

# Polymeric Liquids & Networks: Structure and Properties

William W. Graessley

063  
G735

---

# Polymeric Liquids and Networks

## Structure and Properties

---

**William W. Graessley**  
*Emeritus Professor, Princeton University*  
*Adjunct Professor, Northwestern University*



E200400519

**GS** **Garland Science**  
Taylor & Francis Group  
NEW YORK AND LONDON

## About the Author

William W. Graessley was born in Muskegon, Michigan in 1933. He holds degrees in both Chemistry and Chemical Engineering, as well as a Ph.D. from the University of Michigan. He has worked within academia and industry and has published extensively on radiation cross-linking of polymers, polymerization reactor engineering, molecular aspects of polymer rheology, rubber network elasticity, and the thermodynamics of polymer blends. He is currently a Professor Emeritus at Princeton University and an Adjunct Professor at Northwestern University. His honors include an NSF Predoctoral Fellowship, the Bingham Medal (Society of Rheology), the Whitby Lectureship (University of Akron), the High Polymer Physics Prize (American Physical Society), and membership in the National Academy of Engineering.

Denise T. Schanck, *Vice President*  
Robert L. Rogers, *Senior Editor*  
Liliana Segura, *Editorial Assistant*  
Adam Sendroff, *Marketing Director*  
Randy Harinandan, *Marketing Assistant*

Dennis P. Teston, *Production Director*  
Anthony Mancini Jr., *Production Manager*  
Brandy Mui, *STM Production Editor*  
Mark Lemer, *Art Manager*

Published in 2004 by  
Garland Science  
A member of the Taylor & Francis Group  
29 West 35th Street  
New York, NY 10001  
[www.taylorandfrancis.com](http://www.taylorandfrancis.com)

Published in Great Britain by  
Garland Science  
A member of the Taylor & Francis Group  
11 New Fetter Lane  
London EC4P 4EE  
[www.taylorandfrancis.co.uk](http://www.taylorandfrancis.co.uk)

Copyright © 2004 by Taylor & Francis Books, Inc.

Printed in the United States of America on acid-free paper.

All rights reserved. No part of this book may be reprinted or reproduced or utilized in any form or by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying and recording, or in any information storage or retrieval system, without permission in writing from the publisher.

10 9 8 7 6 5 4 3 2 1

## Library of Congress Cataloging-in-Publication Data

Graessley, W.W. (William Walter)

Polymeric liquids and networks : structure and properties / by William W. Graessley.  
p. cm.

Includes bibliographical references and index.

ISBN 0-8153-4169-5 (alk. paper)

1. Polymer solutions. 2. Polymer networks. I. Title.

QD381.9S65G73 2003  
547'.70454-DC21

2003048324

---

# Polymeric Liquids and Networks

## Structure and Properties

---

To Helen

# Preface

This book is the first of two volumes aimed at a unified view of flexible-chain polymer liquids and networks. The topics range from equilibrium properties, the subject of the present book, to dynamical response, finite deformation behavior, and non-Newtonian flow in Volume 2. Volume 2, subtitled “Dynamics and Rheology,” will appear in about two years. These various aspects of the field were developed over the past seventy years by researchers from many academic disciplines. The infusion of fresh viewpoints continually invigorated and enriched the field, making polymeric liquids and networks a truly interdisciplinary subject. The lack of a common terminology and perspective, however, has led to compartmentalization, thus making it difficult for a newcomer, even one technically trained, to gain a broad appreciation of the field and to see the relationships among its various parts. I hope these two volumes, without diluting the substance, will go some way toward achieving a desirable unity.

The development of the topic emphasizes fundamental principles and the molecular viewpoint. The conceptual basis of the theories underlying each topical area is explained with the derivations sometimes outlined briefly and sometimes in detail; technical terminology is kept to the minimum necessary for a concise coherent presentation. The goal is informed understanding rather than detailed technical proficiency. Theory, experiment, and simulation are woven together as appropriate to achieve a balanced view. Both volumes are aimed to serve academic and industrial needs, consolidating the understanding of topics with both practical and fundamental significance, and written from a technical but nonspecialized perspective.

The books deal primarily with nonpolar and weakly polar species and with the results derived from experiments on structurally well-defined polymer systems. The object is not, of course, to ignore the more complex systems, which are pervasive in both nature and industry and important in their own right. Indeed, much space is devoted to structural distributions, their characterization, and their effect on properties. The object of this book is rather to provide a framework for the better understanding



of all polymeric liquids by identifying, in the simplest possible circumstances, the universal attributes of a chainlike and flexible molecular structure.

Notable omissions from the books (aside from passing reference) are theories of the glass transition, properties of the glassy state, flow properties of multiphase liquids, crystallization phenomena, thermosetting resins, filled polymers, and highly polar polymers. Other topics that would seem natural for volumes like these—block copolymers, polyelectrolyte solutions, and elastically driven flow instabilities—are treated in rather cursory fashion. One reason for this is the author's inexperience in many of these areas; another is the newness and still rapidly evolving character of some topics. Still another is the lack of sufficient systematic experimental studies. The need to keep the size of the books within some reasonable bounds and still do justice to the subjects that are covered was another consideration. Even with the scope narrowed in this way, the amount of relevant material is enormous.

I have long felt that dynamics and flow behavior have been wrongfully neglected in general textbooks on polymers, being regarded as somehow too mathematical, too specialized, or perhaps simply less important in relation to other topics competing for the space. The structure–property relationships for dynamics and rheology abound in universal laws, especially those whose forms are independent of the polymeric species and are of comparatively recent discovery. Many of these are interrelated and can now be understood in quite simple terms. Others belong in introductory polymer textbooks, and I hope these volumes will assist the writers of these future polymer textbooks by giving them a place to find this information without the necessity of digging through a diverse, unfamiliar, and sometimes old literature to find examples and data.

I have also felt that the general subject of polymeric liquids and networks would benefit pedagogically by being developed from a background and language common with the molecular theory of liquids. Chapters 2 and 3 of this volume and the first chapter of Volume 2 begin by summarizing the relevant background for small-molecule substances in the dense liquid state. Many basic principles applied to polymeric liquids grew naturally from earlier considerations of monomeric liquids. It is unfortunate that these subjects are not part of the educational background of most people with interests in the field. Making such commonalities of the liquid state evident helps avoid the idea of polymeric liquids as things apart, somehow subject to different rules than other liquids. The freedom from disciplinary restriction also helps to make clear which features of behavior are unique to liquids and networks containing flexible chainlike molecules—rubberlike elasticity and easily observable viscoelastic response—and which are common to all liquids, such as the glass transition.

Some liberties have been taken, harmlessly I think, with the conventional subdivisions of topics, in order to proceed smoothly with the development while keeping related subjects of similar difficulty as close to one another as possible. Thus, although viscosity and diffusion in dilute polymer solutions are dynamic properties, they are

considered along with the thermodynamic aspects of polymeric size in Chapters 5 and 6 of the present book. To do otherwise would have been artificial, the link between static and dynamic measures of size being otherwise so clear. Other dynamic properties in dilute solution are treated in Volume 2, on dynamics and rheology. Also, the chapters on flow behavior in simple shear histories, which includes nonlinear viscoelastic response, are grouped with those on linear viscoelasticity and diffusion, early in Volume 2. An alternative placement, with other aspects of nonlinear viscoelasticity, would have been formally more logical. However, when presented with some theoretical preliminaries, simple shear behavior, including normal stress effects, follows rather naturally after linear response. The alternative would have inserted some chapters of continuum mechanics between the two, thus spoiling the smooth progression.

I have assembled much of the material in both volumes while developing graduate courses on the various topics. The students came mainly from chemical engineering and materials science backgrounds but with a smattering of chemists and physicists and even some precocious undergraduates as well, first at Northwestern University and then at Princeton. A certain amount of background instruction was always necessary. Based on that experience, I feel the two volumes will quite nicely support a one-year graduate course. I have also written this first volume to stand alone, as a one-semester course, useful in its own right as an introduction to the nonrheologic aspects of the field.

Finally, I wish to thank the many people who have helped make this book possible: my students, associates and colleagues at Northwestern University and Princeton University and my coworkers during employment at Exxon. I am also grateful for the generous research support provided over the years by the National Science Foundation, the United States Department of Energy, and the Petroleum Research Fund. I particularly appreciate the advice of Buckley Crist, Jacques Roovers, Guy Berry, Robert Johnston, and Ralph Colby, who read and commented extensively on the draft of this book. I am also indebted to many others who generously contributed their data and time to discuss various technical matters, including Lew Fetters, Nikos Hadjichristidis, Gary Grest, Frank Bates, Chris Macosko, Scott Milner, Nitash Balsara, Ramanan Krishnamoorti, Tim Lodge, Alan Gent, Tony Habenschuss, Rick Register, David Lohse, Michael Rubinstein, Bruce Eichinger, Ben Chu, Ole Kramer, Claude Cohen, Thomas Sun, Pat Cotts, and Greg Dee.

William W. Graessley  
Montague, Michigan  
September, 2003



# Contents

Introduction .....	xiii
<b>Chapter 1 Introduction .....</b>	<b>1</b>
1.1 Molecular Nature of Polymers.....	1
1.2 Polymeric Structure.....	6
1.2.1 Chemical Microstructure .....	7
1.2.2 Chemical Macrostructure .....	10
1.2.3 Rotational States .....	10
1.3 Polymeric Properties .....	12
1.3.1 Species Dependence.....	13
1.3.2 Architectural Dependence.....	14
Viscosity .....	14
Viscoelastic behavior .....	16
1.4 Macromolecular Heterogeneity .....	17
1.4.1 Averages .....	18
1.4.2 Distribution Functions .....	20
Exponential distribution .....	21
Distributions from branching and scission .....	22
Empirical distribution functions.....	25
1.5 Molecular Simulations .....	27
<b>Chapter 2 Molecular Liquids .....</b>	<b>29</b>
2.1 Microscopic Origin of Liquid Properties.....	35
2.1.1 Intermolecular Forces .....	35
2.1.2 Terminology.....	38
2.1.3 Statistical Thermodynamics .....	40
2.1.4 Pair Distributions and Intermolecular Energy.....	43
2.1.5 Principles of Elastic Scattering .....	46
2.1.6 The Structure Factor .....	52

2.2	Liquid Structure and Properties.....	55
2.2.1	Scattering by Pure Liquids.....	55
2.2.2	The van der Waals Liquid .....	59
2.2.3	Hard Sphere Liquids.....	61
2.3	Generalized van der Waals Theory .....	63
2.3.1	The Longuet-Higgins and Widom Model .....	64
2.3.2	Cell Models .....	66
2.3.3	Lattice Models .....	67
2.3.4	Reduced Equations of State.....	69
2.3.5	Cohesive Energy and Internal Pressure.....	70
<b>Chapter 3</b>	<b>Molecular Mixtures.....</b>	<b>77</b>
3.1	Thermodynamics of Liquid Mixtures .....	77
3.2	Liquid-Liquid Phase Behavior .....	83
3.3	Molecular Aspects of Mixing .....	89
3.4	Simple Mixtures.....	94
3.4.1	Properties of the Interaction Parameter .....	96
3.4.2	Phase Behavior .....	98
3.4.3	Observations.....	100
3.5	Regular Mixtures.....	103
3.5.1	Commentary .....	105
3.5.2	Volume Change on Mixing .....	107
3.6	The Free Volume Effect.....	109
3.6.1	Modified FOV Theory .....	111
3.6.2	The Free Volume Interaction Parameter .....	114
3.6.3	Commentary .....	116
<b>Chapter 4</b>	<b>The Random Coil Model .....</b>	<b>121</b>
4.1	Random Walks.....	123
4.1.1	Average End-to-End Distance .....	124
4.1.2	Radius of Gyration .....	125
4.2	Polymer Chains.....	128
4.2.1	Locally Restricted Conformations .....	129
4.2.2	Step Length Definitions.....	132
4.3	Nonlinear Molecules.....	136
4.3.1	Branched Chains.....	137
4.3.2	Macrocycles .....	140
4.4	Random Coil Asymmetry.....	142
4.5	Conformational Distributions .....	142
4.5.1	The End-to-End Vector Distribution .....	143
4.5.2	The Gaussian Form.....	147
4.5.3	Mass Distribution for Gaussian Coils.....	148
4.6	Properties of Random Coil Ensembles .....	149
4.6.1	Mechanical Properties .....	149
4.6.2	Thermodynamic Properties.....	150

4.7	Scattering Properties .....	152
4.7.1	Form Factors .....	152
	Random coil molecules .....	154
	Pair distributions .....	155
	General properties .....	156
4.7.2	Structure Factors .....	158
	One-component systems .....	159
	Two-component systems .....	160
	Incompressible mixtures .....	160
<b>Chapter 5</b>	<b>Dilute Solution Characterization .....</b>	<b>167</b>
5.1	Thermodynamic Characterization Methods .....	167
5.1.1	Osmotic Pressure .....	168
5.1.2	Light Scattering .....	171
	Fundamentals .....	172
	Dilute solutions .....	175
	Scattering method comparisons .....	182
5.2	Dynamic Characterization Methods .....	184
5.2.1	Dynamic Light Scattering .....	185
5.2.2	Viscometry .....	189
5.3	Chromatographic Methods .....	192
5.3.1	Size Exclusion Chromatography .....	192
5.3.2	Multidetector Methods .....	197
<b>Chapter 6</b>	<b>Dilute Solution Properties .....</b>	<b>203</b>
6.1	Intramolecular Interactions .....	203
6.1.1	Excluded Volume .....	204
	Pervaded volume and self-concentration .....	206
	Self-exclusion .....	208
6.1.2	Hydrodynamic Interaction .....	217
6.2	Linear Polymers .....	222
6.2.1	Limiting Size Ratios .....	223
6.2.2	Expansion Factors .....	224
6.2.3	Good Solvent Master Curves .....	227
	Master curve forms .....	231
	Onset molecular weights .....	232
6.3	Branched and Macrocyclic Polymers .....	235
6.3.1	Lightly Branched Model Structures .....	237
	Regular stars .....	237
	Rings .....	239
	H-Polymers .....	243
	Combs .....	243
6.3.2	Lightly Branched Statistical Structures .....	247
6.3.3	Highly Branched Structures .....	249
	Daoud-Cotton model .....	251

	Many-arm star properties .....	254
	Colloidal analogies .....	255
6.4	Concentration Regimes.....	257
<b>Chapter 7</b>	<b>Polymer Solutions .....</b>	<b>265</b>
7.1	Coil Size Beyond Overlap .....	266
7.1.1	Chain Dimensions in Polymer Melts .....	266
7.1.2	Chain Dimensions in Semidilute Solutions .....	269
	Excluded volume screening .....	269
	Concentration dependence .....	273
	Semidilute–concentrated crossover.....	274
	Observations.....	276
7.2	Osmotic Pressure Beyond Overlap .....	278
7.2.1	Flory-Huggins Predictions.....	280
7.2.2	Scaling Analysis .....	283
7.2.3	Experimental Observations .....	284
7.3	Scattering Beyond Overlap .....	286
7.3.1	Correlation Length .....	286
7.3.2	The Random Phase Approximation.....	293
7.3.3	Interpretation Alternatives.....	295
7.3.4	Branch-Induced Ordering.....	296
7.4	The Interaction Parameter.....	297
7.4.1	Evaluation of $\chi$ .....	298
	Vapor composition and sorption .....	298
	Osmometry.....	299
	Inverse chromatography.....	300
	Scattering .....	300
7.4.2	Interpretation of $\chi$ .....	304
	Free volume effects .....	306
	Impact on dilute solutions.....	312
	Athermal solutions.....	313
7.5	Liquid–Liquid Phase Behavior .....	314
7.5.1	Upper Critical Behavior .....	314
7.5.2	Lower Critical Behavior .....	320
7.5.3	Scattering and Criticality .....	323
7.5.4	The Ginzburg Criterion .....	329
<b>Chapter 8</b>	<b>Polymer Blends .....</b>	<b>341</b>
8.1	Molecular Interactions.....	343
8.2	Isotopic Blends.....	347
8.2.1	Isotopic Interactions.....	348
	Experimental aspects .....	349
8.2.2	Temperature Dependence of the Interactions .....	352
8.2.3	Some Properties of $\chi_{HD}$ .....	355

8.3	Polyolefin Blends.....	356
8.3.1	Measurements.....	357
8.3.2	Observations.....	359
8.3.3	Solubility Parameters .....	364
	Molecular considerations.....	367
	PVT measurements.....	369
	Simulations.....	372
8.3.4	Interaction Properties .....	375
	Temperature dependence .....	375
	Pressure dependence.....	377
	Molecular weight dependence.....	378
	Composition dependence .....	379
8.3.5	Irregular Blends.....	381
8.4	Hydrocarbon Polymer Blends .....	385
8.4.1	Inter-Family Blends.....	388
8.4.2	Intra-Family Blends.....	389
8.4.3	Commentary .....	391
8.5	Blends of Copolymers .....	393
8.5.1	Sequencing Effects .....	393
8.5.2	Mean Composition Effects .....	394
8.6	Blends with Specific Associations.....	399

<b>Chapter 9</b>	<b>Network Structure and Elasticity.....</b>	<b>409</b>
9.1	Equal Reactivity and Random Linking.....	411
9.1.1	Network Connectivity .....	413
9.1.2	Strand Dimensions .....	418
9.1.3	Linking Statistics .....	418
9.2	Structurally Related Observables .....	420
9.2.1	Pre-Gelation Region .....	421
9.2.2	The Gel Curve .....	423
9.3	Elasticity-Related Properties .....	427
9.3.1	Active Junctions and Strands.....	428
9.3.2	Topological and Dynamics-Related Properties.....	431
9.3.3	Architectural Characterization .....	435
9.4	General Considerations on Network Elasticity.....	436
9.5	The Affine Network.....	441
9.5.1	The Logarithmic Contribution.....	443
9.5.2	Effects of Temperature and Volume Change.....	445
9.5.3	Network Pressure.....	446
9.6	The Phantom Network.....	447
9.7	The Entangled Network.....	452
9.7.1	Modulus Magnitude .....	453
9.7.2	Experimental Tests.....	456
9.7.3	Comments .....	466

<b>Chapter 10 Network Properties .....</b>	<b>471</b>
10.1 Stress-Strain Behavior .....	472
10.1.1 The Mooney-Rivlin Form.....	476
10.1.2 Swelling and Supercoiling Effects .....	479
10.1.3 The Ferry-Kan Formulation.....	487
10.2 Swelling Equilibrium .....	490
10.3 Thermoelasticity .....	501
10.4 Observations on Networks.....	508
10.4.1 Microscopic Features .....	509
Orientational correlations .....	509
Neutron scattering .....	509
10.4.2 Macroscopic Features .....	514
10.5 Modeling Uncrossability .....	514
10.5.1 Topological Classification.....	519
10.5.2 Slip-Links.....	522
10.5.3 Constrained Junction Models .....	524
10.5.4 Tube Models .....	524
Affine models.....	526
Constant mesh density models .....	527
Empirical models .....	528
Nonaffine models .....	528
Tube model comparisons .....	530
10.5.5 Commentary .....	530
Appendix A—Symbols .....	537
Subject Index .....	543
Author Index .....	549



# Introduction

This chapter provides an introduction to the general subject of polymeric liquids and networks, referring to both equilibrium and dynamic properties for examples. It begins with the distinction between chemical microstructure and macrostructure in polymer molecules, then specializes the discussion to flexible chain macromolecules. The distinction between species dependence and architectural dependence is considered next, with examples chosen from among the dynamical properties. Polymeric heterogeneity ends the chapter—molecular weight and molecular size averages, the effects of long-chain branching, and crosslinking reactions on polydispersity and distribution functions, both theoretically based and empirical.

## 1.1 Molecular Nature of Polymers

Polymeric materials consist of *macromolecules*, made up of many more-or-less identical molecular subunits, the *mers* or *monomeric units* or *repeating units* that define the polymer species. Polymers are formed from *monomers*, substances whose molecules have the capacity to link chemically with at least two other molecules. The number of polymerizable substances is very large, as is the number of chemical reactions that have been used to form polymers. Molecular size increases with polymerization, and the material properties evolve away from those of the monomer, sometimes in unique and useful ways.

Polymers have been categorized on such attributes as shared properties, synthetic origin, or general areas of application, for example:

- Polymers of biological origin, such as proteins and polysaccharides.
- Covalent network solids, such as epoxy resins and phenolics.
- Flexible-chain polymers, such as acrylics and polyolefins.

Flexible-chain polymers are the substances of particular interest in this book. Some examples of flexible-chain species are listed in Table 1.1. Except at chain

**TABLE 1.1** Monomer, monomeric unit, and common name for selected polymer species

Monomer	Monomeric Unit	Common Name	Acronym
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	$\left[ \begin{array}{cc} \text{H} & \text{H} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{H} \end{array} \right]$	polyethylene	PE
$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	$\left[ \begin{array}{cc} \text{H} & \text{CH}_3 \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{H} \end{array} \right]$	polypropylene	PP
$\begin{array}{c} \text{H} & & \text{CH}_2-\text{CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	$\left[ \begin{array}{cc} \text{H} & \text{C}_2\text{H}_5 \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{H} \end{array} \right]$	poly(1-butene)	PB
$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{CH}_3 \end{array}$	$\left[ \begin{array}{cc} \text{H} & \text{CH}_3 \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{CH}_3 \end{array} \right]$	polyisobutylene	PIB
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{C}=\text{C} & & \text{H} \\ & \diagup & \diagdown \\ & \text{H} & \end{array}$	$\left[ \begin{array}{cc} & \text{H} \\ &   \\ \text{H} & \text{C}=\text{CH}_2 \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{H} \end{array} \right]$	1,2 polybutadiene	PVE
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	$\left[ \begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\   &   &   &   \\ -\text{C} & -\text{C} & =\text{C} & -\text{C}- \\   & & &   \\ \text{H} & & & \text{H} \end{array} \right]$	1,4 polybutadiene	PBD
$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	$\left[ \begin{array}{cccc} \text{H} & \text{CH}_3 & \text{H} & \text{H} \\   &   &   &   \\ -\text{C} & -\text{C} & =\text{C} & -\text{C}- \\   & & &   \\ \text{H} & & & \text{H} \end{array} \right]$	1,4 polyisoprene	PI
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} & -\text{C} \\ & / & \diagdown \\ \text{H} & & \text{O} & \end{array}$	$\left[ \begin{array}{ccc} \text{H} & \text{H} & \\   &   & \\ -\text{C} & -\text{C} & -\text{O}- \\   &   & \\ \text{H} & \text{H} & \end{array} \right]$	poly(ethylene oxide)	PEO
$\begin{array}{c} \text{H} & & \text{Cl} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	$\left[ \begin{array}{cc} \text{H} & \text{Cl} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{H} \end{array} \right]$	poly(vinyl chloride)	PVC

(Continued)

TABLE 1.1 (Continued)

Monomer	Monomeric Unit	Common Name	Acronym
$\begin{array}{c} \text{O} \\ \parallel \\ \text{H} \quad \text{C} \quad \text{C} \quad \text{O}-\text{CH}_3 \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array}$	$\left[ \begin{array}{cc} \text{H} & \text{O} \\   & \parallel \\ -\text{C}- & \text{C}-\text{O}-\text{CH}_3 \\   &   \\ \text{H} & \text{H} \end{array} \right]$	poly(methyl acrylate)	PMA
$\begin{array}{c} \text{O} \\ \parallel \\ \text{H} \quad \text{C} \quad \text{C} \quad \text{O}-\text{CH}_3 \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{CH}_3 \end{array}$	$\left[ \begin{array}{cc} \text{H} & \text{O} \\   & \parallel \\ -\text{C}- & \text{C}-\text{O}-\text{CH}_3 \\   &   \\ \text{H} & \text{CH}_3 \end{array} \right]$	poly(methyl methacrylate)	PMMA
$\begin{array}{c} \text{O} \\ \parallel \\ \text{H} \quad \text{C} \quad \text{C} \quad \text{O}-\text{C}-\text{CH}_3 \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array}$	$\left[ \begin{array}{cc} \text{H} & \text{O} \\   & \parallel \\ -\text{C}- & \text{C}-\text{CH}_3 \\   &   \\ \text{H} & \text{H} \end{array} \right]$	poly(vinyl acetate)	PVAC
$\begin{array}{c} \text{CH}_3 \\   \\ \text{Cl}-\text{Si}-\text{Cl} \\   \\ \text{CH}_3 \end{array}, \quad \text{H}_2\text{O}$	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{CH}_3 \end{array} \right]$	poly(dimethyl siloxane)	PDMS
$\begin{array}{c} \text{H} \quad \text{C}_6\text{H}_5 \\ \diagup \quad \diagdown \\ \text{H} \quad \text{C} = \text{C} \\ \diagdown \quad \diagup \\ \text{H} \quad \text{H} \end{array}$	$\left[ \begin{array}{cc} \text{H} & \text{C}_6\text{H}_5 \\   &   \\ -\text{C}- & \text{C}- \\   &   \\ \text{H} & \text{H} \end{array} \right]$	polystyrene	PS
$\left\{ \begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{HO}-\text{C}-\text{C}-\text{OH} \\   \quad   \\ \text{H} \quad \text{H} \\ \text{H}_3\text{CO}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{OCH}_3 \end{array} \right\}$	$\left[ \begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ -\text{C}-\text{C}_6\text{H}_4-\text{C}-\text{O}-\text{C}-\text{C}- \\ \parallel \quad \quad \parallel \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array} \right]$	poly(ethylene terephthalate)	PET

ends, or at relatively sparse branch points, each monomeric unit is covalently linked with two others. The links define a molecular chain whose backbone, the skeletal structure of the macromolecule, consists of atoms joined by covalent bonds. Side groups complete the covalent bonding of the backbone atoms. These also serve to define the polymer species and to control its properties.