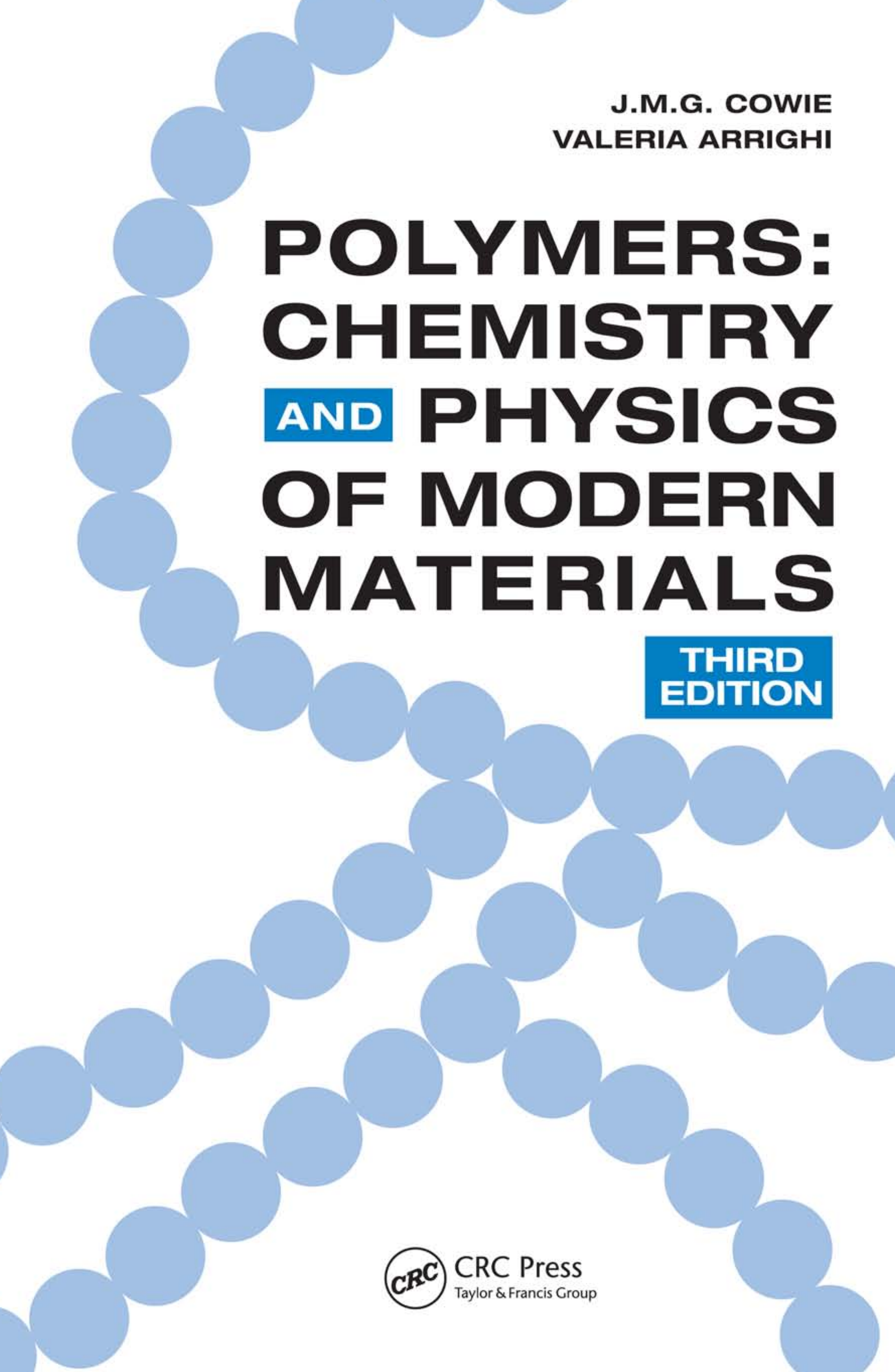


J.M.G. COWIE
VALERIA ARRIGHI

POLYMERS: CHEMISTRY AND PHYSICS OF MODERN MATERIALS

THIRD EDITION

CRC Press
Taylor & Francis Group

POLYMERS: CHEMISTRY AND PHYSICS OF MODERN MATERIALS

THIRD EDITION

POLYMERS: CHEMISTRY AND PHYSICS OF MODERN MATERIALS

THIRD EDITION

J.M.G. COWIE
Heriot-Watt University
Scotland,UK

VALERIA ARRIGHI
Heriot-Watt University
Scotland,UK

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2007 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works
Version Date: 20140113

International Standard Book Number-13: 978-1-4200-0987-3 (eBook - PDF)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (http://www.copyright.com/) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at
http://www.taylorandfrancis.com

and the CRC Press Web site at
http://www.crcpress.com

Contents

Preface xv

The Authors xvii

Chapter 1 Introduction 1

1.1 Birth of a Concept 1
1.2 Some Basic Definitions 2
1.3 Synthesis of Polymers 4
1.4 Nomenclature 4
1.5 Average Molar Masses and Distributions 8
1.6 Size and Shape 10
1.7 Configuration 12
1.8 The Glass Transition Temperature T_g and the Melting Temperature T_m 14
1.9 Elastomers, Fibers, and Plastics 16
1.10 Fiber-Forming Polymers 18
1.11 Plastics 18
1.12 Thermosetting Polymers 21
1.13 Elastomers 21
Problems 25
References 27
Bibliography 27

Chapter 2 Step-Growth Polymerization 29

2.1 General Reactions 29
2.2 Reactivity of Functional Groups 30
2.3 Carothers Equation 31
2.4 Control of the Molar Mass 32
2.5 Stoichiometric Control of M_n 34
2.6 Kinetics 36
2.7 Molar Mass Distribution in Linear Systems 38
2.8 Average Molar Masses 39
2.9 Characteristics of Step-Growth Polymerization 40
2.10 Typical Step-Growth Reactions 40
2.11 Ring Formation 41
2.12 Nonlinear Step-Growth Reactions 42
2.13 Statistical Derivation 43
2.14 Comparison with Experiment 44
2.15 Polyurethanes 46
2.16 Thermosetting Polymers 49
Problems 52
References 56
Bibliography 56

Chapter 3 Free-Radical Addition Polymerization 57

3.1 Addition Polymerization 57
3.2 Choice of Initiators 57
3.3 Free-Radical Polymerization 58
3.4 Initiators 59
  3.4.1 Initiator Efficiency 60
3.5 Chain Growth 62
3.6 Termination 62
3.7 Steady-State Kinetics 63
3.8 High-Conversion Bulk Polymerizations 65
3.9 Chain Transfer 67
  3.9.1 Consequences of Chain Transfer 70
3.10 Inhibitors and Retarders 70
3.11 Activation Energies and the Effect of Temperature 72
3.12 Thermodynamics of Radical Polymerization 73
3.13 Heats of Polymerization 76
3.14 Polymerization Processes 76
3.15 Features of Free-Radical Polymerization 79
3.16 Controlled Radical Polymerization 79
3.17 Nitroxide-Mediated Polymerizations 81
3.18 Atom Transfer Radical Polymerization (ATRP) 82
3.19 Reverse ATRP 83
3.20 Degenerative Chain Transfer Reaction (DT) 84
3.21 Reversible Addition Fragmentation Chain Transfer (RAFT) 84
3.22 CRP of Vinyl Chloride 87
3.23 The Kinetics of CRP Processes 87
3.24 Application to Experimental Data 90
Problems 92
References 96
Bibliography 96

Chapter 4 Ionic Polymerization 99

4.1 General Characteristics 99
4.2 Cationic Polymerization 100
4.3 Propagation by Cationic Chain Carriers 101
4.4 Termination 102
4.5 General Kinetic Scheme 103
4.6 Energetics of Cationic Polymerization 103
4.7 Telechelic Polymers via Cationic Polymerization 104
4.8 Cationic Ring Opening Polymerization 105
4.9 Stable Carbocations 107
4.10 Anionic Polymerization 108
4.11 Living Polymers 109
4.12 Kinetics and Molar Mass Distribution in Living Anionic Systems 110

4.13 Metal Alkyl Initiators 114
4.14 Solvent and Gegen Ion Effects 114
4.15 Anionic Ring-Opening Polymerization 114
Problems 116
References 118
Bibliography 119

Chapter 5 Linear Copolymers and Other Architectures 121

5.1 General Characteristics 121
5.2 Composition Drift 122
5.3 The Copolymer Equation 122
5.4 Monomer Reactivity Ratios 123
5.5 Reactivity Ratios and Copolymer Structure 124
5.6 Monomer Reactivities and Chain Initiation 127
5.7 Influence of Structural Effects on Monomer Reactivity Ratios 127
  5.7.1 Resonance Effects 127
  5.7.2 Polar Effects 129
5.8 The *Q–e* Scheme 129
5.9 Alternating Copolymers 131
5.10 Block Copolymer Synthesis 133
  5.10.1 Transformation Reactions 135
    5.10.1.1 Cationic to CRP 137
    5.10.1.2 Anionic to CRP 138
    5.10.1.3 ROMP to ATRP 139
    5.10.1.4 Step-Growth ATRP 139
  5.10.2 Coupling Reactions 140
  5.10.3 Use of CRP Methods 142
5.11 Graft Copolymer Synthesis 145
5.12 Statistical and Gradient Copolymers 147
5.13 Complex Molecular Architectures 148
5.14 Dendrimers 149
  5.14.1 Divergent Growth 150
  5.14.2 Convergent Growth 151
  5.14.3 Dendrimer Molecular Weight 152
  5.14.4 Properties of Dendrimers 153
  5.14.5 Applications of Dendrimers 154
Problems 155
References 156
Bibliography 156

Chapter 6 Polymer Stereochemistry 157

6.1 Architecture 157
6.2 Orientation 157
6.3 Configuration 158

6.3.1 Monotactic Polymers 159
6.3.2 Ditactic Polymers 160
6.3.3 Polyethers 160
6.4 Geometric Isomerism 162
6.5 Conformation of Stereoregular Polymers 163
6.6 Factors Influencing Stereoregulation 165
6.7 Homogeneous Stereospecific Cationic Polymerizations 167
6.8 Homogeneous Stereoselective Anionic Polymerizations 168
6.9 Homogeneous Diene Polymerization 170
6.10 Summary 172
Problems 172
References 173
Bibliography 173

Chapter 7 Polymerization Reactions Initiated by Metal Catalysts and Transfer Reactions 175

7.1 Polymerization Using Ziegler–Natta Catalysts 175
7.2 Nature of the Catalyst 176
7.3 Nature of Active Centers 177
7.4 Bimetallic Mechanism 177
7.5 Monometallic Mechanism 178
7.6 Stereoregulation 180
7.7 Ring-Opening Metathesis Polymerization (ROMP) 181
7.8 Monocyclic Monomers 182
7.9 Bicyclo- and Tricyclomonomers 183
7.10 Copolyalkenamers 184
7.11 Living Systems 184
7.12 Group Transfer Polymerization (GTP) 186
7.13 Aldol Group Transfer Polymerization 187
7.14 Metallocene Catalysts 188
7.14.1 Metallocene/Aluminoxane Catalysts 189
7.14.2 Stereoregulation 189
7.14.3 Cationic Metallocenes 192
7.14.4 Mechanism of Stereoregulation 192
7.15 Concluding Remarks 193
Problems 194
References 194
Bibliography 194

Chapter 8 Polymers in Solution 197

8.1 Thermodynamics of Polymer Solutions 197
8.2 Ideal Mixtures of Small Molecules 197
8.3 Nonideal Solutions 199
8.4 Flory–Huggins Theory: Entropy of Mixing 199

8.5 Enthalpy Change on Mixing 203
8.6 Free Energy of Mixing 204
8.7 Limitations of the Flory–Huggins Theory 205
8.8 Phase Equilibria 206
8.9 Flory–Krigbaum Theory 208
8.10 Location of the Theta Temperature 210
8.11 Lower Critical Solution Temperatures 213
8.12 Solubility and the Cohesive Energy Density 216
8.13 Polymer–Polymer Mixtures 219
8.14 Kinetics of Phase Separation 223
Problems 224
References 227
Bibliography 227

Chapter 9 Polymer Characterization — Molar Masses 229

9.1 Introduction 229
9.2 Molar Masses, Molecular Weights, and SI Units 229
9.3 Number-Average Molar Mass M_n 229
9.4 End-Group Assay 230
9.5 Colligative Properties of Solutions 230
9.6 Osmotic Pressure 231
9.7 Light Scattering 234
    9.7.1 Scattering from Large Particles 236
9.8 Dynamic Light Scattering 239
9.9 Viscosity 240
    9.9.1 Viscosity-Average Molecular Weight 242
9.10 Gel Permeation Chromatography 243
9.11 MALDI 247
Problems 248
References 251
Bibliography 252

Chapter 10 Polymer Characterization — Chain Dimensions, Structures, and Morphology 253

10.1 Average Chain Dimensions 253
10.2 Freely Jointed Chain Model 254
10.3 Short-Range Effects 255
10.4 Chain Stiffness 255
10.5 Treatment of Dilute Solution Data 256
    10.5.1 The Second Virial Coefficient 256
    10.5.2 Expansion Factor α 257
    10.5.3 Flory–Fox Theory 258
    10.5.4 Indirect Estimates of Unperturbed Chain Dimensions 259
    10.5.5 Influence of Tacticity on Chain Dimensions 259

10.6 Nuclear Magnetic Resonance (NMR) 260
10.7 Infrared Spectroscopy 262
10.8 Thermal Analysis 264
10.9 Wide-Angle and Small-Angle Scattering 265
  10.9.1 Wide-Angle X-Ray Scattering 266
  10.9.2 Small-Angle X-Ray Scattering (SAXS) 267
  10.9.3 Small-Angle Neutron Scattering (SANS) 268
10.10 Microscopy 271
  10.10.1 Optical Microscopy 272
  10.10.2 Scanning Electron Microscopy 273
  10.10.3 Transmission Electron Microscopy 274
  10.10.4 Atomic Force Microscopy and Scanning Tunneling Microscopy 274
Problems 276
References 277
Bibliography 277

Chapter 11 The Crystalline State and Partially Ordered Structures 279

11.1 Introduction 279
11.2 Mechanism of Crystallization 279
11.3 Temperature and Growth Rate 281
11.4 Melting 282
  11.4.1 Effect of Crystallite Size on Melting 282
11.5 Thermodynamic Parameters 282
11.6 Crystalline Arrangement of Polymers 285
  11.6.1 Factors Affecting Crystallinity and T_m 285
    11.6.1.1 Symmetry 285
    11.6.1.2 Intermolecular Bonding 286
    11.6.1.3 Tacticity 287
    11.6.1.4 Branching and Molar Mass 287
11.7 Morphology and Kinetics 287
11.8 Morphology 287
  11.8.1 Crystallites 288
  11.8.2 Single Crystals 288
  11.8.3 Hedrites 289
  11.8.4 Crystallization from the Melt 289
  11.8.5 Spherulites 291
11.9 Kinetics of Crystallization 292
  11.9.1 Isothermal Crystallization 293
  11.9.2 The Avrami Equation 293
  11.9.3 Deviations from Avrami Equation 294
11.10 Block Copolymers 294
11.11 Historical Development of Polymer Liquid Crystals 296
11.12 Liquid Crystalline Phases 297
11.13 Identification of the Mesophases 300

11.14 Lyotropic Main-Chain Liquid Crystal Polymers 302
11.15 Thermotropic Main-Chain Liquid Crystal Polymers 304
11.16 Side-Chain Liquid Crystal Polymers 309
11.17 Chiral Nematic Liquid Crystal Polymers 311
Problems 314
References 318
Bibliography 318

Chapter 12 The Glassy State and Glass Transition 321

12.1 The Amorphous State 321
12.2 The Glassy State 321
12.3 Relaxation Processes in the Glassy State 321
12.4 Glass Transition Region 323
  12.4.1 The Glass Transition Temperature, T_g 323
  12.4.2 Experimental Demonstration of T_g 324
    12.4.2.1 Measurement of T_g from V–T Curves 325
    12.4.2.2 Thermal Methods 326
  12.4.3 Factors Affecting T_g 327
    12.4.3.1 Chain Flexibility 328
    12.4.3.2 Steric Effects 328
    12.4.3.3 Configurational Effects 330
    12.4.3.4 Effect of Cross-Links on T_g 330
12.5 Theoretical Treatments 330
  12.5.1 The Free-Volume Theory 331
  12.5.2 Gibbs–Di Marzio Thermodynamic Theory 335
  12.5.3 Adam–Gibbs Theory 336
12.6 Dependence of T_g on Molar Mass 337
12.7 Structural Relaxation and Physical Aging 338
Problems 339
References 342
Bibliography 343

Chapter 13 Rheology and Mechanical Properties 345

13.1 Introduction to Rheology 345
13.2 The Five Regions of Viscoelastic Behavior 346
13.3 The Viscous Region 347
  13.3.1 Shear Dependence of Viscosity 349
  13.3.2 Kinetic Units in Polymer Chains 351
  13.3.3 Effect of Chain Length 352
  13.3.4 Temperature Dependence of η 353
  13.3.5 Concentration Dependence of Viscosity 353
  13.3.6 Time-Dependent Behavior 354
13.4 Mechanical Properties 355
  13.4.1 Interrelation of Moduli 357

13.5 Mechanical Models Describing Viscoelasticity 357
13.6 Linear Viscoelastic Behavior of Amorphous Polymers 360
  13.6.1 Creep 360
  13.6.2 Stress–Strain Measurements 363
  13.6.3 Effect of Temperature on Stress–Strain Response 363
  13.6.4 Boltzmann Superposition Principle 364
  13.6.5 Stress Relaxation 365
13.7 Dynamic Mechanical and Dielectric Thermal Analysis 366
  13.7.1 Dynamic Mechanical Thermal Analysis (DMTA) 366
  13.7.2 Dielectric Thermal Analysis (DETA) 369
  13.7.3 Comparison Between DMTA and DETA 371
13.8 Time–Temperature Superposition Principle 373
13.9 Dynamic Viscosity 377
13.10 A Molecular Theory for Viscoelasticity 378
13.11 The Reptation Model 380
Problems 382
References 387
Bibliography 388

Chapter 14 The Elastomeric State 389

14.1 General Introduction 389
  14.1.1 Natural Rubber 390
14.2 Experimental Vulcanization 391
14.3 Properties of Elastomers 391
14.4 Thermodynamic Aspects of Rubberlike Elasticity 392
14.5 Nonideal Elastomers 394
14.6 Distribution Function for Polymer Conformation 395
14.7 Statistical Approach 398
  14.7.1 Experimental Stress–Strain Results 398
    14.7.1.1 Simple Extension 398
    14.7.1.2 Simple Compression 400
    14.7.1.3 Pure Shear 400
    14.7.1.4 Large Elastic Deformation 400
14.8 Swelling of Elastomeric Networks 400
14.9 Network Defects 401
14.10 Resilience of Elastomers 403
Problems 405
References 408
Bibliography 408

Chapter 15 Structure–Property Relations 409

15.1 General Considerations 409
15.2 Control of T_m and T_g 409
  15.2.1 Chain Stiffness 410

15.2.2 Intermolecular Bonding 411
15.3 Relation Between T_m and T_g 413
15.4 Random Copolymers 413
15.5 Dependence of T_m and T_g on Copolymer Composition 414
15.6 Block Copolymers 417
15.7 Plasticizers 419
15.8 Crystallinity and Mechanical Response 420
15.9 Application to Fibers, Elastomers, and Plastics 422
15.10 Fibers 422
15.10.1 Chemical Requirements 423
15.10.1.1 Linear Polyesters 425
15.10.2 Mechanical Requirements for Fibers 426
15.10.2.1 Spinning Techniques 426
15.10.2.1.1 Melt Spinning 426
15.10.2.1.2 Wet and Dry Spinning 426
15.10.2.2 Drawing, Orientation, and Crystallinity 427
15.10.2.3 Modulus and Chain Stiffness 428
15.10.2.4 Other Factors 428
15.11 Aromatic Polyamides 429
15.12 Polyethylene 431
15.13 Elastomers and Cross-Linked Networks 434
15.13.1 Cross-Linking 435
15.13.2 Creep in Cross-Linked Polymers 435
15.13.3 Additives 435
15.14 Plastics 435
15.14.1 Plastic Selection for Bottle Crate Manufacture 437
15.14.2 Medical Applications 438
15.15 High-Temperature Speciality Polymers 439
15.16 Carbon Fibers 446
15.17 Concluding Remarks 446
Problems 448
References 453
Bibliography 454

Chapter 16 Polymers for the Electronics Industry 455

16.1 Introduction 455
16.2 Polymer Resists for IC Fabrication 455
16.3 The Lithographic Process 456
16.4 Polymer Resists 457
16.4.1 Sensitivity 458
16.4.2 Resolution 459
16.5 Photolithography 459
16.5.1 Positive Photoresists 459
16.5.2 Negative Photoresists 460
16.6 Electron Beam Sensitive Resists 463

16.6.1 Positive Resists 463
16.6.2 Negative Resists 464
16.7 X-ray and Ion Sensitive Resists 464
16.8 Electroactive Polymers 465
16.9 Conduction Mechanisms 466
16.10 Preparation of Conductive Polymers 467
16.11 Polyacetylene 469
16.12 Poly(*p*-phenylene) 472
16.13 Polyheterocyclic Systems 474
16.13.1 Polypyrrole 475
16.13.2 Sulfur Compounds 475
16.14 Polyaniline 476
16.15 Poly(Phenylene Sulfide) 476
16.16 Poly(1,6-heptadiyne) 476
16.17 Applications 476
16.18 Photonic Applications 477
16.19 Light-Emitting Polymers 477
16.19.1 Applications 478
16.20 Nonlinear Optics 478
16.21 Langmuir–Blodgett Films 481
16.22 Optical Information Storage 483
16.23 Thermorecording on Liquid Crystalline Polymers 486
References 487
Bibliography 487

Index 489

Preface

When the first edition of this book appeared in 1973, it was meant to serve two major functions; the first was to provide a broad-based text on polymer science at an introductory level that would illustrate the interdisciplinary nature of the subject, and the second was to create a high-information, inexpensive text that students would be able to afford. The response to the book over the intervening years has been both surprising and gratifying, and seems to indicate that the stated aims have been achieved.

The same principles are still applied, in this, the third edition, and I have simply attempted to keep abreast of the recent advances in various areas of the subject. Although the basics of polymer science remain unchanged, significant discoveries have been made in the area of control over molecular weight, macromolecular structure, and architecture, and the consequent ability to prepare materials with specific properties. To account for this, the relevant chapters have been expanded to include controlled radical polymerizations, metallocene chemistry, and the preparation of block and graft copolymers, and multiarmed and dendritic structures. Work has also moved steadily into extending the areas where polymeric materials can be used in electronic, biological, and medical applications, and examples of this are included. The chapter on characterization has also been modified to reflect the current approaches where newer techniques have tended to replace or improve on the older methods. Perhaps the most noticeable change is the addition of a series of problems at the end of each chapter. These are designed to test whether the reader has understood the various points raised in each chapter, and in some cases to expand on that knowledge. This feature has been introduced in response to comments from several lecturers who use the book as a text for their courses in polymer science, and I hope this will prove useful to them and their students.

In preparing this third edition I have been ably assisted by Dr. Valeria Arrighi, who, among other contributions, has been largely responsible for compiling all the problems and exercises, and restructuring one or two of the chapters.

The addition of new material has inevitably meant that some sections, present in previous editions, have been omitted, if no longer deemed to be in common use, or have been superseded by modern techniques. However, I hope that the revisions will be acceptable to those who use the text and that it will continue to satisfy the educational needs it was originally designed to meet.

Finally, I would like to dedicate this third edition to my family, Ann, Graeme, and Christian, and grandchildren Emma and Lauren.

The Authors

J.M.G. Cowie, B.Sc., Ph.D., D.Sc., C.Chem., FRSC, FRSE, was educated at Edinburgh University in Scotland, where he graduated in 1955 with a first class honors degree in chemistry. He was appointed to the post of assistant lecturer there in 1956 and was awarded a Ph.D. in 1958 for studies in polysaccharides, particularly starches.

In 1958, he went as a postdoctoral fellow to the National Research Council in Ottawa, Canada, where he worked with Dr. Stan Bywater, and in 1960 he joined the permanent staff of the National Research Council as an associate research officer.

He held this post until 1967 when he returned to the UK as a lecturer at the University of Essex at Colchester. Here he assisted Professor Manfred Gordon to establish a Polymer Research Consortium, involving physicists, mathematicians, and chemists in polymer science problems of common interest. After two years in Essex, he was appointed to a senior lectureship in the new University of Stirling in Scotland, in 1969 and subsequently succeeded Professor R. P. Bell to the chair of chemistry in 1973. From 1974 to 1988 he was Head of Department at Stirling, but moved to Heriot-Watt University as foundation professor of chemistry of materials, the post he held until retirement in 1998. From then to the present, he has been Professor Emeritus (Research) and has continued working with his research group.

In 1976, he was elected a Fellow of the Royal Society of Chemistry and in the following year he was elected Fellow of the Royal Society of Edinburgh. He was visiting professor at the University of Victoria, Canada, in 1979 and the University of Toronto in 1980.

In 1983 he joined the editorial board of *Polymer*, of which he then became main editor, and is also on the editorial boards of *Journal of Applied Polymer Science*, *Polymer Contents*, *Polymers for Advanced Technologies*, *Korean Polymer Journal*, and *Trends in Polymer Science*. He was awarded a D.Sc. from the University of Edinburgh for Research Work on the hydrodynamics of polymer solutions, studies of relaxation processes in the glassy state of polymers, and on physical characterization of polymers. His current interests are centered on phase equilibria in polymer blends, polymer liquid crystals, ion conduction in polymer electrolytes, physical aging, and liquid crystalline cellulose/polymer blends and composites.

He has obtained research grants from industry and Research Councils and has been a consultant for ICI, Courtaulds, International Paint, Hoechst Celanese, DSM, Akzo, API Foils, and a number of smaller companies.

He is author of the textbook, *Polymers: Chemistry and Physics of Modern Materials* and of *Alternating Copolymers* and the editor of several other texts. He has published over 260 papers, together with numerous book chapters, articles for encyclopedias, and general articles.

He has served as chairman of the MacroGroup, British High Polymer Forum, Royal Society of Edinburgh fellowship selection committee (and externally, Council of Disability, Spinal Injuries Scotland and vice chairman of Disability Scotland). He was awarded the MacroGroup Medal for the advancement of polymer science and technology in 2001, and an honorary D.Sc. from Heriot-Watt University in 2005.

Valeria Arrighi, Laurea, Ph.D., D.I.C., C.Chem., FRSC, graduated in Italy from the University of Padova, having completed a five-year degree course in chemistry. After a year spent teaching chemistry at a high school in Trento, Italy, and a short period of employment in industry, she joined Imperial College, UK, in 1988 as a Ph.D. student, under the supervision of Professor Julia Higgins and supported by funding from Enichem (Italy). She was awarded a Ph.D. and a D.I.C. in 1991 for studies on liquid crystalline polymers using neutron and x-ray scattering, and solid state NMR.

From 1992 to 1995, she worked with Professor Higgins as a postdoctoral research associate, and in 1996 she joined the Department of Chemistry at Heriot-Watt University in Edinburgh, as a lecturer in polymer chemistry — the post she is currently holding. She was elected Fellow of the Royal Society of Chemistry in 2001.

Her current research interests include studies of miscibility and physical aging in blends, nanophase separation in polymers with long side-chains, polymer dynamics, liquid crystalline polymers, composites, and systems containing nanoparticles. A common feature of these studies is the use of scattering techniques, especially neutron scattering, to study the local structure, conformation, and dynamics in polymers. She has written various reviews and book chapters in this area and has served on selection panels to allocate beam time at neutron facilities.

Dr. Arrighi has obtained research grants from Research Councils and the European Commission and has over 80 publications, including book chapters and articles for encyclopedias.

1 Introduction

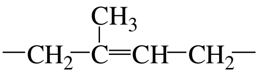
1.1 BIRTH OF A CONCEPT

What is a polymer? If that question had been asked during the latter half of the 19th century and the first quarter of the 20th, it would have been met with either a blank uncomprehending stare or, worse, by derision from sections of the scientific community. This question, which is very much pertinent today, concerns substances that are so pervasive in our everyday lives that we would have difficulty in avoiding them but that may be handled, used, ignored, commented on, and normally taken for granted. Some of these substances are new and recent products resulting from the ingenuity of the chemist; some are naturally occurring and have been used by humans for several thousand years, and some form part of our bodies. All the substances, referred to as polymers or macromolecules, are giant molecules with molar masses ranging from several thousands to several millions.

Today, the concept of a giant molecule is universally accepted by scientists, but this was not always so, and the initial antagonism toward the idea that very large covalently bonded molecules could exist was deep-seated and difficult to dispel. It appears to have stemmed from the different approaches to the interpretation of colloidal behavior. In 1861, the Scotsman Thomas Graham distinguished between *crystalloid* substances, which could diffuse easily when in solution, and *colloids* or gluelike substances, which refused to crystallize, exhibited high viscosities in solution, and diffused slowly when dissolved in liquids. He explained this difference in behavior by assuming that crystalloids were small particles whereas colloids were composed of large particles. This was acceptable to most scientists, but disagreement became apparent when there were attempts at further analysis on the molecular level. This divergence of opinion is embodied in the physical approach as opposed to the chemical approach.

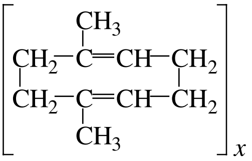
The chemical approach assumed that colloidal substances were, in fact, large molecules and that their behavior could be explained in terms of the size of the individual molecules. The physical approach favored the concept that the molecular sizes were no different in magnitude from those of the crystalloid materials, but that colloidal behavior was a consequence of the formation of aggregates of these smaller molecules in solutions that were held together by physical forces rather than chemical bonds.

The physical approach prevailed because it suited the chemical methodology of the period. Classical organic chemistry demanded the careful preparation and investigation of pure substances with well-defined melting points and molar masses. Even when experimental measurements pointed to the existence of large molecules, the data were rationalized to fit the physical approach. Thus, whereas rubber latex, which showed colloidal behavior, was assigned the correct structural formula I for the individual units, it was postulated to have the ring formation II.



$-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-$

I



II

These rings were thought to form large aggregates in the latex particle. This idea was essential if particle masses of 6500 and 10^5, which had been calculated from ebullioscopic and cryoscopic measurements of rubber particles in solution, were to be explained in accord with the physical approach to the problem.

The majority of scientists were so locked into the mind-warp of believing that only small molecules could exist as chemical entities, that the possibility of the structure I forming long chains, rather than rings, as an alternative way of explaining the high molar masses did not seem to have been seriously considered. Similar work on starch, cellulose, and in the protein field showed the existence of high molar mass species, but here, too, interpretation favored the aggregate hypothesis.

One should not, however, be overly critical of this failure to accept a concept that to us may be obvious. Received wisdom is a deceptively comfortable framework to work within, and it takes a strong-minded, and perhaps equally dogmatic, person to break out of its strictures; the German organic chemist Hermann Staudinger proved to be that person. Building on observations by the English chemist Pickles (who was a fellow skeptic), which cast doubts on the presence of physical forces of aggregation in colloidal systems, and on his own work on the viscosity of materials exhibiting colloidal behavior, he began a long battle of conversion. From 1927 onward, he started to convince other chemists, albeit slowly, that colloidal substances like rubber, starch, and cellulose were, in fact, long, linear, threadlike molecules of variable length, composed of small definable molecular units, covalently bonded to one another to form macromolecules or polymers.

This was no easy task. He was asked by colleagues why he wished to abandon the "beautiful area of the low molecular chemistry" and turn to work in Schmierenchemie (greasy chemistry). Even at the end of the 1920s, he was given the following advice: "Dear colleague, let me advise you to dismiss the idea of large molecules; there are no organic molecules with a molecular mass over 5000. Purify your products, as for instance rubber, and they will crystallize and reveal themselves as low-molecular-weight substances."

Whereas this "greasy" chemistry image of polymer science was a difficult one to erase from some areas of chemical academia, the grease has turned out to be a rich vein of scientific gold. How rich can only be judged by digging deeply into one of the most exciting and diverse areas of science in which the possibilities for innovation seem endless.

1.2 SOME BASIC DEFINITIONS

To place polymer science in the proper perspective, we must examine the subject on as broad a basis as possible. It is useful to consider polymers first on the molecular level, than as materials. These considerations can be interrelated by examining the various aspects in the sequence: synthesis, characterization, mechanical behavior, and application; but before discussing the detailed chemistry and physics, some of the fundamental concepts must be introduced to provide essential background to such a development. We need to know what a polymer is and how it is named and prepared. It is also useful to identify which physical properties are important, and so it is necessary to define the molar mass and the molar mass distribution, obtain an appreciation of the molecular size and shape, and recognize the important transition temperatures.

A *polymer* is a large molecule constructed from many smaller structural units called *monomers*, covalently bonded together in any conceivable pattern. In certain cases, it is more accurate to call the structural or repeat unit a *monomer residue* because atoms are eliminated from the simple monomeric unit during some polymerization processes.

The essential requirement for a small molecule to qualify as a monomer or "building block" is the possession of two or more bonding sites, through which each can be linked to other monomers to form the polymer chain. The number of bonding sites is referred to as the *functionality.* Monomers such as hydroxyacids (HO—R—COOH) or vinyl chloride ($CH_2{=}CHCl$) are bifunctional. The hydroxyacid will condense with the other hydroxyacid molecules through the —OH and —COOH groups to form a linear polymer, and the polymerization reaction in this case consists of a series of simple organic reactions similar to

$$\mathrm{ROH + R'COOH \rightleftharpoons R'COOR + H_2O}$$

The double bond of the vinyl compound is also bifunctional as activation by a free radical or an ion leads to polymer formation

$$\mathrm{H_2C{=}CHCl + R^{\bullet} \longrightarrow RCH_2{-}CHCl{-}CH_2{-}CHCl{\sim\sim}^{\bullet}}$$

Bifunctional monomers form linear macromolecules, but if the monomers are polyfunctional, i.e., they have three or more bonding sites as in glycerol ($CH_2OH.CHOH.CH_2OH$), branched macromolecules can be produced. These may even develop into large three-dimensional networks containing both branches and cross-links.

When only one species of monomer is used to build a macromolecule, the product is called a *homopolymer*, normally referred to simply as a polymer. If the chains are composed of two types of monomer unit, the material is known as a *copolymer*, and if three different monomers are incorporated in one chain, a *terpolymer* results.

Copolymers prepared from bifunctional monomers can be subdivided further into four main categories (see Figure 1.1):

1. *Statistical copolymers* in which the distribution of the two monomers in the chain is essentially random, but influenced by the individual monomer reactivities.
2. *Alternating copolymers* with a regular placement along the chain.
3. *Block copolymers* comprised of substantial sequences or blocks of each.
4. *Graft copolymers* in which blocks of one monomer are grafted on to a backbone of the other as branches.

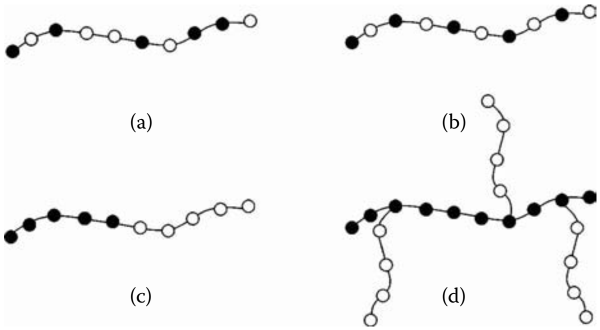
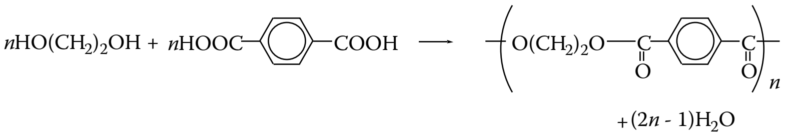


FIGURE 1.1 Schematic diagram of (a) statistical, (b) alternating, (c) block, and (d) graft copolymers.

1.3 SYNTHESIS OF POLYMERS

A process used to convert monomer molecules into a polymer is called *polymerization*, and the two most important groups are step-growth and addition. A step-growth polymerization is used for monomers with functional groups such as —OH, —COOH, —COCl, etc., and is normally, but not always, a succession of condensation reactions. Consequently, the majority of polymers formed in this way differ slightly from the original monomers because a small molecule is eliminated in the reaction, e.g., the reaction between ethylene glycol and terephthalic acid produces a polyester better known as *terylene.*



The addition polymerizations, for olefinic monomers, are chain reactions that convert the monomers into polymers by stimulating the opening of the double bond with a free radical or ionic initiator. The product then has the same chemical composition as the starting material, e.g., acrylonitrile produces polyacrylonitrile without the elimination of a small molecule.

$$nCH_2{=}CHCN \longrightarrow \sim\!\!\sim\!(CH_2CHCN)_n\!\sim\!\!\sim$$

The length of the molecular chains, which will depend on the reaction conditions, can be obtained from measurements of molar masses.

1.4 NOMENCLATURE

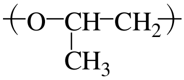
The least ambiguous method of naming a polymer is based on its source. However, a wide variety of trade names are commonly used. The prefix "poly" is attached to the name of the monomer in addition polymers, and so polyethylene, polyacrylonitrile, and polystyrene denote polymers prepared from these single monomers. When the monomer has a multiworded name or has a substituted parent name, then this is enclosed in parentheses and prefixed with poly, e.g., poly(methylmethacrylate), poly(vinyl chloride), poly(ethylene oxide), etc.

Polymers prepared by self-condensation of a single monomer such as ω-amino lauric acid are named in a similar manner, but this polymer, poly(ω-amino lauric acid) (sometimes known as *nylon-12*), can also be prepared by a ring-opening reaction using lauryl lactam and could then be called poly(lauryl lactam). Both names are correct.

International Union of Pure and Applied Chemistry (IUPAC) has attempted to formalize the nomenclature of regular, single-stranded organic polymers and has proposed a set of procedures, some of which are described briefly as follows.

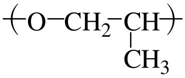
The first step is to select a constitutional repeat unit (CRU), which may contain one or more subunits. The name of the polymer is then the name of the CRU, in parentheses prefixed by poly. Before naming the CRU, it must be orientated correctly. This involves placing the constituent parts in order of seniority with the highest to the left. In descending order, this would be heterocyclic rings, chains with hetero atoms, carbocyclic rings, and chains with only carbon atoms, if such an order is possible chemically.

Thus, $-\!\!(O-CH_2-CH_2)\!\!-$ would be poly(oxy ethylene) rather than $-\!\!(CH_2CH_2-O)\!\!-$ poly(ethylene oxy). If there is a substituent on part of the CRU, then orientation will place the substituent closest to the left of the substituted portion, thus, poly(oxy 1-methyl ethylene):



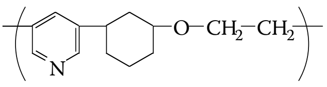
$$-\!\!(O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2)\!\!-$$

is preferred, rather than



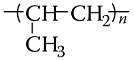
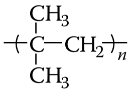
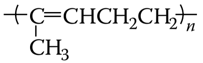
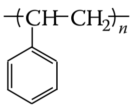
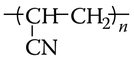
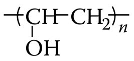
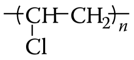
$$-\!\!(O-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}})\!\!-$$

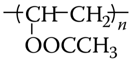
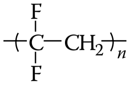
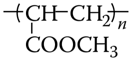
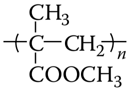
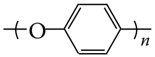
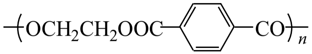
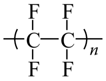
Similarly, a more complex CRU might be orientated as



and named poly(3,5 pyridine diyl-1,3-cyclohexylene oxydimethylene). Other examples are shown in Table 1.1 and the reader is referred to the references listed at the end of the chapter for a more comprehensive coverage.

TABLE 1.1
Nomenclature of Some Common Polymers

Name	Structure	Trivial Name
Poly(methylene)	$-\!\left(\mathrm{CH_2CH_2}\right)_n\!-$	Polyethylene
Poly(propylene)	 $-\!\left(\mathrm{CH(CH_3)\!-\!CH_2}\right)_n\!-$	Polypropylene
Poly(1,1-dimethylethylene)	 $-\!\left(\mathrm{C(CH_3)_2\!-\!CH_2}\right)_n\!-$	Polyisobutylene
Poly(1-methyl-1-butenylene)	 $-\!\left(\mathrm{C(CH_3)\!=\!CHCH_2CH_2}\right)_n\!-$	Polyisoprene
Poly(1-butenylene)	$-\!\left(\mathrm{CH\!=\!CHCH_2CH_2}\right)_n\!-$	Polybutadiene
Poly(1-phenylethylene)	 $-\!\left(\mathrm{CH(C_6H_5)\!-\!CH_2}\right)_n\!-$	Polystyrene
Poly(1-cyanoethylene)	 $-\!\left(\mathrm{CH(CN)\!-\!CH_2}\right)_n\!-$	Polyacrylonitrile
Poly(1-hydroxyethylene)	 $-\!\left(\mathrm{CH(OH)\!-\!CH_2}\right)_n\!-$	Poly(vinylalcohol)
Poly(1-chloroethylene)	 $-\!\left(\mathrm{CH(Cl)\!-\!CH_2}\right)_n\!-$	Poly(vinylchloride)

Poly(1-acetoxyethylene)	 $-\!\!\left(\underset{\substack{\vert\\ \mathrm{OOCCH_3}}}{\mathrm{CH}}-\mathrm{CH_2}\right)_{n}$	Poly(vinylacetate)
Poly(1,1-difluoroethylene)	 $-\!\!\left(\overset{\substack{\mathrm{F}\\ \vert}}{\underset{\substack{\vert\\ \mathrm{F}}}{\mathrm{C}}}-\mathrm{CH_2}\right)_{n}$	Poly(vinylidenefluoride)
Poly(1-(methoxycarbonyl) ethylene)	 $-\!\!\left(\underset{\substack{\vert\\ \mathrm{COOCH_3}}}{\mathrm{CH}}-\mathrm{CH_2}\right)_{n}$	Poly(methylacrylate)
Poly(1-(methoxycarbonyl)-1-methyl-ethylene)	 $-\!\!\left(\overset{\substack{\mathrm{CH_3}\\ \vert}}{\underset{\substack{\vert\\ \mathrm{COOCH_3}}}{\mathrm{C}}}-\mathrm{CH_2}\right)_{n}$	Poly(methylmethacrylate)
Poly(oxymethylene)	$-\!\!\left(\mathrm{OCH_2}\right)_{n}$	Polyformaldehyde
Poly(oxyethylene)	$-\!\!\left(\mathrm{OCH_2\,CH_2}\right)_{n}$	Poly(ethylene oxide) (sometimes called polyethylene glycol)
Poly(oxyphenylene)		Poly(phenyleneoxide)
Poly(oxyethylene-oxyterephthaloyl)		Poly(ethylene terephthalate)
Poly(iminohexamethyl-eneiminoadipoyl)	$-\!\!\left(\mathrm{NH(CH_2)_6NHCO(CH_2)_4CO}\right)_{n}$	Poly(hexamethylene adipamide)
Poly(difluoromethylene)	 $-\!\!\left(\overset{\substack{\mathrm{F}\\ \vert}}{\underset{\substack{\vert\\ \mathrm{F}}}{\mathrm{C}}}-\overset{\substack{\mathrm{F}\\ \vert}}{\underset{\substack{\vert\\ \mathrm{F}}}{\mathrm{C}}}\right)_{n}$	Poly(tetrafluoroethylene)

1.5 AVERAGE MOLAR MASSES AND DISTRIBUTIONS[1]

One of the most important features that distinguishes a synthetic high polymer from a simple molecule is the inability to assign an exact molar mass to a polymer. This is a consequence of the fact that in a polymerization reaction, the length of the chain formed is determined entirely by random events. In a condensation reaction, it depends on the availability of a suitable reactive group and, in an addition reaction, on the lifetime of the chain carrier. Inevitably, because of the random nature of the growth process, the product is a mixture of chains of differing length — a *distribution* of chain lengths — which in many cases can be calculated statistically.

The polymer is characterized best by a molar mass distribution and the associated molar mass averages, rather than by a single molar mass. The typical distributions, shown in Figure 1.2, can be described by a variety of averages. As the methods used for estimating the molar mass of polymers employ different averaging procedures, it is safer to use more than one technique to obtain two or more averages, thereby characterizing the sample more fully.

A colligative method, such as osmotic pressure, effectively counts the number of molecules present and provides a *number-average* molar mass $<M>_n$ defined by

$$\langle M \rangle_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum w_i}{\sum (w_i / M_i)} \tag{1.1}$$

where N_i is the number of molecules of species i of molar mass M_i. The brackets $\langle\ \rangle$ indicate that it is an average value, but by convention these are normally omitted.

The alternative expression is in terms of the mass $w_i = N_i M_i / N_A$ if required, where N_A is Avogadro's constant.

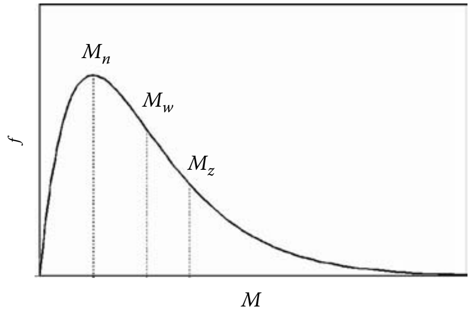


FIGURE 1.2 Typical distribution of molar masses for a synthetic polymer sample, where *f* is the fraction of polymer in each interval of *M* considered.

---

[1] The quantity molar mass is used throughout this text instead of the dimensionless quantity molecular weight, which is usual in polymer chemistry. All the equations in later sections evaluate molar mass rather than the dimensionless quantity molecular weight.

From light-scattering measurements, a method depending on the size rather than the number of molecules, a weight-average molar mass $\langle M\rangle_w$ is obtained. This is defined as

$$\langle M\rangle_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum w_i M_i}{\sum w_i} \tag{1.2}$$

Statistically $\langle M\rangle_n$ is simply the first moment, and $\langle M\rangle_w$ is the ratio of the second to the first moment, of the number distribution.

A higher average, the z-average given by

$$\langle M\rangle_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum w_i M_i^2}{\sum w_i M_i}, \tag{1.3}$$

can be measured in the ultracentrifuge, which also yields another useful average, the $(z + 1)$-average,

$$\langle M\rangle_{z+1} = \frac{\sum N_i M_i^4}{\sum N_i M_i^3}, \tag{1.4}$$

often required when describing mechanical properties.

A numerical example serves to highlight the differences in the various averages. Consider a hypothetical polymer sample composed of chains of four distinct molar masses, 100,000, 200,000, 500,000, and 1,000,000 g mol^{-1} in the ratio 1:5:3:1, than

$$M_n/g\,\text{mol}^{-1} = \frac{(1\times 10^5) + (5\times 2\times 10^5) + (3\times 5\times 10^5) + (1\times 10^6)}{1+5+3+1} = 3.6\times 10^5$$

$$M_w/g\,\text{mol}^{-1} = \frac{\{1\times(10^5)^2\} + \{5\times(2\times 10^5)^2\} + \{3\times(5\times 10^5)^2\} + \{1\times 10^6)^2\}}{(1\times 10^5) + (5\times 2\times 10^5) + (3\times 5\times 10^5) + (1\times 10^6)}$$

$$= 5.45\times 10^5$$

and $M_z = 7.22 \times 10^5$ g mol^{-1}.

The breadth of the distribution can often be gauged by establishing the *heterogeneity index* (M_w/M_n). For many polymerizations, the most probable value is about 2.0, but both larger and smaller values can be obtained, and it is at best only a rough guide.

An alternative method of describing the chain length of a polymer is to measure the *average degree of polymerization x*. This represents the number of monomer units or residues in the chain and is given by

$$x = M/M_0, \tag{1.5}$$

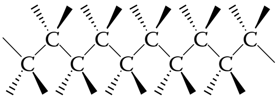
where M_0 is the molar mass of monomer or residue and M is the appropriate average molar mass. Hence, the x average depends on which average is used for M. (To avoid confusion between the mole fraction x and the average degree of polymerization x, the latter will always be subscripted as x_n or x_w to indicate the particular M used in Equation 1.5.)

1.6 SIZE AND SHAPE

Some measure of the polymer size is obtained from the molar mass, but what is the actual length of a chain and what shape does it adopt? We can begin to answer these questions by first considering a simple molecule such as butane and examining the behavior when the molecule is rotated about the bond joining carbon 2 to carbon 3.

The Newman and "saw horse" projections show the trans position in Figure 1.3a with the "dihedral angle" $\phi = 180°$. This is the most stable conformation with the greatest separation between the two methyl groups. Rotation about the C_2—C_3 bond alters ϕ and moves the methyl groups past the opposing hydrogen atoms so that an extra repulsive force is experienced when an eclipsed position (Figure 1.3b) is reached.

The progress of rotation can be followed by plotting the change in potential energy $V(\phi)$ as a function of the dihedral angle, as shown in Figure 1.4. The resulting diagram for butane exhibits three minima at $\phi = \pi$, $\pi/3$, and $5\pi/3$ called the *trans* and ± *gauche* states, respectively, and the greater depth of the trans position indicates that this is the position of maximum stability. Although the gauche states are slightly less stable, all three minima can be regarded as discrete rotational states. The maxima correspond to the eclipsed positions and —CH_3 are angles of maximum instability. These diagrams will vary with the type of molecule and need not be symmetrical, but the butane diagram is very similar to that for the simple polymer polyethylene $\left(CH_2—CH_2 \right)_n$, if the groups are replaced by the two sections of the chain adjoining the bond of rotation. The backbone of this polymer is composed of a chain of tetrahedral carbon atoms covalently bonded to each other so that the molecule can be represented as an extended all trans zigzag chain. For a typical value of $M = 1.6 \times 10^5$ g mol^{-1}, the chain



contains 10,000 carbon atoms; thus in the extended zigzag state, assuming a tetrahedral angle of 109° and a bond length of 0.154 nm, the chain would be about 1260 nm long and 0.3 nm diameter. Magnified one million times, the chain could be represented by a piece of wire 126 × 0.03 cm. This means that polyethylene is a long threadlike molecule, but how realistic is the extended all trans conformation? As every group of four atoms in the chain has a choice of three possible stable rotational states, a total of $3^{10,000}$ shapes are available to this particular chain, only one of which is the all trans state. So, in spite of the fact that the all trans extended conformation has the lowest energy, the most probable conformation will be some kind of randomly coiled state, assuming that no external ordering forces are present and that the rotation about the carbon bonds is in no way impeded. The many possible coiled forms are generated

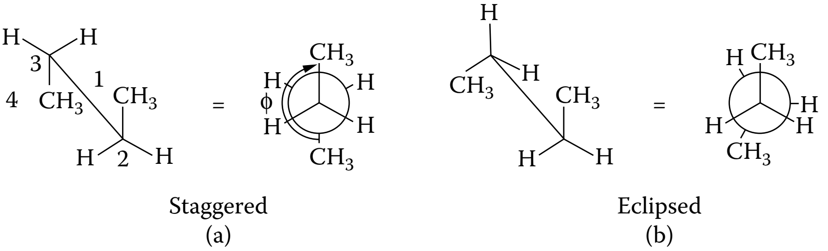


FIGURE 1.3 Newman and "saw horse" projection for *n*-butane, (a) a staggered state with $\phi = \pi$ and (b) an eclipsed position.

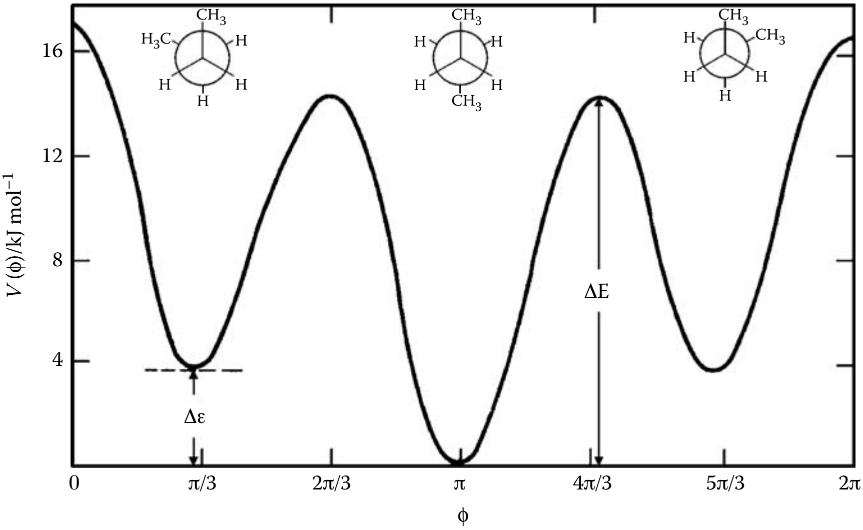


FIGURE 1.4 Potential energy $V(\phi)$ as a function of the dihedral angle ϕ for *n*-butane.

simply by allowing the chain to rotate into a gauche position which moves the atom out of the plane of the adjacent bonds. This is shown more clearly (see Figure 1.5) by considering the various cones of revolution available to a chain over only two bonds. The distribution of trans (*t*) and gauche (*g*) states along a chain will be a function of the temperature and the relative stability of these states. Consequently, there is an unequal distribution of each. The ratio of the number of trans n_t to gauche n_g states is then governed by a Boltzmann factor and

$$n_g/n_t = 2\ \exp\ (-\Delta\varepsilon/kT), \tag{1.6}$$

where k is the Boltzmann constant, $\Delta\varepsilon$ is the energy difference between the two minima, and the 2 arises because of the ± gauche states available. For polyethylene, $\Delta\varepsilon$ is about 3.34 kJ mol^{-1}, and values of (n_g/n_t) for 100, 200, and 300 K are 0.036, 0.264, and 0.524, respectively, showing that the chain becomes less extended and

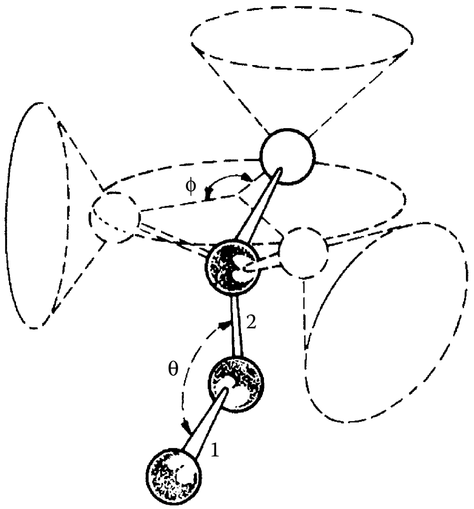


FIGURE 1.5 Diagrammatic representation of the cones or revolution available to the third and fourth bonds of a simple carbon chain with a fixed bond angle θ.

more coiled as the temperature increases. Because of the possibility of rotation about the carbon bonds, the chain is in a state of perpetual motion, constantly changing shape from one coiled conformation to another form, equally probable at the given temperature. The speed of this wriggling varies with temperature (and from one polymer to another) and dictates many of the physical characteristics of the polymer, as we shall see later.

The height of the potential energy barrier ΔE determines the rate of bond interchange between the *t* and the *g* states, and for polyethylene it is about 16.7 kJ mol^{-1}. When ΔE is very high (about 80 kJ mol^{-1}), rotation becomes very difficult, but as the temperature is raised, the fraction of molecules that possess energy in excess of ΔE increases and rotation from one state to another becomes easier.

Realistically, then, a polymer chain is better represented by a loosely coiled ball (Figure 1.6) than an extended rod. For the magnified-polyethylene chain considered earlier, a ball of about 4 cm diameter is a likely size.

The term *conformation* has been used here when referring to a three-dimensional geometric arrangement of the polymer, which changes easily when the bonds are rotated.

There is a tendency to use the term *configuration* in a synonymous sense, but as far as possible, this will be reserved for the description of chains in which the geometric variations can only be interchanged by breaking a bond. Configurational isomers of importance for polymers are discussed in the following section

1.7 CONFIGURATION

For polymers, two types of configurational isomers are of importance: (1) geometric isomerism, e.g., cis and trans and (2) stereoisomers.

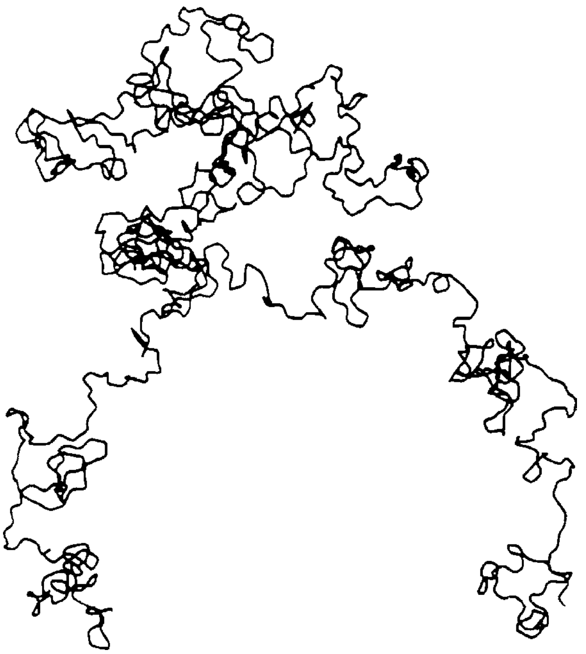
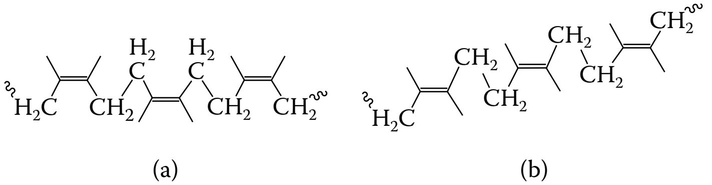


FIGURE 1.6 Random arrangement of a polyethylene chain containing 1000 freely rotating C-C bonds, in which each successive bond has been given a random choice of six equally spaced angular positions. (From Treloar, L.R.G., *Introduction to Polymer Science*, Wykeham Publications, 1970. With permission.)



(a) (b)

FIGURE 1.7 Geometric isomers of 1,4-polybutadiene: (a) cis and (b) trans configuration.

As shown in Figure 1.7, the polymerization of monomers with two double bonds (e.g., butadiene and isoprene) leads to polymer chains with a residual double bond per monomer unit: cis–trans isomerism is possible. Two important polymers that show this type of isomerism are 1,4-polybutadiene and 1,4-polyisoprene. The regularity of the trans configuration makes this type of isomer more crystalline, with a higher melting point compared to the cis configuration.

If the polymer chain contains carbon atoms with two different substituents, then the C atom is asymmetrical. This situation is encountered for vinyl monomers such as polypropylene. For a chain containing asymmetric centers, three different stereoisomers are possible (Figure 1.8):

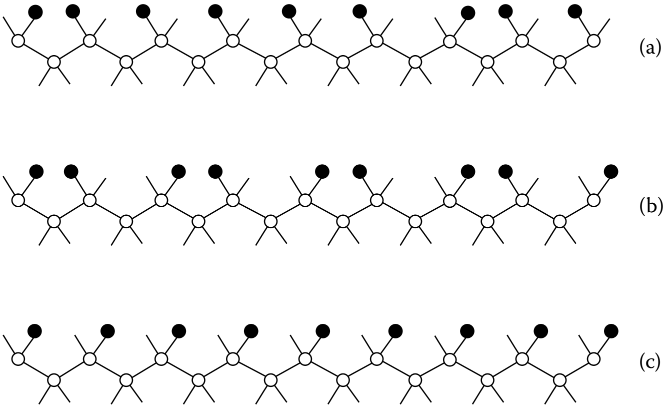


FIGURE 1.8 Sections of polymer chains having different tacticity: (a) atactic, (b) syndiotactic, and (c) isotactic.

1. The *isotactic* configuration in which each substituent is placed on the same side of the chain.
2. The *syndiotactic* structure in which substituents lie on alternate sides of the backbone.
3. A disordered, termed *atactic*, configuration in which substituent groups are placed randomly on either side of the chain.

Of the three stereoisomers, atactic polypropylene was the first to be synthesized. This is because it is the atactic structure that is obtained by conventional polymerization of the monomers when no optically active catalyst is used. It was only when the Ziegler–Natta catalysts were introduced in the 1950s that the production of stereoregular polymers became possible. It is interesting to note that polypropylene did not find any commercial use until the Ziegler–Natta catalysts became available. In fact, the atactic structure that was originally produced leads to a viscous liquid at room temperature of limited use. Isotactic polypropylene instead is one of the most important commercial polymers.

1.8 THE GLASS TRANSITION TEMPERATURE T_g AND THE MELTING TEMPERATURE T_m

At sufficiently low temperatures, all polymers are hard rigid solids. As the temperature rises, each polymer eventually obtains sufficient thermal energy to enable its chains to move freely enough for it to behave like a viscous liquid (assuming no degradation has occurred).

There are two ways in which a polymer can pass from the solid to the liquid phase, depending on the internal organization of the chains in the sample. The different types of thermal response, illustrated by following the change in specific volume, are shown schematically in Figure 1.9.

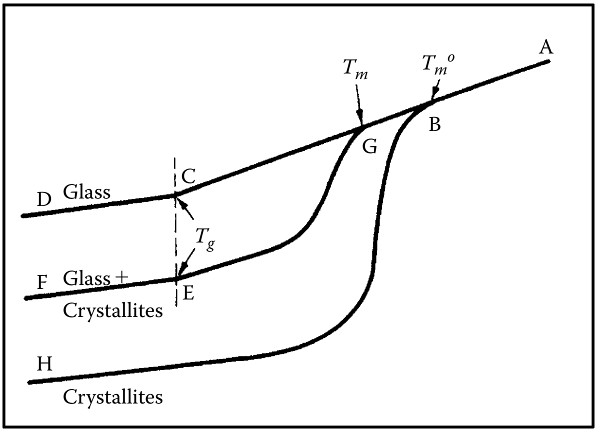


FIGURE 1.9 Schematic representation of the change of specific volume v of a polymer with temperature T for (i) a completely amorphous sample (A–C–D), (ii) a semicrystalline sample (A–G–F), and (iii) a perfectly crystalline material (A–B–H).

A polymer may be completely amorphous in the solid state, which means that the chains in the specimen are arranged in a totally random fashion. The volume change in amorphous polymers follows the curve A–D. In the region C–D the polymer is a glass, but as the sample is heated, it passes through a temperature T_g, called the *glass transition temperature*, beyond which it softens and becomes rubberlike. This is an important temperature because it represents the point where important property changes take place, i.e., the material may be more easily deformed or become ductile above T_g. A continuing increase in temperature along C–B–A leads to a change of the rubbery polymer to a viscous liquid.

In a perfectly crystalline polymer, all the chains would be incorporated in regions of three-dimensional order, called *crystallites*, and no glass transition would be observed because of the absence of disordered chains in the sample. The crystalline polymer, on heating, would follow curve H–B–A; at T_{m}°, melting would be observed, and the polymer would become a viscous liquid.

Perfectly crystalline polymers are not encountered in practice, and instead polymers may contain varying proportions of ordered and disordered regions in the sample. These semicrystalline polymers usually exhibit both T_g and T_m, corresponding to the ordered and disordered portions and follow curves similar to F–E–G–A. As T_{m}° is the melting temperature of a perfectly crystalline polymer of high molar mass, T_m is lower and more often represents a melting range, because the semicrystalline polymer contains a spectrum of chain lengths and crystallites of various sizes with many defects. These imperfections act to depress the melting temperature, and experimental values of T_m can depend on the previous thermal history of the sample.

Nevertheless, both T_g and T_m are important parameters, which serve to characterize a given polymer.

1.9 ELASTOMERS, FIBERS, AND PLASTICS

A large number of synthetic polymers now exist covering a wide range of properties. These can be grouped into three major classes: plastics, fibers, and elastomers; but there is no firm dividing line between the groups. However, some classification is useful from a technological viewpoint, and one method of defining a member of these categories is to examine a typical stress–strain plot (Figure 1.10). Rigid plastics and fibers are resistant to deformation and are characterized by a high modulus and low percentage elongations. Elastomers readily undergo deformation and exhibit large reversible elongations under small applied stresses, i.e., they exhibit elasticity. The flexible plastics are intermediate in behavior. An outline of the structure–property relations will be presented later, but before proceeding further with the more detailed science, we can profitably familiarize ourselves with some of the more common polymers and their uses. Some of these are presented in Table 1.2, where an attempt is made to show that the lines of demarcation used to divide polymers into the three major groups are not clear-cut.

A polymer normally used as a fiber may make a perfectly good plastic if no attempt is made to draw it into a filament. Similarly, a plastic, if used at a temperature above its glass transition and suitably cross-linked, may make a perfectly acceptable elastomer. In the following text, a brief account of some of the more common plastics, fibers, and elastomers is given. The classification is based essentially on their major technological application under standard working conditions.

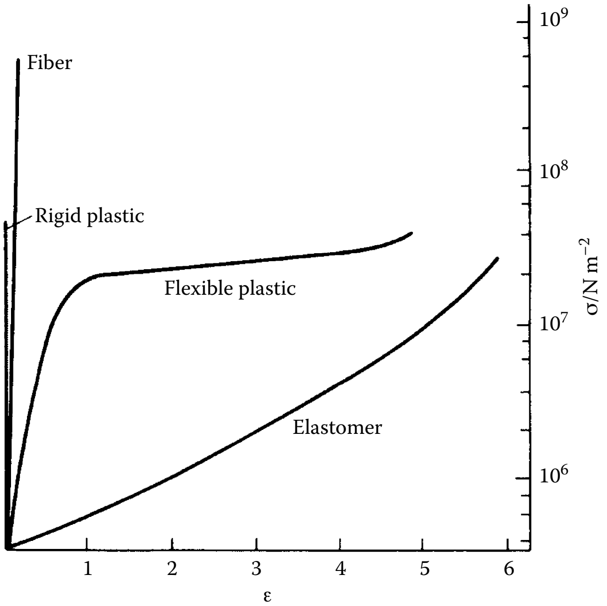


FIGURE 1.10 Typical stress–strain ($\sigma - \varepsilon$) plots for a rigid plastic, a fiber, a flexible plastic, and an elastomer.

TABLE 1.2
Some Common Plastics, Elastomers, and Fibers

Elastomers	**Plastics**	**Fibers**
Polyisoprene	Polyethylene	
Polyisobutylene	Polytetrafluoroethylene	
Polybutadiene	Polystyrene	
	Poly(methylmethacrylate)	
	Phenol-formaldehyde	
	Urea-formaldehyde	
	Melamine-formaldehyde	
◄—— Poly(vinyl chloride) ——	——►	
◄—— Polyurethanes ——	——►	
◄—— Polysiloxanes ——	——►	
	◄——	Polyamide ——►
	◄——	Polyester ——►
	◄——	Polypropylene ——►

1.10 FIBER-FORMING POLYMERS

Whereas there are many fiber-forming polymers, only a few have achieved great technological and commercial success. It is significant that these are polymers of long standing, and it has been suggested that further fiber research may involve the somewhat prosaic task of attempting to improve, modify, or reduce the cost of existing fibers, rather than to look for new and better alternatives. The commercially important fibers are listed in Table 1.3; all are thermoplastic polymers.

The polyamides are an important group of polymers, which include the naturally occurring proteins in addition to the synthetic nylons. The term *nylon*, originally a trade name, has now become a generic term for the synthetic polyamides, and the numerals which follow, e.g., nylon-6,6, distinguish each polymer by designating the number of carbon atoms lying between successive amide groups in the chain. Thus, nylon-6,10 is prepared from two monomers and has the structure

$$-\!\!\left[\mathrm{NH(CH_2)_6NHCO(CH_2)_8CO}\right]_n\!\!-$$

with alternative sequences of six and ten carbon atoms between the nitrogen atoms, whereas nylon-6 is prepared from one monomer and has the repeat formula $-\!\!\left[\mathrm{NH(CH_2)_5CO}\right]_n$ with regular sequences of six carbon atoms between the nitrogen atoms. A nylon with two numbers is termed *dyadic* indicating that it contains both dibasic acid (or acid chloride) and diamine moieties, in which the first number represents the diamine and the second the diacid used in the synthesis. The *monadic* nylons have one number, indicating that synthesis involved only one type of monomer. This terminology means that a poly (α-amino acid) would be nylon-2.

Terylene is an important polyester. It exhibits high resilience, durability, and low moisture absorption, properties that contribute to its desirable “wash and wear” characteristics. The harsh feel of the fiber, caused by the stiffness of the chain, is overcome by blending it with wool and cotton.

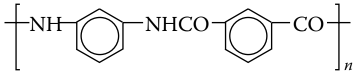
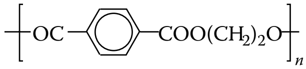
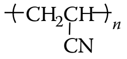
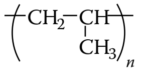
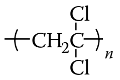
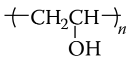
The acrylics and modacrylics are among the most important of the amorphous fibers. They are based on the acrylonitrile unit $\mathrm{—CH_2CH(CN)—}$ and are usually manufactured as copolymers. When the acrylonitrile content is 85% or higher, the polymer is an *acrylic* fiber; but if this drops to between 35 and 85%, it is known as a *modacrylic* fiber. Vinyl chloride and vinylidene chloride are the most important comonomers, and the copolymers produce high-bulk yarns, which can be subjected to a controlled shrinking process after fabrication. Once shrunk, the fibers are dimensionally stable.

1.11 PLASTICS

A plastic is rather inadequately defined as an organic high polymer capable of changing its shape on the application of a force and retaining this shape on removal of this force, i.e., a material in which a stress produces a nonreversible strain.

The main criterion is that plastic materials can be formed into complex shapes, often by the application of heat or pressure, and a further subdivision into those that

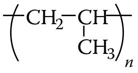
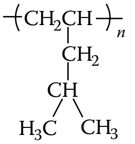
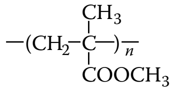
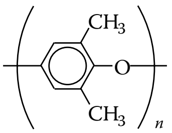
TABLE 1.3
Chemical Structure of Synthetic Fibers

Polymer	Repeat Unit	Trade Names
Polyamides (nylons) (Uses: drip-dry fabrics, cordage, braiding, bristles, and surgical sutures)		
Polycaprolactam	$[\mathrm{NH(CH_2)_5CO}]_n$	Nylon-6, Perlon
Poly(decamethylene carboxamide)	$[\mathrm{NH(CH_2)_{10}CO}]_n$	Nylon-11, Rilsan
Poly(hexamethylene adipamide)	$[\mathrm{NH(CH_2)_6NHCO(CH_2)_4CO}]_n$	Nylon-6,6, Bri-nylon
Poly(*m*-phenylene isophthalamide)		Nomex
Polyesters (Uses: fabrics, tire-cord yarns, and yacht sails)		
Poly(ethylene terephthalate)		Terylene, Dacron
Polyureas		
Poly(nonamethylene urea)	$[\mathrm{NHCONH(CH_2)_9}]_n$	Urylon
Acrylics (Uses: fabrics and carpeting)		
Polyacrylonitrile	 $(\mathrm{CH_2\underset{\mid}{C}H(CN)})_n$ (often as copolymer with >85% acrylonitrile	Orlon, Courtelle, Acrilan, Creslan
Acrylonitrile copolymers	35% < acrylonitrile < 85% + vinyl chloride + vinylidene chloride	Dynel Verel
Hydrocarbons (Uses: carpets and upholstery)		
Polyethylene	$(\mathrm{CH_2CH_2})_n$	Courlene, Vestolen
Polypropylene (isotactic)	 $(\mathrm{CH_2{-}CH(CH_3)})_n$	Ulstron, Herculon, Meraklon
Halogen-Substituted Olefins (Uses: knitwear and protective clothing)		
Poly(vinyl chloride)	$(\mathrm{CH_2CHCl})_n$	Rhovyl, Valren
Poly(vinylidene chloride)	 $(\mathrm{CH_2CCl_2})_n$	Saran, Tygan
Poly(tetrafluoroethylene)	$(\mathrm{CF_2CF_2})_n$	Teflon, Polifen
Vinyl (Uses: fibers, adhesives, paint, sponges, films, and plasma extender)		
Poly(vinyl alcohol)	 $(\mathrm{CH_2CH(OH)})_n$ (normally cross-linked)	Vinylon, Kuralon, Mewlon

are *thermosetting* and those that are *thermoplastic* is useful. The thermosetting materials become permanently hard when heated above a critical temperature and will not soften again on reheating. They are usually cross-linked in this state. A thermoplastic polymer will soften when heated above T_g. It can then be shaped and, on cooling, will harden in this form. However, on reheating, it will soften again and can be reshaped if required before hardening when the temperature drops. This cycle can be carried out repeatedly.

A number of the important thermoplastics are shown in Table 1.4, together with a few examples of their more important uses, determined by the outstanding properties of each. Thus, polypropylene, poly(phenylene oxide), and TPX have good thermal stability and can be used for items requiring sterilization. The optical qualities of polystyrene and poly(methyl methacrylate) are used in situations where

TABLE 1.4
Thermoplastics

Polymer	Repeat Unit	Density (g cm^{-3})	Uses
Polyethylene	$-(CH_2CH_2)_n-$		Household products, insulators, pipes, toys, bottles
High density		0.94–0.96	
Low density		0.92	
Polypropylene	 $-(CH_2-\underset{CH_3}{CH})_n-$	0.90	Water pipes, integral hinges, sterilizable hospital equipment
Poly(4-methylpentene-1) (TPX)		0.83	Hospital and laboratory ware
Poly(tetrafluoroethylene) (PTFE)	$-(CF_2CF_2)_n-$	2.20	Nonstick surfaces, insulation, gaskets
Poly(vinyl chloride) (PVC)	$-(CH_2CHCl)_n-$	1.35–1.45	Records, bottles, house siding, and eaves
Polystyrene	$-(CH_2CH(C_6H_5))_n-$	1.04–1.06	Lighting panels, lenses, wall tiles, flower pots
Poly(methylmethacrylate) (PMMA)	 $-(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-)_n-$	1.17–1.20	Bathroom fixtures, knobs, combs, illuminated signs
Polycarbonates	$-(R.O.COO)-$	1.20	Cooling fans, marine propellers, safety helmets
Poly(2,6-dimethylphenylene oxide)		1.06	Hot water fittings, sterilizable, medical, and surgical equipment

transparency is a premium, whereas the low-frictional coefficient and superb chemical resistance of poly(tetrafluoro-ethylene) make it useful in nonstick cookware and protective clothing. Low-density polyethylene, although mechanically inferior to the high-density polymer, has better impact resistance and can be used when greater flexibility is required, whereas the popularity of poly(vinyl chloride) lies in its unmatched ability to form a stable, dry, flexible material when plasticized. The polyamides and terylene are also important thermoplastics.

1.12 THERMOSETTING POLYMERS

The thermoset plastics generally have superior abrasion and dimensional stability characteristics compared with the thermoplastics, which have better flexural and impact properties. In contrast to the thermoplastics, thermosetting polymers, as the name implies, are changed irreversibly from fusible, soluble products into highly intractable cross-linked resins that cannot be molded by flow and so must be fabricated during the cross-linking process. Typical examples are:

Phenolic resins, prepared by reacting phenols with aldehydes. They are used for electrical fitments, radio and television cabinets, heat resistant knobs for cooking utensils, game parts, buckles, handles, and a wide variety of similar items.

Amino resins are related polymers formed from formaldehyde and either urea or melamine. In addition to many of the uses listed earlier, they can be used to manufacture lightweight tableware, and counter and table surfaces. Being transparent they can be filled and colored using light pastel shades, whereas the phenolics are already rather dark and, consequently, have a more restricted color range.

Thermosetting *polyester resins* are used in paints and surface coatings. In these, oxidation during drying forms a cross-linked film, which provides a tough, resistant finish.

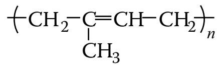
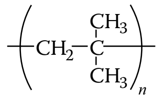
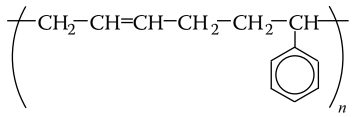
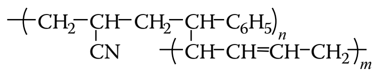
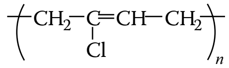
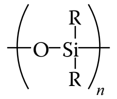
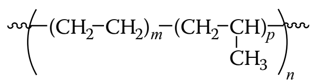
Epoxy resins are polyethers prepared from glycols and dihalides and are extensively used as surface coatings, adhesives, and flexible enamel-like finishes because of their combined properties of toughness, chemical resistance, and flexibility.

1.13 ELASTOMERS

The modern elastomer industry was founded on the naturally occurring product isolated from the latex of the tree *Hevea brasiliensis*. It was first used by indigenous South Americans and was called *caoutchouc*, but, later, simply *rubber*, when it was discovered by Priestley that the material rubbed out pencil marks.

From the early 20th century, chemists have been attempting to synthesize materials whose properties duplicate or at least simulate those of natural rubber, and this has led to the production of a wide variety of synthetic elastomers. Some of these have become technologically important and are listed in Table 1.5, together with their general uses.

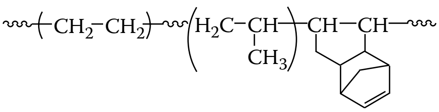
TABLE 1.5
Some Common Elastomers and Their Uses

Polymer	Formula	Uses
Natural rubber (polyisoprene-*cis*)	 $\left(CH_2-\underset{CH_3}{\underset{\mid}{C}}=CH-CH_2 \right)_n$	General purposes
Polybutadiene	$\left(CH_2-CH=CH-CH_2 \right)_n$	Tire treads
Butyl	 $\left(CH_2-\underset{CH_3}{\overset{CH_3}{C}} \right)_n$	Inner tubes, cable sheathing, roofing, tank liners
SBR		Tires, general purposes
ABS	 $\left(CH_2-\underset{CN}{CH}-CH_2-\underset{\left(CH-CH=CH-CH_2 \right)_m}{CH}-C_6H_5 \right)_n$	Oil hoses, gaskets, flexible fuel tanks
Polychloroprene	 $\left(CH_2-\underset{Cl}{\underset{\mid}{C}}=CH-CH_2 \right)_n$	Used when oil resistance, good weathering, and inflammability characteristics are needed
Silicones	 $\left(O-\underset{R}{\overset{R}{Si}} \right)_n$	Gaskets, door seals, medical application flexible molds
Polyurethanes	$\left(R_1-NHCOOR_2OOCHN \right)_n$	Printing rollers, sealing and jointing
EPR	 $\sim\left((CH_2-CH_2)_m-(CH_2-\underset{CH_3}{\underset{\mid}{C}H})_p \right)_n\sim$	Window strips and channeling

Although a large number of synthetic elastomers are now available, natural rubber must still be regarded as the standard elastomer because of the excellently balanced combination of desirable qualities. Presently, it accounts for almost 36% of the total world consumption of elastomers, and its gradual replacement by synthetic varieties is partly a result of demand outstripping natural supply.

The most important synthetic elastomer is styrene-butadiene (SBR) which accounts for 41% of the world market in elastomers. It is used predominantly for vehicle tires when reinforced with carbon black. Nitrile rubber (NBR) is a random copolymer of acrylonitrile (mass fraction 0.2 to 0.4) and butadiene, and it is used when an elastomer that is resistant to swelling in organic solvents is required. The range of properties can be extended when styrene is also incorporated in the chain, forming ABS rubber. Butyl rubber (IIR) is prepared by copolymerizing small quantities of isoprene (3 parts) with isobutylene (97 parts). The elastic properties are poor, but it is resistant to corrosive fluids and has a low permeability to gases. Polychloroprene possesses the desirable qualities of being a fire retardant and resistant to weathering, chemicals, and oils. More recently, ABA triblock copolymers of styrene-(ethene-*stat*-butene)-styrene have become commercially available. These are thermoplastic elastomers, which are unaffected by polar solvents and nonoxidizing acids (alkalis).

Elastomers that fail to crystallize on stretching must be strengthened by the addition of filters such as carbon black. SBR, poly(ethylene-*stat*-propylene), and the silicone elastomers fall into this category. Whereas polyethylene is normally highly crystalline, copolymerization with propylene destroys the ordered structure; and if carried out in the presence of a small quantity of nonconjugated diene (e.g., dicyclopentadiene), a cross-linking site is introduced. The material is an amorphous random terpolymer, which when cross-linked forms an elastomer with a high resistance to oxidation. Unfortunately, it is incompatible with other elastomers and is unsuitable for blending.



The silicone elastomers have a low cohesive energy between the chains, which results in poor thermoplastic properties and an unimpressive mechanical response. Consequently, they are used predominantly in situations requiring temperature stability over a range of 190 to 570 K when conditions are unsuitable for other elastomers.

Extensive use has been made of room temperature vulcanizing silicone rubbers. These are based on linear poly(dimethyl siloxane) chains, with M ranging from 10^4 to 10^5 g mol^{-1}, and hydroxyl terminal groups. Curing can be achieved in a number of ways, either by adding a cross-linking agent and a metallic salt catalyst, such as tri- or tetra-alkoxysilane with stannous octoate, by exposure to light, or by incorporating in the mixture a cross-linking agent sensitive to atmospheric water, which initiates vulcanization. The products are good sealing, encapsulating, and caulking materials; they make good flexible molds and are excellent insulators. They have found a wide application in the building, aviation, and electronics industries. Other room temperature curing adhesives and sealants are listed in Table 1.6.

Having briefly introduced the diversity of structure and property encountered in the synthetic polymers, we can now examine more closely the fundamental chemistry and physics of these materials.

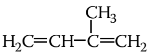
TABLE 1.6
Room Temperature Curing Adhesives and Sealants

Type	General Description	Particular Advantages	Limitations (General Operating Temperature Range)
Moisture curing polyurethanes (PUs)	Sealants (rather than adhesives), which cure by an isocyanate reaction to atmospheric H_2O	Adhesive/sealing effect to a wide range of substrates	Slow curing; usually low modulus (−80°C to +120°C)
RTV (room temperature vulcanizing) silicones	Sealants (rather than adhesives), which cure on exposure to atmospheric moisture by a condensation mechanism that results in release of side products such as acetic acid, alcohols, or amines	Excellent thermal, oxidative, and hydrolytic stability	Unpleasant side products; limited adhesion (−80°C to +200°C)
Anaerobic adhesives and sealants	Fluids, which cure in the absence of air and the presence of metals, heat of UV light by the free-radical mechanism	Very good adhesion to metals and ceramics; resistant to organic solvents	Relatively brittle when cured; curing is sensitive to substrate and to joint geometry (−50°C to +150°C)
Cyanoacrylate adhesives	Relatively low viscosity, which cure anionically in response to substrate-borne atmospheric moisture	Excellent adhesion to a wide range of substrates; very effective on rubber and on most plastics	Brittle when cured; limited thermal and hydrolytic stability (−50°C to +80°C)
Acrylics	Methacrylic adhesives, which cure free radically in response to substrates treated with a primer/hardener; the adhesives usually contain rubber toughener	Forms durable adhesive joints to metallic substrates; high peel strength	Inhibited by atmospheric oxygen; limit cure-through-gap (−50°C to +100°C)

PROBLEMS

1. Consider the following monomers or monomer combinations, and in each case,
   a. Indicate the functionality
   b. Draw the structure of the corresponding polymer or polymers
   c. Indicate whether you would expect polymerization to proceed via a step-growth or chain-growth mechanism.

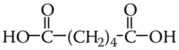
(a)



$H_2C{=}CH{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2$

isoprene

(b)

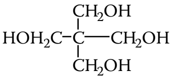


$HO{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}OH$

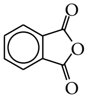
$HO{-}(CH_2)_{10}{-}OH$

adipic acid (hexanedioic acid) and 1,10-decamethylene glycol

(c)



$HOH_2C{-}\underset{CH_2OH}{\underset{|}{\overset{CH_2OH}{\overset{|}{C}}}}{-}CH_2OH$

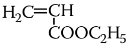


Pentaerythritol and phthalic anhydride

(d) $H_2N(CH_2)_5NH_2$ $ClCO(CH_2)_5COCl$

Pentamethylenediamine and heptanedioyl chloride

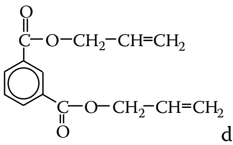
(e)



$H_2C{=}\underset{COOC_2H_5}{\underset{|}{CH}}$

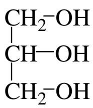
ethyl acrylate

(f)



diallyl isophthalate

2. Consider the reaction of adipic acid with one of the following compounds:



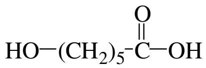
$$\begin{array}{l} CH_2{-}OH \\ | \\ CH{-}OH \\ | \\ CH_2{-}OH \end{array}$$

$HO{-}CH_2CH_2CH_2CH_2{-}OH$ $HO{-}CH_2CH_2CH_2CH_3$

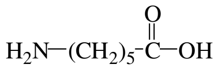
glycerol 1,4-butanediol butanol

In each case, indicate whether a linear polymer or a network is formed.

3. Draw the repeat units of the two polymers obtained by the polymerization of the following two monomers:



$HO-(CH_2)_5-\overset{\displaystyle O}{\overset{\|}{C}}-OH$



$H_2N-(CH_2)_5-\overset{\displaystyle O}{\overset{\|}{C}}-OH$

Which of the two would you expect to exhibit the higher melting point and why?

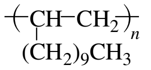
4. Calculate the number-average and weight-average molar mass of the following ternary mixture of monodisperse polymer samples, each characterized by molar mass, M_i, and number of moles, N_i, as reported in the following table:

i	N_i	M_i
1	0.053	10,000
2	0.035	50,000
3	0.012	100,000

Determine the polydispersity of the sample.

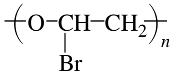
5. Name each of the following polymers by the IUPAC system:

(a)



$\left(\underset{(CH_2)_9CH_3}{\underset{|}{C}H}-CH_2\right)_n$

(b)



$\left(O-\underset{Br}{\underset{|}{C}H}-CH_2\right)_n$

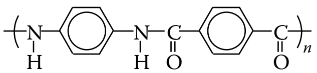
(c) $\left(O-CH_2-CH_2\right)_n$

(d) $\left(HNCO(CH_2)_5CONH(CH_2)_5\right)_n$

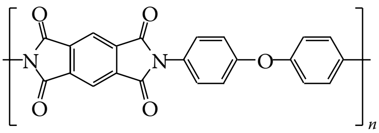
6. The following polymers from DuPont are known by the registered trademarks listed below the structure. Rename them using the IUPAC nomenclature.

$\left(CH_2CHOH\right)_n$

Elvanol®



Kevlar®



Kapton®

7. A polymer sample is composed of a series of fractions:

$M \times 10^{-3}$	Mass (mg)
20–60	40
60–100	160
100–140	360
140–180	720
180–220	440
220–260	228
260–300	140

   Calculate the number average, weight average from these data. Draw the molecular weight distribution curve and indicate in the plot the position of the weight- and number-average molecular weights. Determine the polydispersity of the sample.

8. Identify all the possible isomers (structural and stereoisomers) resulting from the polymerization of 2-methyl butadiene.
9. Polybutadiene samples prepared by anionic polymerization contain a random distribution of *cis*-1,4, *trans*-1,4 and vinyl-1,2 units. Draw structures of a portion of polymer chains consisting of approximately 20 units for PB samples of the following composition:
   a. 38% *cis*-1,4, 51% *trans*-1,4 and 11% vinyl-1,2 units
   b. 11% *cis*-1,4, 13% *trans*-1,4 and 76% vinyl-1,2 units
10. Hydrogenation of the polybutadiene samples in Problem 9 yields a random copolymer. Determine the extended length of the polymers containing 100 repeat units.

REFERENCES

Generic source-based nomenclature for polymers, *Pure Appl. Chem.*, 73(9), 1511, 2001.

Hounshell, D.A. and Smith, J.K., The Nylon Drama, *American Heritage of Invention and Technology*, 4, p. 40, 1988.

Morawetz, H., *Polymers: The Origins and Growth of a Science*, John Wiley and Sons, 1985.

Nomenclature of regular single-strand organic polymers, *Pure Appl. Chem.*, 74(10), 1921, 2002.

Seymour, R.B., *History of Polymer Science and Technology*, Marcel Dekker, 1982.

Treloar, L.R.G., *Introduction to Polymer Science*, Wykeham Publications, 1970.

Use of abbreviations for names of polymeric substances (1986), *Pure Appl. Chem.*, 59, 691, 1987.

Zandvoort, H., *Studies in the History and Philosophy of Science*, 19(4), 489, 1988.

BIBLIOGRAPHY

Allcock, H.R., Mark, J.E., and Lampe, F.W., *Contemporary Polymer Chemistry*, 3rd ed., Prentice Hall, 2003.

Allen, G. and Bevington, J.C., Eds., *Comprehensive Polymer Science: The Synthesis, Characterization, Reactions, and Applications of Polymers*, Pergamon Press, 1989.

Billmeyer, F.W., *Textbook of Polymer Science*, 3rd ed., Interscience Publishers, 1984.

Bovey, F.A. and Winslow, F.H., *Macromolecules: An Introduction to Polymer Science*, Academic Press, 1979.

Brandrup, J., Immergut, E.H., Grulke, E.A., Abe, A., and Bloch, D.R., Eds., *Polymer Handbook*, 4th ed., John Wiley and Sons, 2005.

Carraher, C.E., Jr., *Seymour/Carraher's Polymer Chemistry*, 6th ed., CRC Press, 2003.

Elias, H.G., *An Introduction to Polymer Science*, John Wiley and Sons, 1996.

Elias, H.G., *Macromolecules*, Vol. 1, 2, John Wiley and Sons, 2006.

Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press, 1953.

Hiemenz, P.C. and Lodge, T., *Polymer Chemistry*, 2nd ed., CRC Press, 2007.

Mark, H.F., *Encyclopedia of Polymer Science and Technology*, 12 volume set, 3rd ed., John Wiley and Sons, 2004.

Munk, P. and Aminabhavi, T.M., *Introduction to Macromolecular Science*, 2nd ed., John Wiley and Sons, 2002.

Odian, G., *Principles of Polymerization*, 4th ed., John Wiley and Sons, 2004.

Painter, P.C. and Coleman, M.M., *Fundamentals of Polymer Science: An Introductory Text*, Technomic Publishing, 1997.

Ravve, A., *Principles of Polymer Chemistry*, Plenum Press, 2000.

Rodriguez, F., Cohen, C., Ober, C.K., and Archer, L., *Principles of Polymer Systems*, 5th ed., Taylor and Francis, 2003.

Rosen, S.L., *Fundamental Principles of Polymeric Materials*, 2nd ed., John Wiley and Sons, 1993.

Sperling, L.H., *Introduction to Physical Polymer Science*, 4th ed., Wiley-Interscience, 2005.

Stevens, M., *Polymer Chemistry: An Introduction*, 3rd ed., Oxford University Press, 1998.

Young, R.J. and Lovell, P.A., *Introduction to Polymers*, 2nd ed., Chapman and Hall, 1991.

References

1 Chapter 1. Introduction

Hounshell, D.A. and Smith, J.K., The Nylon Drama, American Heritage of Invention and Technology, 4, p. 40, 1988.

Morawetz, H., Polymers: The Origins and Growth of a Science, John Wiley and Sons, 1985. Nomenclature of regular single-strand organic polymers, Pure Appl. Chem., 74(10), 1921, 2002. Seymour, R.B., History of Polymer Science and Technology, Marcel Dekker, 1982.

Oshinski, A.J., Keskkula, H., and Paul, D.R., Polymer, 37, 4891, 1996.

Flory, P.J., Principles of Polymer Chemistry, Cornell University Press, 1953, chap. 3.

Frazer, A.H., High Temperature Resistant Polymers, Interscience Publishers, 1968.

Lenz, R.W., Organic Chemistry of Synthetic High Polymers, Interscience Publishers, 1967, chap. 3.

Mark, H.F. and Whitby, G.S., The Collected Papers of Wallace Hume Carothers, Interscience Publishers, 1940.

Nielson, P.O., Properties of Epoxy Resins, Hardeners and Modifiers, Adhesives Age, Vol. 42, 1982. Odian, G., Principles of Polymerization, 4th ed., John Wiley and Sons, 2004, chap. 2. Oertel, G., Ed., Polyurethane Handbook, 2nd ed., Hanser Gardner Publications, Munich, 1994. Potter, W.G., Epoxide Resins, Butterworth, 1970. Rempp, P. and Merrill, E.W., Polymer Synthesis, 2nd ed., Hüthig and Wepf, 1991. Rogers, M.E. and Long, T.E., Synthetic Methods in Step Growth Polymers, John Wiley and Sons, 2003. Solomon, D.H., The Chemistry of Organic Film Formers, John Wiley and Sons, 1967.

3 Chapter 3. Free-Radical Addition Polymerization

Goto, A. et al., Macromolecules, 34, 402, 2001.

Melville, H.W., J. Chem. Soc., 247, 1947.

Olaj, O.F., Bitai, I., and Hinkelmann, F., Makromol. Chem., 188, 1689, 1987.

Overberger et al., J. Am. Chem. Soc., 71, 2661, 1949.

Palit, S.R. and Das, S.K., Proc. R. Soc. London 226A, 82, 1954.

Schulz, G.V., Chem. Ber., 80, 232, 1947.

Allen, G. and Bevington, J.C., Eds., Comprehensive Polymer Science, Vol. 3, 4, Pergamon Press, 1989.

Alter, H. and Jenkins, A.D., Chain-reaction polymerization, in Encyclopedia of Polymer Science and Technology, Interscience Publishers, 1965. Bamford, C.H. and Tipper, C.F.H., Eds., Free Radical Polymerization, Comprehensive Chemical Kinetics, Vol. 14A, Elsevier, 1976. Billmeyer, F.W., Textbook of Polymer Science, 3rd ed., John Wiley and Sons, 1984. Blackley, D.C., Emulsion Polymerization, John Wiley and Sons, 1975. Bouton, T.C., Henderson, J.N., and Bevington, J.C., Eds., Polymerization Reactors and Processes, ACS Symposium Series 104, 1979. Flory, P.J., Principles of Polymer Chemistry, Cornell University Press, 1953, chap. 4. Ham, G.E., Vinyl Polymerization, Vol. I, Marcel Dekker, 1967. Jenkins, A.D., The reactivity of polymer radicals, in Advances in Free Radical Chemistry, Vol. 2, Logos Press, 1967. CTA Percentage Conversion 2.5 30 2.5 50 2.5 70 2.5 90 2.0 50 1.5 50 1.0 50 Lenz, R.W., Organic Chemistry of Synthetic High Polymers, Interscience Publishers, 1967, chap. 9–11.

Margerison, D. and East, G.C., Introduction to Polymer Chemistry, Pergamon Press, 1967, chap. 4. Napper, D.H., Polymer Stabilization of Colloidal Dispersions, Academic Press, 1984. Odian, G., Principles of Polymerization, 4th ed., John Wiley and Sons, 2004. Rempp, P. and Merrill, E.W., Polymer Synthesis, Hüthig and Wepf Verlag, 1986. Smith, D.A., Addition Polymers, Butterworths, 1968, chap. 2.

4 Chapter 4. Ionic Polymerization

Hogen-Esch, T.E. and Smid, J., Eds., Recent Advances in Anionic Polymerization, Elsevier Science Publishing, 1987.

Hsieh, H.L. and Quirk, R.P., Recent Anionic Polymerization: Principles and Practical Applications, Marcel Dekker, 1996. Ivin, K.J. and Saegusa, T., Eds., Ring Opening Polymerization, Elsevier Applied Science Publishers, 1984. Kennedy, J.P. and Marechal, E., Carbocationic Polymerization, Krieger Publishing Company, 1990. Lenz, R.W., Organic Chemistry of Synthetic High Polymers, Interscience Publishers, 1967, chap. 13, 14. Morton, M., Anionic Polymerization: Principles and Practice, Academic Press, 1983. Plesch, P.H., The Chemistry of Cationic Polymerization, Pergamon Press, 1963. Puskas, J.E. and Kaszas, G., Carbocationic polymerization, in Encyclopedia of Polymer Science and Technology, John Wiley and Sons, 2003. Quirk, R.P., Anionic polymerization, in Encyclopedia of Polymer Science and Technology, John Wiley and Sons, 2002. Smith, D.A., Addition Polymers, Butterworths, 1968, chap. 3. Szwarc, M., Carbanions, Living Polymers and Electron Transfer Processes, Interscience Publishers, 1968.

5 Chapter 5. Linear Copolymers and Other Architectures

Mayo, F.R., Walling, C., Lewis, F.M., and Hulse, W.F., J. Am. Chem. Soc., 70, 1523, 1948.

Cowie, J.M.G., Alternating Copolymers, Plenum Press, 1985.

Folkes, M.J., Eds., Processing, Structure and Properties of Block Copolymers, Elsevier Applied Science Publishers, 1985.

Noshay, A. and McGrath, J.E., Block Copolymers: Overview and Critical Survey, Academic Press, 1977.

Odian, G., Principles of Polymerization, 4th ed., John Wiley and Sons, 2004.

Rempp, P. and Merrill, E.W., Polymer Synthesis, Hüthig and Wepf, 1986.

6 Chapter 6. Polymer Stereochemistry

Bawn, C.E.H. and Ledwith, A., Q. Rev., 16, 361, 1962.

Hirabayashi, T., Yamamoto, H., Kojima, T., Takasu, A., and Inai, Y., Macromolecules, 33, 4304, 2000.

Natta, G. and Corradini, P., Rubber Chem. Technol., 33, 703, 1960.

Vogl, O., J. Macromol. Sci. Chem., A21, 1725, 1984.

Cooper, W., Stereospecific polymerization, in Progress in High Polymers, Vol. I, Academic Press, 1961.

Goodman, M., Concepts of polymer stereochemistry, Topics in Stereochemistry, Vol. 2, WileyInterscience, 1967.

Ketley, A.D., The Stereochemistry of Macromolecules, Vol. I–III, Edward Arnold, 1968.

Natta, G., Precisely constructed polymers, Sci. Am., 205, 33, 1961.

Schildknecht, G.E., Stereoregular polymers, in Encyclopedia of Chemistry, Reinhold Publishing, 1966.

Seymour, R.B., Introduction to Polymer Chemistry, McGraw-Hill, 1971, chap. 6.

7 Chapter 7. PolymerizationReactions Initiated by Metal Catalysts and Transfer Reactions

Boor, J., Ziegler-Natta Catalysis and Polymerization, Academic Press, 1979.

Dragutan, V., Balaban, A.T., and Dimonie, M., Olefin Metathesis and Ring Opening Polymerization of Cyclo Olefins, John Wiley, 1985.

Hiemenz, P.C. and Lodge, T., Polymer Chemistry, 2nd ed., CRC Press, 2007, chap. 5. (a) rac-Me 2 Si(2Me-4-Ph-1-Ind) 2 ZrCl 2 (b) meso-Me 2 Si(4-Ph-1-Ind) 2 ZrCl 2 (c) Me 2 C(Cp)(9-Flu) ZrCl 2 Ivin, K.J., Olefin Metathesis, Academic Press, 1983. Kaminsky, W. and Sinn, H., Eds., Transition Metals and Organometallics as Catalysts for Olefin Polymerization, Springer-Verlag, 1988.

Keii, T., Kinetics of Ziegler-Natta Polymerization, Chapman and Hall, 1972.

Mark, H.F., Encyclopedia of Polymer Science and Technology, 12 volume set, 3rd ed., John Wiley and Sons, 2004.

Odian, G., Principles of Polymerization, 4th ed., John Wiley and Sons, 2004, chap. 8.

Quirk, R.P., Ed., Transition Metal Catalysed Polymerizations, Harwood Academic Press, 1983.

Stevens, M., Polymer Chemistry: An Introduction, 3rd ed., Oxford University Press, 1998.

Koningsveld, R., Onclin, M.H., and Kleintjens, L.A., in Polymer Compatibility and Incompatibility, Harwood Academic Publishers, 1982. Kurata, M., Thermodynamics of Polymer solutions, Gordon and Breach, 1982. Morawetz, H., Macromolecules in Solution, 2nd ed., John Wiley and Sons, 1975. Olabisi, O., Robeson, L.M., and Shaw, M.T., Polymer-Polymer Miscibility, Academic Press, 1969. Paul, D.R. and Bucknall, C.B., Eds., Polymer Blends: Formulation and Performance, Vol. 1, 2, John Wiley and Sons, 2000. Paul, D.R. and Newman, S., Eds., Polymer Blends, Vol. 1, 2, Academic Press, 1978. B xyB x yB x y B x y blend AC BC AD = + − + − + − − ( ) ( ) ( )( ) 1 1 1 1 B x x B y y B BD AB CD − − − −( ) ( )1 1 Tompa, H., Polymer Solutions, Butterworths, 1956. Van Krevelen, D.W., Properties of Polymers, 3rd ed., Elsevier, 1990. Yamakawa, H., Modern Theory of Polymer Solutions, Gordon and Breach, 1982.

9 Chapter 9. Polymer Characterization — Molar Masses

Debye, P., J. Phys. Coll. Chem., 51, 18, 1947. M ω × 10 -6 (g mol -1) [η] 4.00 1.60 1.54 1.01 1.40 0.93 1.25 0.90 0.84 0.69 0.66 0.64 0.48 0.52 0.22 0.36 0.09 0.23 V (min) M (g mol -1) 10.83 8500000 11.58 3040000 12.45 1030000 13.66 330000 14.45 156000 15.09 66000 15.96 28500 16.75 9200 18.08 3250 η � � � � = × − 8 6 10 2 0 5 . . M Fox, T.G., Kinsinger, J.B., Mason, H.F., and Schuele, E.M., Polymer, 3, 71, 1962. Grubisic, Z., Rempp, P., and Benoit, H., J. Polym. Sci.: Polym. Lett., 5, 753, 1967.

Wyatt, P.J., Anal. Chim. Acta, 272, 1, 1993.

Zimm, B.H., J. Chem. Phys., 16, 1093, 1948a.

10 Chapter 10. Polymer Characterization — Chain Dimensions, Structures, and Morphology

Brownstein, S., Bywater, S., and Worsfold, D.J., Makromol. Chem., 58, 127, 1961.

Krigbaum, W.R., J. Am. Chem. Soc., 76, 3758, 1954.

Matsushita, Y., Mori, K., Saguchi, R., Nakao, Y., Noda, I., and Nagasawa, M., Macromolecules, 23, 4393, 1990.

11 Chapter 11. The Crystalline State and Partially Ordered Structures

Imura, K., Koide, N., and Takeda, M., Synthesis and characterization of some thermotropic liquid crystalline polymers, Curr. Top. Polym. Sci., 1, 1987.

Keith, H.D. and Padden, F.J., J. Appl. Phys., 35, 1286, 1964.

Keller, A., Lester, G.R., and Morgan, L.B., Phylos. Trans. R. Soc. London, 247A, 13, 1954.

Krigbaum, W.R., Watanabe, J., and Ishikawa, T., Macromolecules, 16, 1271, 1983.

Leibler, L., Macromolecules, 13, 1602, 1980.

Lenz, R.W. and Jin, J.I., Liquid crystal polymers: a new state of matter, Polymer News, 11, 200, 1986.

Mandelkern, L., Rubber Chem. Technol., 32, 1392, 1949.

Marker, L., Early, R., and Aggarwal, S.L., J. Polym. Sci., 38, 369, 1959.

Matsen, M.W. and Schick, M., Phys. Rev. Lett., 72, 2660, 1994.

McArdle, C.B., Ed., Side Chain Liquid Crystals Polymers, Blackie and Sons, 1989.

McCrum, N.B., Buckley, C.P., and Bucknall, C.B., Principles of Polymer Engineering, 2nd ed., Oxford University Press, 1997.

McCrum, N.B., Buckley, C.P., and Bucknall, C.B., Principles of Polymer Engineering, Oxford University Press, 1988. Platé, N.A. and Shibaev, V.P., Comb-Shaped Polymers and Liquid Crystals, Plenum Press, 1987. Sadler, D.M., Static and Dynamic Properties of the Polymeric Solid State, Pethrick, R.A. and Richards, R.W., Eds., D. Reidel Publishing Co., 1982. Sharples, A., Introduction to Polymer Crystallization, Edward Arnold, 1966. Sperling, L.H., Introduction to Physical Polymer Science, 4th ed., Wiley-Interscience, 2005. Tobolsky, A.V. and Mark, H., Polymer Science and Materials, Wiley-Interscience, 1971, chap 8.

12 Chapter 12. The Glassy State and Glass Transition

Doi, M. and Edwards, S.F., The Theory of Polymer Dynamics, Oxford University Press, 1986.

Ferry, J.D., Viscoelastic Properties of Polymers, 3rd ed., John Wiley and Sons, 1979.

de Gennes, P.G., Scaling Concepts in Polymer Physics, Cornell University Press, 1979. Mark, J.E., Ngai, K., Graessley, W., Mandelkern, L., Samulski, E., Koenig, J.L., and Wignall, G., Physical Properties of Polymers, 3rd ed., Cambridge University Press, 2004. Meares, P., Polymers: Structures and Bulk Properties, Van Nostrand 1965, chap. 10. Pethrick, L.H. and Richards, R.W., Eds., Static and Dynamic Properties of the Polymeric Solid State, D. Reidel Publishing Co., 1982. Sperling, L.H., Introduction to Physical Polymer Science, 4th ed., John Wiley and Sons, 2005. Tobolsky, A.V. and Mark, H., Polymer Science and Materials, Wiley-Interscience, 1971, chap. 6.

Ward, I.M., Mechanical Properties of Solid Polymers, 2nd ed., John Wiley and Sons, 1983.

13 Chapter 13. Rheology and Mechanical Properties

FIGURE 13.33 Log a T vs. T-T o for polystyrene (open circles) and polyisobutylene (slotted

circles). (From Williams, M.L. et al., J. Am. Chem. Soc., 77, 3701, 1955. With permission.) -20 0 20 40 60 80 100 120 -4 -2 0 2 T-T o /K l o g a T S M 2 1 2/ / Fox, T.G. and Flory, P.J., J. Phys. Chem., 55, 221, 1951. Graessley, W.W., Viscoelasticity and flow in polymer melts and concentrated solutions in Physical Properties of Polymers, 3rd ed., Cambridge University Press, 2004. Grentzer, T. and Leckenby, J., Intl. Lab., 19(6), 34–38, July–August, 1989.

Ishida, Y. et al., Koll. Z. 180, 108, 1962.

McCrum, N.G. et al., Anelastic and Dielectric Effects in Polymeric Solids, John Wiley and Sons, NY, 1976. Morris, E.R., Carbohydr. Polym., 13, 85, 1990. Pearson, D.S., ver Strate, G., von Meerwall, E., and Schilling, F.C., Macromolecules, 20, 1133, 1987.

Thompson, A.B. and Woods, D.W., Trans. Faraday Soc., 52, 1383, 1956.

Wetton, R.E. et al., Intl. Lab., March, 1986.

Chaper 14. The Elastomeric State

Beevers, R.B., Experiments in Fibre Physics, Butterworths, 1970.

Flory, P.J., Ind. Eng. Chem., 38, 417, 1946.

Grumbell, S.M., Mullins, L., and Rivlin, R.S., Trans. Faraday Soc., 49, 1495, 1953.

Mark, J.E., J. Chem. Ed., 58, 898, 1981.

Meyer, K.H. and Ferri, C., Helv. Chim. Acta, 18, 570, 1935.

Mullins, L., I. R. I. Trans., 22, 235, 1947.

Shen, M., McQuarrie, D.A., and Jackson, J.L., J. Appl. Phys., 38, 791, 1967.

Treloar, L.R.G., Introduction to Polymer Science, Wykeham Publications, 1970.

Treloar, L.R.G., Trans. Faraday Soc., 40, 59, 1944.

Allen, G. and Bevington, J.C., Eds., Comprehensive Polymer Science, Vol. 2, Pergamon Press, 1989.

Beevers, R.B., Experiments in Fibre Physics, Butterworths, 1970.

Blackley, D.C., Synthetic Rubbers: Their Chemistry and Technology, Elsevier, 1983.

Bueche, F., Physical Properties of Polymers, Interscience Publishers, 1962, chap. 1.

Flory, P.J., Principle of Polymer Chemistry, Cornell University Press, 1953, chap. 11.

Koenig, L., Physical Properties of Polymers, American Chemical Society, 1984.

Mark, J.E. and Erman, B., Rubberlike Elasticity — A Molecular Primer, John Wiley and Sons, 1988.

Mark, J.E., Ngai, K., Graessley, W., Mandelkern, L., Samulski, E., Koenig, J.L., and Wignall, G., Physical Properties of Polymers, 3rd ed., Cambridge University Press, 2004.

Odian, G., Principles of Polymerization, 4th ed., Wiley, 2004.

Sperling, L.H., Introduction to Physical Polymer Science, 4th ed., Wiley-Interscience, 2005.

Tobolsky, A.V. and Mark, H., Polymer Science and Materials, Wiley Interscience, 1971, chap. 9.

Treloar, L.R.G., Introduction to Polymer Science, Wykeham Publications, 1970.

Treloar, L.R.G., Physics of Rubber Elasticity, 3rd ed., Clarendon Press, 1975.

Ward, I.M. and Sweeney, J., An Introduction to the Mechanical Properties of Solid Polymers, John Wiley and Sons, 2004.

15 Chapter 15. Structure-Property Relations

Drumm, M.F., Dodge, C.W.H., and Nielsen, L.E., Ind. Eng. Chem., 48, 76, 1956.

Edgar, O.B. and Hill, R., J. Polym. Sci., 8, 1, 1951.

Gaudiana, R.A., Minns, R.A., Sinta, R., Weeks, N., and Rogers, H.G., Amorphous rigid rod polymers, Prog. Polym. Sci., 14, 47, 1989.

Hegenrother, P.M., Polym. J., 19, 73, 1987.

Hill, R., Fibres from Synthetic Polymers, Elsevier, 1953.

Hill, R. and Walker, E.E., J. Polym. Sci., 3, 609, 1948.

Hirroka, M. and Kato, T., J. Polym. Sci., Polym. Lett. Ed., 9, 199, 1971. Kelley, F.N. and Bueche, F., J. Polym. Sci., 50, 549, 1961. Krigas et al., J. Polym. Sci., Polym. Phys. Ed,. 23, 509, 1985. Lopez, L.C. and Wilkes, G.L., Poly(phenylene sulphide), Rev. Macromol. Chem. Phys., C29, 83, 1989. Nielsen, E., Mechanical Properties of Polymers and Composites, Marcel Dekker, 1974. Richards, R.B., J. Appl. Chem., 1, 370, 1951. Tanner, D., Fitzgerald, J.A., and Phillips, B.R., The Kevlar story, Angew. Chem. Int. Ed. Engl. Adv. Mater., 28, 649, 1989. Tonelli, A.E., Macromolecules, 8, 544, 1975.

16 Chapter 16. Polymers for the Electronics Industry

Kuzmany, H., Mehring, M., and Roth, S., Electronic Properties of Polymers and Related Compounds, Springer-Verlag, 1985. Platé, N.A. and Shibaev, V.P., Comb-Shaped Polymers and Liquid Crystals, Plenum Press, 1987. Seanor, D.A., Ed., Electrical Properties of Polymers, Academic Press, 1982. Skotheim, T.A., Ed., Handbook of Conducting Polymers, Vol. I, II, Marcel Dekker, 1986. Thompson, L.F., Willson, C.G., and Bowden, M.J., Eds., Introduction to Microlithography, ACS Symposium, Series 219, American Chemical Society, 1983. Thompson, L.F., Willson, C.G., and Frechet, J.M.T., Eds., Materials for Microlithography, ACS Symposium, Series 266, American Chemical Society, 1984.