

# Contents

<b>Preface</b> .....	VII
<b>About the Author</b> .....	IX
<b>Foreword</b> .....	XI
<b>1 General Introduction</b> .....	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
<b>2 Polymer Molecular Structure</b> .....	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
<b>3 Polymers in Solution .....</b>	<b>55</b>
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
<b>4 Polymer Solid-State Morphology .....</b>	<b>89</b>
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
<b>5</b>	<b>Polymer Synthesis</b>	<b>119</b>
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

<b>6 Polymer Molecular Weight and Distribution</b> .....	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
<b>7 Polymer Thermal Behavior</b> .....	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
<b>8</b>	<b>Polymer Crystallization Kinetics . . . . .</b>	<b>219</b>
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

<b>9</b>	<b>Polymer Mechanical Behavior</b>	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
<b>10</b>	<b>Experiments in Polymer Science .....</b>	<b>281</b>
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
<b>11 Further Reading .....</b>	<b>337</b>
<b>12 Appendix A .....</b>	<b>341</b>
12.1 Terminology .....	341
12.2 Abbreviations .....	348
<b>13 Appendix B .....</b>	<b>351</b>
<b>Index .....</b>	<b>363</b>