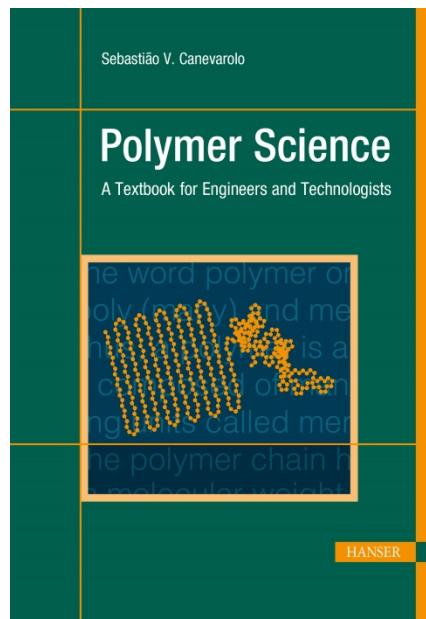


HANSER



Sample Pages

Polymer Science
Sebastião V. Canevarolo Jr.

ISBN: 978-1-56990-725-2

E-Book ISBN: 978-1-56990-726-9

For further information and order see

www.hanserpublications.com (in the Americas)

www.hanser-fachbuch.de (outside the Americas)

Preface

The idea of writing this book was to create a reference for the undergraduate and graduate students of polymer science in the Materials Engineering course of the Federal University of São Carlos, Brazil, where I have been lecturing for the past four decades. During this period much has been developed and discovered in the area of synthesis and technology of polymer materials. Despite all this frenetic development, the fundamental concepts discussed here, defined mainly by the great researchers in polymer science – Staudinger and Carothers in the 1920s, Ziegler and Natta in the 1950s, and Flory, to name a few – have remained constant because by being general they have the greatness of universality. Deeply understanding concepts such as degree of crystallinity, melting and glass transition temperature, and mechanical behavior and applying them to our needs has made it possible to scientifically solve the everyday problems polymer engineers face. I hope the way I set and discuss the basic concepts of the plastics world may help you too to tackle your everyday problems. Read it unhurriedly, reflect on each concept, go beyond the text itself, give wings to your logical imagination; this will give you confidence in the basic fundamentals of the ever-increasing modern commodity that plastics have become.

To better discuss the matters, I included in every chapter some problems and presented their solution. I hope that I have chosen examples that are sufficiently comprehensive and representative. More important than this, I hope the answers I have proposed are a way of showing the reader how to tackle the problem and solve it. At the end of each chapter a list of exercises was added, with the main intention of testing the clarity with which the concepts covered were understood by the reader, helping to assimilate each one of them in the best possible way.

I hope this text is light, having a minimum number of words, only those necessary to express the idea well. On the other hand, I would like it to be faithful to what many bright and tireless researchers thought, tested, and, after verifying that their ideas made sense, shared with us. A light text only in its approach, but dense in concept, indeed, as every textbook should be.

Thanks for choosing it and good reading.

S. V. Canevarolo

São Carlos, Brazil

October 2019

About the Author



Sebastião Vicente Canevarolo was born on 30/May/1956 in São Carlos, SP, Brazil. In 1978, he finished the undergraduate course of Materials Engineering in the Department of Materials Engineering of the Federal University of São Carlos (UFSCar), joining immediately this same department as a lecturer, and is currently still working there.

He completed the Master's Program in Materials Engineering at UFSCar in 1982 and got his Ph.D. at the Institute of Polymer Technology at Loughborough University of Technology, England in 1986. He carried out a postdoctoral program at the Dipartimento di Ingegneria Chimica ed Alimentare of the University of Salerno, Italy from Jun/93 to Jul/94, and is a Researcher Fellow of CNPq (Brazilian National Council for Scientific and Technological Development) since 1994 and Full Professor at UFSCar since 2015.

In different periods, he has been the Vice-Head of DEMa (<http://www.dema.ufscar.br>), Supervisor of the Polymer Laboratories, Coordinator of the Polymer Group, member of the Department Council, Head of the Graduate Program in Science and Materials Engineering (<http://www.ppgcem.ufscar.br>), founder and for 20 years Director of the Brazilian Polymer Association, ABPol (<http://www.abpol.com.br>), Editor-in-Chief of the Brazilian polymers journal *Polímeros: Ciência e Tecnologia* (ISSN 1678-5169 and 0104-1428, www.revistapolimeros.org.br), honorary member of the Brazilian Association of Thermal Analysis and Calorimetry-ABRATEC, and member of the Editorial Board of Materials Research (<http://www.materialsresearch.org.br>). He has participated in the organizing committee of various congresses in the polymer area in Brazil (XIICBECIMAT, 4CBPol, 1CBRATEC, 1SBE, 9CBPol, 11CBPol) and abroad (PPS-18, Portugal).

His research field is developing optical techniques to characterize in real time (in-line) the extrusion process, constructing the hardware (slit-die, optical cell, in-line turbidimeter, in-line rheo-polarimeter, in-line colorimeter, in-line LALLS), and developing the software (in LabView). He has two patent applications, published one

chapter in an English-language book and two Portuguese-language books: *Ciência dos Polímeros*, ISBN 85-88098-10-5, 2010, and *Técnicas de Caracterização de Polímeros*, ISBN 85-88098-19-9, 2004, both from Artliber. The first one has become a standard reference in the area, being used as bibliographic source for all Brazilian undergraduate and graduate polymer courses, and its content is the basis for this book.

Canevarolo has published 55 original papers in international journals, 17 in Brazilian journals, and participated in presenting 130 articles in national and international congresses. He has given 23 invited conferences in national and international events, supervised three postdoc researches, nine Ph.D. theses, and 29 Master theses. He has participated in the CNPq PRONEX project and the FAPESP Thematic Program, coordinates an international cooperation agreement between Brazil and Portugal, and is the Brazilian National Representative in the Polymer Processing Society (PPS). Currently, he is Full Professor at DEMA/UFSCar and Research Fellow from CNPq PQ-2. He has an h-index of 13, with 775 citations.

<http://www.researcherid.com/rid/G-3880-2012>

CV LATTES: <http://lattes.cnpq.br/4153664441338178>

ORCID: 0000-0002-7959-1872

Foreword

Dear reader, if you are in any way involved with plastic materials and looking for a direct but not superficial text, deep but easy to understand, rich in information without being boring, I believe this is the book that you were looking for. Read it once or twice and have it on hand for a quick look: its figures, charts, tables, and appendices have been prepared not only to illustrate the text but mainly to be accessed when necessary. An efficient and productive professional is not one who knows by heart hundreds of phone numbers but the one who knows where to find them.

In its over 350 pages, *Polymer Science: A Textbook for Polymer Engineers* tries to summarize in a didactic way the vast field of knowledge that was developed in the twentieth century in the area of polymers. Better known as plastics, these new materials started their lives in a timid way but quickly gained their space due to both their superior performance and the acceptance of the increasingly demanding consumers. Their low price, light weight, easy molding, good chemical, thermal, and mechanical resistance, easy coloring, and great functionality, permitting the production of goods with complicated shapes, are the reason for their total acceptance by the modern designer. All these characteristics, almost gifted, are not obtained for free. It is necessary that the technician/engineer who is choosing knows their particularities deeply so that the choice is not a “shot in the foot”. This book attempts to provide practitioners who are in some way involved with polymer materials, whether in obtaining, selecting, or molding, technical/scientific information that will enable them to act knowingly. The empirical method of trial and error has no place in the twenty-first century; professionals with decision-making power have to be aware of the basic fundamentals, their intricacies, and implications.

Finally, the purpose of this book is to give you technical knowledge about the vast and economically attractive field of plastic materials. It is easy to remember that having the information, not necessarily known by heart but definitely within reach, is what counts. Good reading and good business!

S. V. Canevarolo

Contents

Preface	VII
About the Author	IX
Foreword	XI
1 General Introduction	1
1.1 History	1
1.2 Polymer Concept	5
1.2.1 Reactive Double Bonds	6
1.2.2 Reactive Functional Groups	7
1.3 Terminology	7
1.4 Sources of Raw Materials	8
1.4.1 Natural Products	8
1.4.2 Mineral Coal	9
1.4.3 Petroleum	10
1.5 Problems	11
2 Polymer Molecular Structure	13
2.1 Molecular Forces in Polymers	13
2.1.1 Primary or Intramolecular Bonds	13
2.1.1.1 Ionic or Electrovalent Bonds	13
2.1.1.2 Coordinate Bonds	14
2.1.1.3 Metallic Bonds	14
2.1.1.4 Covalent Bonds	14
2.1.2 Secondary or Intermolecular Bonds	16
2.1.2.1 Van der Waals Forces	17
2.1.2.2 Hydrogen Bonds	19
2.1.3 Summary	21

2.2	Monomer Functionality	21
2.3	Types of Chains	23
2.3.1	Linear Chain	23
2.3.2	Branched Chain	24
2.3.2.1	Random Chain Architecture	24
2.3.2.2	Star or Radial Chain Architecture	24
2.3.2.3	Comb Chain Architecture	25
2.3.3	Cross-linked Chain	25
2.4	Copolymer	27
2.4.1	Random Copolymer	27
2.4.2	Alternating Copolymer	27
2.4.3	Block Copolymer	28
2.4.4	Graft Copolymer	28
2.5	Classification of Polymers	29
2.5.1	Chemical Structure	29
2.5.1.1	Carbon Chain Polymers	30
2.5.1.2	Heterogeneous Chain Polymers	34
2.5.2	Method of Preparation	37
2.5.2.1	Addition Polymers	37
2.5.2.2	Condensation Polymers	37
2.5.3	Mechanical Behavior	38
2.5.3.1	Plastics	38
2.5.3.2	Elastomers	39
2.5.3.3	Fibers	40
2.5.4	Mechanical Performance	40
2.5.5	Commodity Thermoplastics	40
2.5.6	Special Thermoplastics	40
2.5.7	Engineering Thermoplastics	40
2.5.8	Special Engineering Thermoplastics	41
2.6	Configuration of Polymer Chains	41
2.6.1	Polymer Chaining	41
2.6.1.1	Head-to-Tail Chaining	42
2.6.1.2	Head-to-Head (or Tail-to-Tail) Chaining	42
2.6.1.3	Mixed Chaining	42
2.6.2	Isomerism in Dienes	43
2.6.3	Tacticity	46
2.6.3.1	Isotactic Polymer	46
2.6.3.2	Syndiotactic Polymer	46
2.6.3.3	Atactic Polymer	47
2.7	Conformation of Polymer Chains	48
2.7.1	Random Coil	49

2.7.2 Planar Zig-Zag	50
2.7.3 Helical	51
2.7.4 Mnemonic Rule	52
2.8 Problems	53
3 Polymers in Solution	55
3.1 Technological Importance	55
3.2 Conformation of the Polymer Chain in Solution	55
3.2.1 Free Joined Chain Model	56
3.2.2 Free Tetrahedral Rotation Chain Model	57
3.2.3 Restricted Movement Chain Model	58
3.2.4 Characteristic Ratio	59
3.2.5 Expansion Factor	61
3.3 Theta Condition	61
3.4 The Excluded Volume	65
3.5 Polymer Solubility	68
3.5.1 Basic (Empirical) Rules of Polymer Solubility	69
3.5.2 Effect of Polymer Chain Type on Solubility	69
3.5.3 Cohesive Energy Density in Polymers, CED	70
3.5.4 Hildebrand Solubility Parameter	71
3.5.5 Generalized or Hansen Solubility Parameter	72
3.5.6 Methods for Determining the Solubility Parameter	80
3.5.6.1 Molar Attraction Constant, G	80
3.5.6.2 Solvent Swelling	81
3.5.7 Polymer Fractionation	81
3.5.7.1 Addition of a Non-Solvent	82
3.5.7.2 Evaporation of the Solvent	82
3.5.7.3 Temperature Reduction	82
3.6 Problems	88
4 Polymer Solid-State Morphology	89
4.1 Introduction	89
4.2 Morphological Models of Polymer Crystallization	90
4.2.1 Fringed Micelle Model	90
4.2.2 Folded Chains, Lamellae, or Single Crystal Model	91
4.3 Molecular Chain Packing	93
4.4 Crystalline Structures Derived from the Crystallization Process	95
4.4.1 Spherulitic Crystallization Structure	95
4.4.2 Shish-Kebab Crystallization Structure	98

4.5	Interlamellar Links	99
4.6	Unit Cells of Some Semi-Crystalline Polymers	100
4.6.1	Polyethylene (PE)	100
4.6.2	Polypropylene (PP)	103
4.6.3	Polyhexamethylene Adipamide (Nylon 6,6)	104
4.6.4	Polyethylene Terephthalate (PET)	105
4.7	Crystallinity Degree	106
4.7.1	Determination of the Degree of Crystallinity from the Specific Volume	107
4.7.2	Determination of the Degree of Crystallinity from the Density ..	108
4.7.3	Determination of the Degree of Crystallinity from the Melt Enthalpy	111
4.7.4	Determination of the Degree of Crystallinity from Specific Heat	113
4.8	Factors That Alter the Degree of Crystallinity	114
4.8.1	Polymer Structural Factors	114
4.8.1.1	Chain Linearity	114
4.8.1.2	Tacticity	114
4.8.1.3	Side Chain Group	114
4.8.1.4	Configuration around Double Bonds	115
4.8.1.5	Polarity	115
4.8.1.6	Stiffness or Flexibility of the Main Chain	116
4.8.1.7	Copolymerization	116
4.8.2	External Factors	116
4.8.2.1	Impurities and Additives	116
4.8.2.2	Nucleating and Clarifying Agents	117
4.8.2.3	Polymeric Second Phase	117
4.8.3	Processing Conditions	117
4.8.3.1	Shear Rate	117
4.8.3.2	Cooling Rate	118
4.9	Problems	118
5	Polymer Synthesis	119
5.1	Introduction	119
5.2	Classification of the Polymerization Processes	119
5.2.1	Number of Monomers	119
5.2.2	Type of Chemical Reaction	120
5.2.3	Polymerization Kinetics	120
5.2.4	Type of Physical Arrangement Methods	120
5.3	Step Polymerization	121

5.3.1 Characteristics of Step Polymerization	121
5.3.2 Some Factors Affecting Step Polymerization	122
5.3.2.1 Reaction Time and Temperature.....	122
5.3.2.2 Catalyst	122
5.3.2.3 Non-Equimolar Addition of the Reagents	122
5.3.2.4 Functionality of the Third Reagent	123
5.3.2.5 Ways of Stopping Step Polymerization	123
5.4 Chain Polymerization	124
5.4.1 Free-Radical Chain Polymerization	125
5.4.1.1 Initiation	125
5.4.1.2 Propagation	126
5.4.1.3 Termination	126
5.4.2 Inhibitors and Retarders	130
5.5 Ionic Polymerization	131
5.5.1 Cationic Polymerization	131
5.5.1.1 Initiation	131
5.5.1.2 Propagation	131
5.5.1.3 Termination	132
5.5.2 Anionic Polymerization	132
5.5.2.1 Initiation	133
5.5.2.2 Propagation	133
5.5.2.3 Termination	133
5.6 Ring-Opening Polymerization	134
5.7 Copolymerization	135
5.8 Methods of Polymerization According to the Physical Arrangement ...	136
5.8.1 Bulk Polymerization	136
5.8.2 Solution Polymerization	137
5.8.3 Suspension Polymerization	137
5.8.4 Emulsion Polymerization	137
5.9 Degradation	139
5.9.1 Depolymerization	139
5.9.2 Chain Scission	139
5.9.2.1 Nylon Hydrolysis	140
5.9.2.2 Thermo-Mechanical Degradation of Polypropylene	140
5.9.2.3 Thermo-Mechanical Degradation of Polyethylene	142
5.9.3 Loss of Side Groups	143
5.10 Problems	144

6 Polymer Molecular Weight and Distribution	147
6.1 Introduction	147
6.2 Types of Average Molecular Weights	148
6.2.1 Number Average Molecular Weight (\overline{M}_n)	148
6.2.2 Weight Average Molecular Weight (\overline{M}_w)	149
6.2.3 Viscosity Average Molecular Weight (\overline{M}_v)	149
6.2.4 z-Average Molecular Weight (\overline{M}_z)	150
6.3 Methods for Measuring Average Molecular Weights	151
6.3.1 Number Average Molecular Weight (\overline{M}_n)	151
6.3.1.1 Chain-End Analysis	151
6.3.1.2 Colligative Properties	151
6.3.2 Weight Average Molecular Weight (\overline{M}_w)	153
6.3.2.1 Light Scattering	153
6.3.2.2 Ultracentrifugation	154
6.3.3 Viscosity Average Molecular Weight (\overline{M}_v)	155
6.3.3.1 Viscosimetry of Dilute Polymer Solutions	155
6.3.4 z-Average Molecular Weight (\overline{M}_z)	160
6.4 Molecular Weight Distribution Curve	160
6.4.1 Size Exclusion Chromatography (SEC)	165
6.5 Most Probable Molecular Weight Distribution Function	169
6.5.1 Polycondensation with Linear Chains	169
6.5.2 Chain Polymerization	172
6.5.2.1 Chain Transfer Termination	172
6.5.2.2 Combination Termination	172
6.5.2.3 Polymerization without Termination	172
6.6 Molecular Weight and Chain Length	173
6.7 Molecular Weight Fractioning Principles	176
6.7.1 Precipitation from a Polymer Solution	176
6.7.2 Preparative Size Exclusion Chromatography (Prep-SEC)	177
6.8 Problems	177
7 Polymer Thermal Behavior	179
7.1 Characteristic Transition Temperatures in Polymers	179
7.1.1 Glass Transition Temperature or T_g	179
7.1.2 Crystalline Melting Temperature or T_m	180
7.1.3 Crystallization Temperature or T_c	183
7.1.4 Other Transition Temperatures sub- T_g	184
7.2 Free Volume Theory	185

7.3	Flory's Theory for the Reduction of the Melt Temperature	188
7.3.1	Effect of the Diluent on T_m	189
7.3.2	Effect of the Polymer Molecular Weight in its T_m	191
7.3.3	Effect of the Comonomer Content in the Copolymer's T_m	192
7.4	Engineering Polymer Temperatures	192
7.5	Main Experimental Techniques for the Determination of Transition Temperatures	193
7.5.1	Differential Scanning Calorimetry, DSC	193
7.5.2	Dynamic-Mechanical Thermal Analysis, DMTA	196
7.5.3	Vicat and HDT Softening Temperatures	198
7.6	Effect of the Chemical Structure on T_g and T_m	199
7.6.1	Structural Symmetry of the Main Chain	200
7.6.2	Rigidity/Flexibility of the Main Chain	201
7.6.3	Polarity of the Main Chain	203
7.6.4	Steric Effect of the Main Chain Side Group	205
7.6.4.1	Side Group Volume	206
7.6.4.2	Side Group Length	206
7.6.5	Residual Double Bond Isomerism	207
7.6.6	Copolymerization	208
7.6.6.1	Homogeneous, Miscellaneous, or Single-Phase Systems	208
7.6.6.2	Heterogeneous, Immiscible, or Polyphasic Systems	211
7.6.7	Polymer Molecular Weight	213
7.6.8	Branching	215
7.7	Influence of External Factors on T_g and T_m	216
7.8	Summary of the Factors Affecting Crystallinity, T_g , and T_m	217
7.9	Problems	218
8	Polymer Crystallization Kinetics	219
8.1	Crystal Nucleation	219
8.1.1	Nucleation Rate	221
8.2	Crystal Growth	221
8.3	Total Isothermal Crystallization	224
8.4	Avrami's Isothermal Crystallization Kinetics Theory	225
8.4.1	Measuring Crystallization Kinetics via Dilatometry	226
8.4.2	Measuring Crystallization Kinetics via Differential Scanning Calorimetry (DSC)	229
8.5	Isothermal Crystallization Rate	234
8.6	Equilibrium Melting Temperature	235
8.7	Problems	236

9 Polymer Mechanical Behavior	237
9.1 Introduction	237
9.2 Polymer Viscoelasticity	238
9.2.1 Linear Viscoelasticity Models	239
9.2.1.1 Maxwell Model	241
9.2.1.2 Voigt Model	242
9.2.1.3 Combined Maxwell-Voigt Model	243
9.2.2 Creep and Stress Relaxation	243
9.2.3 Rubber Elasticity	246
9.3 Considerations upon Polymer Mechanical Testing	249
9.3.1 Testing Recording Stress–Strain Curves	249
9.3.2 Testing under Impact	253
9.4 Fracture Characteristics	255
9.4.1 Brittle Fracture Mechanism	255
9.4.2 Ductile Fracture Mechanism in Toughened Systems	256
9.4.2.1 Shear Yielding	256
9.4.2.2 Crazing	257
9.5 Parameters Affecting Polymer Mechanical Behavior	257
9.5.1 Chemical Structure	257
9.5.2 Degree of Crystallinity	258
9.5.3 Molecular Weight	259
9.5.4 Molecular Orientation	260
9.5.4.1 Peterlin Molecular Reorientation Model	260
9.5.4.2 Characterization of Molecular Orientation via Dichroic Ratio in Polarized Infrared	261
9.5.5 Copolymerization	264
9.5.6 Plasticization	264
9.5.7 Elastomer Toughening	267
9.5.8 Fiber Reinforcing	268
9.6 Superposition Principles	269
9.6.1 Boltzmann Stress Superposition Principle	269
9.6.2 Time–Temperature Superposition Principle	270
9.7 Reptation Theory	272
9.8 Polymer Physical States	273
9.9 Physico–Chemical Methods for Polymer Transformation	275
9.9.1 Physical Methods	275
9.9.1.1 Orientation	275
9.9.1.2 Plasticization	276
9.9.1.3 Solubilization	276

9.9.1.4 Foaming	276
9.9.1.5 Reinforcing	277
9.9.1.6 Toughening	277
9.9.2 Chemical Methods	277
9.9.2.1 Mastication	277
9.9.2.2 Cross-linking	278
9.9.2.3 Grafting	278
9.9.2.4 Oxidation	278
9.10 Problems	278
10 Experiments in Polymer Science	281
10.1 Identification of Plastics and Rubbers	281
10.1.1 Objective	281
10.1.2 Introduction	281
10.1.3 Materials	283
10.1.4 Equipment	283
10.1.5 Method	283
10.1.6 Results	284
10.2 Observation of Polymer Solubilization	286
10.2.1 Objective	286
10.2.2 Introduction	286
10.2.3 Materials	287
10.2.4 Equipment	287
10.2.5 Method	287
10.2.6 Results	288
10.2.7 Questions	288
10.3 Observation of the Precipitation of a Polymer Solution	289
10.3.1 Objective	289
10.3.2 Introduction	289
10.3.3 Materials	289
10.3.4 Equipment	290
10.3.5 Method	290
10.3.6 Results	291
10.3.7 Questions	292
10.4 Identification of Polymers by Infrared Absorption Spectroscopy	293
10.4.1 Objective	293
10.4.2 Introduction	293
10.4.3 Materials	296
10.4.4 Equipment	296
10.4.5 Method	296

10.4.6 Results	296
10.4.7 Questions	297
10.5 Characterization of Polymers by Infrared Absorption Spectroscopy	297
10.5.1 Introduction	297
10.5.2 Determination of <i>Cis/Trans</i> /Vinyl Isomer Concentration in Polybutadiene	298
10.5.2.1 Objective	298
10.5.2.2 Materials	298
10.5.2.3 Equipment	298
10.5.2.4 Method	299
10.5.2.5 Results	299
10.5.3 Quantification of the Components in a Binary Polymer Blend	301
10.5.3.1 Objective	301
10.5.3.2 Materials	301
10.5.3.3 Equipment	301
10.5.3.4 Method	301
10.5.3.5 Results	302
10.5.3.6 Questions	304
10.6 Characterization of Polymer Molecular Orientation via the IR Dichroic Ratio	304
10.6.1 Objective	304
10.6.2 Introduction	304
10.6.3 Materials	305
10.6.4 Equipment	305
10.6.5 Method	305
10.6.6 Results	307
10.6.7 Questions	308
10.7 Observation of the Spherulitic Crystallization in Polymers	308
10.7.1 Objective	308
10.7.2 Introduction	308
10.7.3 Materials	309
10.7.4 Equipment	309
10.7.5 Method	309
10.7.6 Results	311
10.7.7 Supplementary Activities	311
10.8 Determination of the Degree of Crystallinity by Density Measurements	313
10.8.1 Objective	313
10.8.2 Introduction	313
10.8.3 Materials	314
10.8.4 Equipment	315

10.8.5 Preparation of the Liquid Mixture Having the Same Density as the Sample	315
10.8.6 Pycnometry	315
10.8.7 Results	316
10.8.8 Questions	318
10.9 Determination of the Degree of Crystallinity by Differential Scanning Calorimetry (DSC)	318
10.9.1 Objective.....	318
10.9.2 Introduction	318
10.9.3 Materials	319
10.9.4 Equipment	319
10.9.5 Method	319
10.9.6 Results	320
10.9.7 Questions	320
10.10 Free-Radical Bulk Polymerization of Methyl Methacrylate	321
10.10.1 Objective.....	321
10.10.2 Introduction	321
10.10.3 Materials	322
10.10.4 Equipment	322
10.10.5 Method	322
10.10.6 Results	323
10.10.7 Questions	323
10.10.8 Supplementary Activities	323
10.11 Determination of the Viscosity Average Molecular Weight	324
10.11.1 Objective.....	324
10.11.2 Introduction	324
10.11.3 Materials	325
10.11.4 Equipment	325
10.11.5 Method	325
10.11.6 Results	327
10.11.7 Questions	328
10.12 Determination of the Melt Flow Index (MFI)	328
10.12.1 Objective.....	328
10.12.2 Introduction	329
10.12.3 Materials	329
10.12.4 Equipment	329
10.12.5 Method	330
10.12.6 Results	331
10.12.7 Questions	331
10.13 Determination of Vicat Softening Temperature	331

10.13.1 Objective.....	331
10.13.2 Introduction	331
10.13.3 Materials	332
10.13.4 Equipment	332
10.13.5 Method	333
10.13.6 Results	333
10.13.7 Questions	334
10.14 Determination of Cross-linking Density in Vulcanized Rubbers	334
10.14.1 Objective.....	334
10.14.2 Introduction	334
10.14.3 Materials	335
10.14.4 Equipment	335
10.14.5 Method	335
10.14.6 Results	336
10.14.7 Questions	336
11 Further Reading	337
12 Appendix A	341
12.1 Terminology	341
12.2 Abbreviations	348
13 Appendix B	351
Index	363

3

Polymers in Solution

■ 3.1 Technological Importance

For formulation, production, and quality control in the paint, varnish, and adhesive industries, it is necessary to obtain stable solutions (which do not undergo major changes in viscosity with storage time), with safe handling (the use of flammable solvents should be avoided if possible) at a competitive cost (an expensive solvent may be replaced by a mixture of other organic liquids to produce a thinner with the power to solubilize the solids). That is, what is the best thinner (or mixture of solvents) to solubilize a given formulation (or mixture of polymers)?

The melt viscosity shown by a polymer while being processed is due to the difficulty polymer chains face to change conformation during flow. This difficulty is created by the large number of entanglements, formed among the long polymer chains. Thus, it is important to know and control the average molecular weight obtained during the polymerization. The molecular weight is an average of the length (or weight) of all chains measured individually. For this measurement, it is necessary to separate the chains, which can be done in a practical manner by solubilizing the polymer in a suitable solvent.

■ 3.2 Conformation of the Polymer Chain in Solution

The conformation of a polymer chain defines the spatial geometric arrangement of the atoms forming the molecule. This arrangement can undergo many spatial changes as long as the carbon tetrahedral geometry is maintained. This usually occurs by rotation of single covalent C-C bonds, keeping the distance and the angle of the bonds fixed. Despite these two constraints, there are a large number of positions in which the carbon atoms of the main chain can place themselves, since

all points in the cone defined by the equidistant locus of the previous carbon atom by a fixed distance (bond length) forming a fixed angle (bond angle) can be used. Figure 3.1 shows a schematic representation of a polymeric chain in solution when subjected to a change in temperature or solvent power.

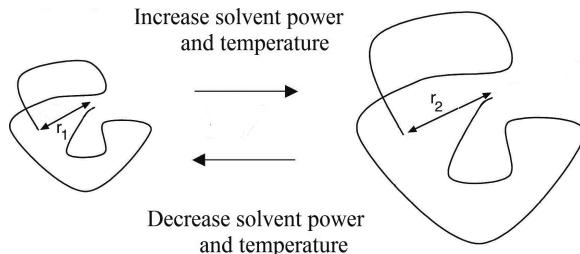


Figure 3.1 Schematic representation of the change in the volume occupied by a polymer chain in solution and its end-to-end chain distance when subjected to a change in temperature or solvent power

The most stable conformation in solution is the random coil conformation. In the presence of a good solvent and/or high temperatures, the hydrodynamic volume occupied by the polymer chain increases. Likewise, in the presence of a poor solvent and/or low temperatures, the volume occupied by the molecule in solution tends to decrease. A practical way to quantify the hydrodynamic volume size is by estimating the geometric mean distance between the chain ends. For this purpose, the square root of the mean squares of the distances between chain ends is calculated as:

$$\bar{r} = \left(\overline{r^2} \right)^{1/2} \quad (3.1)$$

In an attempt to calculate the average distance between the two ends of a chain, several theoretical models were developed by Prof. Paul John Flory (19/Jun/1910–9/Sep/1985), physicochemical professor at Stanford University, California, USA, Nobel prize in chemistry of 1974, with different levels of detail. The most known are:

3.2.1 Free Joined Chain Model

This is the simplest model where it is assumed that the chain is formed by a sequence of bars with a fixed length (l) connected by the tips without restriction of the angle formed between them. This model can also be seen as that of a Brownian movement or “the walking drunk man”. In this case, the mean square distance that the drunkard will walk after n steps with fixed length l will be:

$$\bar{r} = \left(\bar{r}^2 \right)^{1/2} = l\sqrt{n} \quad (3.2)$$

Figure 3.2 shows a possible conformation of a polymer chain obtained from a numerical simulation using random bond angles (open points). The simulation took 100 single C-C bonds with unit bond length, following the predicted freely joined chain model. This model is two-dimensional and does not take into account short- and long-range interactions. This allows the crossing of two segments, something that is impossible in reality, making a much more closed conformation than the real one. In any case, it serves as a starting point in the development of other simulations, presenting results that are closer to reality.

3.2.2 Free Tetrahedral Rotation Chain Model

If the bond angle is set as fixed, the constraint increases and the mean square distance between the chain ends becomes:

$$\bar{r} = \left(\bar{r}^2 \right)^{1/2} = l\sqrt{n} \left[\frac{1 - \cos\theta}{1 + \cos\theta} \right]^{1/2} \quad (3.3)$$

which, in the case of the carbon–carbon single bond, reduces to:

$$\bar{r} = \left(\bar{r}^2 \right)^{1/2} = l\sqrt{2n} \quad (3.4)$$

The tetrahedral angle $\theta = 109^\circ 28'$ then $\cos\theta = -1/3$. This results in a mean square distance of the free tetrahedral rotation chain model 41% higher than the value calculated by the free joined chain model.

$$\left(\bar{r}_{\text{tetrahedral}}^2 \right)^{1/2} = \sqrt{2} \left(\bar{r}_{\text{random}}^2 \right)^{1/2} = 1.41 \left(\bar{r}_{\text{random}}^2 \right)^{1/2} \quad (3.5)$$

Figure 3.2 also shows the result of a simulation using the free tetrahedral rotation chain model (full points) for a chain with 100 C-C single bonds.

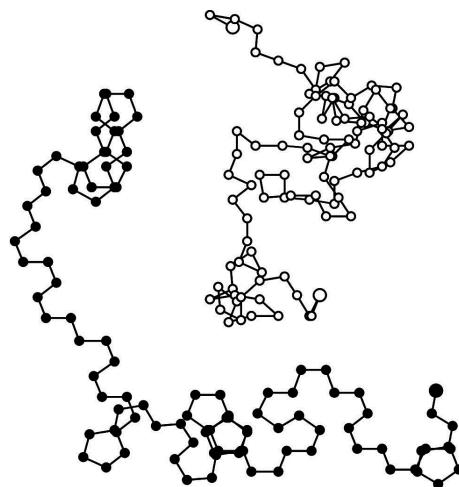


Figure 3.2 Conformations of a polymer chain according to the model of the free joined chain (open points) and with the free tetrahedral rotation chain (full points). Simulation with 100 C-C single bonds and unitary bond length. The restriction imposed at the C-C-C angle by the free tetrahedral rotation model creates a more expanded chain (with a higher hydrodynamic volume) and a larger quadratic mean distance between chain ends

3.2.3 Restricted Movement Chain Model

One can further restrict movement by considering that repulsion effects present in a given position will also be present on the other side of the molecule (action symmetry). Thus, the angle of rotation of the chain ϕ is defined as the angle the next carbon atom makes relative to the plane formed by the three carbon atoms prior to it in the chain. Figure 3.3 shows a diagram with the angle of rotation ϕ .

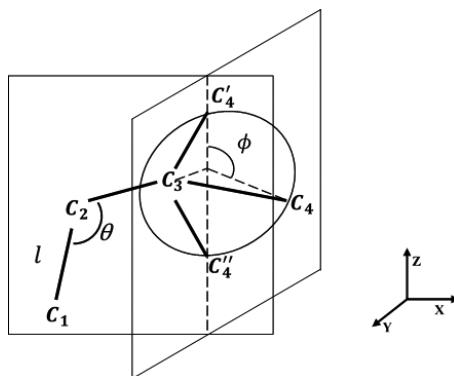


Figure 3.3 Diagram of a sequence of four single bonded carbon atoms showing the bond length l , bond angle θ , and the rotation angle ϕ



Solved problem 4.1

Calculate the densities of the orthorhombic and monoclinic crystalline phases of polyethylene.

Taking the top view of the *orthorhombic polyethylene unit cell* as shown in Figure 4.9b, it is possible to observe that it is formed of a quarter of a mer in each corner plus an integer mer in the center, that is, $4 \times 1/4 + 1 = 2$ mers/unit cell. A polyethylene mer contains $2 \times C + 4 \times H$, i.e., it weighs $2 \times 12 + 4 \times 1 = 28$ g/mol. Then we can calculate the density of the orthorhombic unit cell of polyethylene, which is equal to the density of the crystal or crystalline phase, by:

$$\rho = \frac{m}{V} = \frac{2 \times \frac{28 \text{ g/mol}}{\text{mer}} / 6.02 \times 10^{23} \text{ mers/mol}}{7.42 \text{ \AA} \times 4.95 \text{ \AA} \times 2.55 \text{ \AA} \times (10^{-8} \text{ cm}/\text{\AA})^3} = 0.993 \text{ g/cm}^3$$

This value is very close to the experimental value of 1.011 g/cm^3 , with an error of only -1.8% .

The calculation using the *monoclinic unit cell* follows the same methodology, using Figure 4.9c. The unit cell forms the geometric figure of a trapeze that has as its area:

$$\begin{aligned} A_{UC\text{ monoclinic}} &= \text{Base} \times \text{Height} = \text{side a} \times (\text{side b} \times \sin 72.1^\circ) \\ &= 8.09 \times (4.79 \times 0.9516) = 36.87 \text{ \AA}^2 \end{aligned}$$

It is also formed from a quarter of a mer in each corner plus half a mer on each side, that is, $4 \times 1/4 + 2 \times 1/2 = 2$ mers/unit cell.

$$\rho = \frac{m}{V} = \frac{2 \times \frac{28 \text{ g/mol}}{\text{mer}} / 6.02 \times 10^{23} \text{ mers/mol}}{36.87 \text{ \AA} \times 2.55 \text{ \AA} \times (10^{-8} \text{ cm}/\text{\AA})^3} = 0.989 \text{ g/cm}^3$$



Solved problem 4.2

Calculate the number of PE chains required to produce a 100 nm (1000 \AA) diameter fibril. Assume an orthorhombic unit cell (UC).

We start by calculating the number of PE chains per unit cell:

$$\frac{\text{no. of chains}}{\text{UC}} = 4 \frac{1}{4} + 1 \times 1 = 2 \text{ chains/UC}$$

The area of a UC is: $A_{gross\text{ UC}} = a \times b = 7.42 \times 4.95 = 37.5 \text{ \AA}^2$

The cross-sectional area of a fibril is: $A_{fibril} = \frac{\pi D^2}{4} = \frac{\pi (1000 \text{ \AA})^2}{4} = 7.85 \times 10^5 \text{ \AA}^2$

The number of UCs per fibril is: $n_{UC} = \frac{A_{fibril}}{A_{cross\ UC}} = 7.85 \times 10^5 \text{ \AA}^2 / 37.5 \text{ \AA}^2$
 $n_{UC} = 20.933$

Finally, the number of PE chains per fibril is:

$$n_{chains\ per\ fibril} = 2 \times 20.933 \cong 42.000$$

4.6.2 Polypropylene (PP)

Isotactic polypropylene PPi has a monoclinic unit cell with the following unit cell parameters: $a = 6.65 \pm 0.05 \text{ \AA}$; $b = 20.96 \pm 0.15 \text{ \AA}$; $c = 6.50 \pm 0.04 \text{ \AA}$; and angles $\alpha = \gamma = 90^\circ$ and $\beta = 99^\circ 20'$. Figure 4.10 shows a view along the c -axis, i.e., the axis of the main chain. The circular arrows at the center of the chains indicate the direction of rotation of the helix and the fractional numbers next to the carbon atom of the side group $-\text{CH}_3$, its partial height inside the unit cell, counted from the basal plane, subdivided into 12 fractions.

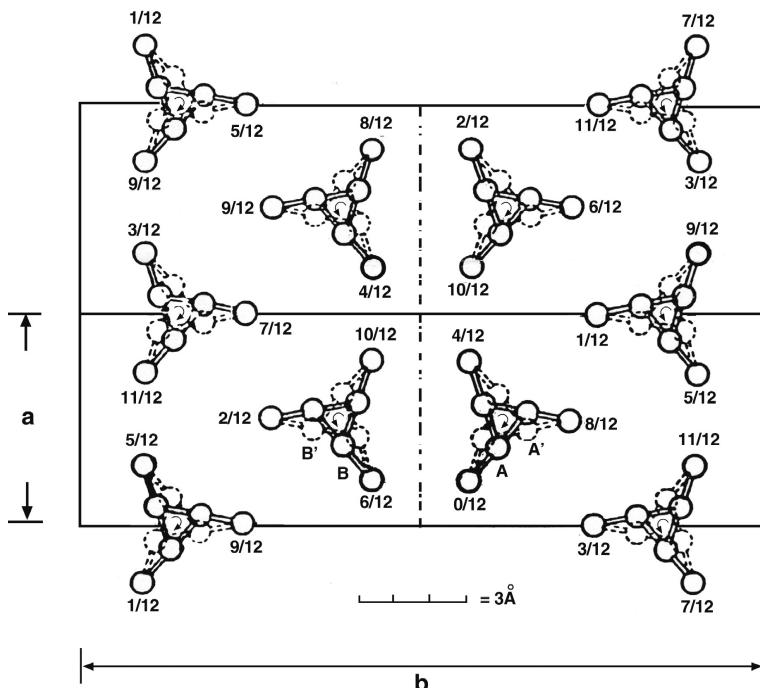


Figure 4.10 Projection of the monoclinic crystalline unit cell of the polypropylene seen along the c -axis, i.e., the main-chain axis

4.6.3 Polyhexamethylene Adipamide (Nylon 6,6)

The crystalline phase of nylon 6,6 may be present in at least three distinct crystallographic forms. At room temperature, the forms α and β are stable, both triclinic, with a planar zig-zag conformation. Figure 4.11 shows the unit cell of the α form.

The γ form only appears at high temperatures and is not yet well defined.

The unit cell parameters of the α and β forms are:

α form	β form
$a = 4.9 \text{ \AA}$	$a = 4.9 \text{ \AA}$
$\alpha = 48.5^\circ$	$\alpha = 90^\circ$
$b = 5.4 \text{ \AA}$	$b = 8.0 \text{ \AA}$
$\beta = 77^\circ$	$\beta = 77^\circ$
$c = 17.2 \text{ \AA}$	$c = 17.2 \text{ \AA}$
$\gamma = 63.5^\circ$	$\gamma = 67^\circ$

The hydrogen bond formed between the $-\text{NH}$ and $-\text{C=O}$ groups creates strong secondary intermolecular links, aligning the zig-zag planes of the layered chains where the bonding forces between the chain segments within each layer are greater than the intermolecular dispersion forces between the layers.

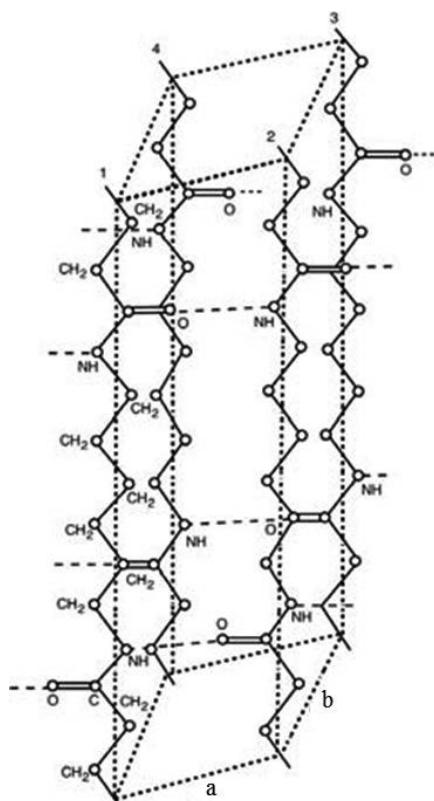


Figure 4.11 Triclinic unity cell of the α form of nylon 6,6

4.6.4 Polyethylene Terephthalate (PET)

The crystallization conformation of polyethylene terephthalate (PET) is planar zig-zag forming a triclinic unit cell with the following parameters: $a = 4.56 \text{ \AA}$; $b = 5.94 \text{ \AA}$; $c = 10.75 \text{ \AA}$ and angles $\alpha = 98.5^\circ$; $\beta = 118^\circ$; $\gamma = 112^\circ$. To allow more packing, the terephthalic acid group makes a small angle with the axis of the polymer chain. Figure 4.12 shows several views of the PET unit cell.

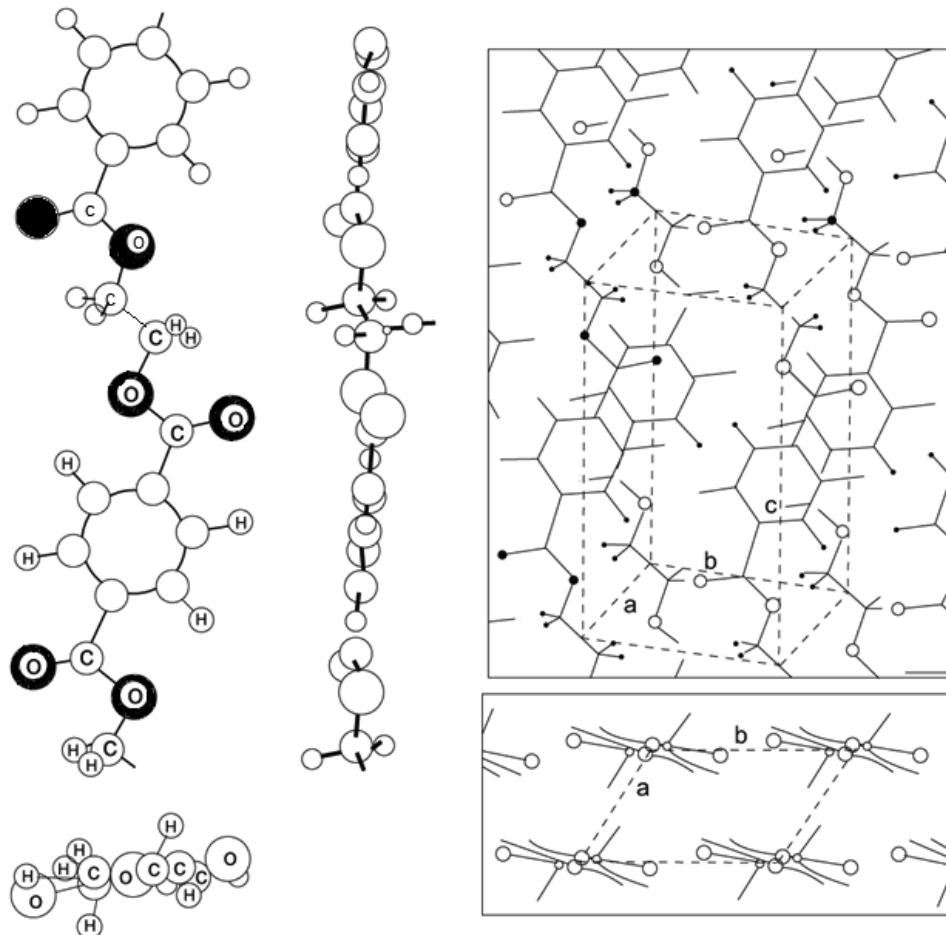


Figure 4.12 Planar zig-zag crystallization conformation of the PET chains and its triclinic unit cell

$$\overline{M_n} = \frac{\sum h_i}{\sum N_i} = \frac{390}{4.85 \times 10^{-3}} = 80,400 \text{ g/mol};$$

$$\overline{M_w} = \frac{\sum N_i (M_i)^2}{\sum h_i} = \frac{3.46 \times 10^7}{390} = 88,700 \text{ g/mol};$$

$$\overline{M_z} = \frac{\sum N_i (M_i)^3}{\sum N_i (M_i)^2} = \frac{3.83 \times 10^{12}}{3.46 \times 10^7} = 110,700 \text{ g/mol};$$

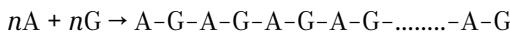
and the polydispersity $PD = \frac{\overline{M_w}}{\overline{M_n}} = \frac{88,700}{80,400} = 1.1$

■ 6.5 Most Probable Molecular Weight Distribution Function

It is theoretically possible to predict the width of the molecular weight distribution depending on the type of polymerization reaction. Thus, polycondensation tends to produce mainly linear chains that grow with the polymerization reaction time. On the other hand, the chain polymerization will be dependent on its preferential type of termination mechanism.

6.5.1 Polycondensation with Linear Chains

The polycondensation reaction of two initial bifunctional materials yields a long linear chain where each component enters alternately during the chaining. This produces the so-called **most probable distribution function**. Assuming the reaction of a diacid (A) with a dialcohol (G, glycol) forms a linear polyester chain, as shown:



then if for the formation of this chain a total of x molecules of the reactants (half of the molecules of diacid and half of glycol) are used, then $x-1$ bonds are formed. Assuming that the probability of each of these esterification reactions to occur is p , also known as reaction extension, one can conclude that the probability of a molecule being formed with exactly x units is n_x given by:

$$n_x = p^{x-1} (1-p) \quad (6.25)$$

the first term relating to the probability that the same reaction (p) happens $x-1$ consecutive times, and the second term appears to ensure that the chain stops growing exactly after these $x-1$ reactions. Thus, the number of molecules (N_x) with a size of exactly x is the total number of molecules available (N) times their probability of existing n_x :

$$N_x = N \times n_x \quad (6.26)$$

or

$$N_x = N (1-p) \times p^{x-1} \quad (6.27)$$

but the total number of molecules available is the total number of unreacted molecules (N_0), i.e.,

$$N = N_0 \times (1-p) \quad (6.28)$$

Replacing these equations, the **number most probable molecular weight distribution function** is:

$$N_x = N_0 \times (1-p)^2 \times p^{x-1} \quad (6.29)$$

which can be converted into **weight function** by neglecting the loss of mass due to the elimination of molecules of low molecular weight after each condensation reaction (water in the case of formation of the ester bond).

$$w_x = x \times \frac{N_x}{N_0} \quad (6.30)$$

that is, obtaining the **weight most probable molecular weight distribution function** as:

$$w_x = x \times (1-p)^2 \times p^{x-1} \quad (6.31)$$

Figure 6.11a graphically shows the number most probable MWD function and Figure 6.11b shows the weight most probable MWD function, calculated for four probability values: $p = 0.90, 0.96, 0.98$, and 0.99 . The higher the probability of the polymerization reaction, the greater the number of initial molecules that will react, generating larger chains and shifting the curves to the right. With the lowest probability, $p = 0.90 = 90\%$, the average number of reacted molecules, defined by the peak of the weight function, is only $x \approx 10$. By increasing the probability to $p = 0.96 = 96\%$, the average number of molecules that react to form the chain increases

to $x \approx 25$, and if we reach $p = 0.99 = 99\%$, it increases even more to $x \approx 140$, the typical value of a commercial poly(ethylene terephthalate) PET polymer.

The **number average polymerization degree** (\overline{x}_n) can also be estimated as:

$$\overline{x}_n = \sum x \times n_x = \sum x \times p^{x-1} \times (1-p) = \frac{1}{1-p} \quad (6.32)$$

and in weight fraction (\overline{x}_w) as:

$$\overline{x}_w = \sum x \times w_x = \sum x \times x \times p^{x-1} \times (1-p) = \frac{1+p}{1-p} \quad (6.33)$$

Thus, the width of the most probable MW distribution curve of a polycondensation with linear chain is:

$$\frac{\overline{x}_w}{\overline{x}_n} = 1 + p \quad (6.34)$$

assuming $p \approx 1$, then one can say that

$$\frac{\overline{x}_w}{\overline{x}_n} \approx 2 \quad (6.35)$$

i.e., the polydispersity calculated for a polycondensation is approximately 2 (see Table 6.5). Nylons are polymers obtained by this type of polymerization and commercial products have $PD \approx 2$.

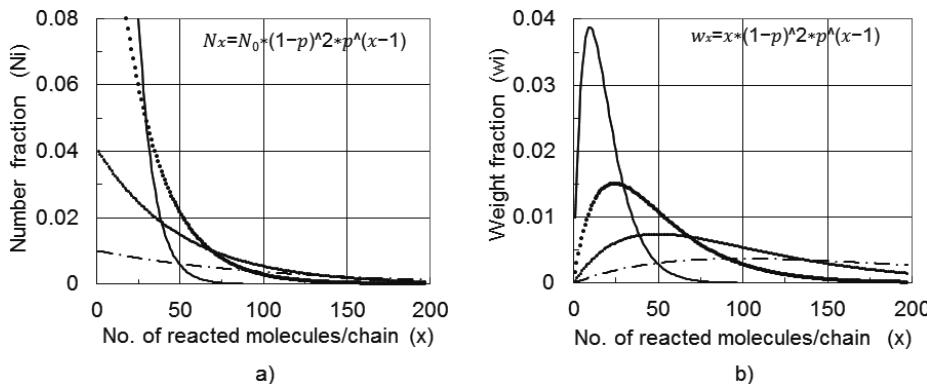


Figure 6.11 (a) Number most probable MW distribution function and (b) weight most probable MW distribution function, simulated for four different reaction probabilities: $p = 0.90, 0.96, 0.98$, and 0.99

6.5.2 Chain Polymerization

This polymerization presents three types of preferential terminations:

6.5.2.1 Chain Transfer Termination

The hydrogen is transferred from the solvent molecule to the reactive growing chain end, terminating the polymerization. In this case, the most probable molecular weight distribution function can be applied, in the same way it was for the polycondensation or step polymerization. In order to synthesize a polyethylene with degree of polymerization $x = GP = 1000$, it is necessary that the probability of the ethylene addition reaction has at least 3 nines, that is, $p \geq 99.9\%$.

6.5.2.2 Combination Termination

In this case, two growing radical chains meet and react by forming a single covalent bond. The molecular weight of the final chain will be the sum of the initial two that formed it. In this case, the **distribution function** is narrower than the most probable:

$$w_x = \frac{x}{2} (x-1) \times (1-p)^3 \times p^{x-2} \quad (6.36)$$

6.5.2.3 Polymerization without Termination

This type of termination occurs specially in anionic polymerizations. The distribution function follows **Poisson's distribution**:

$$N_x = \frac{e^{-\nu} \times \nu^{(x-1)}}{(x-1)!} \quad (6.37)$$

and

$$w_x = \frac{\nu \times x \times e^{-\nu} \times \nu^{(x-2)}}{(\nu+1) \times (x-1)!} \quad (6.38)$$

ν being the number of reacted monomers per polymer chain. The distribution width in the anionic polymerization is:

$$\frac{\overline{x_w}}{x_n} = 1 + \frac{\nu}{(\nu+1)^2} \quad (6.39)$$

If ν is big then:

$$\frac{\overline{x_w}}{x_n} \cong 1 + \frac{1}{\nu} \cong 1 \quad (6.40)$$

1. **Vicat softening temperature:** is the temperature that, during heating at a constant and predetermined rate, a flat tip needle with an area of 1 mm^2 ($1.120 \text{ mm} < D < 1.137 \text{ mm}$), penetrates the sample at a depth of $1 \pm 0.01 \text{ mm}$, subject to a constant and predetermined load. Two types of loads, $10 \pm 0.2 \text{ N}$ ($1 \text{ kg} = 9.80665 \text{ N}$) or $50 \pm 1.0 \text{ N}$, are used and heating rates of $50 \pm 5 \text{ }^{\circ}\text{C/h}$ or $120 \pm 10 \text{ }^{\circ}\text{C/h}$. ASTM 1525 standardizes this method.
2. **Heat distortion temperature, HDT:** is the temperature that, during heating at a constant rate of $2 \pm 0.2 \text{ }^{\circ}\text{C/min}$, a rectangular section bar of 13 mm thickness and length between supports of 100 mm , positioned in its side and tensioned in the center, deforms the bar 0.25 mm (0.01 in). The maximum fiber tension (S) should be 0.455 MPa (66 psi) or 1.82 MPa (264 psi). ASTM 648 standardizes this method.

■ 7.6 Effect of the Chemical Structure on T_g and T_m

Since the T_g and T_m transition temperatures refer to overcoming secondary forces and giving mobility to the polymer chain, any factor leading to an increase in secondary intermolecular forces and chain stiffness will increase both T_g and T_m . Figure 7.7 shows the positioning in the space T_m vs T_g , with values presented in degrees Celsius, of a long list of semi-crystalline polymers. The maximum range of the T_g is $-100 \text{ }^{\circ}\text{C} \leq T_g \leq 300 \text{ }^{\circ}\text{C}$ and for the T_m is $0 \text{ }^{\circ}\text{C} \leq T_m \leq 400 \text{ }^{\circ}\text{C}$, making a total span of $400 \text{ }^{\circ}\text{C}$ in both cases. These ranges are extremely convenient because they provide polymers for many types of commercial applications with varying levels of thermal stability. For example, applications where the material is expected to perform exclusively at room temperature and do not require any high mechanical strength can be provided by polyolefin, whose range is $100 \text{ }^{\circ}\text{C} \leq T_m \leq 200 \text{ }^{\circ}\text{C}$, which is considered a low melting temperature range. On the other hand, applications where the materials will have to perform at constant temperatures in the range of $100 \text{ }^{\circ}\text{C}$ should have a range of $200 \text{ }^{\circ}\text{C} \leq T_m \leq 300 \text{ }^{\circ}\text{C}$, which is considered a medium-high melting temperature, requiring the use of engineering thermoplastics.

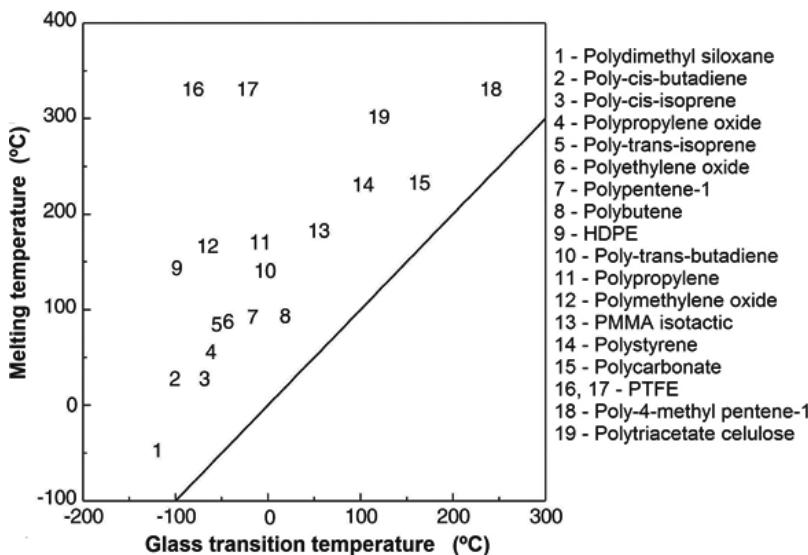


Figure 7.7 Relationship between the T_m and T_g values of various commercial polymers. The line represents $T_m = T_g$

The large variation in the values of T_g and T_m presented by the polymers is dependent on particular structural factors. The most important are listed, commented on, and exemplified in the next section. It is also possible in some cases to change them further by making use of external factors, which will be discussed in the next section of this chapter.

7.6.1 Structural Symmetry of the Main Chain

In Figure 7.7, it can be seen that most of the polymers present a difference between the transition temperatures of the order of 110 °C. On the other hand, some polymers present a greater difference. According to the **Boyer/Beaman Law**, the greater the symmetry of the polymer chain with respect to its side groups, the greater the difference between T_g and T_m . Taking the temperature in Kelvin, one gets:

1. $\frac{T_g}{T_m} \cong 0.5$ for **symmetrical polymers** either without a lateral group, as in PE, POM, etc., or with two groups symmetrically placed on both sides of the same carbon atom, as for PTFE, PVDC, etc.
2. $\frac{T_g}{T_m} \cong 0.75$ for **asymmetrical polymers** either with only one side group, as for PP, PS, PVC, etc., or two that should be very different in size, as in the case of PMMA.

The presence of side groups may not increase T_g and T_m at the same level when they are arranged symmetrically with respect to the main chain axis. This allows for better-balanced motions of the molecule, not requiring high levels of energy to achieve mobility. This effect is confirmed by the values of the transition temperatures of polyvinylidene chloride, PVDC, which are lower than those of polyvinyl chloride, PVC, although the former presents twice as many chlorine atoms as the PVC (and therefore a lateral group with double the volume) but they are disposed symmetrically, with a chlorine atom on each side of the polymer chain, as seen in Table 7.1.

Table 7.1 T_g and T_m of Some Vinyl Polymers

Polymer	Mer	T_g (°C)	T_m (°C)	T_g/T_m (K/K)
Polyvinyl chloride PVC		87	212	0.74
Polyvinylidene chloride PVDC		-19	198	0.54

7.6.2 Rigidity/Flexibility of the Main Chain

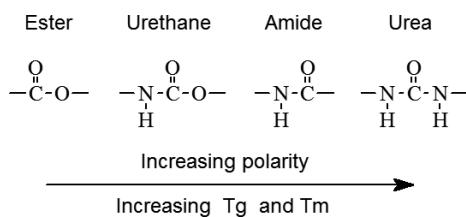
The presence of rigid groups within the main chain will promote rigidity, leading to an increase in both T_g and T_m . An example is the ***p*-phenylene rigid group** with two single bonds flat within the plane defined by the benzene ring. This is found in PET with $T_g = 69$ °C and $T_m = 265$ °C. In contrast, another polymer with a similar chemical structure, but not containing the *p*-phenylene group, polyethylene adipate (PEA), has much lower values ($T_g = -46$ °C and $T_m = 45$ °C); it, therefore, has fewer commercial applications. The same happens with other polymers (polyamides, polyesters, etc.) where ethylene sequences are replaced by *p*-phenylene groups. On the other hand, some elements can generate chain flexibility as in the case of **oxygen** and **sulfur** atoms because they form flexible bonds with carbon. Thus, polyethylene oxide, which has a flexible ether bond $-C-O-C-$ within the main chain, has a $T_m = 66$ °C, much lower than the value given by polyethylene, which is $T_m = 135$ °C. For a comparative analysis between various chemical structures, analyze the examples presented in Table 7.2.

Table 7.2 Stiffening Effect of the *p*-Phenylene Group on Some Condensation Polymers

Polymer	Mer	T_g (°C)	T_m (°C)
Polyethylene (PE)	$\left[\text{CH}_2\text{CH}_2 \right]_n$	-100	135
Polyethylene <i>p</i> -phenylene	$\left[\text{CH}_2\text{---} \text{C}_6\text{H}_4\text{---} \text{CH}_2 \right]_n$		380
Polyethylene oxide	$\left[\text{CH}_2\text{CH}_2\text{O} \right]_n$		66
Polyethylene adipate (PEA)	$\left[\text{H} \text{---} \text{O} \text{---} \text{C} \text{---} \text{O} \text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{C} \text{---} \text{O} \text{---} \text{O} \text{---} \text{C} \text{---} \text{O} \text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{OH} \right]_n$	-46	45
Polyethylene terephthalate (PET)	$\left[\text{H} \text{---} \text{O} \text{---} \text{C} \text{---} \text{O} \text{---} \text{CH}_2\text{---} \text{C}_6\text{H}_4\text{---} \text{CH}_2\text{---} \text{C} \text{---} \text{O} \text{---} \text{O} \text{---} \text{C} \text{---} \text{O} \text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{OH} \right]_n$	69	265
Polyoctene sebacate	$\left[\text{O} \text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{O} \text{---} \text{C} \text{---} \text{O} \text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{C} \text{---} \text{O} \right]_n$		75
Aromatic polyester	$\left[\text{O} \text{---} \text{CH}_2\text{---} \text{C}_6\text{H}_4\text{---} \text{CH}_2\text{---} \text{O} \text{---} \text{C} \text{---} \text{O} \text{---} \text{CH}_2\text{---} \text{C}_6\text{H}_4\text{---} \text{CH}_2\text{---} \text{C} \text{---} \text{O} \right]_n$		146
Polyhexamethylene adipamide (nylon 6,6)	$\left[\text{H} \text{---} \text{N} \text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{N} \text{---} \text{C} \text{---} \text{O} \text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{C} \text{---} \text{O} \right]_n$	87	263
Polyhexamethylene terephthalamide (nylon 6T)	$\left[\text{H} \text{---} \text{N} \text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{CH}_2\text{---} \text{N} \text{---} \text{C} \text{---} \text{O} \text{---} \text{CH}_2\text{---} \text{C}_6\text{H}_4\text{---} \text{CH}_2\text{---} \text{C} \text{---} \text{O} \right]_n$		350

7.6.3 Polarity of the Main Chain

The existence of polar groups in polymer macromolecules causes a strong attraction between the chains, bringing them closer together and increasing the secondary forces. Thus, the presence of **polarity** increases T_g and T_m , and they are greater the higher the polarity value. Common polar groups in polymers include the carbonyl group, $-\overset{\text{O}}{\underset{\text{C}}{\text{||}}}-$, in which its polarity value will be affected depending on the type of atom bonded laterally to it. Nitrogen atoms tend to donate and oxygen to withdraw electrons, respectively. Ester, urethane, amide, and urea polar groups have increasing polarity in this order and therefore polymers with similar chemical structures (changing only the polar group but keeping their content along the polymer chain constant) increase T_g and T_m in this order.



This effect can also be seen in Figure 7.8 where the change of the melting temperature of several homologous series (with the same functional group) of aliphatic polymers (with linear CH_2 -methylene sequences) is shown as a function of the number of CH_2 groups connecting the functional groups. For the same number of methylenes, the higher the polarity of the functional group present, the greater the T_m of the polymer. On the other hand, the higher the number of CH_2 s, the lower the concentration of the functional groups per unit length of molecule and, therefore, the lower its attraction effect. In this way, the values of T_m are close to that presented by a very long sequence of methylenes, which is no more than polyethylene itself. Table 7.3 exemplifies the latter case for a series of linear aliphatic polyamides. When the number of methylenes is even, both N-H and C=O bonds are placed at the same side of the main chain; when it is odd, they sit on opposite sides. This particular configuration affects the crystallization kinetics and the melting temperature.

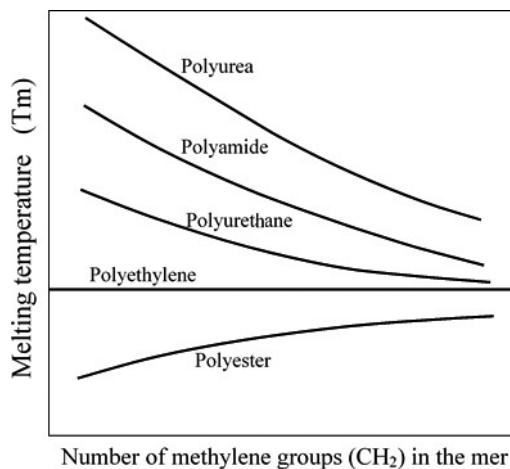


Figure 7.8 Variation of T_m for several homologous series of aliphatic polymers

Table 7.3 Melting Temperatures of Some Polyamides (Nylon N)

Nylon type	Mer of some nylon types	T_m (°C)
3	$\left[\begin{array}{c} \text{H} \\ \\ \text{N} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{C} = \text{O} \\ \\ \text{O} \end{array} \right]_n$	320-330
4	$\left[\begin{array}{c} \text{H} \\ \\ \text{N} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{C} = \text{O} \\ \\ \text{O} \end{array} \right]_n$	260-265
5	$\left[\begin{array}{c} \text{H} \\ \\ \text{N} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{C} = \text{O} \\ \\ \text{O} \end{array} \right]_n$	260
6	$\left[\begin{array}{c} \text{H} \\ \\ \text{N} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{C} = \text{O} \\ \\ \text{O} \end{array} \right]_n$ Polycaproamide	215-220
7	$\left[\begin{array}{c} \text{H} \\ \\ \text{N} - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{C} = \text{O} \\ \\ \text{O} \end{array} \right]_n$	225-230

2. Discuss how copolymerization and chain branching affect the radius of interaction R . What experimental technique makes use of this property to characterize different types of homopolymers and copolymers?
3. Justify why Eq. (10.2) (from Chapter 3, Section 3.5.4) is valid. What is the advantage of it being valid for the commercial production of a thinner?

$$\delta^m = \sqrt{\left(\delta_d^m\right)^2 + \left(\delta_h^m\right)^2 + \left(\delta_p^m\right)^2} \quad (10.2)$$

■ 10.4 Identification of Polymers by Infrared Absorption Spectroscopy

10.4.1 Objective

Use the infrared absorption spectroscopy FTIR technique for a qualitative analysis in the identification of the chemical structure, molecular configuration, components, formulation, etc., of pure polymers, their blends, and composites.

10.4.2 Introduction

Infrared absorption spectroscopy is one of the most widely used tools for identifying and characterizing polymeric materials. The vibrational analysis of polymers can provide information on three important structural aspects: chemical composition, configurational, and conformational structure. It also provides indications of interatomic forces due to the presence of molecular interactions. The technique of characterization of materials by absorption in the infrared is based on the observation of the frequency (qualitative analysis identifying the type of chemical bond) and intensity (quantitative analysis measuring the chemical bond concentration) of absorbed infrared radiation when a beam of this radiation crosses the sample. The infrared region corresponds to the range of wavelengths of the electromagnetic spectrum of 1 micron to 1 mm.

For a molecule to absorb infrared radiation, a change in the dipole moment of the molecule must occur during its axial and angular deformation movements. The incidence of infrared radiation in the molecule at the same frequency as the vibration of one of its bonds absorbs part of the incident energy with increasing amplitude of this vibration. By measuring the decreases in intensity of the transmitted radiation, a spectrum of the absorbed infrared radiation, characteristic of the material being analyzed, is generated.

The atoms that make up a molecule are in continuous motion due to various types of vibrations. They can be classified into two fundamental modes: **axial deformation** (or stretch) and **angular deformation**, shown in Figure 10.2 for a triatomic molecule. These vibrations occur only on some quantized frequencies, that is, they are unique and characteristic of each chemical bond.

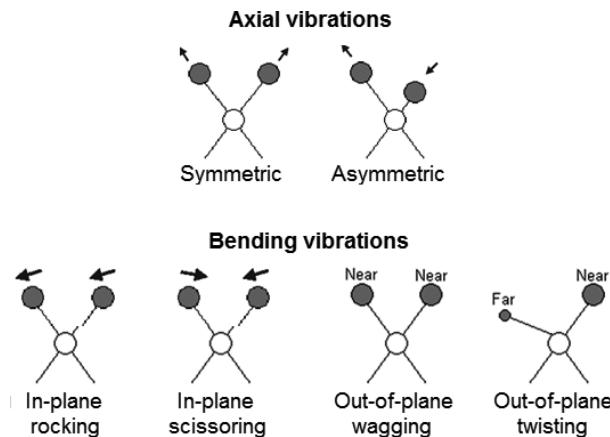


Figure 10.2 Vibration modes of a simple three-atomic molecule

If a radiant energy of known intensity at all wavelengths of its spectrum is supplied to the sample through an incident beam and the intensities at each particular wavenumber of the transmitted beam are analyzed, it may be seen that the intensity will be lower with some particular wavenumbers. This means that chemical bonds present in the sample selectively absorb at these frequencies. Such knowledge allows the identification of some of the bonds present in the sample contributing to their identification. In practical terms, spectra of the unknown sample can be compared with standard sample spectra facilitating the identification of the material. Figure 10.3 shows the infrared absorption spectrum of polystyrene.

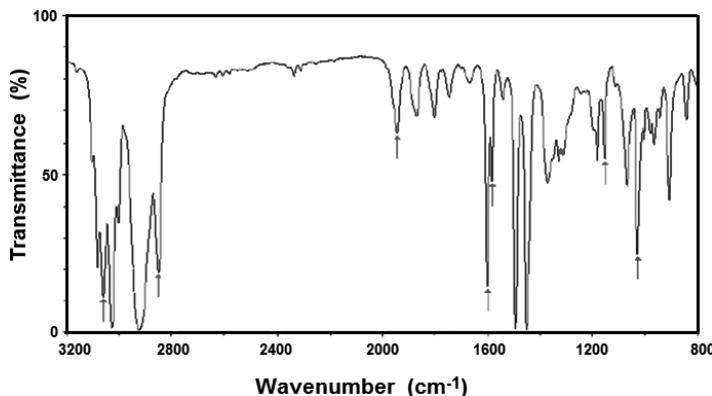


Figure 10.3 Infrared absorption spectrum of a polystyrene PS thin film. The arrows indicate some of the bands used to calibrate the equipment

A large number of polystyrene characteristic bands can be used for spectrophotometer calibration. Table 10.4 shows these reference bands, some with precision to the first decimal place (in cm^{-1}). The table also gives an indication of the relative intensity of each band, assuming the strongest ones have a maximum intensity of 10.

Table 10.4 Wavenumber for Some Absorption Bands Characteristic of Polystyrene and Their Relative Intensity, Normalized between Zero (baseline) to 10 (Highest Absorption)

Wavenumber (cm^{-1})	Relative intensity	Wavenumber (cm^{-1})	Relative intensity	Wavenumber (cm^{-1})	Relative intensity
3027.1	9	1583.1	5	1154.3	4
2924	10	1495	10	1069.1	6
2850.7	7	1454	10	1028.0	8
1944.0	3	1353	5	906.7	3
1871.0	3	1332	5	842	3
1801.6	3	1282	3	752	10
1601.4	9	1181.4	4	698.9	10

The identification of an unknown sample is done by analyzing the position and intensity of the absorption bands present in the spectrum, comparing them with standard tables. In this experiment, it is initially suggested to try the identification of pure and known polymers. After the operator has acquired some experience, it is recommended that they identify polymer plastic products found on the market such as packaging, pipes, pots, films, injected parts, etc.

Index

Symbols

ε -caprolactam 134
 θ condition 158

A

absorption bands 262
absorption coefficient 298, 300
absorptivity 300
acetylation 120
activated monomer 125, 131–133
adipic acid 122
alternating copolymer 27
amidation 120
amide bond 134, 140
amide group 19
amorphous state 274
angular deformation 294
anionic polymerization 131–133
atactic polymer 47
average chain length 174, 175
average molecular weight 148–151, 153, 155, 156, 158, 160–164, 173, 175
average molecular weight between cross-links 247, 248
Avrami's constant 225
Avrami's equation 225
Avrami's exponent 225
Avrami's plot 226, 229, 232
axial deformation 294

B

back biting 127
Bakelite 1, 34, 39
Beer–Lambert law 297
Beilstein test 282, 284, 285
benzene 9
benzoyl peroxide 125, 144
biaxial orientation 275
bifunctional 22, 23, 37
birefringence compensators 313
block copolymer 28
blowing agent 276
Boltzmann stress superposition principle 269
bond energy 15, 19
bond length 15, 19, 21
branched chain 24
brittle behavior 250, 251, 253
brittle fracture 253, 255
bulk polymerization 136, 145
by-products 121

C

calibration curve 166, 167
carbonyl group 19
cast from solution 276
catalyst–cocatalyst complex 131
cationic polymerization 131, 145
cavitation 256
cellulose 8
chain cleavage 278
chain-end analysis 151

chain end segments 247
chain length 173
chain polymerization 120
chain scission 139–142
chain scission distribution function 142
chain stiffness 199, 217
chain terminator 129, 133
chain transfer 128
chain transfer termination 172
characteristic ratio 59, 60
cis isomer 31, 45, 48
cis isomerism 300
clarifying agent 117
cloud point 63, 289, 291
coal 9
cocatalyst 131
cohesive energy 70
cold crystallization 194–196
cold drawing 260, 262, 306, 307, 314
cold flow 150
comb chain architecture 25
combination 126
combination termination 172
condensation 2, 7
conductive polymers 4
configuration 3, 20, 41, 44, 46, 47, 52, 53
copolymer 27
copolymerization 120, 135
counter-ion 132
covalent bonds 5, 14
Crankshaft mechanism 185
crazing 256, 257
creep 237, 243–245, 278
critical radius 220, 221
critical strain intensity factor 255
critical temperature 63, 64
cross-linked chain 25
cross-linking 278
cross-linking density 25, 270–272, 335
cryoscopy 153
crystal growth rate 221, 223
crystalline melting temperature 179, 194, 196, 210, 212, 217
crystalline state 274
crystallinity index 107
crystallization enthalpy 193–195
crystallization fractionation 86
crystallization temperature 179, 183, 193, 194, 196
crystal stability parameter 235
cure 276, 278
cured epoxy resin 253, 269

D

degradation 139
degree of crystallinity 89, 91, 93, 95, 107–114, 116–118, 182, 194–196, 206, 212, 239, 257–260, 275, 279, 308, 313–315, 317–320, 334
degree of molecular orientation 260, 262, 304, 305, 307
degree of polymerization 148, 158–160, 172, 174
density 89, 90, 93–95, 97, 100–102, 108–110, 114, 118
depolymerization 139
diacid 2, 7
dichroic ratio 261, 262, 304, 305, 307, 308
differential scanning calorimetry 193, 318
dilatometry 226–228, 232
dioctyl phthalate 264, 265, 276
dispersion forces 17
disproportion 127
Doolittle's equation 185
ductile behavior 250, 251
ductile fracture 255
dynamic crystallization 183
dynamic-mechanical thermal analysis 193, 196

E

ebulliometry 152, 153
elastomer toughening 267
elongational flow 98
elution volume 166–168, 177
emulsifying agent 137

emulsion polymerization 137
 enthalpy 229, 231, 232
 epoxy resins 9, 34
 equilibrium melting temperature 181, 235, 236
 equimolar ratio 122
 esterification 2, 120, 169
 ethene addition 120
 ethylene-propylene-diene-monomer copolymer 30
 excluded volume 3, 59, 61, 65, 66
 expansion factor 61

F

fiber reinforcing 268
 fibers 5
 Flory–Rehner equation 335
 Flory's equation 189
 Flory's interaction parameter 189
 foaming 276
 folded chains 91
 fold period 91
 fold plane 91
 forced termination 132
 formaldehyde 1, 9
 fracture toughness 255
 free joined chain model 56
 free-radical chain polymerization 125
 free-radical mass polymerization 321
 free surface energy 181
 free tetrahedral rotation chain model 57
 free volume 186, 187, 213, 215
 fringed micelle 90, 91, 106, 118
 full-wave retardation plate 311
 functionality 6, 123

G

glass transition temperature 17, 18, 39, 47, 179, 184, 193, 194, 196–198, 213, 215–217, 257, 264, 267, 270, 271, 275
 glycol 2, 7
 graft copolymer 28
 grafting 278

H

half-time crystallization 234
 Hampton equation 298
 Hansen solubility parameter 72
 head-to-tail chaining 42
 heat distortion temperature 199
 helicoidal 4
 heterogeneous nucleation 221
 Hevea Brasiliensis 1
 hexagonal unit cell 101
 hexamethylene adipamide 122
 hexamethylene diamine 122
 high density polyethylene 4
 high-impact polystyrene 267
 Hildebrand solubility parameter 71
 Hoffman–Weeks plot 236
 homogeneous nucleation 221
 homopolymerization 120
 hydrodynamic volume 56, 58, 61, 62, 65, 67, 82
 hydrogen bonds 8, 17, 19, 35, 265, 266
 hydrogen transfer 132
 hydroquinone 129

I

induction forces 19
 induction time 130
 infrared absorption spectroscopy FTIR 293
 inherent viscosity 156
 inhibitor 119, 129, 130, 145, 322
 initiation 124–126
 initiator 119, 121, 125, 134, 136–138, 321–323
 interaction radius 73, 75, 77, 292
 interlamellar links 99, 260
 intermolecular bonds 16
 intermolecular forces 20, 32, 33, 180, 199, 217
 intramolecular bonds 13
 intramolecular forces 14, 20, 53
 intrinsic viscosity 150, 156–159, 324, 325, 327, 328
 ionic polymerization 131

isocyanates 9
isomerism 207, 217
isotactic polymer 46
isothermal crystallization 183, 222–236
isothermal crystallization rate 234

L

lamellae 91, 118
lamellar morphology 258
Lewis acid 131
Lewis base 133
light scattering 153, 314
linear chain 23
linear polarizers 309
linear thermal expansion 181
living polymers 161
long-range order 273, 274
loss modulus 196
loss of side groups 143
loss tangent 197

M

macromolecular theory 2
maleic anhydride 123
Maltese Cross 95, 96, 308, 310
Mark–Houwink–Sakurada equation 156, 160, 325
master curve 271, 272
mastication 277
maximum crystal growth rate 223
maximum crystallization conversion rate 183
Maxwell model 241–245
mean square distance 56, 57, 59–62, 66, 67
melamine-formaldehyde 9
melt flow index 329, 331
melting enthalpy 111, 112, 188, 194–196, 319, 320
mer 5
methacrylate polymers 207
methanol 132
Michel–Lévy color chart 312
molar attraction constant 80

molecular orientation 260, 261, 263, 274, 275
molecular weight 3–6
molecular weight distribution curve 150, 151, 155, 160, 161, 163, 168, 175, 176
molecular weight regulator 129
monoclinic unit cell 101
monofunctional 21
monomer 4–8
most probable distribution function 169

N

naphtha 10
natural rubber 3, 8, 9
nominal degree of crystallinity 224
non-oriented state 274
norbornadiene 30
notch tip 254
nucleating agent 117, 219
nucleation rate 221, 222
number average molecular weight 148
number average molecular weight between cross-links 336
number average polymerization degree 171
number most probable molecular weight distribution function 170
number of cross-links per chain 247
nylon 6 2, 122, 123, 134
nylon 6,6 2, 22, 23, 38, 122, 123
nylon 9 9
nylon 11 9
nylon hydrolysis 140
nylon salt 122, 123

O

olefin elastomers 268
optical path difference 312
oriented state 274
orthorhombic unit cell 101
osmometry 151, 153
osmotic pressure 151–153
oxidation 129, 140, 278

P

particle scattering factor 154
 p-benzoquinone 129
 peptizing agents 277
 permanent dipole-induced dipole interaction 19
 permanent dipole-permanent dipole interaction 18
 PET bottle 274
 Peterlin model 260, 261, 275
 petroleum 10, 11
 phenol 1, 9, 11
 phenol-formaldehyde 9
 plasticization 264, 276
 plasticizer 257, 264–266, 276
 plastics 5
 Poisson's distribution 172
 polarized infrared radiation 261, 262, 304
 polarizing filter 304, 305, 310
 polyacetal 34
 polyaddition 120, 124
 polyamides 2
 polybutadiene 24, 28, 31, 43–45, 47, 48, 298, 299
 polycondensation 120, 123, 169, 171, 172
 polydispersity 161–164, 166, 169, 171, 173, 177
 polyesters 2
 polyethylene 6, 9
 polyethylene oxide 201
 polyethylene unit cell 263
 polymer 1–8, 10, 12
 polymer chaining 41
 polymer fractionation 81
 polymerization 119, 120, 122, 144
 poly(methyl methacrylate) 321
 polymorphism 90, 100
 polytetrafluoroethylene 3, 33
 polyvinyl acetate 34
 polyvinyl chloride 6, 9
 polyvinylidene chloride 32
 preparative size exclusion chromatography 177
 propagation 124, 126, 131, 133, 134

PS sub-inclusions 267
 pycnometry 313, 315

R

radial chain architecture 24
 radius of the notch tip 254
 random chain architecture 24
 random coil conformation 56
 Rayleigh ratio 154
 reactive compatibilization 278
 reactive functional groups 6, 7, 22, 37
 reactivity ratio 135, 136
 rearrange with the counter-ion 132
 reduced viscosity 156
 refractive index 313
 reinforcing 277
 relative viscosity 156
 relaxation time distribution 270
 reptation theory 4, 272
 restricted movement chain model 58
 retarder 322
 retarders 130, 145
 ring-opening polymerization 120, 134
 rubber elasticity 237
 rubber equation 247, 248
 rubbers 5
 rubbery state 273

S

sapphire 113
 SBR 27, 31, 32, 43
 secondary crystallization 224, 225
 shear yielding 256
 shish-kebab 98, 118, 275
 short-range order 273, 274
 side groups 14, 18, 36, 41, 42, 45, 46, 50, 51
 single crystal 91
 size exclusion chromatography 151, 153, 163, 165, 177
 solution polymerization 137
 specific heat 113
 specific viscosity 156

specific volume 93, 107–109, 180–184
spherulite 95–97, 308–311
stabilized morphology 278
step polymerization 120, 121
stereoblock isotactic polypropylene 232
stereoregular synthesis 4
storage modulus 196, 198
strain rate 240, 244, 253, 272
stress relaxation 237, 243–245, 271, 272,
 278
stress–strain curves 251–253, 259
stretching direction 260, 263
styrene 9
styrene–butadiene triblock copolymer
 28
styrene–isoprene triblock copolymer 28
Styrofoam 32
super-cooling 219, 221, 234
surfactant 137, 138
suspension agent 137
suspension polymerization 137
swelling 69, 70, 80, 81
swollen gel 286
symmetrical polymers 200
syndiotactic polymer 46
synthetic rubber 3

T

tacticity 46
temperature rising elution fractionation
 83
tensile stress–strain curve 250, 253,
 258, 279
termination 126, 132–134
terpolymerization 120
thermal degradation 304, 321
thermal expansion 180, 181, 186
thermo-mechanical degradation 140,
 142
thermoplastic 2
thermosets 25
theta condition 3, 61
thinner 55, 76–79, 82, 88, 288, 289, 293,
 325, 326

time–temperature equivalence 270
time–temperature superposition principle
 270
toughening 277
toughening mechanisms 277
toughness 250, 255, 260, 279
transfer to the solvent 129
trans isomer 44, 45
trans isomerism 300
triclinic unity cell 104
true solution 287, 289

U

Ubbelohde viscometer 324, 325, 327
ultracentrifugation 153, 154, 160
urea-formaldehyde 9, 36

V

van der Waals forces 17
Van't Hoff equation 152
Vicat softening temperature 199,
 331–334
vinyl chloride 6, 9
vinyl isomers 44
vinyl terminal double bond 132
viscoelasticity 237, 238, 278
viscosimetry 155, 159
viscosity average molecular weight 149,
 324, 325, 327
viscous state 273
vitreous state 273
Voigt model 242–245
volumetric expansion coefficient 186,
 187, 213
vulcanization 1, 30, 31, 39, 44, 45, 278
vulcanized rubber 15, 25, 39

W

water absorption 265, 266
weight average molecular weight 149,
 162

weight most probable molecular weight
distribution function 170
WLF equation 187, 188, 270

Z

z-average molecular weight 150, 160
Ziegler-Natta 23, 30, 31, 44, 47
Zimm plot 154