# **CRYSTALS AND CRYSTALLINITY IN POLYMERS**

### **Diffraction Analysis of Ordered and Disordered Crystals**

#### **CLAUDIO DE ROSA**

Dipartimento di Scienze Chimiche Università di Napoli Federico II Complesso Monte Sant' Angelo Napoli, Italy

#### FINIZIA AURIEMMA

Dipartimento di Scienze Chimiche Università di Napoli Federico II Complesso Monte Sant' Angelo Napoli, Italy

### WILEY

### CONTENTS

#### Preface

#### xi

#### 1 Configuration and Conformation of Macromolecules in Polymer Crystals 1

- 1.1 Crystals of Polymers, 1
- 1.2 Constitution and Configuration of Crystalline Polymers, 3
  - 1.2.1 Constitution, 3
  - 1.2.2 Configuration, 5
  - 1.2.3 Relative Configurations, 14
- 1.3 Conformation, 18
- 1.4 Relationships among Internal Parameters of Macromolecules, 19
- 1.5 Conformation of Polymer Chains in the Crystalline State, 21
  - 1.5.1 Basic Principles, 21
  - 1.5.2 The Equivalence Principle, 21
    - 1.5.2.1 Symmetry Relations for Cylindrical Coordinates, 29
    - 1.5.2.2 Application of the Equivalence Principle: Stereoregular Vinyl Polymers, 31
  - 1.5.3 Principle of Minimum Conformational Internal Energy, 33
  - 1.5.4 Relationships between Internal Coordinates and Conformational Parameters, 36
- 1.6 Helical Conformations in Isotactic and Syndiotactic Polymers, 46
- 1.7 Conformational Energy Calculations, 51
  - 1.7.1 Setting Up Molecular Models: Coordinate Transformations, 521.7.2 Calculation of the Conformational Energy for Isotactic and Syndiotactic Polymers, 54
- 1.8 Helical Conformation and Optical Activity, 66
- 1.9 Alternating Copolymers, 68
- 1.10 Polydienes, 73
- 1.11 Nonhelical Chain Conformations of Isotactic Polymers, 78 References, 81

#### 2 Packing of Macromolecules in Polymer Crystals

- 2.1 General Principles, 88
- 2.2 The Principle of Density (Entropy)-Driven Phase Formation in Polymers, 92

#### 88

¥

#### vi CONTENTS

- 2.3 Symmetry Breaking, 96
- 2.4 Impact of Chain Folding on Crystal Structure Symmetry, 103
- 2.5 Frustrated Polymer Crystal Structures, 107
- 2.6 Chiral Crystallization of Polymers with Helical Chain Conformations, 110
- 2.7 Packing Effects on the Conformation of Polymer Chains in Crystals: The Case of Aliphatic Polyamides, 113 References, 118

#### 3 Methods in Crystal Structure Determination from X-Ray Diffraction 123

- 3.1 X-Ray Diffraction of Semicrystalline Polymers, 123
   3.1.1 Basic Principles, 123
   2.1.2 Encoded and Tacketing on the Polymera Countel
  - 3.1.2 Experimental Techniques for Polymer Crystals, 128
- 3.2 Fourier Synthesis and the Phase Problem in Crystallography, 134
- 3.3 X-Ray Fiber Diffraction Analysis, 140
  - 3.3.1 Determination of the Fiber Period and the Bragg Distances of Diffraction Peaks, 140
  - 3.3.2 Analysis of Nonhelical and Helical Structures, 142
  - 3.3.3 The Structure Factor of a Single Molecule: The Continuous Helix, 144
  - 3.3.4 CCV Formula for Helical Structures, 147
  - 3.3.5 The Case of Incommensurable Helices, 153
  - 3.3.6 Calculation of Structure Factors of a Single Helical Chain, 162
  - 3.3.7 Calculation of Structure Factors of Crystals of Helical Molecules Including More Than One Chain per Unit Cell, 163
- 3.4 Determination of Parameters of the Unit Cell and Indexing of the Diffraction Pattern, 165
   2.4.1 X Bey Diffraction Data from Oriented Fibers, 165
  - 3.4.1 X-Ray Diffraction Data from Oriented Fibers, 165
  - 3.4.2 X-Ray Diffraction Data from Powder Samples, 170
- 3.5 Measure of the Integrated Intensities of the Reflections and Corrections for Geometric (Lorentz), Polarization, and Absorption Factors, 171
- 3.6 Calculation of Structure Factors, 174
- 3.7 Structural Refinement, 180
- 3.8 Form of Diffraction Pattern and Broadening due to the Laue Function, 181 References, 183

#### 4 Defects and Disorder in Polymer Crystals

- 4.1 Classification of Different Types of Structural Disorder, 185
- 4.2 Crystals with Partial Three-Dimensional Order (Class A): Disorder with Three-Dimensional Periodicity Maintained for Only Some Characterizing Points of the Structure, 191
  - 4.2.1 Substitutional Isomorphism of Different Chains, 192
    - 4.2.1.1 Disorder in the Positioning of Right- and Left-Handed Helical Chains, 192
    - 4.2.1.2 Disorder in the Positioning of Up and Down Chains, 195
    - 4.2.1.3 Disorder in the Orientation of Chains around the Chain Axis, 197

- 4.2.2 Substitutional Isomorphism of Different Monomeric Units, 200
- 4.2.3 Conformational Isomorphism, 202
- 4.2.4 Disorder in the Stacking of Ordered Layers of Chains (Stacking Fault Disorder), 204
  - 4.2.4.1 Stacking Faults in Form I and Form II of sPP, 204
  - 4.2.4.2 Stacking Faults in  $\alpha$  and  $\gamma$ -Forms of iPP, 206
  - 4.2.4.3 Stacking Faults in the  $\beta$ -Form of sPS, 209
- 4.2.5 Conformational Kink-Band Disorder, 211
  - 4.2.5.1 Conformational Kink-Band Disorder in PVDF, 212
  - 4.2.5.2 Conformational Kink-Band Disorder in PE, 215
  - 4.2.5.3 Conformational Kink-Band Disorder in sPP, 216
  - 4.2.5.4 The Role of Kink-Band Disorder in the Cooperative Crystal–Crystal Polymorphic Transitions, 218
- 4.3 Solid Mesophases, 219
  - 4.3.1 LCs in Small Molecules and Polymers, 222
  - 4.3.2 Solid Mesophases in Polymers, 227
  - 4.3.3 Solid Mesophases of Class B: Crystals with Three-Dimensional Long-Range Order of Not-Point-Centered Features, 229
    - 4.3.3.1 Solid Mesophase in 1,4-*trans*-Poly(1,3-butadiene) (*trans*-PBD), 230
    - 4.3.3.2 Poly(ε-caprolactame) (Nylon 6), 232
    - 4.3.3.3 Poly(acrylonitrile) (PAN), 235
    - 4.3.3.4 Ethylene–Propylene Random Copolymers, 239
    - 4.3.3.5 Pseudohexagonal Form of PE at High Pressure and Temperature, 243
    - 4.3.3.6 Poly(tetrafluoroethylene) (PTFE), 245
    - 4.3.3.7 Random Copolymers of Tetrafluoroethylene with Fluorinated Comonomers, 251
    - 4.3.3.8 Alternating Ethylene–Tetrafluoroethylene (ETFE) Copolymers, 255
    - 4.3.3.9 Alternating Ethylene-Norbornene Copolymers (ENCs), 264
    - 4.3.3.10 Comblike Polymers, 271
  - 4.3.4 Solid Mesophases of Class C: Crystals with Long-Range Positional Order in Only One or Two Dimensions, 271
    - 4.3.4.1 Poly(ethylene terephthalate) (PET), 272
    - 4.3.4.2 Isotactic Polypropylene (iPP), 275
    - 4.3.4.3 Copolymers of iPP with Branched Comonomers, 276
    - 4.3.4.4 Syndiotactic Polypropylene (sPP), 279
    - 4.3.4.5 Copolymers of sPP, 284
    - 4.3.4.6 Syndiotactic Polystyrene (sPS) and Methyl-Substituted Polystyrenes, 286

References, 287

## 5 Methods of Analysis of Diffuse Scattering from Disordered Structures of Polymers

- 5.1 Structural Disorder and Diffuse Scattering, 296
- 5.2 Methods of Diffraction Analysis from Disordered Crystals, 298
- 5.3 Long-Range Order in Disordered Lattices of Class A, 300
- 5.4 SRO in Disordered Crystals of Class A, 302
- 5.5 Short-Range Order in Disordered Crystals with Substitution-Type Disorder, 305

- 5.6 Short-Range versus Long-Range Order in Disordered Crystals of Classes B and C (Solid Mesophases), 309
- 5.7 Disordered Models with Perturbations Occurring over Continuous Ranges, 311
- 5.8 Basic Formulas for the Calculation of X-Ray Diffraction Intensity from Disordered Model Structures of Polymers, 316
  - 5.8.1 Brief Overview of Basic Formalism in X-Ray Modeling, 316
  - 5.8.2 Effect of Longitudinal Translational Disorder and Rotational Displacements of Chains about Their Axes: Explicit Formulas, 319
    5.8.3 Substitutional and Translational Disorder in One Dimension, 321
- 5.9 Examples of Calculation of Average Diffracted Intensity of Structures Disordered in One Dimension, 328
  - 5.9.1 Substitution-Type Disorder, 328
  - 5.9.2 Translation-Type Disorder, 331
  - 5.9.3 Stacking Fault Disorder in the  $\beta$ -Form of sPS, 333
- 5.10 Line and Surface Integration Method of Diffraction Intensity for Fibers and Powders of Polycrystalline Samples, 337 References, 338

#### 6 Crystal Habits

- 6.1 Basic Remarks, 341
- 6.2 Rounded Lateral Habits, 347
- 6.3 Chain Folding, Molecular Orientation, and Sectorization, 3496.3.1 Chain Tilting, 3496.3.2 Sectorization, 350
  - 6.3.2 Sectorization, 350
  - 6.3.3 Nonplanar Lamellae, 352
- 6.4 Twinning and Secondary Nucleation Theory, 355
- 6.5 Homoepitaxy, Morphology, Stem Orientation, and Polymorphism, 359 References, 367

#### 7 Influence of Crystal Defects and Structural Disorder on the Physical and Mechanical Properties of Polymeric Materials 369

- 7.1 Introduction, 369
- 7.2 Stress-Induced Phase Transformations during Deformation, 371
- 7.3 Isotactic Polypropylene (iPP), 373
  - 7.3.1 Influence of Stereo- and Regiodefects on the Crystallization Behavior of iPP, 374
  - 7.3.2 Influence of Stereo- and Regiodefects on the Mechanical Properties of iPP, 378
  - 7.3.3 Stress-Induced Phase Transformations of iPP during Tensile Deformation, 382
  - 7.3.4 Elastic Properties and Phase Transformations in Stereodefective iPP, 388
  - 7.3.5 Influence of Constitutional Defects on the Crystallization Behavior of iPP, 390
  - 7.3.6 Influence of Constitutional Defects on the Physical Properties of iPP, 397
  - 7.3.7 Influence of Conditions of Crystallization on the Physical Properties of iPP: The Mesomorphic Form, 406
    - 7.3.7.1 Morphology of the Solid Mesophase of iPP, 407
    - 7.3.7.2 Mechanical Properties of the Solid Mesophase of iPP, 412

- 7.3.7.3 Mechanical Properties of the  $\gamma$ -Form and Solid Mesophase in Metallocene iPPs, 417
- 7.4 Syndiotactic Polypropylene (sPP), 422
  - 7.4.1 Influence of Stereodefects on the Crystallization Behavior of sPP, 424
  - 7.4.2 Influence of Stereodefects on the Crystallization of the Mesomorphic Form of sPP, 427
  - 7.4.3 Influence of Stereodefects on the Crystallization of *trans*-Planar and Helical Forms of sPP in Oriented Fibers: Stress-Induced Phase Transformations during Deformation, 428
  - 7.4.4 Influence of Constitutional Defects on the Crystallization Behavior of sPP, 431
  - 7.4.5 Physical and Mechanical Properties of sPP, 434
    - 7.4.5.1 Influence of Stereodefects on the Mechanical Properties of sPP, 434

7.4.5.2 Mechanical Properties of the Solid Mesophase of sPP, 440 References, 442

Index