frac{-d[M]}{dt} = k_p \left(\frac{2fk_d}{k_t} \right)^{1/2} [M][I]^{1/2} \quad (13)$$

The rate of polymerization $R_{gross} \approx R_p$ is thus directly proportional to the monomer concentration, under ideal kinetics conditions. Larger initiator concentrations lead to higher polymerization rates and to lower kinetic chain length, ν , defined as the number of monomer molecules that are added to an initiator radical before the resulting macroradical is terminated. The kinetic chain length is given by the ratio of the rate of propagation, R_p , to the sum of the rates of all terminations; the type of termination does not matter (Eq. 14).

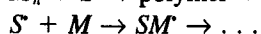
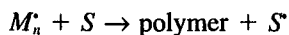
$$\nu = \frac{R_p}{\sum_i R_{t,i}} \quad (14)$$

The ideal polymerization kinetics are rarely followed in practical polymerizations. One complication is related to the “gel effect”: toward the end of a polymerization, the reaction mixture becomes extremely viscous, resulting in a rapid increase in the rate of polymerization, R_p , as a result of the decrease in k_t . Another complication results from undesired chain transfer reactions, which terminate the polymerization prematurely, and consequently, polymers of molecular weights lower than predicted will be formed. There are several mechanisms for chain transfer, for example:

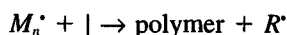
Chain transfer to monomer:



Chain transfer to solvent:



Chain transfer to initiator



Chain transfer agents may be added intentionally to a polymerization mixture as a way of controlling the (low) molecular weight of a polymer. Such compounds are known as “regulators.” When used in large amounts, they are called telogens, since they produce low-molecular-weight polymers, or telomers. Examples of chain transfer agents are mercaptans, alkyl halides, phenols, and alcohols. The chain transfer reaction decreases the average chain length in accordance with the concentration of chain transfer agent $[S]$. The deMayo equation (Eq. 15) can be used to predict the molecular weight of a polymer upon addition of a chain transfer agent:

$$\frac{1}{DP} = \frac{1}{DP_0} + C_s \frac{[S]}{[M]} \quad (15)$$

In this equation, DP and DP_0 are the degrees of polymerization of the polymer with and without chain transfer agent, respectively, $[S]$ is the concentration of chain transfer agent, $[M]$ is the monomer concentration, and C_s is the chain transfer constant or the ratio of the rate of termination by transfer to the rate of propagation. This constant is related to relative bond strengths in the chain transfer agent and the stability of the new free radical produced.

D. Polymer Analog Reactions (30,31)

In polymer analog modifications, a reaction takes place along the polymer chain to convert certain chemical functionalities into different functions, without altering the degree of polymerization of the starting polymer. This approach is particularly useful for the transformation of naturally occurring polymers, but it is applied also to modify synthetic polymers. For example, saturated polymers, such as polyethylene, can be chlorinated or oxidized. Polyenes, such as rubber, can be hydrogenated, halogenated, or epoxidized. Pendant groups, such as the ester groups in poly(vinyl acetate), can be hydrolyzed by transesterification with butanol or methanol to yield poly(vinyl alcohol). The latter can be modified further by reactions typical of alcohols, such as ether formation, esterification, or formation of acetal by treatment with butyraldehyde to form poly(vinyl butyral). The hydroxyl groups in polysaccharides are converted to corresponding ethers and esters. Cellulose ethers, for example, result from the reaction of cellulose with ethylene oxide or propylene oxide (see Chapter 8). Hydrophobically modified polymers such as the cationic cellulose ether derivative, Quatrisoft LM-200 (Amerchol), are obtained via polymer analog reactions (see later chapters).

Esters, amides, or nitriles pendant groups can be converted to the corresponding car-

boxylic acids. Poly(carboxylic acids) may be dehydrated upon heating to poly(carboxylic acid anhydrides). Phenyl pendant groups, such as those in polystyrene, undergo the characteristic reactions of aromatic rings, such as alkylation, halogenation, or sulfonation. In all cases, competing polymer degradation may take place. It is important to assess whether the molecular weight of the polymer is affected by the chemical transformation.

III. DISTRIBUTION OF MOLECULAR WEIGHTS

With the exception of naturally occurring proteins, all polymers are mixtures of many molecular weights. They are polydisperse: in any polymer sample, the individual polymer chains do not all have the same size. The distribution of molecular weights has been shown to be important in many applications, including the flow of melts or solutions, adhesion, flocculation, or aging behavior. Because of the difficulties involved in measuring a distribution of molecular weights in detail, several mathematical forms are used and related to the averages measured experimentally. As described below, the type of average determined will depend on the experimental method used to measure it.

A. Types of Molecular Weight (32,33)

The simplest average is the number-average molecular weight, M_n , where n_i is the number of species with molecular weight M_i (Eq. 16). Physically, the number-average molecular weight can be determined by any technique that “counts” molecules based on the colligative properties of solutions (34), such as freezing point depression, boiling point elevation, and osmometry.

The weight-average molecular weight, M_w , is given by Eq. 17, where wt_i is the weight of all species with molecular weight M_i . Weight-average molecular weights are determined from techniques such as size-exclusion chromatography, in which each macromolecule makes a contribution to the measured value relative to its size. The weight average is more dependent on the number of heavier molecules than is M_n , which depends simply on the total number of polymers. The z-average molecular weight M_z , obtained, for instance, by ultracentrifugation techniques, is defined by Eq. 18:

$$M_n = \frac{\sum_i n_i M_i}{\sum_i M_i} \quad (16)$$

$$M_w = \frac{\sum_i wt_i M_i}{\sum_i wt_i} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \quad (17)$$

$$M_z = \frac{\sum_i wt_i M_i^2}{\sum_i wt_i M_i} = \frac{\sum_i n_i M_i^3}{\sum_i n_i M_i^2} \quad (18)$$

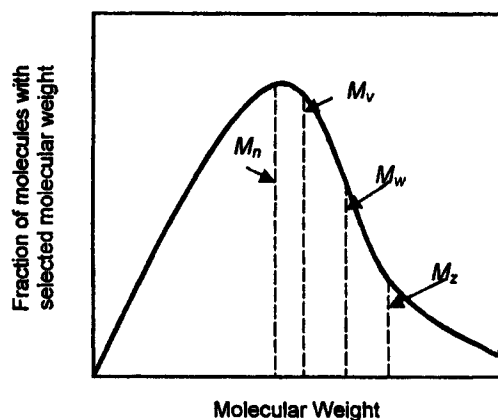


Figure 5 Molecular weights of polymers.

For systems heterogeneous in size, the three average molecular weights are such that $M_n < M_w < M_z$ (Fig. 5). The ratio M_w/M_n , called the polydispersity, is a useful measure of the spread of a polymer distribution. Larger values of M_w/M_n (>2) indicate a very wide spread with substantial amounts of material at both extremes. When $M_w/M_n \sim 1$, all polymer molecules have the same molecular weight.

Viscosity measurements yield yet another average molecular weight, M_v . Its value is usually intermediate between M_n and M_w . It is obtained from the Mark-Houwink-Sakurada equation (see below).

B. Experimental Methods for Determining Molecular Weight and Molecular Weight Distribution (35)

Absolute methods yield experimental data that can be used to determine molecular weights without any assumption about the polymer structure. Listed below are some of the well-known experimental techniques for determining absolute molecular weights of polymers:

1. Methods yielding number-average molecular weights: osmotic pressure, melting point depression, boiling point elevation
2. Methods yielding weight-average molecular weights: diffusion, light scattering
3. Methods yielding z-average molecular weights: ultracentrifugation

Relative methods for determining molecular weights require calibrations with standards of known molecular weight and molecular weight distribution. They are influenced by the chemical and physical nature of the polymer and its interactions with solvent molecules. Gel permeation chromatography, fractional precipitation, and electrophoresis are used most frequently, with electrophoresis particularly useful to determine the molecular weight of proteins.

Gel permeation chromatography (GPC) (36–38) is a type of liquid-solid elution chromatography that separates polydisperse samples into fractions by means of the sieving action of a cross-linked gel. Such gels, which serve as the stationary phase, are commer-

cially available with a wide distribution of pore sizes ($1-10^6$ nm). Since the smaller molecules permeate the gels preferentially, the larger molecules elute faster than the smaller ones. Therefore, molecules are separated on the basis of their size. The separation can be carried out with polymers soluble in organic solvent, with calibration against polystyrene standard samples, or with water-soluble polymers, using poly(ethylene oxides) or dextrans standards.

Equivalent methods require information about the chemical structure of a polymer. End-group determinations allow the calculation of relative molar masses if the constitution of end groups is known (39). The sensitivity of end-group determinations depends on the experimental methods. ^{13}C NMR spectrometry can yield information on polymers of molecular weight up to ~ 8000 . Titrations are applicable if the end group is either an acid or a base. They yield molecular weights up to $\sim 40,000$.

Mass spectrometry is the only method that delivers the mass of a molecule, as the ratio of molecular mass to the number z of charges per molecule. Until recently mass spectrometry was of little use for the analysis of polymers, since polymers could not be vaporized in the spectrometer without thermal decomposition. However, newer techniques, such as matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS), which uses a volatile carrier, "the matrix," to transport nonvolatile polymers to the magnetic field of the spectrometer, allow the determination of molecular masses of polymers up to 200,000.

IV. PHYSICAL PROPERTIES OF POLYMERS IN THE BULK

A. Polymer Morphology (40–42)

When polymers are irradiated by a beam of X-rays, scattering produces diffuse halos on the screen for some polymers, whereas for others a series of sharply defined rings superimposed on a diffuse background is recorded. The former pattern is characteristic of amorphous polymers and illustrates the fact that a limited amount of short-range order exists in all polymer solids. The latter pattern indicates considerable three-dimensional order and is typical of polycrystalline samples containing a large number of unoriented crystallites associated with amorphous regions. No bulk polymer is completely crystalline. Some commercial polymers, for example polyethylenes, are highly crystalline materials with well-defined crystalline morphology consisting of chain-folded lamellae joined in supramolecular structures called "spherulites." Another important polymer, poly(vinylchloride), has a very low level of crystallinity. Many other polymers, such as atactic polystyrene or poly(methyl methacrylate), are totally amorphous. In each case the presence of crystalline structure controls to a significant level the physical, thermal, and mechanical properties of the material. Polymer microstructure depends first on molecular parameters, such as the chemical structure of the base unit and the molecular weight of the polymer, but it is influenced also by the processing techniques employed to manufacture a specific material.

To appreciate how polymers attain their morphology, let us consider what may happen when an initially molten polymer is cooled down gradually. In the melt, a polymer can be viewed as made up of highly entangled chains that have a considerable segmental motion and conformational freedom. The polymer melt behaves like a liquid. As the temperature decreases, the viscosity of the molten polymer increases. When the temperature has come down far enough, individual chains undergoing the strongest attraction start

to solidify. These chains separate from the molten polymer as crystallites. Then, as the temperature decreases further, the remaining polymer chains solidify as amorphous unorganized domains outside the domains of crystallinity (Fig. 6). The difference between flexible and rubbery polymeric materials arises from the significant degree of crystallinity of the former, as opposed to an almost totally amorphous state in the latter.

1. The Amorphous State

Polystyrene and poly(methyl methacrylate) are typical glassy polymers (43) at ambient temperature. They are rigid and optically transparent materials. As thin samples, they become slightly flexible. They have moderate strength and some impact resistance, but can be shattered quite easily. If a small stress is applied, the glass exhibits a rapid elastic response resulting from local deformations. However, the sample has no means of dissipating large stresses other than by rupture. A polymer glass is therefore brittle and prone to fractures.

Elastomers (44) exhibit many of the properties of liquids: they change shape and flow readily when subjected to weak forces. But unlike liquids they reassume their original shape once the distorting force has been removed. This unique behavior is a consequence of the large size of polymer chains, compared to typical low-molecular-weight liquids, coupled with a high mobility of backbone bonds, compared to glassy polymers. The ability of an elastomer to reassume its original shape after deformation can be attributed to en-

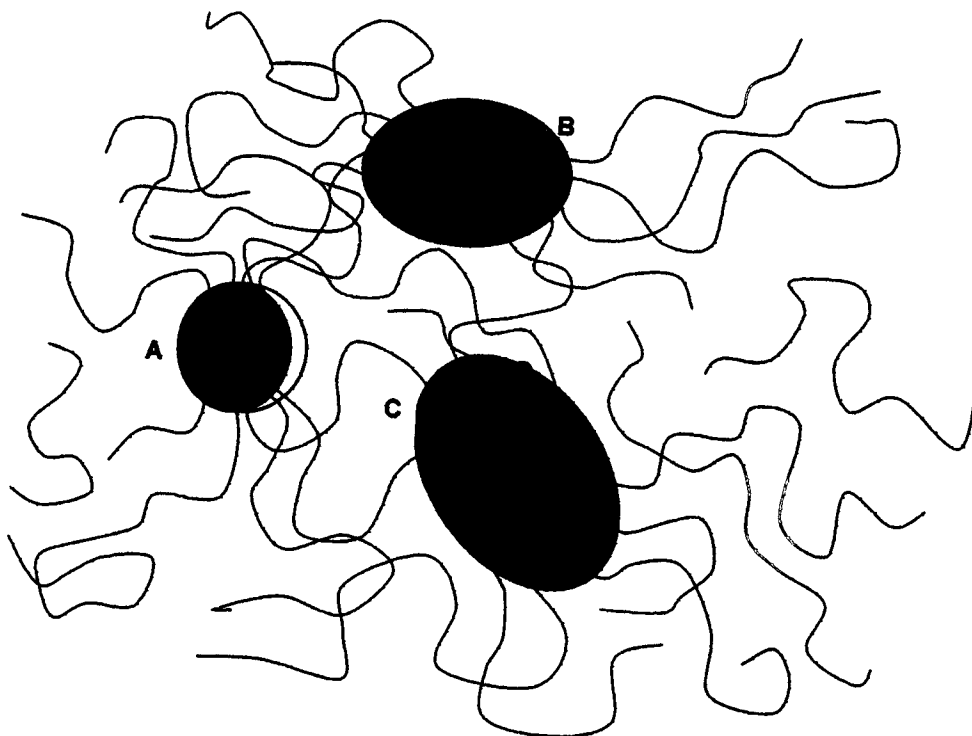


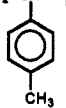
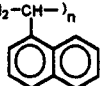
Figure 6 Schematic representation of a thermoplastic polymer (semicrystalline state). Each line corresponds to the backbone of polymer chain. The encircled zones A, B, and C represent zones of crystallinity.

tropic features: a stretched chain will tend to contract to allow maximization of the entropy, once the tension is released.

At low enough temperatures, all amorphous polymers are stiff and glassy. On warming, polymers soften in a characteristic temperature range, known as the glass transition temperature (T_g) range (45–47). The transition from the glass to the rubber-like state is an important characteristic of amorphous polymers, because it marks the region of dramatic changes in their physical properties, such as stiffness and elasticity. For most common polymers this temperature ranges between -120°C and $+200^\circ\text{C}$. Structural factors influencing the magnitude of T_g include: (1) the molecular structure in particular possible steric effects, (2) the chain flexibility, (3) the molecular weight, and (4) the degree of branching and cross-linking. The relative importance of each of these factors is illustrated by the examples listed in Table 2.

a. Measurement of the Glass Transition Temperature. The glass temperature of a polymer can be observed experimentally by measuring basic thermodynamic, physical, mechanical, or electrical properties as a function of temperature. Thermal methods are

Table 2 Relationships Between the Structure of Polymers and Their Glass Transition Temperature (T_g)

Polymer structure	Main chain unit	$T_g(^{\circ}\text{C})$
<i>Chain flexibility</i>		
Polyethylene	$-(\text{CH}_2\text{CH}_2)_n-$	-125
Polydimethylsiloxane	$-(\text{O}-\text{Si}(\text{CH}_3)_2)_n-$	-123
Polyethylene oxide	$-(\text{CH}_2\text{CH}_2\text{O})_n-$	-47
<i>Steric restrictions and substituent sizes</i>		
Polyethylene	$-(\text{CH}_2\text{CH}_2)_n-$	-125
Polystyrene	$-(\text{CH}_2\text{CH}(\text{C}_6\text{H}_5))_n-$	+100
Poly(4-methylstyrene)	$-(\text{CH}_2-\text{CH})_n-$ 	+115
Poly(α -vinyl naphthalene)	$-(\text{CH}_2-\text{CH})_n-$ 	+135
<i>Size of the substituent group</i>		
Poly(methyl methacrylate)	$-(\text{CH}_2\text{CH}(\text{COOCH}_3))_n-$	+105
Poly(ethyl methacrylate)	$-(\text{CH}_2\text{CH}(\text{COOCH}_2\text{CH}_3))_n-$	+65
Poly(propyl methacrylate)	$-(\text{CH}_2\text{CH}(\text{COOCH}_2\text{CH}_2\text{CH}_3))_n-$	+35
<i>Interchain forces (H-bonds, dipole-dipole interactions)</i>		
Polyethylene	$-(\text{CH}_2\text{CH}_2)_n-$	-125
Polyoxymethylene	$-(\text{OCH}_2)_n-$	-85
Polypropylene	$-(\text{CH}_2\text{CH}(\text{CH}_3))_n-$	-15
Polyvinylchloride	$-(\text{CH}_2\text{CHCl})_n-$	+80
Polyacrylonitrile	$-(\text{CH}_2\text{CH}(\text{CN}))_n-$	+105
Polycaprolactone	$-[(\text{CH}_2)_5-\text{COO}]_n-$	-60
Polycaprolactam (nylon 6)	$-[(\text{CH}_2)_5-\text{CONH}]_n-$	+60

used routinely (48,49). Two closely related thermal methods dominate, an older method, differential thermal analysis (DTA), and a newer method, differential scanning calorimetry (DSC) (50). In making DTA measurements, the temperature of a sample is compared with a reference material, such as powdered alumina. Both the sample and the reference are heated at a uniform rate, typically 10–20°C/min. Since the two materials have different heat capacities, each maintains slightly different temperatures throughout the scan. The difference in temperature, ΔT , is monitored as a function of the temperature T . The glass transition temperature will be marked by a significant deviation in the otherwise smooth profile of ΔT versus temperature (or time) (Fig. 7). The DSC method uses a servo system to supply energy at a varying rate to the sample and the reference, so that the two stay at equal temperature (50). A DSC trace plots energy supplied against average temperature. The area under the peaks corresponding to the glass transition temperature can be related directly to the enthalpy change associated with the transition. Melting temperatures of crystalline polymers (see below) are also measured by DSC.

b. Molecular Interpretation of the Glass Transition (48). In the amorphous state the distribution of polymer chains in the matrix is completely random. At sufficiently high molecular weight interpenetrating chains form flow-restricting entanglements. The minimum polymer chain length, or critical molecular weight (M_c), for the formation of stable entanglements is an important characteristic of a polymer. Relatively flexible chains, such as polystyrene, have high M_c , while stiffer chains, such as polycarbonates, have relatively lower M_c . A second parameter of importance is M_e , the molecular weight between entanglements. Typically the molecular weight of commercial polymers (100,000–500,000) is much larger than M_e (10,000–30,000). Therefore, in most commercial polymers the individual chains are highly entangled. The question then arises: how can long-range motion of the chains take place as the polymer is heated through its glass transition temperature?

Several models have been proposed to describe the motion of a single polymer chain in an entangled network of chains. In the reptation model, proposed by De Gennes (51),

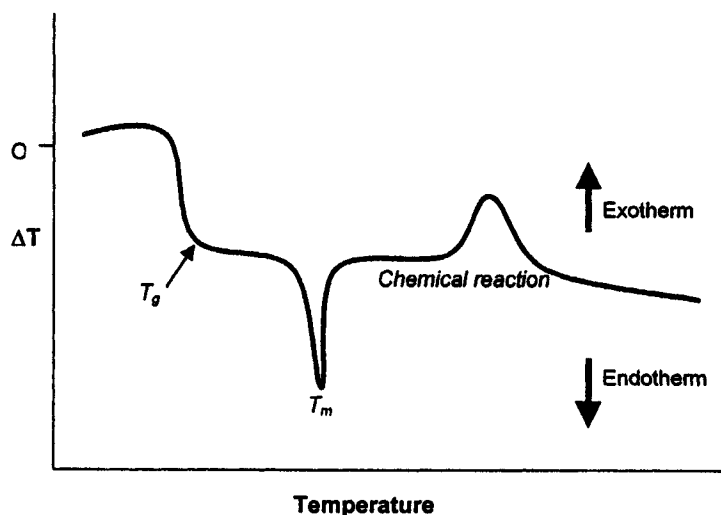


Figure 7 Schematic differential thermal analysis plot (DTA).

the chain is assumed to be contained in a hypothetical tube placed in the network. The “knots” in the network are seen as obstacles around which the chain must “wriggle” during translation. Two types of motions can be envisaged: (1) conformational changes within the confines of the tube; and (2) reptation, a snake-like motion that translates the chain within the tube until it finally escapes at the tube end (Fig. 8). The theory of reptation has been applied with large success to develop theories describing the dynamics and viscoelastic properties of entangled polymers.

The most severe mechanism for decreasing molecular freedom in a polymeric material is by chemical cross-linking: linking polymer chains through chemical bonds. This can be made either during the polymerization process, by use of polyfunctional monomers, or in a separate process, often described as a curing step (52). A number of extreme changes accompany cross-linking. If previously soluble, the polymer will no longer dissolve. In the presence of a solvent, a cross-linked polymer swells as the solvent molecules penetrate the network. A solvent-swollen polymer forms a gel. If the gel particles are very small these are called microgels, which can be viewed as tightly packed spheres suspended in solvents (53). These materials have found many applications, as support for solid-phase reactions and delivery systems (54).

2. The Crystalline and Semicrystalline States (55–58)

The formation of stable crystalline regions in a polymer requires that a closely packed arrangement of chains can be achieved in three dimensions and that a favorable change in internal energy is obtained during the crystallization process. This imposes restrictions on the type of chains that can be crystallized with ease. Polyesters, polyamides, and polyethylene, which have a high degree of symmetry, are expected to crystallize readily. General factors influencing the crystallinity of a polymer include: (1) the symmetry of the chain, (2) the occurrence of intermolecular bonding (van der Waals forces, hydrogen bonding, dipole-dipole interactions), (3) the tacticity, (4) the branching (if the chain is substantially branched the packing efficiency deteriorates), and (5) the molecular weight of the polymer.

Crystalline polymers are generally tougher, stiffer, more opaque, more resistant to solvents, and of higher density than their amorphous counterparts. The higher the degree of crystallinity, the more pronounced are these properties. The superior mechanical properties are a reflection of the greater cohesive strength arising from more effective intermolecular secondary forces among the closely packed chains. Examples of highly crystalline

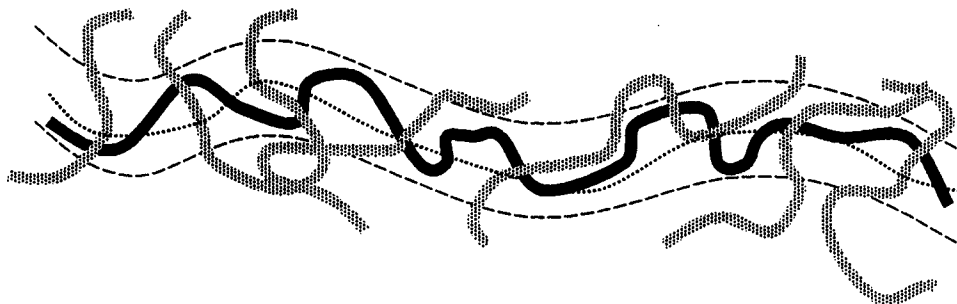


Figure 8 Reptation of a chain within a tube. (A test chain [black] reptates through a tube with “walls” formed by segments of the chains [gray]).

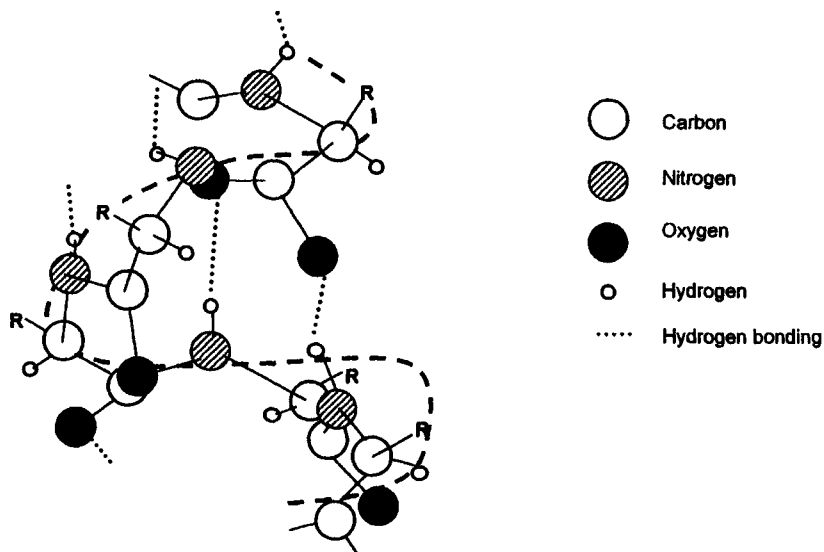


Figure 9 Section of α -helix of α -keratin.

polymers include proteins, polysaccharides, such as cellulose, and synthetic polymers, such as certain forms of polyethylene.

Proteins tend to form stable geometries, generally those that allow the greatest degree of hydrogen bonding. The conformation of a protein chain is referred to as its secondary structure. X-ray analysis, notably by Linus Pauling, has shown that a right-handed helical arrangement, called the α -helix, is probably the most important secondary structure. Such an arrangement allows room for bulky substituents present in most amino acids. It is stabilized by intramolecular hydrogen bonding between the amide nitrogen atoms and the carbonyl oxygens. A short section of the peptide chain of α -keratin, the main constituent of hair and nails, is shown in Figure 9 (59). Proteins that have predominantly small substituents, for example silk fibroin (60), can assume a configuration that is essentially an extended chain, but with some contraction so that crowding between substituents of one chain and those of a neighboring chain is minimized. The chains can lie side by side in a sheet-like arrangement, referred to as a pleated sheet or beta-arrangement (Fig. 10).

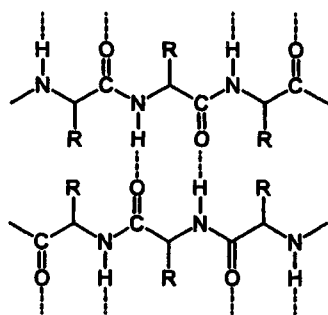


Figure 10 Pleated sheet structure (β -arrangement) of silk fibroin.

The shape of protein molecules is not given completely by their secondary structure. Sections of peptide chains may be linked chemically through sulfur bonds of cysteine groups, as in the case of keratins, or by salt bridges between carboxyl groups and ammonium groups, such as the glutamic acid-lysine links present in α -keratin (59). This overall three-dimensional structure of a protein molecule is known as its tertiary structure. In addition to tertiary structure, a protein may exhibit a quaternary structure that originates from associations of several proteins or of proteins and nonprotein substances.

B. Rheology and Mechanical Properties of Polymers (61,62)

In the course of their use, polymers are subjected to various physical treatments, first during product manufacture and then during use in their intended applications. Therefore, the mechanical properties of polymeric materials need to be controlled and tested rigorously. Mechanical properties of polymers include their resistance to deformation and their ultimate failure as static or dynamic loads are applied. Deformations can be generated by drawing, shearing, pressurizing, compressing, bending, or torsion.

1. Deformation Under Tension (63)

The simplest mechanical test method is tensile testing, where a rectangular or dumbbell-shaped specimen is placed between two clamps and then uniaxially drawn with constant speed (64,65). In the case of pure elastic deformation, the stress σ and the resulting deformation are proportional to each other. The original dimensions of the test specimen are completely and immediately restored after removal of the stress. The proportionality constant E is called the modulus. It is given by Hooke's law (Eq. 19), where σ is the tensile stress ($N\ m^{-2}$), γ the strain, and E Young's modulus ($N\ m^{-2}$):

$$\sigma = E\gamma \quad (19)$$

Polymers behave very differently upon drawing. They can be subdivided into six classes (Table 3) according to moduli and stress-strain behavior. The changes of Young's modulus E with temperature give a good insight into the properties and applicability of a polymer over a given temperature range. For an amorphous non-cross-linked polymer five regions exist, as shown in Figure 11. It is clear that amorphous polymers below T_g have high E values that remain reasonably constant below T_g (region 1). At the glass transition temperature the polymer does not immediately become a viscous liquid ($E = 0$), as would be observed for low-mass compounds, but rather it undergoes a series of changes in mechanical behavior. In region 2, the modulus drops by a factor of 10^3 over a 20–30°C range. The behavior of the polymer in this region is described as leathery. Region 3 is

Table 3 Classification of Polymers According to Their Tensile Behavior

Class	E	σ	ϵ	Example
Rigid-brittle	Large	—	Small	Polystyrene
Rigid-strong	Large	Large	Small	Poly(methyl methacrylate)
Rigid-ductile	Large	Large	Large	Polycarbonate
Soft-ductile	Small	Small	Large	Low-density polyethylene
Soft-strong	Small	Small	Small	Poly(tetrafluoroethylene) (teflon)
Soft-elastic	Small	Large	Large	Styrene/butadiene/styrene copolymer

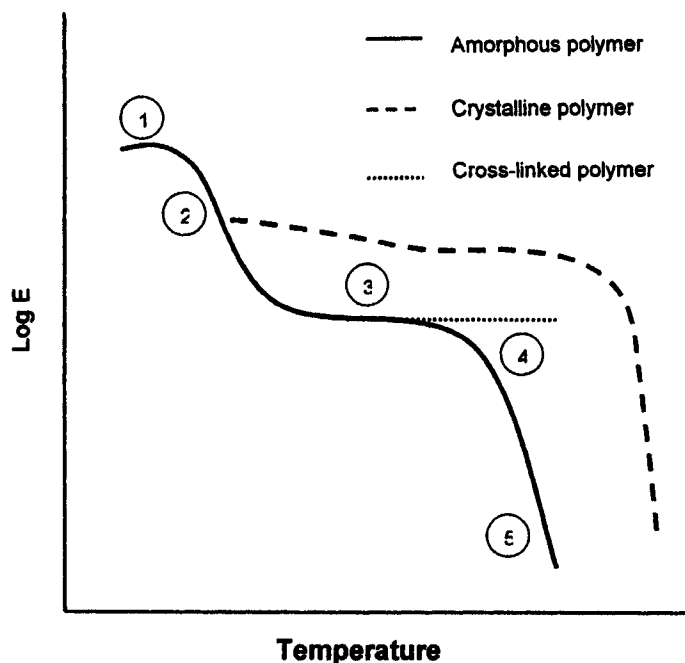


Figure 11 Five regions of viscoelastic behavior for a linear, amorphous polymer.

the rubbery plateau region. After a sharp drop, the modulus reaches a value that remains constant over a large temperature range. In the rubbery plateau, polymers exhibit long-range rubber elasticity, which means that they can be stretched maybe several hundred percent and snap back to nearly their original length. As the temperature is raised past the rubbery plateau, the polymer reaches the rubbery flow region (4), and finally the liquid flow region (5) at still higher temperatures.

A typical stress-strain curve of keratin, a crystalline polymer, is shown in Figure 12. If a keratin fiber is extended progressively under constant temperature and humidity conditions, once it is straightened, the stress-strain curve exhibits a nearly linear region. With further extension an increase in stress occurs with small increases in strain (yield region). Then the stress increases more rapidly with increasing strain. This region of increase in fiber stiffness is called the postyield region. The longitudinal stress-strain curves of α -keratin vary markedly with temperature, humidity, and time.

2. Deformations Under Shear

Instead of elongating or compressing a solid, we can subject it to various shearing or twisting motions. The ratio of the shear stress, σ , to the shear strain, γ , defines the shear modulus G (Eq. 20):

$$\sigma = G\gamma \quad (20)$$

Normally a body shrinks in volume upon exposure to increasing external pressure. The bulk modulus B is defined by Eq. 21, where P is the pressure and V the volume of the body. The inverse of the bulk modulus is the compressibility β .

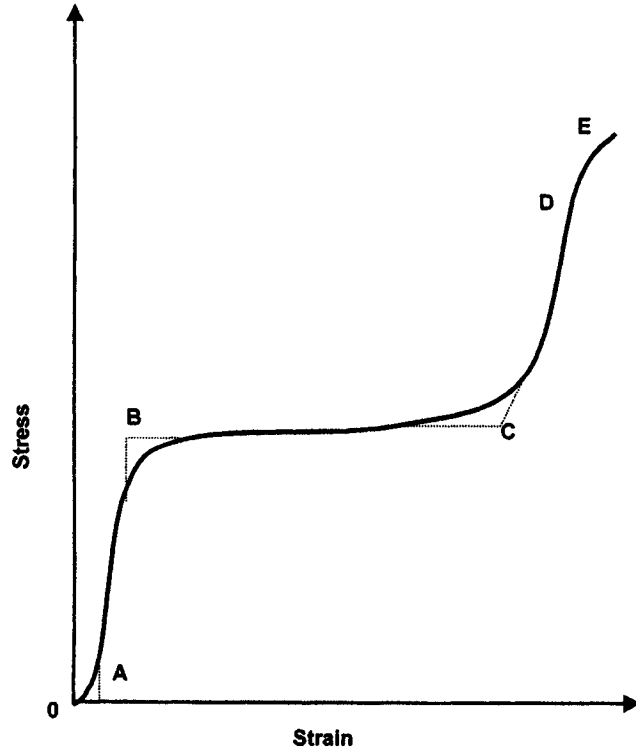


Figure 12 Typical stress-strain curve of an α -keratin fiber showing the Hookean region (AB), the yield region (BC), and the postyield region (CDE).

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T \quad (21)$$

The modulus B is a measure of stiffness or hardness of an object. The compliance J is a measure of its softness. In regions far from transitions, the elongation compliance J is defined as in Eq. 22:

$$J \equiv \frac{1}{E} \quad (22)$$

In a creep experiment the dimensions of a specimen are observed as a function of time under constant load. Usually a constant stress is applied to a sample and the dimensions are recorded as a function of time. The experiments can be generalized to include shear motions, compressions, etc. Creep experiments are usually reported as time-dependent compliance $J(t)$.

The quantities E and G refer to quasi-static measurements. When cyclic motions of stress and strain are involved, it is more convenient to use dynamical mechanical moduli. The complex Young's modulus is then defined as $E^* = E' + iE''$, where E' is the storage modulus and E'' the loss modulus. The storage modulus is a measure of the energy stored elastically during deformation; the loss modulus is a measure of the energy converted to heat. Similar definitions hold for G^* , J^* , and other mechanical properties.

3. Models for Analyzing Stress Relaxation and Creep

When dealing with very small deformations of materials with both elastic and viscous nature (viscoelastic materials) it is usual to combine a linear, Hookean stress-strain relationship with a linear Newtonian viscous relationship to illustrate the behavior of real materials. In these models, spring and dashpot elements are frequently used to model creep and relaxation measurements. A spring behaves like a purely elastic material, such as a metallic spring, stretching instantly under stress and holding the stress indefinitely. A dashpot is full of a purely viscous fluid. Under stress the plunger moves through the fluid at a rate proportional to the stress. On removal of stress there is no recovery. Springs and dashpots can be put together to model the viscoelastic behavior of polymers. Two simple arrangements are the Maxwell and Kelvin (or Voigt) elements (Fig. 13). In the Maxwell element, the spring and dashpot are in series; in the Kelvin element, they are in parallel. In the Maxwell element both the spring and the dashpot are subjected to the same stress but are permitted to have independent strains. The inverse is true for the Kelvin element. On application of stress to the Maxwell element, the spring instantly responds, as illustrated by the vertical line in Figure 14. The spring then remains extended as the dashpot gradually pulls out, yielding a line slanted upward. The spring and dashpot undergo concerted motions. On the other hand, in the Kelvin element the dashpot responds slowly to the stress and gradually transfers it to the spring as it becomes extended, resulting in the asymptotic behavior as a function of time depicted in Figure 14.

A few viscoelastic behaviors can be modeled adequately by a two-element model, but usually it is necessary to combine Maxwell and Kelvin elements. A series arrangement of the two elements, known as the four-element model, is the simplest model that exhibits all the features of viscoelasticity (Fig. 15). It is beyond the scope of this introductory chapter to derive the mathematical equations that describe the various models. Several excellent texts exist and can be consulted (66–68).

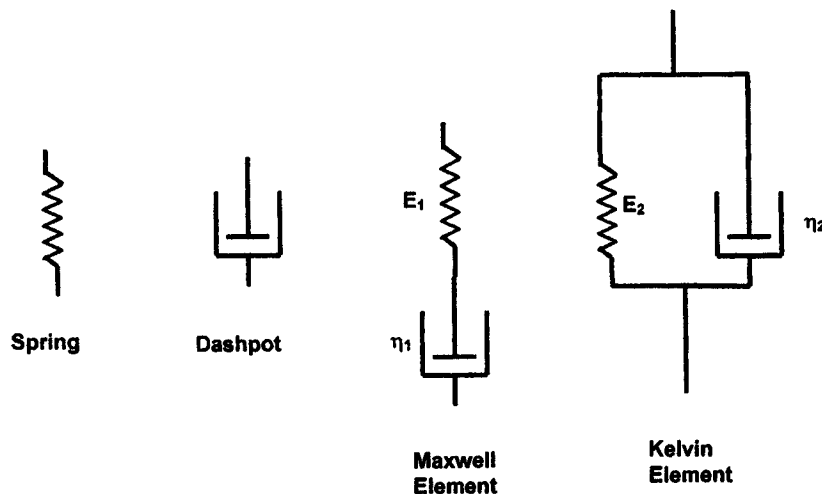


Figure 13 The Maxwell and Kelvin elements, representing simple series and parallel arrays of springs and dashpots.

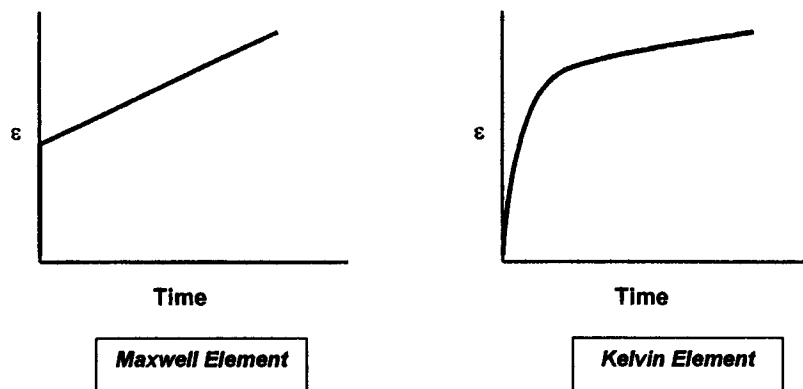


Figure 14 Creep behavior of the Maxwell and Kelvin elements. The Maxwell element exhibits viscous flow throughout the deformation, whereas the Kelvin element reaches an asymptotic limit to deformation.

V. POLYMER SOLUTIONS

Polymers are probably best known for their use as bulk materials, as discussed in the previous section. However, they also play an important role in the control of solution and dispersion rheology. This application includes fields as diverse as fuels, lubricants, water treatment chemicals, foodstuffs, and cosmetic formulations. In these areas polymers affect the flow behavior, and thereby the performance, of a fluid during and after application.

When one attempts to dissolve a polymer in solvents selected at random, many, per-

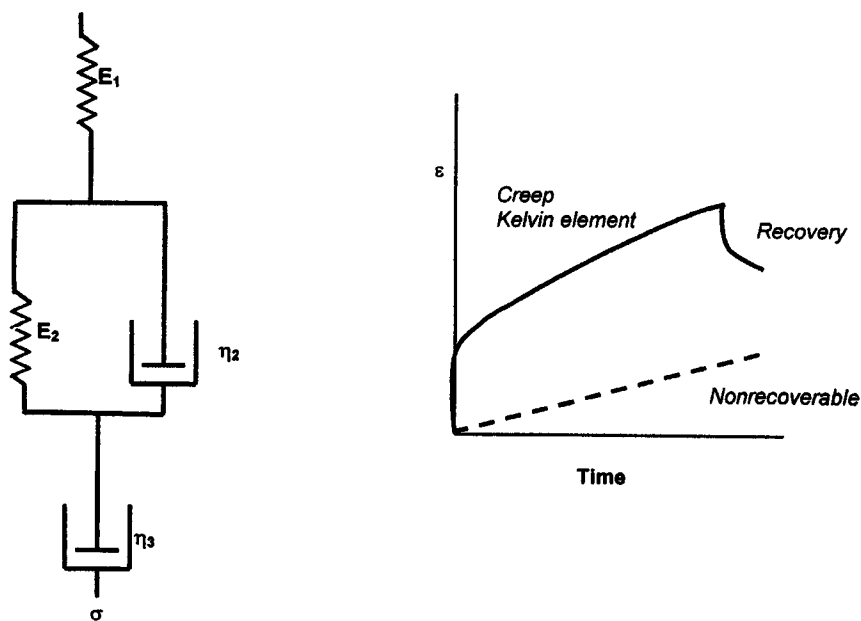


Figure 15 The four-element model and the creep behavior predicted by this model.

haps most, will not work. The experimentalist rapidly finds out that the higher the molecular weight of the polymer, the more difficult it is to select a good solvent. Attempts to understand polymer-solvent and polymer-polymer mutual interactions in a solvent, especially by Flory in the 1950s (69) and De Gennes in the 1970s, have led to many new theoretical developments in the thermodynamics of polymers in solution.

A. Thermodynamics of Polymers in Solution

One of the simplest notions in chemistry is that “like dissolves like.” Qualitatively, “like” can be defined in terms of similar chemical groups or similar polarities. Quantitatively, solubility of one component in another is governed by the free energy of mixing, ΔG_M (Eq. 23), where T is the absolute temperature, ΔS_M is the entropy of mixing, and ΔH_M is the enthalpy of mixing.

$$\Delta G_M = \Delta H_M - T\Delta S_M \quad (23)$$

A negative value of ΔG_M indicates that the dissolution process will occur spontaneously. The term $T\Delta S_M$ is generally positive, as there is usually an increase in entropy (disorder) on mixing. Hence the sign of ΔG_M depends primarily on the sign of the enthalpy of mixing. Surprisingly, the enthalpy of mixing is usually positive, opposing mixing. This is true for most small molecules and polymers alike. Exceptions occur when the solute and solvent attract each other in some way, for example through hydrogen bonding as is often the case during the dissolution process in water.

Historically, the theoretical understanding of how polymers interact with solvent molecules is credited to the pioneering work of Flory and Huggins (69). They introduced the idea of contact energy as the cause of the heat of mixing of polymer solutions. In this treatment, the energy change on mixing is assumed to arise from the formation of new solvent-polymer contacts, which replace some of the solvent-solvent and polymer-polymer contacts present in pure solvent and in the pure polymer, respectively (Fig. 16). By assuming that the size of polymer units, or segments, is similar to that of a solvent molecule, Flory and Huggins derived an expression for the partial molar Gibbs free energy, which included a dimensionless parameter, known as the Flory-Huggins interaction parameter, χ_i . This parameter is defined in Eq. 24, where the term ΔH_M is the contact energy, k is Boltzmann constant, T the absolute temperature, n_1 the number of solvent molecules, and V_2 the polymer volume fraction. The interaction parameter can be used as a measure of solvent power. It has a value of at least 0.5 for poor solvents and decreases for good solvents.

$$\chi_i = \frac{\Delta H_M}{kn_1V_2} \quad (24)$$

To overcome some of the limitations of his early model, Flory, together with Krigbaum (70), made a second assumption. They postulated the presence of the excluded volume, the volume occupied by a polymer chain that exhibits long-range intramolecular interactions. These interactions were introduced as an enthalpic term (K_1) and an entropic term ω_1 , as described later. The two terms are equal if $\Delta G_M = 0$. The temperature at which these conditions prevail in a given solvent is the θ temperature. At this temperature the effects of the excluded volume are eliminated and the polymer chain adopts its unperturbed conformation in dilute solution. In other words, the θ temperature is the lowest temperature at which a polymer of infinite molecular weight is completely soluble in a given solvent.

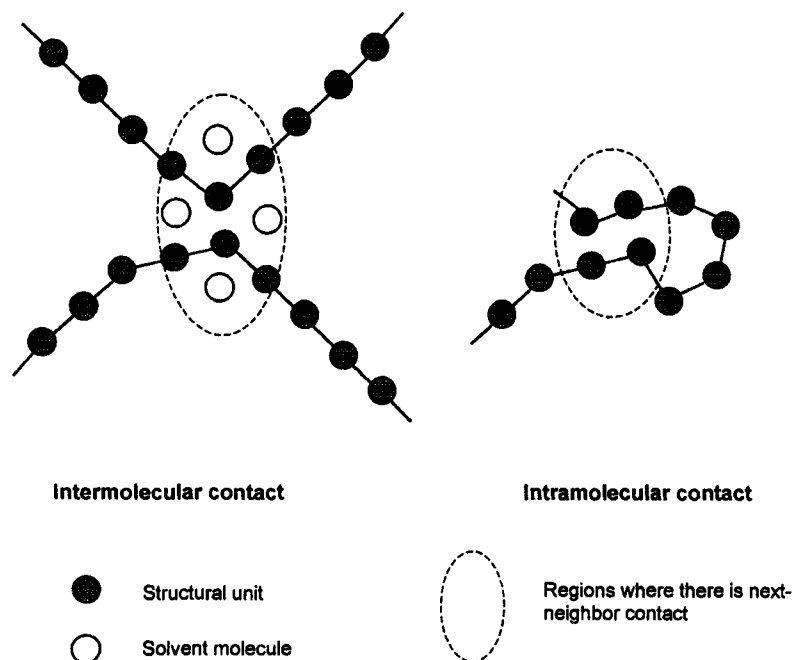


Figure 16 Schematic representation of polymer/polymer and polymer/solvent contacts in solution.

Above this temperature the coil expands and below this temperature the coil collapses with concomitant macroscopic phase separation.

1. Solubility Parameters and Cohesive Energy Density (71)

As there is no simple rule for predicting the solubility of a polymer in a specific solvent, polymer chemists and technologists use empirical relationships to guide solvent selection. In the early 1930s, both Scatchard and Hildebrand independently suggested that the enthalpy of mixing, ΔH_M , involved in the mixing of solute and solvent could be derived using the heat of vaporization of a liquid in binary mixtures. The cohesive energy density (CED) was introduced as a measure of the strength of the internal forces between polymer chains in the bulk. In this approach the enthalpy of mixing is obtained from Eq. 25:

$$\Delta H_M = V_M \left[\left(\frac{\Delta E_1^v}{V_1} \right)^{1/2} - \left(\frac{\Delta E_2^v}{V_2} \right)^{1/2} \right]^2 \chi_1 \chi_2 \quad (25)$$

where ΔE_i^v is the energy of vaporization of the two species ($i = 1$: solvent, $i = 2$: polymer), $V_M = V_1 n_1 + V_2 n_2$ is the total volume of the solution with V_i and n_i , the molar volume and the number of moles of each component, respectively, and x_i is the molar fraction of each component. The quantity $\Delta E^v/V$ is taken as a measure of “internal pressure” or cohesive energy density. The square root of $\Delta E^v/V$ is defined as the solubility parameter, δ . Thus, we can write the following relations:

$$\Delta H_M = V_M (\delta_1 - \delta_2)^2 \chi_1 \chi_2 \quad (26)$$

$$\text{or } \delta = \left(\frac{\Delta H_M - RT}{V_M} \right)^{1/2} \quad (27)$$

Therefore knowing the values of V_M and ΔH_M at a given temperature, T , it is possible to determine the value of δ for any solvent and polymer.

It is reasonably easy to use Eq. 26 to determine the solubility parameter of a solvent, but since the heat of vaporization of polymers is usually not known, other methods are needed to determine the solubility parameters of polymers. There are several experimental methods, based on polymer swelling measurements or on the determination of the intrinsic viscosity of polymer solutions. Alternatively, solubility parameters can be predicted from knowledge of the chemical structure of each component. The latter method is due to Small (72) and Hoy (73), who supplied values for molar attraction constants (G) of a large number of functional groups (Table 4). The constants G are additive. With these values it is possible to estimate the solubility parameter of any polymer using Eq. 28, where ρ represents the density and M the molecular weight of the polymer.

$$\delta = \frac{\rho \sum G}{M} \quad (28)$$

Solubility parameters of common solvents and polymers are given in Table 5 and Table 6, respectively. (For a comprehensive list of solubility parameters, see Ref. 74.) These tables provide a strong basis to predict the solubility of a polymer in a given solvent. It is usually found that polymers will dissolve in solvents having solubility parameters within about one unit of their own. Referring to Tables 5 and 6, it is easy to understand why polyethylene (δ 7.9) is not soluble in water (δ 23.4) or methanol (δ 14.5) but dissolves readily in *n*-hexane (δ 7.28).

2. Statistical Thermodynamics of Mixing

In the previous section the solubility of a polymer in a solvent was described in terms of the respective solubility parameters, which are controlled only by the heat of mixing. However, it is the free energy of mixing, $\Delta G_M = \Delta H_M - T\Delta S_M$, that ultimately controls polymer solubility in a given solvent. Therefore, the entropy of mixing needs to be taken into account as well. An expression of the entropy of mixing of a polymer in a solvent was derived by Flory and Huggins, using a simple lattice model. A representation of a lattice model in the case of mixing of two low-molecular-weight components is given in Figure 17a. The lattice sites are chosen to be the size of a solvent molecule. The solute

Table 4 Representative Group Molar Attraction Constants G [(cal/cm³)^{1/2} mol⁻¹] at 25°C

Group	G	Group	G
—CH ₃	214	—CO— (ketone)	275
—CH ₂	133	—COO— (ester)	310
>CH—	28	—CN	310
>C<	-93	—SH—	315
Six-membered ring	95-105	—S—	225
—CH=CH—	111	—Cl (primary)	270
>C=CH—	19	—Si—	-38
Phenyl	735	—CF ₃	274
—O— (ether)	70		

Table 5 Solubility Parameters of Common Solvents

Solvent	δ (cal cm ⁻³) ^{1/2}
<i>n</i> -Hexane	7.28
Carbon tetrachloride	8.70
Toluene	8.90
Benzene	9.09
Chloroform	9.29
Tetrahydrofuran	9.48
Chlorobenzene	9.58
Acetone	9.82
Methylene chloride	9.92
1,4-Dioxane	10.0
<i>N</i> -Methyl-2-pyrrolidone	11.2
Dimethylformamide	12.1
Methanol	14.5
Water	23.4

molecule (component 2) is assumed to have the same size as the solvent molecule (component 1). The increase in entropy due to mixing of solvent and solute, ΔS_M , is obtained from Boltzmann's relation (Eq. 29), where Ω gives the total number of ways of arranging n_1 molecules of solvent and n_2 solute molecules in a lattice with $N = n_1 + n_2$ number of sites. The probability function is given by Eq. 30:

$$\Delta S_M = k \ln \Omega \quad (29)$$

$$\Omega = \frac{N!}{n_1! n_2!} \quad (30)$$

Using Stirling's approximation ($\ln n! = n \ln n - n$) leads to the expression for the entropy of mixing (Eq. 31), where R is the ideal gas constant, $x_1 = n_1/(n_1 + n_2)$ the molar fraction of the solvent, and $x_2 = n_2/(n_1 + n_2)$ the molar fraction of the solute.

$$\Delta S_M = -k (n_1 \ln x_1 + n_2 \ln x_2) = -R (x_1 \ln x_1 + x_2 \ln x_2) \quad (31)$$

Table 6 Solubility Parameters of Polymers

Polymer	δ (cal cm ⁻³) ^{1/2}
Polybutadiene	8.4
Polyethylene	7.9
Poly(methyl methacrylate)	9.45
Polytetrafluorethylene	6.2
Polyisobutene	7.85
Polystyrene	9.10
Cellulose triacetate	13.60
Nylon 66	13.6
Polysulfone	9.92
Poly(vinyl chloride)	10.5
Polyacrylonitrile	12.4

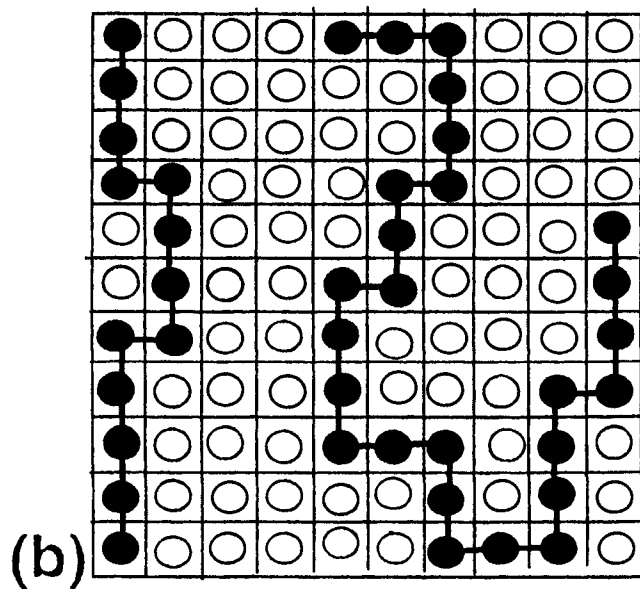
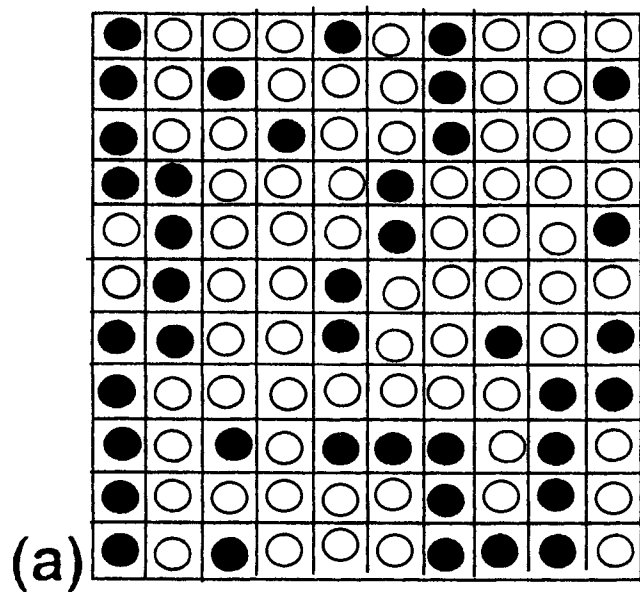


Figure 17 Lattice model for (a) a low-molecular-weight solute in solution (filled circle: solute; open circle: solvent molecule); (b) a polymer solution (filled circle: monomer segment; open circle: solvent molecule).

Flory derived general equations to describe the changes in molecular configuration of the polymer in the presence of a solvent using the lattice theory, which had been applied previously to describe solutions of small molecules. The central point is the filling of lattice sites in a three-dimensional space by polymer segments and solvent molecules (see Fig. 17b), neglecting the interaction potentials existing between polymer segments. A segment was defined by Flory as “that portion of a polymer molecule requiring the same space as a molecule of solvent.” Thus, we assume that the polymer segment and the solvent molecule are of equal volume and that a lattice site is filled with either a solvent molecule or a polymer segment. Solvent molecules can be placed in any unoccupied site available. The possibilities for placing polymer segments are limited, since adjacent segments have to occupy adjacent sites (see Fig. 17b). Let y be the number of segments in a chain, n_1 the number of solvent molecules, n_2 the number of polymer chains, and N the total number of lattice sites; hence $N = n_1 + yn_2$. The derivations, described very clearly by Flory (75), lead to the expression of ΔS_M represented by Eq. 32, where ϕ_1 and ϕ_2 are the lattice volume fractions of solvent and polymer, respectively.

$$(32) \quad \Delta S_M = -k (n_1 \ln \phi_1 + n_2 \ln \phi_2)$$

$$\phi_2 = \frac{yn_2}{n_1 + yn_2} \quad (33)$$

$$\phi_1 = \frac{n_1}{n_1 + yn_2} \quad (34)$$

Combining the expressions for the entropy (Eq. 32) and the enthalpy of mixing (derived from Eq. 24) gives the Gibbs free energy of mixing of a polymer in a solvent (Eq. 35):

$$\Delta G_M = -kT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_1 \phi_2^2) \quad (35)$$

The Flory-Huggins theory in its simplest form considers all lattice sites to be occupied by one component or the other, in other words, incompressible solutions. It can be applied only to solutions sufficiently concentrated to have uniform segment density. It also assumes that there are no energetically preferred arrangements of polymer segments and solvent molecules in the lattice. Newer theories have extended the treatment to lattices with empty sites.

3. Miscibility and Phase Equilibria (76)

The mutual solubility, or miscibility, of a polymer and a solvent, or of two polymers, is governed by the sign of ΔG_M , the free energy of mixing of the two components. Three different cases can be envisaged. If ΔG_M is positive over the entire composition range (case I) the polymer and solvent are totally immiscible. They will coexist at equilibrium as two distinct phases. For total miscibility of polymer and solvent, two conditions have to be met: (1) the free energy of mixing must be negative for all compositions, and (2) the second derivative of ΔG_M with respect to the volume fraction of solvent or polymer must be positive over the entire composition range (Eq. 36):

$$\left(\frac{\partial^2 \Delta G_M}{\partial \phi_2^2} \right)_{P,T} > 0 \quad (36)$$

If condition (2) is not satisfied, the solution will phase-separate at equilibrium into two phases containing different concentrations of each component.

Phase equilibria are strongly affected by temperature: raising the temperature of a solution may increase the miscibility of the two components or, less frequently, may result in a decrease of their miscibility. In the first case, as depicted in the phase diagram in Figure 18, the two components are totally miscible above a point known as the upper critical solution temperature (UCST). At any temperature below the UCST, compositions lying outside the curve constitute homogeneous phases, while compositions inside the curve are thermodynamically unstable and will phase-separate. When the miscibility of a polymer in a solvent decreases as the temperature increases, the mixture possesses a lower critical solution temperature (LCST; Fig. 18). For temperatures below this point, the two components are totally miscible.

Phase diagrams presenting a UCST are often reported for polymers in nonpolar solvents. In these systems, ΔS_M is normally positive but weighted heavily by T , so the solubility depends mainly on the magnitude of ΔH_M , which is normally positive (endothermic dissolution process). Consequently when T decreases, $\Delta G_M = \Delta H_M - T \Delta S_M$, eventually becomes positive and phase separation takes place. Miscibility curves featuring an LCST are often observed in solutions of polymers in polar solvents, in particular in water. The occurrence of an LCST in water is a result of hydrogen-bond formation between the polymer and solvent, which enhances the solubility of the polymer at low temperature. As hydrogen bonds are thermally labile, a rise in temperature reduces the number of hydrogen bonds and causes eventual phase separation. Phase diagrams of polymer solutions may also present a miscibility gap between the two types of curves, as in the case of polystyrene in acetone.

B. Size and Shape of Polymers in Solution

One of the classic problems in polymer science has been the conformation of polymer chains in space. Over the years, several models have been proposed, based on theory and backed up by experimental determinations of the macromolecules' dimensions by scatter-

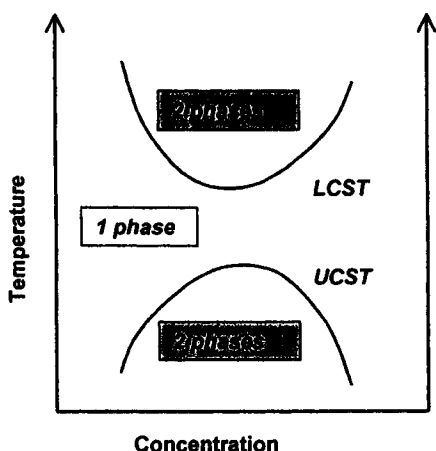


Figure 18 Phase diagram of a polymer solution with UCST (upper-critical-solution temperature) and LCST (lower-critical-solution temperature)

ing of light (77,78), X-rays (79), or neutrons (80). Polymer chain dimensions can also be obtained indirectly from size exclusion chromatography data, the viscosity of dilute solutions, and other hydrodynamic properties. The size and shape of single macromolecules can only be studied in solution, unlike small molecules that can be vaporized and observed in the gas phase, in the absence of solvent molecules. In solutions, solvent/polymer interactions cannot be ignored. In melts, macromolecules surrounding a single chain may be viewed as a type of solvent. The shape of a macromolecule will depend on inherent structural factors, such as the chemical structure of the base unit and the level of branching. It will also vary with solvent, temperature, and flow. The influence of the shape of macromolecules on their physical properties and performances cannot be overlooked. It may be as strong as the effect of chain constitution and configuration.

1. Dilute Solutions (81,82)

Once a polymer-solvent pair has been selected, the physical properties of the resulting solution are controlled by how the polymer behaves among the solvent molecules. Particularly important is the resultant size, or hydrodynamic volume, of the macromolecule. A polymer in solution can be pictured as a coil, continuously changing its shape, and hence its size, under the action of thermal fluctuations. Therefore, the only meaningful chain dimensions are those averaged over many conformations and chain lengths. If the polymer were fully extended, its size could easily be determined from the knowledge of bond lengths and bond angles. This is not the case with most common polymers. Two average dimensions are particularly useful:

The average root mean square distance between chain ends, $\langle r^2 \rangle^{1/2}$

The average root mean square radius of gyration, $\langle s^2 \rangle^{1/2}$, which is a measure of the average distance of a chain segment from the center of gravity of the coil (Fig. 19)

For simple linear chains, the two quantities are related, in the absence of excluded volume effects, by:

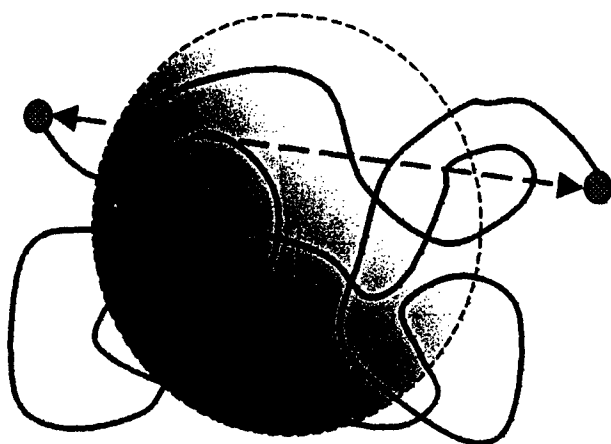


Figure 19 Coil conformation of a macromolecule in solution. The distance between chain ends and the radius of gyration are indicated.

$$\langle r^2 \rangle^{1/2} = \langle 6s^2 \rangle^{1/2} \quad (37)$$

Various models have been proposed to calculate the end-to-end distances of single linear chains. In simple cases only short-range interactions need to be considered. These involve two to five neighboring segments of the polymer chain. Long-range interactions are defined as those between spatially proximate groups that are separated along the chain by many segments. Both interaction types are intramolecular. The various models for random coils with short-range interactions are all nonspecific with respect to the type of interactions (Van der Waals, dipole-dipole, etc.). They differ in the number of interacting chain atoms and the restrictions applied to valence angles and torsion angles.

It is convenient to express r and s in terms of two factors, an unperturbed dimension (r_0 or s_0) and an expansion factor (α). Thus:

$$\bar{r}^2 = r_0^2 \alpha^2 \quad (38)$$

$$\bar{s}^2 = s_0^2 \alpha^2 \quad (39)$$

The unperturbed dimension refers to the size of the molecule, exclusive of solvent effects. It arises from a combination of free rotations and intermolecular steric and polar interactions. The expansion factor arises from interactions between the polymer and the solvent. In a "good solvent" α will be greater than 1 and the actual (perturbed) dimensions of the polymer will exceed its unperturbed dimensions. The greater the value of α , the better the solvent. For the special case where $\alpha = 1$, the polymer adopts its unperturbed dimensions and behaves as an "ideal statistical coil".

2. Semidilute and Concentrated Solutions

Random coils of polymer molecules are very loose entities. They occupy a large volume per mass. At very low polymer concentrations, they are separated from each other by many solvent molecules. With increasing polymer concentration, less and less space is available between the coils and finally a concentration is reached where they start to touch each other and then overlap. This critical concentration is known as the overlap concentration, c^* . If the concentration is increased to a point slightly higher than c^* , the coils become entangled and a network of mesh size ξ is formed. The parameter ξ refers to the distance between two entanglement points or two intersection points. The chain interactions and entanglements in the three concentration regimes are represented in Figure 20.

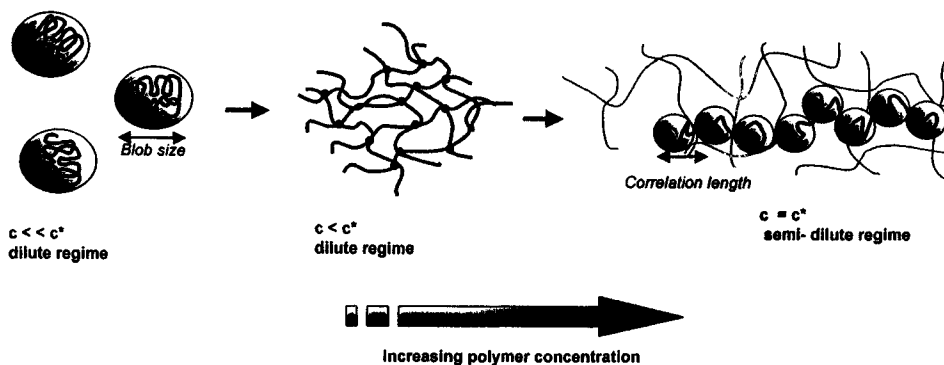


Figure 20 Chain entanglement.

In the dilute region an individual polymer chain can be conceived as confined in a blob of radius r or ξ . In the semidilute regime many chains interpenetrate into each other to form a mesh of size ξ . Still in the semidilute region, but with a concentration slightly higher than c^* , the same individual chain is in the form of a succession of blobs of radius ξ . The parameter ξ is known as the correlation length. In the concentrated region c'' , the length ξ becomes smaller than the coil size. When the concentration is very high, ξ becomes similar to the monomer unit size. The chain exists in the collapsed state.

The phase diagram of a typical polymer solution is shown in Figure 21, where $\tau = (T - \theta)/\theta$ is the reduced temperature. Region I is the dilute region. Region II is the semidilute region, bound by the lines corresponding to the c^* and c'' . An interesting quantity in region II is the screening length, ξ , which represents the average distance between nearest chain contacts. At c^* , ξ can be identified as the radius of gyration. If the polymer is cross-linked it corresponds to the mesh size. Region III consists of the semidilute and concentrated θ state. Region IV occurs in the negative τ range. It is bound by the coexistence phase diagram curve (dashed line). Phase I' represents the θ state.

3. Polymer Association

Coil overlap, described in the previous section, is a nonspecific event that is due only to the increased competition for space of segments of macromolecules as the polymer concentration increases. In many cases an increase in concentration induces *specific* interactions between certain groups or segments. These lead to polymer association and gelation. Specific interactions tend to begin at polymer concentrations well below c^* . Polymer association is a reversible process under thermodynamic control. This process should not be confused with polymer aggregation, an irreversible process. Association may occur within a single macromolecule, or intrapolymeric association. Alternatively, it may involve several chains (interpolymeric association). Intramolecular association leads to the contraction of the polymer coils. The coils become more compact and overall viscosity of the solution decreases. Intramolecular association shows no concentration dependence. On the contrary, interpolymeric associations increase with increasing polymer concentra-

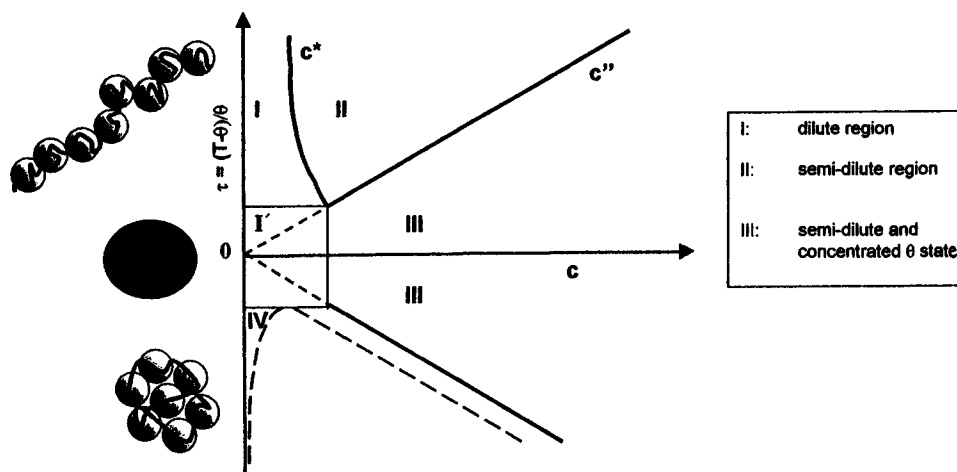


Figure 21 Phase diagram of a typical polymer solution. The quantity τ represents the reduced temperature, $(T - \tau)/\theta$ where θ is the Flory θ -temperature.

tion. They tend to induce an increase in the viscosity of the solution. Important advances have been made in the last two decades in unraveling the structure and dynamics of polymer association, especially in the case of aqueous polymers (83,84).

C. Rheology of Polymer Solutions

The simplest rheological properties are viscosity and elasticity. Liquids such as water or liquid paraffin have viscosity but no elasticity. They flow under even the smallest force, spending all the force in flowing. By contrast, materials such as rubber have elasticity but no viscosity. When they are subjected to a force, they change shape and the energy applied is stored, instead of being consumed. In cosmetics, the liquid state is usually handled as a purely viscous fluid, but disperse systems, such as milky lotions and creams, demonstrate complex rheological properties, displaying both viscosity and elasticity. Polymers strongly influence the rheological properties of these fluids as described in the following sections.

1. The Viscosity of Polymer Solutions

It is a common observation that, usually, polymer solutions flow more slowly through a tube than do pure solvents, under the same pressure. Viscosity is a measure of the energy dissipated by a fluid in motion as it resists an applied shearing force. Solution viscosity is a measure of the resistance to flow and thus, for polymer solutions, it is directly related to the size of the macromolecules and can be used to characterize the molecular weight of polymers. Practically, the flow of a polymer solution is measured and compared to the flow of the solvent alone. The ratio of the viscosity of a polymer solution, η , to that of the solvent, η_0 , or relative viscosity, η_r , is used to define an important parameter of a polymer in a given solvent, the intrinsic viscosity $[\eta]$ (Eq. 40).

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta - \eta_0}{c \eta_0} = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (40)$$

The extrapolation to zero concentration is performed to eliminate the effects of molecular interferences likely to occur even in dilute solutions and obtain the influence of an isolated polymer coil on the viscosity of the solution. Only η and η_0 have the dimensions of viscosity (Poise or Pa. s). Specific viscosity and relative viscosity are dimensionless. Intrinsic viscosity, reduced viscosity, and inherent viscosity all have the dimension of inverse concentration. The nomenclature of viscosity parameters is given in Table 7.

A relationship between molecular weight and intrinsic viscosity was derived independently by Mark and Houwink in the late 1930s (Eq. 41):

$$[\eta] = KM^a \quad (41)$$

where K and a are constants (the Mark-Houwink constants) that vary with solvent and polymer. The exponent a is a function of the shape of the molecule in solution and a measure of the interaction of solvent and polymer, increasing in value as the polymer expands in a good solvent. For most polymer/solvent pairs, the coefficient a ranges between 0.5 and 0.8. In a θ -solvent, it takes a value of 0.5, characteristic of the ideal random coil. An extensive compilation of a and K values can be found, for example, in the *Polymer Handbook* for a large number of solvent/polymer pairs (85). Measurements of viscosity for the determination of molecular weight are usually done using a glass capillary viscometer, such as the Ostwald-Fenske or the Ubbelohde viscometer. Precise experimental conditions are described in various textbooks (86).

Table 7 Commonly Used Viscometry Terms

Common name	IUPAC name	Definition	Symbol	Common Units
Solution viscosity		η	η	Poise or Pa s
Solvent viscosity		η_0	η_0	Poise or Pa s
Relative viscosity	Viscosity ratio	η/η_0	$\eta_{rel} = \eta_r$	Dimensionless
Specific viscosity		$(\eta/\eta_0) - 1$ or $\eta_p - 1$	η_{sp}	Dimensionless
Reduced viscosity	Viscosity number	η_{sp}/c	η_{red}	dl/g
Inherent viscosity	Logarithmic viscosity number	$\ln (\eta_r)/c$	η_{inh}	dl/g
Intrinsic viscosity	Limiting viscosity number	$\lim(\eta_{sp}/c)_{c \rightarrow 0}$	$[\eta]$ or LVN	dl/g

When dealing with solutions of charged water-soluble polymers, the linear Huggins relationship no longer holds as a result of the strong ionic interactions between polymer chains and solvent molecules. Charged polymers have been shown to follow the empirical relationship proposed by Fuoss and Strauss (Eq. 42) (87). The reciprocal of Eq. 42 yields a linear relationship between (c/η_{sp}) and $c^{1/2}$, with the slope given by B/A and the intercept by $(1/A)$. Physically, the value of A corresponds to the intrinsic viscosity.

$$\frac{\eta_{sp}}{c} = \frac{A}{1 + Bc^{1/2}} \quad (42)$$

2. Rheological Properties of Polymer Solutions (38)

In many practical systems, polymers are added to solutions to control their flow characteristics. The attractive feature of polymeric additives is that even in rather low concentrations they can dramatically affect the rheology of a fluid, imparting to a solution properties intermediate between those of elastic solids and those of viscous fluids. The elastic behavior is dominant in solids. It is described by Hooke's law ($\sigma = E\gamma$, Eq. 19, see above). Viscous behavior is dominant in simple liquids. It is described by Newton's law (Eq. 43), which states that the applied stress σ is proportional to the rate of strain $d\gamma/dt$, with a proportionality constant η , the viscosity.

$$\sigma = \eta \frac{d\gamma}{dt} = \eta \dot{\gamma} \quad (43)$$

Therefore, a liquid is said to exhibit Newtonian flow, if η is independent of $\dot{\gamma}$. Substances that show deviations from this flow pattern are termed non-Newtonian. There are two broad classes of non-Newtonian fluids:

1. Fluids with shear stresses that at any point depend on the shear rates only, and are independent of time. These include Bingham plastics, or materials that require a minimum amount of stress (yield stress) before deformation, pseudo-plastics or shear-thinning fluids, which exhibit a decrease of shear stress with shear rate, and dilatants, or shear-thickening fluids, for which the stress increases with the shear rate.
2. Fluids in which the ratio of shear stress to shear rate depends on time. They fall into two categories: thixotropic fluids, in which the microstructure of the fluid progressively breaks down and the viscosity decreases, and rheopectic fluids, where the applied shear promotes gradual formation of structure, and the viscosity increases with shear.

Most polymer solutions fall into one (or several) of these categories in certain concentration ranges. The nature and shape of the viscosity curves depend on a series of additional factors, such as polymer molecular weight and weight distribution, polymer molecular structure, and solvent power. A typical flow curve exhibits two Newtonian plateaus, one at low shear, or "zero-shear condition," and one at high shear, or "infinite shear condition." A shear-thinning region lies between the two limiting conditions. It may extend over several orders of magnitudes of shear rates (Fig. 22).

To understand the complex effect of shear on the flow of polymer solutions, one needs to consider its influence on the molecular interactions at play in solution. Shear-thinning behavior, for instance, reflects the effect of shear on entanglements, as illustrated

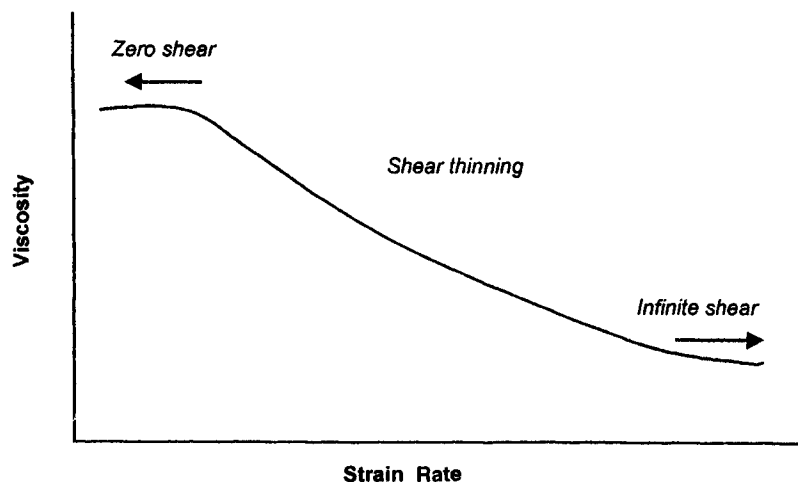


Figure 22 Typical viscosity curve of a polymer solution.

in Figure 23. At low shear rates, the entanglements impede shear flow, and therefore viscosity is high. As the shear rate increases, chains begin to orient in the flow direction and disentangle from one another, and the viscosity begins to drop. Finally the macromolecules become fully oriented in the flow direction at very high shear rates. At this point stable entanglements are no longer possible and the viscosity reaches a low level that is again independent of shear rate.

In some cases the viscosity of a fluid increases with increasing shear rate. This behavior is uncommon for polymers in organic solvents, where it was observed for the first time in ionomer solutions (89). Ionomers are hydrophobic polymers that carry a charged group at each chain end. When dissolved in organic solvents, the charged polymers associate via their ionic groups. The observed shear thickening of the solution is interpreted in terms of an increase in temporary associations among chains made possible by elongation under flow of the charged polymers. The phenomenon is highly dependent on chemical composition and is maximized with only a few associating groups per chain. Shear-thickening effect is observed also with certain water-soluble polymers, especially various new types of hydrophobically modified polymers, such as hydrophobically-modified ethylene oxide urethanes (HEUR) and hydrophobically-modified alkali-swellable emulsions (HASE) (90). In these solutions shear thickening is brought about by formation of polymer networks via hydrophobic interactions (91). The addition of small amounts of surfactant to these polymeric solutions may also result in exceptionally intense shear thickening.

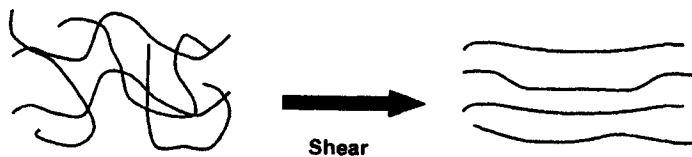


Figure 23 Idealized view of the effect of shear on the entanglements of concentrated polymer solutions and polymer melts.

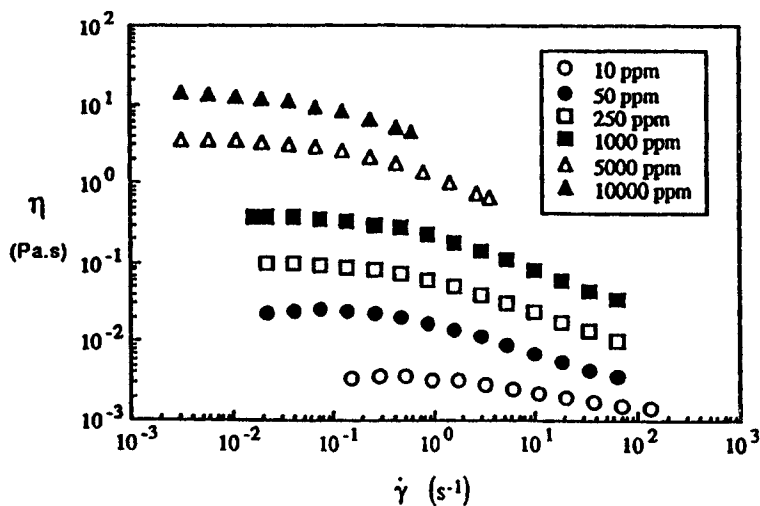


Figure 24 Shear-dependent viscosity of polyacrylamide solutions. (From KC Tam and C Tiu, Water-soluble polymers (rheological properties) in Polymeric Materials Encyclopedia, JC Salamone, ed. Boca Raton, FL: CRC Press, 1996, p. 8655.)

a. Effect of Polymer Concentration. Figures 24 and 25 show typical viscosity curves for two classes of polymers, the flexible poly(acrylamide) and the semirigid xanthan gum, in aqueous solutions. Shear-thinning behavior is observed in both cases, starting at a very low concentration in the case of the xanthan gum. The curves are identical for the two polymers at low concentration, despite considerable structural differences between the two. In the semidilute and concentrated regions ($c > 2$ g/L) the xanthan solutions are much more viscous than the polyacrylamide solutions and shear thinning starts at much lower shear rates, compared to the poly(acrylamide). The viscosity at low shear (η_0) is

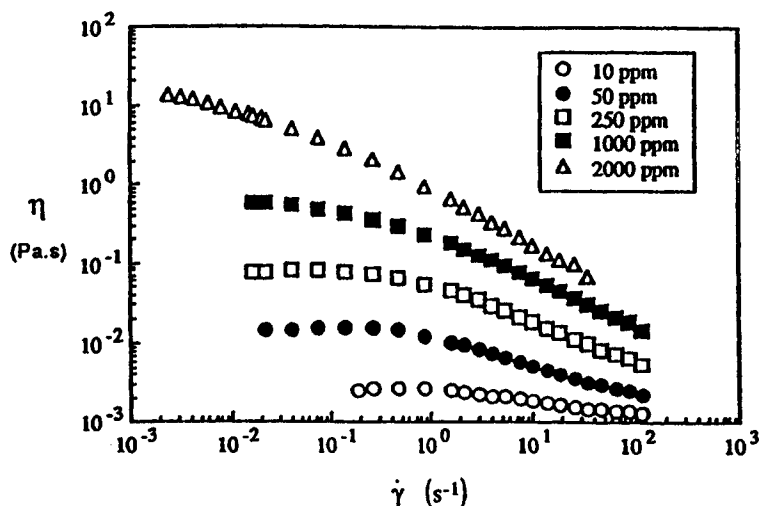


Figure 25 Shear-dependent viscosity of xanthan gum solutions. (From KC Tam and C Tiu, Water-soluble polymers (rheological properties) in Polymeric Materials Encyclopedia, JC Salamone, ed. Boca Raton, FL: CRC Press, 1996, p. 8655.)

often correlated as a function of $c[\eta]$ and the result is used as an approximate guide to identify various concentration regimes of a polymer solution. For many polymers, the dilute solution regime occurs up to $c[\eta]$ of 1.0, where the slope of η_0 versus $c[\eta]$ is about 1.0. This regime is followed by a transition zone between $1 < c[\eta] < 10$ with a varying slope, corresponding to the semidilute regime. Finally, when $c[\eta]$ exceeds about 10, the curve reaches a second linear region with a slope of about 3.4, corresponding to the concentrated solution regime. In the case of polyelectrolytes the interactions between charges on the polymer chains greatly affect the shape and size of the polymer coil, and hence the solution viscosity. In general, the values of zero-shear viscosity vary greatly among polymers for solutions of identical concentrations, even in the case of neutral polymers.

b. Temperature Effects. Temperature changes can dramatically affect the rheology of polymer solutions. Thus, the ability to predict the variations of the steady shear and dynamic properties with respect to temperature is critical in many applications. Newtonian fluids usually obey an Arrhenius-type exponential dependence on temperature (Eq. 44) where the constant B_T can be estimated from thermodynamic properties (92).

$$\eta(T) = A \exp\left(\frac{B_T}{T}\right) \quad (44)$$

Solutions of high-molecular-weight polymers exhibit similar temperature dependence, but the coefficient B_T cannot be predicted from thermodynamic properties. It depends on the structural and thermal properties of the polymer. Data are analyzed in terms of mathematical representations of viscosity in which appropriate coefficients are related to structural considerations.

c. Effects of Electrolytes. Polyelectrolytes in water are highly charged species producing a strong electrical field that attracts counterions. The electrical field is screened out when the concentration of small ions is large enough. This may be achieved by addition of simple electrolyte, such as sodium chloride. The effects of mono- and divalent salts on the zero shear viscosity and onset of shear thinning are illustrated in the case of polyacrylamide (Fig. 26).

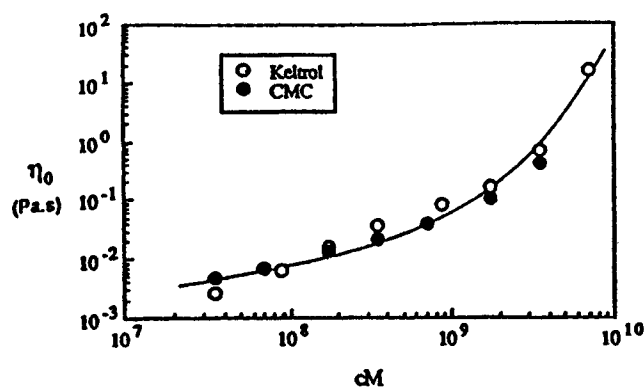


Figure 26 Dependence of zero-shear viscosity and critical shear rate concentration on salt concentration for polyacrylamide aqueous solutions. (From KC Tam and C Tiu, Water-soluble polymers (rheological properties) in Polymeric Materials Encyclopedia, JC Salamone, ed. Boca Raton, FL: CRC Press, 1996, p. 8655.)

d. Oscillatory Properties. When polymer solutions are subjected to oscillatory stresses of high frequency, their characterization as fluids with a viscosity η is no longer adequate, since their response to the applied stress also contains an elastic component (93). If the shearing strain in the $x - y$ plane is $\gamma_{xy} = \gamma_{xy}^0 \sin(\omega t)$, where $\omega/2\pi$ is the frequency of the oscillations, the shearing stress s_{xy} has an elastic component in phase with γ_{xy} and a viscous component proportional to $d\gamma_{xy}/dt$, such that Eq. 45 is obeyed, where the shear storage modulus G' and the shear loss modulus G'' are functions of ω .

$$\sigma_{xy} = \gamma_{xy}^0 [G' \sin(\omega t) + G'' \cos(\omega t)] \quad (45)$$

The shapes of G' and G'' versus ω curves for polymer solutions have been described by Ferry (93). At low frequency, G' and G'' are proportional to ω^2 and ω , respectively. As the frequency increases, the slope of these curves decreases. On a molecular basis this suggests that as the polymer concentration increases, the number density of macromolecules in solution increases, resulting in larger G' and G'' values. The effects of temperature on dynamic properties are similar to those on the steady shear behavior of polymer solutions. Also, similar to the steady shear properties, the presence of electrolytes significantly alters the elastic properties of polyelectrolyte solutions. Divalent salts have a much greater effect on the relaxation time, as the shielding effect is much stronger than in the case of monovalent salts. Therefore, addition of divalent salts to a polyelectrolyte solution will induce coiling of the chain in a more compact polymer coil. Such behavior results in a reduction in the effectiveness of a polymer as a drag-reducing agent when high salt concentrations are encountered.

e. Treatment of Viscosity Data: Master Curves. We have seen that the viscosity-shear rate curves for polymer solutions are dependent on a number of factors. It is possible to evaluate the effects of molecular structure on $\eta(\dot{\gamma})$ in terms of reduced variables. Graessley showed that such dependence can be represented by the characteristic relaxation time in spring-bead models, where β is given by Eq. 46 (94).

$$\frac{\eta - \eta_s}{\eta_0 - \eta_s} = f(\beta) \quad (46)$$

$$\beta = \frac{(\eta_0 - \eta_s)M}{cRT} \dot{\gamma} = \lambda \dot{\gamma}$$

A classic example is the master curve obtained for concentrated polystyrene solutions in *n*-butylbenzene (94). The method is also applicable for dilute aqueous solutions of poly(acrylamide), xanthan gum and poly(ethylene oxide). In the case of polyelectrolytes, the method gives satisfactory results only in limited concentration ranges. Further refinements have to be added to the general method (95).

f. Correlation Between Steady-Shear and Oscillatory Data. The viscosity function is by far the most widely used and the easiest viscometric function determined experimentally. For dilute polymer solutions dynamic measurements are often preferred over steady-shear normal stress measurements for the determination of fluid elasticity at low deformation rates. The relationship between viscous and elastic properties of polymer liquids is of great interest to polymer rheologists. In recent years, several models have been proposed to predict fluid elasticity from shear viscosity data.

VI. CONCLUSION

Polymers are important components of most cosmetics and their role can be critical. Understanding the physical chemistry of polymer solutions is essential in designing cosmetic formulations and ensuring their stability. The rheological properties of cosmetics, controlled to a great extent by the incorporation of polymers, are of prime importance, not only from the standpoint of their final use and acceptance by the customer, but also in the design of manufacture processes. The dramatic effects that are often triggered by small modifications of polymer-containing fluids cannot be overlooked, as demonstrated in the following chapters.

ACKNOWLEDGMENTS

I thank Dr. E. D. Goddard for his constant support, his enthusiasm, and his excellent advice. Thanks are due also to Dr. V. Gruber for providing an early version of the chapters he wrote in this book and to Dr. K. Szczubialka (Jagiellonian University, Krakow, Poland) for his careful proofreading of the manuscript.

REFERENCES

1. Morawetz H. *Polymers: The Origins and Growth of a Science*. New York: Wiley, 1985.
- 1a. Meikle JL. *American Plastic: A Cultural History*. New Brunswick, NJ: Rutgers University Press, 1995.
2. Carraher CE Jr. *Polymer Chemistry, an Introduction*, 4th ed. New York: Marcel Dekker, 1996.
3. Allcock HR, Lampe FW. *Contemporary Polymer Chemistry*, 2nd ed. Englewood Cliffs, NJ: Prentice-Hall, 1990.
4. Fried JR. *Polymer Science and Technology*. Englewood Cliffs, NJ: Prentice-Hall, 1995.
5. Elias H-G. *An Introduction to Polymer Science*. Weinheim, Germany: VCH, 1997.
6. Campbell IM. *Introduction to Synthetic Polymers*. Oxford, UK: Oxford Science Publications, Oxford University Press, 1994.
7. Cowie JMG. *Polymers, Chemistry and Physics of Modern Materials*, 2nd ed. London: Blackie Academic & Professional, Chapman Hall, 1991.
8. Brandrup J, Immergut EH, eds. *Polymer Handbook*, 3rd ed. New York: Wiley, 1989.
9. Mark H, Overberger C, Menges G, Bikales NM, eds. *Encyclopedia of Polymer Science and Engineering*, 2nd ed. New York: Wiley, 1985 ff, 18 vols, and supplements.
10. Salamone JC, ed. *Polymeric Materials Encyclopedia*. Boca Raton, FL: CRC Press, 1986.
11. Allen G, Bevington JC, eds. *Comprehensive Polymer Science*. Oxford, UK: Pergamon Press, 1989.
12. Semlyen JA, ed. *Cyclic Polymers*. New York: Elsevier, 1986.
13. Ikeda Y. Characterization of graft copolymers. *Adv Polym Sci* 1978; 29:47.
14. Bywater S. Preparation and properties of star-branched polymers. *Adv Polym Sci* 1979; 30: 89.
15. Tomalia DA, Naylor AM, Goddard WA III. Starburst dendrimers. *Angew Chem Int Ed Engl* 1990; 29:138.
16. Sperling LH. *Interpenetrating Networks and Related Materials*. New York: Plenum Press, 1981.
17. Rempp P, Merrill EW. *Polymer Synthesis*, 2nd ed. Basel: Hüthig and Wepf, 1992.
18. Odian G. *Principles of Polymerization*, 3rd ed. New York: Wiley, 1992.

19. Kricheldorf HR, ed. *Handbook of Polymer Synthesis*. New York: Marcel Dekker, 1992. 2 vols.
20. Millich F, Carraher CE, eds. *Interfacial Synthesis*. New York: Marcel Dekker, 1977. 2 vols.
21. *Free-Radical Polymerization*, *Comprehensive Chemical Kinetics*, 14A. Amsterdam: Elsevier, 1976
22. Piirma I. *Emulsion Polymerization*. New York: Academic Press, 1982.
23. Morton M. *Anionic Polymerization: Principle and Practice*. New York: Academic Press, 1983.
24. Hsieh HL, Quirk RP. *Anionic Polymerization*. New York: Marcel Dekker, 1996.
25. Kennedy JP, Iván B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*. Munich: Hanser, 1992.
26. Matyjaszewski K, ed. *Cationic Polymerizations*. New York: Marcel Dekker, 1996.
27. Kissin YV. *Isospecific Polymerization of Olefins*. Berlin: Springer-Verlag, 1986.
28. Fink G, Mülhaupt R, Brintzinger HH, eds. *Ziegler Catalysts*. Berlin: Springer-Verlag, 1995.
29. Kucera M. *Mechanism and Kinetics of Addition Polymerizations*. Amsterdam: Elsevier, 1992.
30. Carraher CE, Moore JA. *Modification of Polymers*. New York: Plenum Press, 1983.
31. Moore JA. *Reactions of Polymers*. Boston: D. Reidel, 1974.
32. Peebles LH. *Molecular Weight Distribution in Polymers*. New York: Interscience, 1971.
33. Slade PE Jr. *Polymer Molecular Weights*. New York: Marcel Dekker, 1975. 2 vols.
34. Laidler KJ, Meiser JH. *Physical Chemistry*, 2nd ed. Boston: Houghton Mifflin, 1995, Chapter 5.
35. Billingham NC. *Molar Mass Measurements in Polymer Science*. New York: Wiley, 1977.
36. Yau WW, Kirkland IJ, Bly DD. *Modern Size Exclusion Liquid Chromatography*. New York: Wiley, 1979.
37. Glöckner G. *Polymer Characterization by Liquid Chromatography*. Amsterdam: Elsevier, 1986.
38. Wu CS. *Handbook of Size Exclusion Chromatography*. New York: Marcel Dekker, 1995.
39. Garmon RG. End group determinations. *Techn Methods Polym Eval* 1975; 4(1):31.
40. Bassett DC. *Principles of Polymer Morphology*. Cambridge: Cambridge University Press, 1981.
41. Woodward AE. *Understanding Polymer Morphology*. Cincinnati: Hanser-Gardner, 1995.
42. Corradini P, Guerra G. Polymorphism in polymers. *Adv Polym Sci* 1992; 100:183.
43. Haward RN, ed. *The Physics of Glassy Polymers*. New York: Wiley, 1973.
44. Cheremisinoff NP, ed. *Elastomer Technology Handbook*. Boca Raton, FL: CRC Press, 1993.
45. Bartenev GM, Zenlenev YV, eds. *Relaxation Phenomena in Polymers*. New York: Halsted, 1974.
46. Strobl G. *The Physics of Polymers*, 2nd ed. Berlin: Springer-Verlag, 1997, Chapter 5.
47. Eisenberg A. The glassy state and the glass transition. In: Mark JE, Eisenberg A, Graessley WW, Mandelkern L, Samulski ET, Koenig JL, Wignall GD, eds. *Physical Properties of Polymers*, 2nd ed. Washington, DC: American Chemical Society, 1993:61–95.
48. Turi EA, ed. *Thermal Characterisation of Polymeric Materials*, 2nd ed. New York: Academic Press, 1982.
49. Mathot VBF, ed. *Calorimetry and Thermal Analysis of Polymers*. Cincinnati: Hanser, 1994.
50. Bershtein VA, Egorov VM. *Differential Scanning Calorimetry of Polymers*. Chichester: Ellis Horwood, 1973.
51. De Gennes P-G. *Scaling Concepts in Polymer Physics*. Cornell: Cornell University Press, 1979.
52. Guven O. *Cross-Linking and Scission of Polymers*. Dordrecht: Kluwer, 1990.
53. Burchard W, Ross-Murphy SB, eds. *Physical Networks*. London: Elsevier, 1990.
54. Guenet JM. *Thermoreversible Gelation of Polymers and Biopolymers*. London: Academic Press, 1992.
55. Tadokoro H. *Structure of Crystalline Polymers*. New York: Wiley, 1979.

56. Hall IH, ed. *Structure of Crystalline Polymers*. London: Elsevier, 1984.
57. Rhodes G. *Crystallography Made Crystal Clear. A Guide for Users of Macromolecular Models*. New York: Academic Press, 1993.
58. Mandelkern L. In: Mark JE, Eisenberg A, Graessley WW, Mandelkern L, Samulski ET, Koenig JL, Wignall GD, eds. *The Crystalline State in Physical Properties of Polymers*, 2nd ed. Washington, DC: American Chemical Society, 1993:145–200.
59. Fraser RDB, MacRae TP, Rogers GE. *Keratins: Their Composition, Structure, and Biosynthesis*. Springfield, IL: Charles C Thomas, 1972.
60. Bendit EG. In: Parry DA, Creamer LK, eds. *Fibrous Proteins: Scientific, Industrial, and Medical Aspects*. New York: Academic Press, 1980.
61. Ward IM, Hadley DW. *An Introduction to the Mechanical Properties of Solid Polymers*. Chichester: Wiley, 1993.
62. Nielsen LE, Landel RF. *Mechanical Properties of Polymers and Composites*, 2nd ed. New York: Marcel Dekker, 1993.
63. Bartener G. *Mechanical Strength and Failure of Polymers*. Engelwood Cliffs, NJ: Prentice-Hall, 1993.
64. Crompton TR. *Practical Polymer Analysis*. New York: Plenum Press, 1993.
65. Williams JG. *Stress Analysis of Polymers*. London: Longmans, 1973.
66. Aklonis JJ, MacKnight WJ. *An Introduction to Polymer Viscoelasticity*, 2nd ed. New York: Wiley, 1983.
67. Mark JE, Erman B. *Rubberlike Elasticity: A Molecular Primer*. New York: Wiley, 1988.
68. Matsuoka S. *Relaxation Phenomena in Polymers*. Cincinnati: Hanser-Gardner, 1992.
69. Flory JP. *Principles of Polymer Chemistry*. Ithaca: Cornell University Press, 1953.
70. Flory JP, Kriegbaum WR. *J Chem Phys* 1950; 18:1086.
71. Barton AFM. *Solubility Parameters and Other Cohesion Parameters*, Boca Raton, FL: CRC Press, 1983.
72. Small PA. *J Appl Chem* 1953; 3:71.
73. Hoy KL. *J Paint Technol* 1970; 42:76.
74. Grulke EA. In: Brandrup J, Immergut EH, eds. *Polymer Handbook*, 3rd ed. New York: Wiley, 1989:519–559.
75. Flory PJ. *Disc Far Soc* 1970; 49:7.
76. Morawetz H. *Macromolecules in Solution*, 2nd ed; New York: Wiley, 1975.
77. Kratochvil P. *Classical Light Scattering from Polymer Solutions*. Amsterdam: Elsevier, 1987.
78. Chu B. *Laser Light Scattering*. San Diego: Academic Press, 1990.
79. Glatter O, Kratky O. *Small Angle X-Ray Scattering*. New York: Academic Press, 1982.
80. Higgins JS, Benoit HC. *Polymers and Neutron Scattering*. Oxford: Clarendon Press, 1994.
81. Forsman WC, ed. *Polymers in Solution, Theoretical Considerations and Newer Methods of Characterisation*. New York: Plenum Press, 1983.
82. Mattice WL, Suter UW. *Conformational Theory of Large Molecules*. New York: Wiley, 1994.
83. Dubin P, ed. *Microdomains in Polymer Solutions*. New York: Plenum Press, 1982.
84. Stroeve P, Balazs AC, eds. *Macromolecular Assemblies in Polymer Systems*. Washington, DC: American Chemical Society, 1992.
85. Kurata M, Tsunashima Y. In: Bandrup J, Immergut EH, eds. *Polymer Handbook*, 3rd ed. New York: Wiley, 1989:1–59.
86. Bohdanecky M, Kovar J. *Viscosity of Polymer Solutions*. Amsterdam: Elsevier, 1982.
87. Fuoss RM, Strauss UP. *J Polym Sci* 1948;3:246.
88. Barnes HA, Hutton JF, Walters K. *An Introduction to Rheology*. Amsterdam: Elsevier, 1989.
89. Glass JE, ed. *Polymers as Rheology Modifiers*. Washington, DC: American Chemical Society, 1991, Chapters 7 and 9.
90. Glass JE, ed. *Polymers as Rheology Modifiers*. Washington DC: American Chemical Society, 1991, Chapters 10, 13, and 14.

91. English RJ, Gulati HS, Jenkins RD, Khan, SA. Solution rheology of a hydrophobically modified alkali-soluble associative polymer. *J Rheol* 1997;41:427–444.
92. Bird RB, Stewart WE, Lightfoot EN. *Transport Phenomena*. New York: Wiley, 1960
93. Ferry JD. *Viscoelastic Properties of Polymers*, 3rd ed. New York: Wiley, 1980.
94. Graessley WW. *Adv Polym Sci* 1974; 16:1.
95. Tam KC, Tiu CJ. *Non-Newt Fluid Mech* 1993;46:275.

APPENDIX I: GLOSSARY

A	Arrhenius prefactor
a	Mark-Houwink coefficient
B	bulk modulus
c^*	overlap concentration
E	Young's modulus of elasticity
E'	storage modulus
E''	loss modulus
ΔG	change in Gibbs free energy
G	modulus
G	molar attraction constant (Small and Hoy)
G'	shear storage modulus
G''	shear loss modulus
ΔH	change in enthalpy
J	elongation compliance
K	Mark-Houwink coefficient
k	rate constant
M	modulus
M_n	number-average molecular weight
M_v	viscosity molecular weight
M_w	weight-average molecular weight
R	ideal gas constant
$\langle r^2 \rangle^{1/2}$	average root mean square end to end distance
ΔS	change in entropy
$\langle s^2 \rangle^{1/2}$	radius of gyration
T_g	glass transition temperature
T_m	melting point
x	molar fraction
α	expansion factor
β	compressibility
δ	solubility parameter (Hildebrandt)
γ	strain
η	viscosity
η_r	reduced viscosity
η_{rel}	relative viscosity
η_{sp}	specific viscosity
$[\eta]$	intrinsic viscosity
θ	Flory critical miscibility temperature
μ	dipole moment

ν	kinetic chain length
ρ	density
σ	tensile strength
τ	relaxation time
ϕ	volume fraction
ω	frequency
ξ	screening length
ζ	correlation length
χ_1	Flory-Huggins interaction parameter
CED	cohesive energy density
DP	degree of polymerization
DS	degree of substitution
DSC	differential scanning calorimetry
DTA	differential thermal analysis
GPC	gel permeation chromatography
IPN	interpenetrating network
LCST	lower critical solution temperature
MALDI-MS	matrix-assisted laser desorption ionization mass spectrometry
MWD	molecular weight distribution
NMR	nuclear magnetic resonance
TGA	thermal gravimetric analysis
UCST	upper critical solution temperature

APPENDIX II: Definitions of Terms Commonly Used in Polymer Science

Amorphous polymer: noncrystalline polymer or noncrystalline areas in bulk polymer.

Anionic polymerization: a polymerization initiated by an anion.

Bingham plastic: a polymer which does not flow until the applied stress exceeds a threshold stress value.

Blend: mixture of different polymers, in which the polymers are mixed intimately in either one or two phases.

Branched polymer: a polymer having extensions of the polymer chain attached to the polymer backbone (or main chain), such as in low-density polyethylene (LDPE).

Cationic polymerization: a polymerization initiated by a cation, such as sulfuric acid.

Chain-growth polymerization: a polymerization method that consists of a least three steps: initiation, propagation, and termination. The polymerization can be initiated by a free radical, a cation, or an anion.

Chain transfer: a process in which a growing chain becomes a dead polymer by abstracting a group from some other compound, thereby generating a new active site.

Cloud point: some systems, notably poly(ethylene oxide) in water, have an inverse solubility/temperature relation and exhibit a cloud point on heating. The cloud point is the temperature at which a polymer starts to precipitate from a solution when the temperature is raised.

Composite: mixture, on a macroscopic level of different polymers, one forming a continuous phase and another a discontinuous phase.

Conformations: various shapes of polymers resulting from the rotation of single bonds in the chain. Not to be confused with configurations, which are related chemical structures produced by the breaking and making of covalent bonds.

Contour length: the fully extended length of a polymer chain, equal to the product of the length of each repeat unit (l) times the number of units (or mers, n), thus the product nl is the full contour length.

Copolymer: a polymer chain containing more than one monomeric species of different chemical structure.

Creep: cold flow of a polymer under stress.

Critical chain length: the minimum chain length required for entanglement of the polymer chains.

Crystalline polymer: a polymer with ordered structure, such as high-density polyethylene (HDPE) and cellulose. Semicrystalline polymers consist of regions of crystallinity or crystallites dispersed in amorphous regions.

Dipole-dipole interactions: moderate secondary forces between polar groups in different molecules or in different locations in the same molecule.

Elastomer: a polymer, such as polyisoprene, that readily undergoes deformation and exhibits large reversible elongations under applied stress.

End-to-end distance: the shortest distance between the ends of a polymer chain.

Excluded volume: the volume that must be disregarded because only one atom of a chain may occupy any specific space at any specific time.

Flory-Huggins parameter (or χ parameter): a quantity obtained by application of the lattice theory to polymer solutions. It describes the thermodynamic goodness of a solvent for a polymer.

Gel permeation chromatography: a type of liquid solution elution chromatography that separates solutions of polydisperse polymers into fractions by means of a sieving action through swollen cross-linked polymer beads of controlled pore sizes.

Glass transition temperature: a characteristic temperature at which glassy amorphous polymers become flexible or rubber-like because of segmental motion. It corresponds to the lowest temperature at which segmental motion of a polymer chain can take place.

HEUR polymers (Hydrophobe-modified Ethoxylated Urethane polymers): a class of rheology modifiers consisting of poly(ethylene oxide) fragments connected by isocyanate units. Aqueous solutions of HEUR polymers exhibit increased viscosity at low shear rate.

Homopolymer: a polymer made up of only one repeating unit, in contrast to a copolymer, which is made up of more than one repeat unit.

Hydrogen bonding: strong secondary force between a hydrogen atom in one molecule and an oxygen, nitrogen, or fluorine atom in another molecule. These forces may also exist between a hydrogen atom in one location and oxygen, nitrogen, or fluorine atoms in another location of the same molecule. Intermolecular hydrogen bonds are responsible for the high strength of fibers, such as keratin and nylon. Helices in some polymers are the result of intramolecular hydrogen bonds.

Impact modifier: a material that improves the resistance of polymers to stress.

Interfacial polymerization: a polymerization in which the reaction takes place at the interface of two immiscible liquids.

Interpenetrating networks: intimate combination of two polymers both in network form, where at least one of the polymers is synthesized or cross-linked in the presence of the other.

Ionomer: a water-insoluble polymer with relatively few electrically charged groups along the chain.

Latex: a stable dispersion in water of polymer particles produced by emulsion polymerization.

Lattice theory: a theory that describes solutions in terms of three-dimensional lattices, where each lattice site is occupied by a segment, either a monomeric unit or a solvent molecule.

Linear polymer: a polymer that consists of a linear chain without extending branches.

Living polymer: a charged polymer chain or macroion, which carries one ionic group, usually at one chain end.

Melt index: a measure of flow, related inversely to melt viscosity, the time for 10 g of a polymer to pass through a standard orifice at a specified time and temperature.

Modulus: the ratio of stress to strain, which is a measure of stiffness of a polymer. A high modulus polymer is stiff and has very low elongation. Some systems, especially solutions of high molecular weight or cross-linked polymers, show "complex" behavior under stress. They possess an elastic modulus, G' , and a loss modulus, G'' , representing the recoverable and irrecoverable strain, respectively.

Molecular weight distribution: a probability curve used to describe the distribution of molecular weights in a polydisperse sample. The number-average molecular weight is the simple arithmetic mean, determined experimentally from colligative properties of polymer solutions. The weight-average molecular weight is the second power average, determined experimentally by light scattering. For polydisperse samples the number-average molecular weight is smaller than the weight-average molecular weight.

Monodisperse: a polymer made up of molecules of one specific molecular weight, such as a protein.

Newtonian fluid: a fluid whose viscosity is proportional to the applied viscosity gradient.

Oligomer: very-low-molecular-weight polymer, usually with a degree of polymerization of 10 or less.

Overlap concentration: the concentration of a polymer solution where individual polymer coils begin to overlap without undergoing chain contraction. This concentration is frequently not very high; thus it is often called the semidilute regime.

Plasticizer: a nonvolatile liquid or solid, which is compatible with a hard plastic and which reduces the glass transition temperature of this polymer, and thus increases the flexibility of hard polymers.

Polydisperse: a polymer consisting of molecules of many different molecular weights, such as most commercial polymers.

Polyelectrolytes: water-soluble polymers with many electrically charged groups per molecule. They form polyions on dissociation, either polyanions, as in the case of dissociated polyacrylic acid, or polycations, as in the case of protonated poly(vinylamine). They may also be polysalts, as in the case of the sodium salt of polyacrylic acid.

Pseudoplastic: a system where the shear rate increases faster than the applied stress; also known as shear-thinning system.

Radius of gyration: the root-mean-square distance of a chain end to the center of gravity of a polymer coil.

Reactivity ratio: the relative reactivity of one monomer compared to another during a polymerization.

Reptation model: a theoretical model to account for the ability of long polymer chains to move through a polymer matrix. In this approach the chain is assumed to be contained

in a hypothetical tube that is placed in a three-dimensional network formed by the entangled chains. The contours of the tube are defined by the position of the entanglement points in the network.

Rheopectic liquid: a liquid that exhibits an increase in viscosity as a function of time.

Shear: stress caused by planes sliding by each other, as in greasing or polishing a flat surface.

Solubility parameter: a numerical value, which can be used to predict solubility. It is equal to the square root of the cohesive energy density or heat of vaporization per unit volume.

Step-growth polymerization: a polymerization method, in which the polymer chain grows slowly in a step-like manner. Also known as polycondensation, the process used to prepare polyesters and polyamides, for example.

Stress: force per unit area.

Suspension polymerization: a process in which liquid monomers are polymerized as liquid droplets suspended in water.

Tacticity: a property that describes the steric order of a polymer chain. Polymers with a unique way of coupling the monomer units are called isotactic. If the coupling of monomer units varies, but in a regular way, the polymers are called syndiotactic. Atactic polymers are polymers with an irregular steric structure. Polystyrene, for example, can adopt all types of tacticities, depending on the process of synthesis.

Theta solvent: a solvent in which a polymer exists as a statistical coil. Under these conditions the χ parameter takes a value of 0.5.

Thixotropic liquid: a liquid that exhibits a decrease in viscosity as a function of time.

Viscoelastic: having the properties of a liquid and a solid.

Polymer Adsorption: Fundamentals

Timothy M. Obey

University of Bristol, Bristol, England

Peter C. Griffiths

Cardiff University, Cardiff, Wales

I. GENERAL FEATURES OF POLYMER ADSORPTION

The adsorption of a polymer from solution onto a surface is usually described in terms of an adsorption isotherm. This relates the amount of polymer at the particle surface (mg/m^2) with the amount of polymer in solution (ppm or mg/L). In contrast with the Langmuir-type low-affinity isotherms displayed by small molecules, polymers tend to show high-affinity isotherms of the type shown in Figure 1.

Initially all the polymer molecules are adsorbed from solution (point A). As the concentration of polymer is further increased, osmotic forces between neighboring molecules cause the polymer chains to start to repel each other. An equilibrium between the attraction of the surface for more polymer and the repulsive lateral osmotic forces between neighboring polymer segments results in the adsorption of an approximately constant amount of polymer at the surface and observation of the so-called *pseudo-plateau*.

Small molecules usually reach equilibrium adsorption levels relatively quickly, but for polymer molecules steady states may take much longer to achieve. Two factors contribute to this: first, polymer molecules have much lower diffusion coefficients compared to small molecules, and second, polymer molecules require a finite time to rearrange from their solution conformation to their adsorbed conformation. The first effect is rate determining at low concentration and the second is rate determining at high concentration. These effects are further complicated if the polymers are polydisperse since the more rapidly diffusing small molecules will gradually be replaced at the surface by the slower-diffusing large molecules (1).

The size of the polymer molecule makes it extremely unlikely that all the segments of the macromolecule will be in contact with the surface at any one time, and as a result the polymer adopts a conformation consisting of *tails*, *loops*, and *trains*, shown schematically in Figure 2.

Multipoint attachment of the molecule to the surface makes it difficult for all the

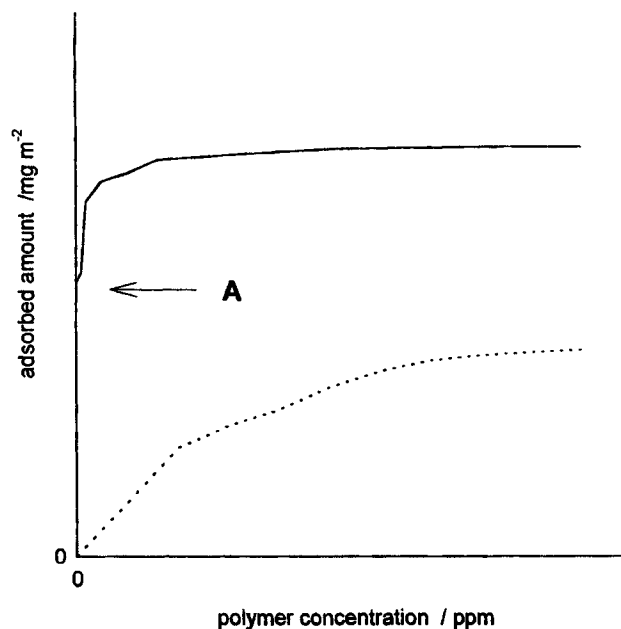


Figure 1 A high-affinity polymer adsorption isotherm, which relates the amount of polymer at the particle surface to the amount of polymer in solution (solid line) and a low-affinity Langmuir-type isotherm (broken line).

segments to desorb simultaneously. Polymer adsorption can, thus, be thought of as an essentially irreversible phenomenon even though each of the individual polymer segments may be reversibly adsorbed.

II. DRIVING FORCE FOR ADSORPTION

For any spontaneous process to occur chemical thermodynamics tells us that there must be a lowering of the free energy, ΔG , of the system. The driving force for polymer adsorption is thus the competition between the net energy change on adsorption (enthalpy of adsorption), the loss of conformational entropy of the adsorbed polymer, and the gain in entropy of solvent molecules released from the surface and polymer upon adsorption.

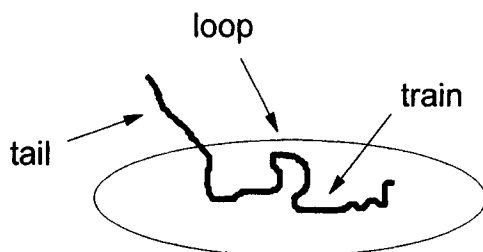


Figure 2 The *tails*, *loops*, and *trains* representation of the conformation of a polymer adsorbed at a surface.