
Contents

1 Shifting Paradigms in Polymer Crystallization

<i>Murugappan Muthukumar</i>	1
1.1 Introduction	1
1.2 Classical View	3
1.2.1 Lamellar Thickness	3
1.2.2 Lamellar Growth	3
1.3 Results	6
1.3.1 Nucleation of a Lamella	7
1.3.2 Free Energy Landscape	8
1.3.3 Spontaneous Selection of Lamellar Thickness and Shape ..	9
1.3.4 Growth Front	11
1.3.5 Kinetics at the Growth Front	11
1.4 Conclusions	15
References	16

2 Theoretical Aspects of the Equilibrium State of Chain Crystals

<i>Jens-Uwe Sommer</i>	19
2.1 Introduction	19
2.2 Thermodynamic Considerations about the Equilibrium Shape of a Polymer Single Crystal	20
2.3 The Brush State of the Amorphous Fraction is Thermodynamically Suppressed	23
2.4 Extended Chain Crystals and Sliding Entropy	24
2.5 The Slip-Loop Model for the Entropy of the Amorphous Fraction of a Single Chain Crystal	26
2.6 Tight Loops and Effective Fold Surface Tension for Single Chain Crystals	29
2.7 Many Chain Crystals	32
2.8 The Role of Bending Rigidity for the Formation of Small Loops ..	34
2.9 Tilting in Extended Chain Crystals	36

2.10	Summary and Conclusion	38
	References	43
3 Intramolecular Crystal Nucleation		
	<i>Wenbing Hu</i>	47
3.1	Nucleation Mechanism of Polymer Crystallization	47
3.2	Concept of Molecular Nucleation	51
3.3	Intramolecular Nucleation Model	52
	3.3.1 Primary Crystal Nucleation in a Single Chain	52
	3.3.2 Secondary Crystal Nucleation in a Single Chain	55
	3.3.3 From Molecular Nucleation to Intramolecular Nucleation .	59
3.4	Concluding Remarks	60
	References	61
4 Kinetic Theory of Crystal Nucleation Under Transient Molecular Orientation		
	<i>Leszek Jarecki</i>	65
4.1	Introduction	65
4.2	Time Evolution of the Chain Distribution Function	67
4.3	Free Energy and Orientation Distribution of the Chain Segments .	72
4.4	Crystal Nucleation Rate	77
4.5	Conclusions	84
	References	85
5 Precursor of Primary Nucleation in Isotactic Polystyrene Induced by Shear Flow		
	<i>Toshiji Kanaya, Yoshiyuki Takayama, Yoshiko Ogino, Go Matsuba and Koji Nishida</i>	87
5.1	Introduction	87
5.2	Experimental	88
5.3	Results and Discussion	89
5.4	Conclusion	95
	References	95
6 Structure Formation and Glass Transition in Oriented Poly(Ethylene Terephthalate)		
	<i>Koji Fukao, Satoshi Fujii, Yasuo Saruyama, Naoki Tsurutani</i>	97
6.1	Introduction	97
6.2	Experiments	99
6.3	Structural Change at Isothermal Annealing Process	100
	6.3.1 X-ray Diffraction Patterns	100
	6.3.2 Integrated Intensity as a Function of Annealing Time ...	103
	6.3.3 Kinetic Model Analysis	104
6.4	Structural and Thermal Change During the Heating Process	109
	6.4.1 X-ray Scattering Patterns During the Heating Process ...	109
	6.4.2 Thermal Properties of Oriented PET	110

6.5	Concluding Remarks	115
	References	116

7 How Do Orientation Fluctuations Evolve to Crystals?

Zhicheng Xiao, Jan Ilavsky, Gabrielle G. Long, Yvonne A. Akpalu 117

7.1	Introduction	117
7.2	Materials and Methods	119
7.2.1	Sample Preparation	119
7.2.2	Differential Scanning Calorimetry (DSC)	120
7.2.3	Simultaneous WAXS and SAXS	120
7.2.4	USAXS Measurements	121
7.2.5	Small Angle Light Scattering (SALS)	122
7.3	Results and Discussion	123
	References	130

8 Role of Chain Entanglement Network on Formation of Flow-Induced Crystallization Precursor Structure

Benjamin S. Hsiao 133

8.1	Introduction	133
8.2	Current Opinions on Flow-Induced Crystallization Precursor Structures	134
8.3	Role of High Molecular Weight Species in Flow-Induced Crystallization	138
8.4	New Insights on the Molecular Mechanism of Shish-Kebab Formation	142
8.4.1	Kebab Growth Follows the Diffusion-Controlled Like Process	142
8.4.2	Thermal Stability of Flow-Induced Shish-Kebab Scaffold	143
8.5	Relationship between Micro-rheology and Precursor Morphology	146
8.6	Concluding Remarks	147
	References	147

9 Full Dissolution and Crystallization of Polyamide 6 and Polyamide 4.6 in Water and Ethanol

Marjoleine G.M. Wevers, Vincent B.F. Mathot, Thijs F.J. Pijpers, Bart Goderis, Gabriel Groeninckx 151

9.1	Introduction	151
9.2	Experimental Section	153
9.2.1	Materials	153
9.2.2	Preparation and Characterization of the Samples	154
9.3	Results and Discussion	156
9.3.1	Dissolution and Crystallization of PA6 in Water by DSC	156
9.3.2	Influence of Dissolution of PA6 on Molar Mass Distribution by SEC	158
9.3.3	Influence of Dissolution of PA6 on the Crystallinity Found by DSC	160

9.3.4 Dissolution and Crystallization of PA6 by WAXD 161
 9.3.5 Dissolution of Other Polyamides and in Various Solvents . 165
 9.4 Conclusions 166
 References 167

10 Small Angle Scattering Study of Polyethylene Crystallization from Solutions

Howard Wang 169
 10.1 Introduction 169
 10.2 Experiment 171
 10.3 Results and Discussion 171
 10.4 Conclusion 177
 References 177

11 Morphologies of Polymer Crystals in Thin Films

Günter Reiter, Ioan Botiz, Laetitia Graveleau, Nikolay Grozev, Krystyna Albrecht, Ahmed Mourran, Martin Möller 179
 11.1 Introduction 179
 11.2 Experimental Section 182
 11.3 Results and Discussion 183
 11.3.1 Changes in Morphology with Crystallization Temperature 183
 11.3.2 Dependence of Morphology on Initial Film Thickness . . . 186
 11.3.3 The Kinetics of Crystal Growth and the Effect of Changing Temperature 190
 11.3.4 “Decoration” of Flat-On Lamellar Crystals by Ripples and Spirals 193
 11.3.5 Orientation of the Crystalline Lamellae with Respect to the Substrate 195
 11.4 Conclusions 197
 References 198

12 Crystallization of Frustrated Alkyl Groups in Polymeric Systems Containing Octadecylmethacrylate

Elke Hempel, Hendrik Budde, Siegfried Höring, Mario Beiner 201
 12.1 Introduction 201
 12.2 Side-chain Crystallization in Poly(*n*-octadecylmethacrylate) 203
 12.3 Confined Crystallization in Microphase-separated Poly(styrene–*block*–octadecylmethacrylate) Copolymers 212
 12.4 Conclusions 224
 References 226

13 Crystallization in Block Copolymers with More than One Crystallizable Block

Alejandro J. Müller, María Luisa Arnal, Vittoria Balsamo 229
 13.1 Introduction 229
 13.2 Double Crystalline AB and ABA Copolymers 230

13.3	ABC Triblock Linear and Star Shaped Terpolymers	251
13.4	Conclusions	256
	References	257

14 Monte Carlo Simulations of Semicrystalline Polyethylene: Interlamellar Domain and Crystal-Melt Interface

	<i>Markus Hütter, Pieter J. in 't Veld, Gregory C. Rutledge</i>	261
14.1	Introduction, Motivation	261
14.2	Methodology	263
	14.2.1 Force Field, Virial Calculation of Stress	263
	14.2.2 Simulation Setup	264
	14.2.3 Thermal and Elastic Properties of Interlamellar Domain	267
	14.2.4 Energy and Stresses in the Crystal-Melt Interface	268
14.3	Results and Discussion	270
	14.3.1 Conformational Properties	270
	14.3.2 Thermal and Elastic Properties of Interlamellar Domain	271
	14.3.3 Properties of the Crystal-Melt Interface	275
	14.3.4 Internal Energy of the Interface	278
	14.3.5 Interface Stresses	278
14.4	Summary and Discussion	279
	14.4.1 Entire Interlamellar Domain	280
	14.4.2 Sharp Crystal-Melt Interface	280
	14.4.3 Perspectives	281
	References	282

15 The Role of the Interphase on the Chain Mobility and Melting of Semi-crystalline Polymers; A Study on Polyethylenes

	<i>Sanjay Rastogi, Dirk R. Lippits, Ann E. Terry, Piet J. Lemstra</i>	285
15.1	Introduction	286
15.2	Control of Entanglement Density Upon Crystallization	289
	15.2.1 Crystallization via Dilute Solution	289
	15.2.2 Exploitation of the Hexagonal Phase in Polyethylene	292
	15.2.3 Via Synthesis	293
15.3	Influence of the Interphase on Molecular Mobility in Crystalline Domains	295
15.4	From the Interphase to the Interface: The Welding of Semi-crystalline Polymers	296
15.5	Influence of Chain Folding on the Unit Cell	297
	15.5.1 Monodisperse Ultra-long Linear Alkanes	298
	15.5.2 Monodisperse Ultra-long Branched Alkanes	302
	15.5.3 Homogeneous Copolymers of Ethylene-1-Octene	308
15.6	Beyond Flexible Polymers: Rigid Amorphous Fraction	313
15.7	Influence of the Interphase on the Polymer Melt	315

15.7.1	Heating Rate Dependence on the Chain Dynamics – from Disentangled to Entangled Melt	321
15.8	Conclusions	323
	References	325
16	Polymer Crystallization Under High Cooling Rate and Pressure: A Step Towards Polymer Processing Conditions	
	<i>Andrea Sorrentino, Felice De Santis, Giuseppe Titomanlio</i>	329
16.1	Introduction	329
16.2	Material and Methods	333
16.2.1	DTA Experiments	333
16.2.2	High Cooling Rates Device	333
16.2.3	Rapid Solidification Under Pressure	334
16.2.4	Morphological Characterization	336
16.3	Experimental Results	336
16.4	Discussion	340
16.5	Conclusions	342
	References	343
17	Stress-Induced Phase Transitions in Metallocene-Made Isotactic Polypropylene	
	<i>Claudio De Rosa, Finizia Auriemma</i>	345
17.1	Introduction	345
17.2	Mechanical Properties of Unoriented Films	349
17.3	Stress-induced Phase Transitions in Unoriented Fims	357
17.4	Oriented Fibers of Elastomeric Samples	365
17.5	Conclusions	368
	References	370
18	Insights into Polymer Crystallization from In-situ Atomic Force Microscopy	
	<i>Jamie K. Hobbs</i>	373
18.1	Introduction	373
18.2	In-situ Observation of Thin Film Growth	374
18.2.1	In-situ Observation of Polyethylene Thin-film Crystallization	375
18.2.2	In-situ Observation of Polyethylene Oxide Dendritic Crystallization	377
18.3	Observations on Growth of Shish Kebabs	380
18.4	Imaging of Precursors to Crystal Growth?	382
18.5	Developments in Atomic Force Microscopy – High Speed AFM ...	384
18.6	Conclusions	387
	References	388

19 Temperature and Molecular Weight Dependencies of Polymer Crystallization

<i>Norimasa Okui, Susumu Umemoto, Ryuichiro Kawano, Al Mamun</i>	391
19.1 Introduction	391
19.2 Temperature Dependence of Crystallization	393
19.2.1 Temperature Dependence of Linear Crystal Growth Rate	393
19.2.2 Temperature Dependence of Nucleation Rate	399
19.3 Molecular Weight Dependence of Nucleation and Crystal Growth Rates	409
19.3.1 Molecular Weight Dependence of Crystal Growth Rate	409
19.3.2 Molecular Weight Dependence of Nucleation Rate	416
19.3.3 Molecular Weight Dependence of Overall Crystallization	419
19.4 Conclusions	422
References	423

20 Step-scan Alternating Differential Scanning Calorimetry Studies on the Crystallisation Behaviour of Low Molecular Weight Polyethylene

<i>Kinga Pielichowska, Krzysztof Pielichowski</i>	427
20.1 Introduction	427
20.2 Experimental	428
20.2.1 Materials	428
20.2.2 Techniques	428
20.3 Results and Discussion	430
20.4 Conclusions	433
References	433

21 Order and Segmental Mobility in Crystallizing Polymers

<i>Aurora Nogales, Alejandro Sanz, Igors Šics, Mari-Cruz García-Gutiérrez, Tiberio A. Ezquerro</i>	435
21.1 Introduction	435
21.2 Description of the Experimental Set-up for Simultaneous Small and Wide Angle X-ray Scattering and Dielectric Spectroscopy (SWD)	438
21.3 Dielectric Relaxation of Amorphous Polymers: Poly(ethylene terephthalate)	441
21.4 Time Resolved Cold Crystallization by SWD	443
21.4.1 Poly(ethylene terephthalate)	443
21.4.2 Poly(ethylene terephthalate)/Poly(ethylene naphthalene 2,6-dicarboxylate) Blends	445
21.5 Development of the Rigid Amorphous Phase (RAP) as Revealed by SWD	450
21.5.1 Aromatic Polyesters: Poly(ethylene terephthalate), Poly(butylene isophthalate)	450
21.5.2 Confined Crystallization of PET in PET/PEN Blends	452

21.6	Conclusions	454
	References	455
22	Atomistic Simulation of Polymer Melt Crystallization by Molecular Dynamics	
	<i>Numan Waheed, Min Jae Ko, Gregory C. Rutledge</i>	457
22.1	Introduction	457
22.2	Methods	460
22.3	Results and Discussion	461
	22.3.1 Nucleation	461
	22.3.2 Growth	468
22.4	Conclusions	476
	References	478
23	A Multiphase Model Describing Polymer Crystallization and Melting	
	<i>Gert Strobl</i>	481
23.1	Introduction	481
23.2	Experimental Findings	483
	23.2.1 Crystallization Line and Melting Line	483
	23.2.2 Effects of Counits and Diluents	485
	23.2.3 Recrystallization Processes	488
23.3	A Multiphase Model of Polymer Crystallization and Melting	492
	23.3.1 Thermodynamic Scheme	494
23.4	Examples of Application	496
23.5	Conclusion	500
	References	502
	Index	503