

The Effect of Temperature and other Factors on Plastics and Elastomers

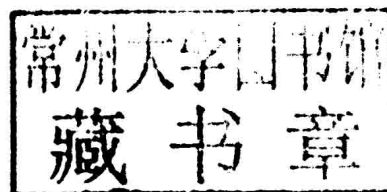
Third Edition

Laurence W. McKeen

THE EFFECT OF TEMPERATURE AND OTHER FACTORS ON PLASTICS AND ELASTOMERS

Third Edition

Laurence W. McKeen



AMSTERDAM • BOSTON • HEIDELBERG • LONDON • NEW YORK • OXFORD
PARIS • SAN DIEGO • SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

William Andrew is an imprint of Elsevier



William Andrew is an imprint of Elsevier
225 Wyman Street, Waltham, MA 02451, USA
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK

Third edition 2014

Copyright © 2014 Elsevier Inc. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means electronic, mechanical, photocopying, recording or otherwise without the prior written permission of the publisher

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone (+44) (0) 1865 843830; fax (+44) (0) 1865 853333; email: permissions@elsevier.com. Alternatively you can submit your request online by visiting the Elsevier web site at <http://elsevier.com/locate/permissions>, and selecting *Obtaining permission to use Elsevier material*

Notice

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made

British Library Cataloguing-in-Publication Data

A catalog record for this book is available from the British Library

Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

ISBN: 978-0-323-31016-1

For information on all William Andrew publications
visit our website at books.elsevier.com

Typeset by MPS Limited, Chennai, India
www.adi-mps.com

Printed and bound by CPI Group (UK) Ltd, Croydon, CR0 4YY

14 15 16 17 18 10 9 8 7 6 5 4 3 2 1



Working together
to grow libraries in
developing countries

www.elsevier.com • www.bookaid.org

THE EFFECT OF TEMPERATURE AND OTHER FACTORS ON PLASTICS AND ELASTOMERS



PLASTICS DESIGN LIBRARY (PDL)

PDL HANDBOOK SERIES

Series Editor: Sina Ebnesajjad, PhD

President, FluoroConsultants Group, LLC

Chadds Ford, PA, USA

www.FluoroConsultants.com

The **PDL Handbook Series** is aimed at a wide range of engineers and other professionals working in the plastics industry, and related sectors using plastics and adhesives.

The PDL is a series of data books, reference works and practical guides covering plastics engineering, applications, processing, and manufacturing, and applied aspects of polymer science, elastomers and adhesives.

Recent titles in the series

Biron, Thermoplastics and Thermoplastic Composites, Second Edition (ISBN: 9781455778980)

Drobny, Ionizing Radiation and Polymers (ISBN: 9781455778812)

Ebnesajjad, Polyvinyl Fluoride (ISBN: 9781455778850)

Ebnesajjad, Plastic Films in Food Packaging (ISBN: 9781455731121)

Ebnesajjad, Handbook of Adhesives and Surface Preparation (ISBN: 9781437744613)

Ebnesajjad, Handbook of Biopolymers and Biodegradable Plastics (ISBN: 9781455774425)

Fink, Reactive Polymers, Second Edition (ISBN: 9781455731497)

Fischer, Handbook of Molded Part Shrinkage and Warpage, Second Edition (ISBN: 9781455725977)

Giles Jr., Wagner, Jr., Mount III, Extrusion, Second Edition (ISBN: 9781437734812)

Goodman & Dodiuk, Handbook of Thermoset Plastics, Third Edition (ISBN: 9781455731077)

Kutz, Applied Plastics Engineering Handbook (ISBN: 9781437735147)

Kutz, PEEK Biomaterials Handbook (ISBN: 9781437744637)

McKeen, The Effect of Long Term Thermal Exposure on Plastics and Elastomers (ISBN: 9780323221085)

McKeen, The Effect of Sterilization on Plastics and Elastomers, Third Edition (ISBN: 9781455725984)

McKeen, The Effect of UV Light and Weather on Plastics and Elastomers (ISBN: 9781455728510)

McKeen, Film Properties of Plastics and Elastomers, Third Edition (ISBN: 9781455725519)

McKeen, Permeability Properties of Plastics and Elastomers, Third Edition (ISBN: 9781437734690)

McKeen, The Effect of Creep and other Time Related Factors on Plastics and Elastomers, Second Edition (ISBN: 9780815515852)

Modjarrad and Ebnesajjad, Handbook of Polymer Applications in Medicine and Medical Devices (ISBN: 9780323228053)

Niaounakis, Biopolymers Reuse, Recycling, and Disposal (ISBN: 9781455731459)

Sastri, Plastics with Medical Devices, Second Edition (ISBN: 9781455732012)

Sin, Rahmat and Rahman, Polylactic Acid (ISBN: 9781437744590)

Wagner, Multilayer Flexible Packaging (ISBN: 9780815520214)

Woishnis & Ebnesajjad, Chemical Resistance, Volumes 1 & 2, Chemical Resistance of Thermoplastics (ISBN: 9781455778966)

Woishnis & Ebnesajjad, Chemical Resistance, Volume 3, Chemical Resistance of Specialty Thermoplastics (ISBN: 9781455731107)

To submit a new book proposal for the series, please contact Sina Ebnesajjad, Series Editor

sina@FluoroConsultants.com

or

Matthew Deans, Senior Publisher

m.deans@elsevier.com

This book is an update to one of the first of a series of PDL books covering the properties of plastic and elastomer materials. The last edition was published in 2008. A lot has changed in the field since 2008. There has been a huge turnover in ownership of the plastic producing companies. There has been a lot of consolidation, which of course means discontinued products.

Plastics of similar polymer types are grouped into nine chapters. Each of these chapters is split into sections covering a specific type of plastic polymer. Included is a brief explanation of the chemistry of the polymers used in the plastics of that section.

Chapter 1 has been updated to provide background to polymer chemistry and plastic formulations. It is an introductory chapter that summarizes the chemistry of making polymers, the formulation of plastics, testing and test methods, and plastic selection.

Most plastic products and parts are expected to be used in environments other than room temperature and standard humidity conditions. Chapters 2–10 are a data bank that serves as an evaluation of plastics as they are exposed to varying operating conditions at different temperatures, humidity, and other factors. In these chapters, several new plastic types have been added along with newly available data. Over 1200 uniform graphs for more than 60 generic families of plastics are contained in these chapters. The following types of graphs may be included.

A. Properties as functions of temperature:

1. Flexural modulus/strength
2. Tensile modulus/strength
3. Shear modulus/strength
4. Impact strength

5. Hardness
6. Torsional modulus
7. Coefficient of thermal expansion
8. Dielectric constant
9. Dissipation factor
10. Water absorption
11. Specific volume/heat
12. Pressure–volume–temperature plots

B. Stress vs. strain curves at various temperatures:

1. Strain rates
2. Humidity levels

C. Mechanical properties as a function of:

1. Strain rate
2. Humidity level

D. Electrical properties as a function of:

1. Humidity level
2. Frequency

E. Also included:

1. Properties vs. thickness
2. Dimensions vs. moisture
3. Properties vs. glass content and other formulation factors

Chapter 11 contains extensive mechanical and electrical data in tabular form. These tables contain data on several thousand plastics. Similarly, Chapter 12 contains thermal data on several thousand plastics.

Data from the previous editions have only been removed if those products were discontinued, and many products were. Product names and manufacturers have been updated.

Laurence W. McKeen
2014

Contents

Preface	x
1 Introduction to Plastics, Polymers, and Their Properties	1
1.1 Polymer/Plastic Chemistry	1
1.1.1 Polymerization.....	1
1.1.1.1 Addition Polymerization	1
1.1.1.2 Condensation Polymerization	1
1.1.2 Copolymers.....	2
1.1.3 Linear, Branched, and Cross-linked Polymers	3
1.1.4 Polarity	3
1.1.5 Unsaturation	3
1.1.6 Steric Hindrance.....	5
1.1.7 Isomers	5
1.1.7.1 Structural Isomers	5
1.1.7.2 Geometric Isomers	6
1.1.7.3 Stereoisomers—Atactic, Isotactic, and Syndiotactic.....	6
1.1.8 Inter- and Intramolecular Attractions in Polymers.....	7
1.1.8.1 Hydrogen Bonding	7
1.1.8.2 Van der Waals Forces	7
1.1.8.3 Chain Entanglement.....	8
1.1.9 General Classifications.....	8
1.1.9.1 Molecular Weight.....	8
1.1.9.2 Thermosets vs. Thermoplastics.....	9
1.1.9.3 Crystalline vs. Amorphous.....	9
1.2 Plastic Compositions	10
1.2.1 Fillers, Reinforcement, Composites.....	11
1.2.2 Combustion Modifiers, Fire, Flame Retardants, and Smoke Suppressants.....	11
1.2.3 Release Agents	12
1.2.4 Slip Additives/Internal Lubricants.....	12
1.2.5 Antiblock Additives	13
1.2.6 Catalysts	13
1.2.7 Impact Modifiers and Tougheners.....	13
1.2.8 UV/Radiation Stabilizers	14
1.2.9 Optical Brighteners	14
1.2.10 Plasticizers	14
1.2.11 Pigments, Extenders, Dyes, and Mica	14
1.2.11.1 Titanium Dioxide	14
1.2.11.2 Carbon Black.....	14

1.2.12 Coupling Agents.....	14
1.2.13 Thermal Stabilizers	14
1.2.14 Antistats.....	15
1.3 Testing of Plastics	15
1.3.1 Mechanical Property Testing of Plastics	15
1.3.1.1 Tensile Properties.....	16
1.3.1.2 Compressive Properties.....	18
1.3.1.3 Shear Properties.....	19
1.3.1.4 Flexural Properties	22
1.3.1.5 Impact Property Testing of Plastics.....	22
1.3.2 Thermal Property Testing of Plastics	23
1.3.2.1 Heat Deflection Temperature.....	25
1.3.2.2 Vicat Softening Temperature.....	26
1.3.2.3 Melt Flow Index.....	26
1.3.2.4 Glass Transition Temperature (T_g)	28
1.3.2.5 Melting Point (T_m)	31
1.3.2.6 Coefficient of Thermal Expansion.....	32
1.4 Principles of Plastic Product Design	32
1.4.1 Rigidity of Plastic Materials	33
1.4.2 The Assessment of Maximum Service Temperature	34
1.4.3 Assessment of Thermal Stability	34
1.4.4 Toughness.....	36
1.4.5 The Assessment of Impact Strength	39
1.4.6 Time-Dependent Behavior	40
1.4.7 Selection Guides.....	40
1.5 Summary.....	45
References.....	45
 2 Styrenic Plastics	 47
2.1 Acrylonitrile Butadiene Styrene (ABS).....	47
2.2 Methyl Methacrylate—Acrylonitrile—Butadiene—Styrene (MABS) Polymer.....	48
2.3 Acrylonitrile Styrene Acrylate (ASA).....	60
2.4 Polystyrene (PS).....	62
2.5 Styrene Acrylonitrile (SAN)	66
2.6 Styrenic Butadiene Block Copolymers (SBC)	72
2.7 Styrene Maleic Anhydride (SMA).....	72
2.8 Styrenic Blends and Alloys.....	83
References.....	90
 3 Polyether Plastics.....	 91
3.1 Acetals—Polyoxymethylene (POM or Acetal Homopolymer).....	91
3.2 Polyoxymethylene Copolymer (POM-Co or Acetal Copolymer).....	91
3.3 Modified Polyphenylene Ether/Polyphenylene Oxides (PPE or PPO)	102
References.....	142

4	Polyesters	143
4.1	Polycarbonate (PC)	143
4.2	Polybutylene Terephthalate (PBT)	143
4.3	Polyethylene Terephthalate (PET)	144
4.4	Liquid Crystalline Polymer (LCP)	144
4.5	Polycyclohexylene—Dimethylene Terephthalate (PCT)	170
4.6	Polyethylene Naphthalate (PEN) and Polybutylene Naphthalate (PBN)	178
4.7	Polyester Blends and Alloys	179
	References	197
5	Polyimides	199
5.1	Polyimide (PI)	199
5.1.1	Standard PIs	199
5.1.2	Thermoplastic PIs	199
5.2	Polyamide—Imide (PAI)	199
5.3	Polyetherimide (PEI)	210
	References	232
6	Polyamides (Nylons)	233
6.1	Nylon 6 (PA6)	233
6.2	Nylon 11 (PA11)	234
6.3	Nylon 12 (PA12)	245
6.4	Nylon 46 (PA46)	251
6.5	Nylon 66 (PA66)	256
6.6	Nylon 610 (PA610)	257
6.7	Nylon 612 (PA612)	257
6.8	Nylon 6/66 (PA666)	291
6.9	Nylon 1010 (PA1010)	291
6.10	Nylon Amorphous	308
6.11	Polyarylamide (PAA)	309
6.12	Polyphthalamide (PPA)	315
6.13	Polyamide Blends and Alloys	339
	References	339
7	Polyolefins and Acrylics	341
7.1	Polyethylene (PE)	341
7.2	Polypropylene (PP)	342
7.3	Polymethylpentene (PMP)	343
7.4	Rigid Polyvinyl Chloride (PVC)	356
7.5	Cyclic Olefin Copolymer (COC)	362
7.6	Polyacrylics	363
	References	370
8	Thermoplastic Elastomers	371
8.1	Thermoplastic Polyurethane Elastomers (TPUs)	371
8.2	Olefinic Thermoplastic Elastomers (TPO)	381

8.3 Thermoplastic Copolyester Elastomers (TPE-Es or COPEs).....	381
8.4 TPEs—Polyether Block Amide (PEBA)	395
References.....	398
9 Fluoropolymers	399
9.1 Polytetrafluoroethylene (PTFE)	399
9.2 Ethylene Chlorotrifluoroethylene (ECTFE)	401
9.3 Ethylene Tetrafluoroethylene (ETFE)	405
9.4 Fluorinated Ethylene Propylene (FEP)	410
9.5 Perfluoroalkyl Vinyl Ether (PFA/MFA).....	419
9.5.1 PFA.....	427
9.5.2 MFA.....	434
9.6 Polychlorotrifluoroethylene (PCTFE).....	434
9.7 Polyvinylidene Fluoride (PVDF)	435
9.8 Polyvinyl Fluoride (PVF).....	442
9.9 Amorphous Fluoropolymer: Teflon [®] AF	452
References.....	461
10 High Temperature Polymers.....	463
10.1 Polyketones (PAEK)	463
10.1.1 Polyether Ether Ketones (PEEK).....	463
10.1.2 Polyether Ketones (PEK)	465
10.1.3 Polyether Ketone Ether Ketone Ketones (PEKEKK)	465
10.1.4 Polyaryletherketones (PAEK)	479
10.1.5 Blends.....	482
10.2 Polyethersulfone (PES)	489
10.3 Polyphenylene Sulfide (PPS)	489
10.4 Polysulfone (PSU).....	501
10.5 Polyphenylsulfone (PPSU).....	512
10.6 Parylene (Poly(<i>p</i> -xylylene))	525
References.....	527
11 Tables of Selected ISO 10350 Properties of Selected Plastics	529
11.1 Styrenic Plastics	532
11.2 Polyethers	543
11.3 Polyesters.....	553
11.4 Polyimides	581
11.5 Polyamides (Nylons).....	582
11.6 Polyolefins and Acrylics	622
11.7 Thermoplastic Elastomers.....	629
11.8 Fluoropolymers.....	633
11.9 High Temperature Plastics	642
12 Tables of Selected Thermal Properties of Selected Plastics	649
12.1 Styrenic Plastics	650
12.2 Polyethers	659

12.3 Polyesters.....	667
12.4 Polyimides	693
12.5 Polyamides (Nylons)	696
12.6 Polyolefins and Acrylics	715
12.7 Thermoplastic Elastomers	721
12.8 Fluoropolymers.....	725
12.9 Miscellaneous High Temperature Plastics.....	726
Appendix 1: Abbreviations	731
Appendix 2: Conversion Factors.....	733
Index	737

1 Introduction to Plastics, Polymers, and Their Properties

The most basic components of plastic and elastomer materials are polymers. The word polymer is derived from the Greek term for “many parts.” Polymers are large molecules comprised of many repeat units called monomers that have been chemically bonded into long chains. Since World War II, the chemical industry has developed a large quantity of synthetic polymers to satisfy the material needs for a diverse range of products, including paints, coatings, fibers, films, elastomers, and structural plastics. Literally thousands of materials can be called “plastics,” although the term today is typically reserved for polymeric materials, excluding fibers, which can be molded or formed into solid or semisolid objects. As of the beginning of 2014, IDES The Plastics Web® (<http://www.ides.com>) listed over 85,900 different grades of plastic from over 900 suppliers.

1.1 Polymer/Plastic Chemistry

This section provides a basic understanding of polymers and plastics from a chemistry point of view.

1.1.1 Polymerization

Polymerization is the process of chemically bonding monomer building blocks to form large molecules. Commercial polymer molecules are usually thousands of repeat units long. Polymerization can proceed by one of several methods. The two most common methods are called addition polymerization and condensation polymerization.

1.1.1.1 Addition Polymerization

In *addition polymerization* (sometimes called *chain-growth polymerization*), a chain reaction adds new monomer units to the growing polymer molecule one at a time through double or triple bonds in

the monomer. The polymerization process takes place in three distinct steps:

1. *Chain initiation*—Usually by means of an initiator which starts the polymerization process. The reactive initiation molecule can be a radical (free radical polymerization), cation (cationic polymerization), anion (anionic polymerization), and/or organometallic complex (coordination polymerization).
2. *Chain propagation*—A monomer adds onto the chain and each new monomer unit creates an active site for the next attachment. The net result is shown in Figure 1.1.
3. *Chain termination*—The radical, cation, or anion is “neutralized,” stopping the chain propagation.

Many of the plastics discussed in later chapters of this book are formed in this manner. Some of the plastics made by addition polymerization include polyethylene (PE), polyvinyl chloride (PVC), acrylics, polystyrene (PS), and polyoxymethylene (acetal).

1.1.1.2 Condensation Polymerization

The other common method is *condensation polymerization* (also called *step-growth polymerization*), in which the reaction between monomer units and the growing polymer chain end group releases a small molecule, often water, as shown in Figure 1.2. The monomers in this case have two reactive groups. This reversible reaction will reach equilibrium and halt unless this small molecular by-product is removed. Polyesters and polyamides are among the plastics made by this process.

Understanding the polymerization process used to make a particular plastic gives insight into the nature of the plastic. For example, plastics made via condensation polymerization, in which water is released, can degrade when exposed to water at high temperature. Polyesters such as polyethylene terephthalate (PET)

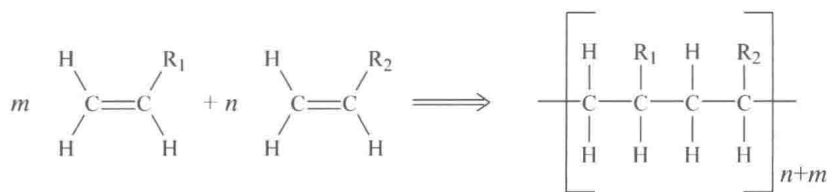


Figure 1.1 Addition polymerization.

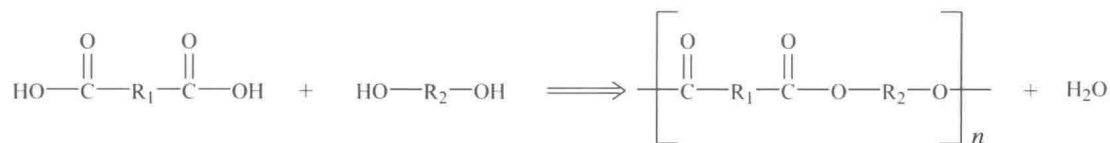


Figure 1.2 Condensation polymerization.

can degrade by a process called hydrolysis when exposed to acidic, basic, or even some neutral environments, severing the polymer chains. The polymer's properties are degraded as a result.

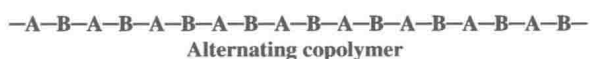
1.1.2 Copolymers

A copolymer is a polymer formed when two (or more) different types of monomers are linked in the same polymer chain, as opposed to a homopolymer where only one monomer is used. If exactly three monomers are used, it is called a terpolymer.

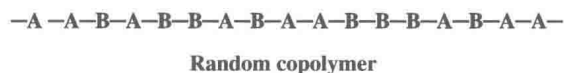
Monomers are only occasionally symmetric; the molecular arrangement is the same regardless of which end of the monomer molecule you are looking at. The arrangement of the monomers in a copolymer can be head-to-tail, head-to-head, or tail-to-tail. Since a copolymer consists of at least two types of repeating units, copolymers can be classified based on how these units are arranged along the chain. These classifications include:

- Alternating copolymer
- Random copolymer (statistical copolymer)
- Block copolymer
- Graft copolymer

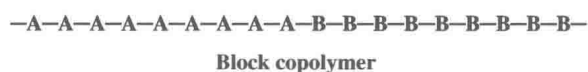
In the following examples, A and B are different monomers that do not have to be present in a one-to-one ratio. When the two monomers are arranged in an alternating fashion, the polymer is called an alternating copolymer:



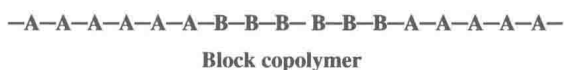
In a random copolymer, the two monomers may link in any order:



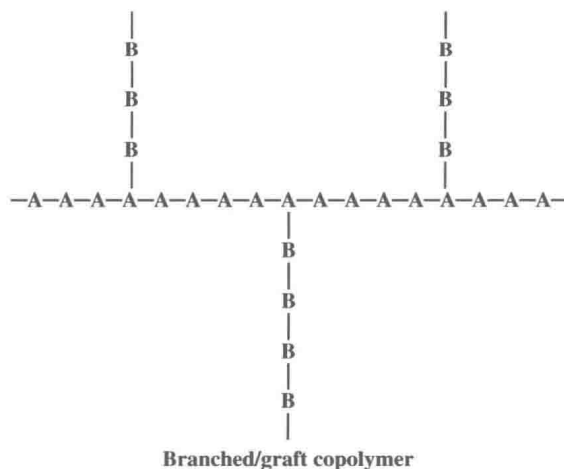
In a block copolymer, all monomers of one type are grouped together and all monomers of the other type are grouped together. A block copolymer can be thought of as two homopolymers joined together at the ends:



A polymer that consists of large grouped blocks of each of the monomers is also considered as a block copolymer:



When chains of a polymer made of monomer B are grafted onto a polymer chain of monomer A we have a graft copolymer:



High-impact polystyrene (HIPS) is a graft copolymer. It is a PS backbone with chains of polybutadiene grafted onto the backbone. PS gives the material strength, but the rubbery polybutadiene chains give resilience to make it less brittle.

1.1.3 Linear, Branched, and Cross-linked Polymers

Some polymers are linear—a long chain of connected monomers. PE, PVC, Nylon 66, and polymethyl methacrylate (PMMA) are some linear commercial examples found in this book. Branched polymers can be visualized as a linear polymer with side chains of the same polymer attached to the main chain. While the branches may in turn be branched, they do not connect to another polymer chain. The ends of the branches are not connected to anything. Special types of branched polymers include star polymers, comb polymers, brush polymers, dendronized polymers [1], ladders, and dendrimers. A cross-linked polymer, sometimes called a network polymer, is one in which different chains are connected. Essentially the branches are connected to different polymer chains on the ends. These three polymer structures are shown in Figure 1.3.

1.1.4 Polarity

A molecule is two or more atoms joined by a covalent bond. Basically the positively charged atom nuclei share the negatively charged electrons. However, if the atoms are different they may not share the electrons equally. The electrons will be denser around one of the atoms. This makes that end more negatively charged than the other end and that creates a negative pole and a positive pole (a *dipole*), and such a bond is said to be a *polar bond* and the molecule is polar and has a *dipole moment*. A measure of how much an atom attracts electrons is *electronegativity*. The electronegativity of common atoms in polymers follows:



The polarity of a molecule affects the attraction between molecular chains, which affects the structure of the polymer and the attraction of polar molecules, so one would expect polarity to affect solubility which affects permeability.

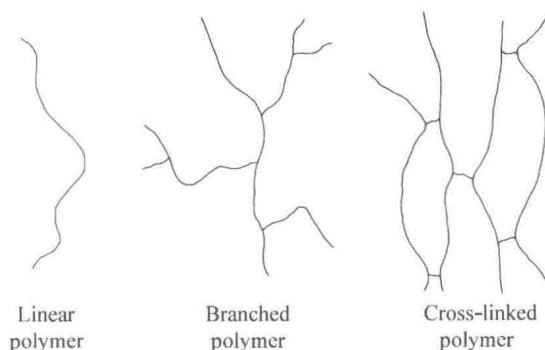


Figure 1.3 Linear, branched, and cross-linked polymers.

How does one predict molecular polarity? When there are no polar bonds in a molecule, there is no permanent charge difference between one part of the molecule and another, so the molecule is nonpolar. For example, the Cl_2 molecule has no polar bonds because the electron charge is identical on both atoms. It is therefore a nonpolar molecule. The C—C and C—H bonds in hydrocarbon molecules, such as ethane, C_2H_6 , are not significantly polar, so hydrocarbons are nonpolar molecular substances and hydrocarbon polymers such as PE or polypropylene (PP) are also nonpolar.

A molecule can possess polar bonds and still be nonpolar, however. If the polar bonds are evenly (or symmetrically) distributed, the bond dipoles cancel and do not create a molecular dipole. For example, the three bonds in a molecule of CCl_4 are significantly polar, but they are symmetrically arranged around the central carbon atom. No side of the molecule has more negative or positive charge than another side, and so the molecule is nonpolar. Dipole moments in some small molecules are given in Table 1.1.

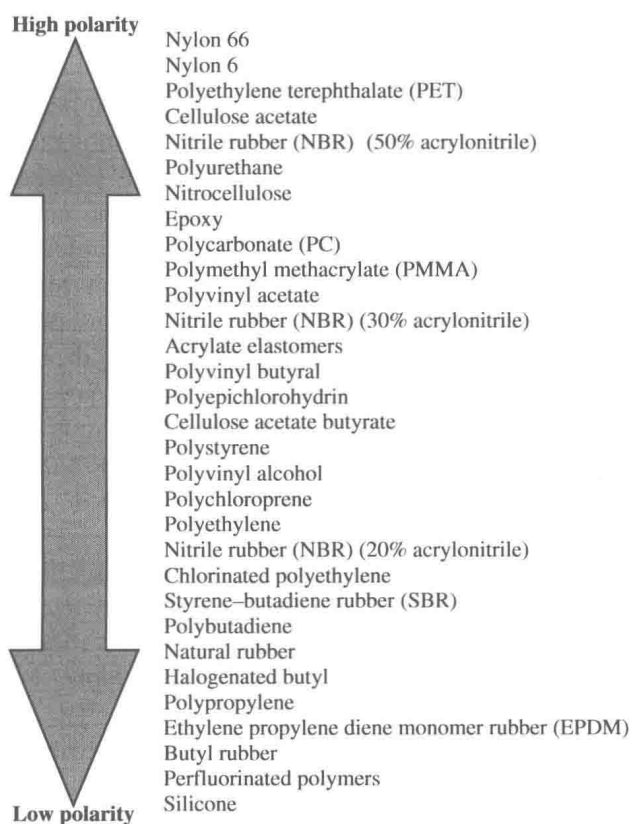
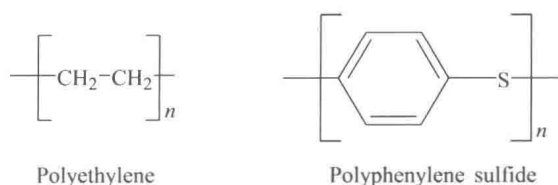
Generally polar polymers are more permeable to water than nonpolar polymers. Figure 1.4 shows a qualitative ranking of some polymer polarities.

1.1.5 Unsaturation

Up to this point in the discussion of polymer chemistry, the atom to atom structure has not been discussed. The covalent bonds between atoms in a polymer can be single, double, triple bonds, or even rings. The presence of bonds higher than single bonds generally makes the polymer molecule stiffer and reduces freedom of rotation along the

Table 1.1 Dipole Moments in Some Small Molecules

Molecule	Dipole Moment	Molecule	Dipole Moment	Molecule	Dipole Moment
H ₂	0	HF	1.75	CH ₄	0.0
O ₂	0	H ₂ O	1.84	CH ₃ Cl	1.86
N ₂	0	NH ₃	1.46	CCl ₄	0
Cl ₂	0	NF ₃	0.24	CO ₂	0
Br ₂	0	BF ₃	0		

**Figure 1.4** Qualitative ranking of polymer polarities.**Figure 1.5** Example polymer structures.

polymer chain, and that can affect its properties. It is easier to discuss molecules first and then extend that discussion to polymers. Saturated molecules only contain single bonds with no rings.

Often when talking about molecular unsaturation, the *degree of unsaturation* (DoU) is noted. The formula to calculate DoU, if the molecular formula is given, is

$$\text{DoU} = \frac{2C + 2 + N - X - H}{2} \quad (1.1)$$

where

C , number of carbons

N , number of nitrogens

X , number of halogens (F, Cl, Br, I)

H , number of hydrogens

Oxygen and sulfur are not included in the formula because saturation is unaffected by these elements.

Examples:

$$\begin{aligned} \text{Ethylene: } \text{C}_2\text{H}_4 \quad \text{DoU} &= \frac{2C + 2 + N - X - H}{2} \\ &= \frac{2 \times 2 + 2 + 0 - 0 - 4}{2} = 1 \end{aligned} \quad (1.2)$$

$$\begin{aligned} \text{Benzene: } \text{C}_6\text{H}_6 \quad \text{DoU} &= \frac{2C + 2 + N - X - H}{2} \\ &= \frac{2 \times 6 + 2 + 0 - 0 - 6}{2} = 4 \end{aligned} \quad (1.3)$$

When polymers are used, the formula shown is often the repeating unit as shown in Figure 1.5. This will often have two bonds that are shown to which the repeating unit is supposed to attach. If applying a DoU formula to the repeating unit, one would remove the “+2” in the formula.

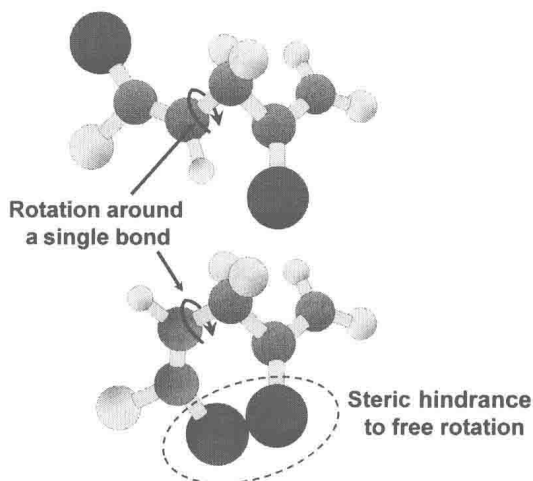


Figure 1.6 Steric hindrance shown with a ball-and-stick molecular model.

Examples:

Polyethylene: $-(\text{CH}_2 - \text{CH}_2)_n -$

$$\text{DoU} = \frac{2C + N - X - H}{2} = \frac{2 \times 2 + 0 - 0 - 4}{2} = 0 \quad (1.4)$$

Polyphenylsulfone: $-(\text{C}_6\text{H}_4 - \text{S})_n -$

$$\text{DoU} = \frac{2C + N - X - H}{2} = \frac{2 \times 6 + 0 - 0 - 4}{2} = 4 \quad (1.5)$$

1.1.6 Steric Hindrance

As described earlier in this chapter, polymers are long chains of atoms linked together. They may be flexible and bendable. To explain this, one may visualize them as a ball-and-stick model. In chemistry, the ball-and-stick model is a molecular model of a chemical substance which aims to display both the three-dimensional position of the atoms and the bonds between them. The atoms are typically represented by spheres, connected by rods which represent the bonds. Double and triple bonds are usually represented by two or three curved rods, respectively. The chemical element of each atom is often indicated by the sphere's color and size. The top of Figure 1.6 shows a drawing of a ball-and-stick model of a molecule. Figure 1.6 also indicates that there is free rotation around the single bonds. If there was a double or triple bond, there would not be any rotation possible around those bonds.

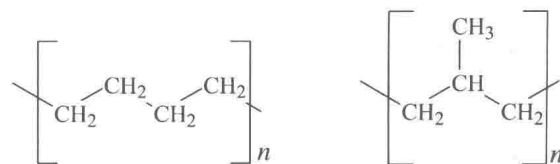


Figure 1.7 Structural isomers.

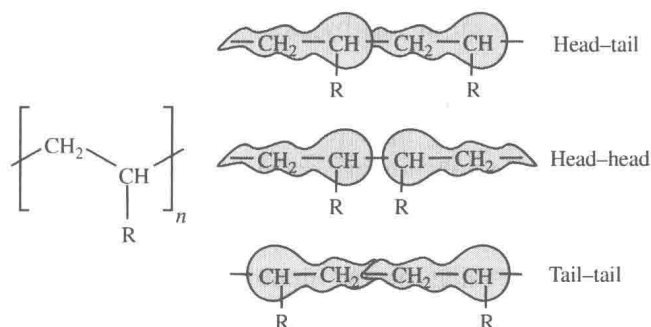


Figure 1.8 Head-to-tail isomers [8].

Similarly, ring structures, while they might flex a little bit, inhibit rotation. In some cases, such as shown in the bottom of Figure 1.6, large atoms or bulky side groups might bump into each other as the molecule rotates around single bonds. This is called *sterically hindered* or *steric hindrance*. Hindered or inhibited rotation stiffens the polymer molecule and dramatically affects its physical properties.

1.1.7 Isomers

Isomers (from Greek *isomerēs*; *isos* = “equal,” *méros* = “part”) are compounds with the same molecular formula but a different arrangement of the atoms in space. There are many kinds of isomers and the properties can differ widely or almost not at all.

1.1.7.1 Structural Isomers

Structural isomers have the atoms arranged in a completely different order as shown in Figure 1.7. Here both polymer repeating groups have the same formula, $-\text{C}_4\text{H}_8-$, but the atoms are arranged differently. The properties of structural isomers may be very different from each other.

Often the repeating group in a polymer is exactly the same formula, but the repeating group is flipped over as shown in Figure 1.8. If one views the

repeating group as having a head and a tail then the different ways to connect neighboring repeating units are head—tail, head—head, and tail—tail.

1.1.7.2 Geometric Isomers

When there is a carbon—carbon double bond in a molecule, there might also be two ways to arrange the groups attached to the double bonds. This is best seen in side-by-side structures as shown in Figure 1.9.

These are called *geometric isomers* that owe their existence to hindered rotation about double bonds. If the substituents are on the same side of the double bond then the isomer is referred to as *cis*- (Latin: on this side). If the substituents are on the opposite side of the double bond then it is referred to as *trans*- (Latin: across).

1.1.7.3 Stereoisomers—Atactic, Isotactic, and Syndiotactic

Stereoisomerism occurs when two or more molecules have identical molecular formula and the same structural formula (i.e., the atoms are arranged in the same order). However, they differ in their 2D or 3D spatial arrangements of their bonds—which mean different spatial arrangement of the atoms—even though they are bonded in the same order. This may best be understood by example.

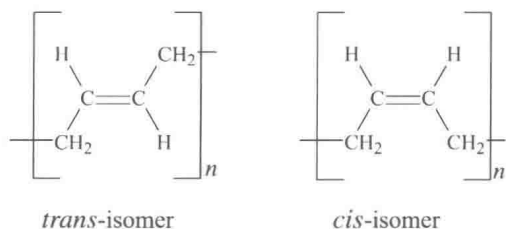


Figure 1.9 *cis*- and *trans*-isomers.

PPs all have the same simplified structural polymer formula of polypropylene as shown in Figure 1.10.

However, there are subtle differences in the ways to draw this structure. Figure 1.11 shows a longer structure of polypropylene and also some three-dimensional structure. This structure shows how some bonds (the dotted lines) are behind the plane of the paper and others stick out of the paper (the ones on the ends of the little triangular wedges). In this structure, some of the methyl ($-\text{CH}_3$) groups are above the paper plane and others are behind the paper plane. This is called *atactic* polypropylene.

Atactic polypropylene has at random about 50% of hydrogen/methyl groups in front of/behind the C—C—C chain viewing plane. This form of polypropylene is amorphous (noncrystalline, discussed in Section 1.1.9.3) and has an irregular structure due to the random arrangement of the methyl groups attached to the main carbon—carbon chain. It tends to be softer and more flexible than the other forms (described below) and is used for roofing materials, sealants, and other weatherproof coatings.

Isotactic polypropylene has all of the methyl groups in front of the C—C—C chain viewing plane and all of the Hs behind as shown in Figure 1.12. This stereoregular structure maximizes the molecule—molecule contact and so increases the intermolecular forces compared to the atactic form. This regular structure is much stronger (than the atactic form above) and is used in sheet and film form for packaging and carpet fibers.

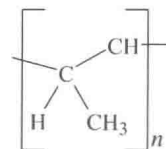


Figure 1.10 The structure of polypropylene.

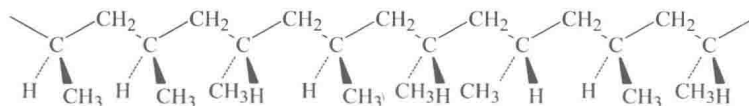


Figure 1.11 The structure of atactic polypropylene.

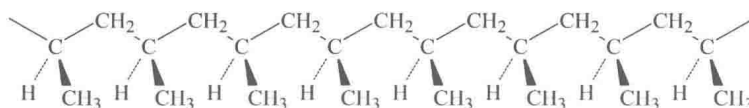


Figure 1.12 The structure of isotactic polypropylene.