

Nello Pasquini (Ed.)

Polypropylene Handbook



2nd Edition

HANSER

Contents

Foreword	V
Preface	VII
I Polypropylene – The Product	1
1 Introduction	3
<i>N. Pasquini, Edward P. Moore, Jr.</i>	
1.1 Scope	3
1.2 Chemistry	4
1.3 History	6
1.3.1 Before Ziegler and Natta	6
1.3.2 Ziegler	8
1.3.3 Natta	9
1.3.4 Patent Rights	10
1.4 Commercial Significance	11
2 Catalysts for Polymerization	15
2.1 Ziegler–Natta Catalysts and Polymerizations	15
<i>E. Albizzati, G. Cecchin, J. C. Chadwick, G. Collina, U. Giannini, G. Morini, L. Noristi</i>	
2.1.1 Introduction	15
2.1.2 History and Development of Stereospecific Ziegler–Natta Catalysts ...	16
2.1.2.1 First Generation Catalysts	16
2.1.2.2 Second Generation Catalysts	16
2.1.2.3 Third Generation Catalysts	17
2.1.2.4 Fourth Generation Catalysts	17
2.1.2.5 Fifth Generation Catalysts and Beyond	17
2.1.3 Ziegler–Natta Catalysts: Synthesis, Chemistry, and Structure	18
2.1.3.1 First Generation TiCl_3 Catalysts	18
2.1.3.2 Second Generation TiCl_3 Catalysts	24
2.1.3.3 MgCl_2 -Supported Catalysts	26
2.1.4 Mechanism of Propylene Polymerization	49
2.1.4.1 The Active Metal–Carbon Bond	49
2.1.4.2 Insertion Mode and Regioselectivity	50
2.1.4.3 Stereochemistry of the Insertion Reaction	51
2.1.4.4 Steric Control of Monomeric Unit Insertion	52
2.1.4.5 Catalytic Site Models	54
2.1.5 Polymerization Kinetics	64
2.1.5.1 Kinetic Models	64

2.1.5.2	Catalyst Concentration	65
2.1.5.3	Cocatalyst Concentration	65
2.1.5.4	Monomer Concentration	65
2.1.5.5	Hydrogen Concentration	66
2.1.5.6	Temperature	67
2.1.5.7	Polymerization Time	68
2.1.5.8	Polymerization Medium	69
2.1.5.9	Number of Active Centers and Value of Propagation Rate Constant	69
2.1.5.10	The Rate Determining Step	72
2.1.5.11	Active Site Heterogeneity	72
2.1.5.12	Chain Termination	73
2.1.5.13	Replication and Polymer Morphology	75
2.1.5.14	Mechanism of Polypropylene Particle Growth and Related Technological Implications	78
2.1.6	Copolymerization	83
2.1.6.1	Introduction	83
2.1.6.2	Statistical (Random) Copolymerization	83
2.1.6.3	Sequential Copolymerization	86
2.1.7	Latest Developments and Industrial Applications of Ziegler–Natta Catalysts	90
2.1.8	Comparison between Homogeneous and Heterogeneous Catalysts ...	91
2.2	Metallocene Catalysts for Propylene Polymerization	107
<i>L. Resconi, C. Fritze</i>		
2.2.1	General Introduction	107
2.2.1.1	The Tools of the Trade: Metals, Ligands, and Activators	108
2.2.1.2	Mechanisms of Olefin Insertion and Symmetry Rules for Stereocontrol	109
2.2.1.3	Mechanisms of Chain Release Reactions	113
2.2.2	Trying to Catch up with Ziegler–Natta Catalysts: Isotactic PP	116
2.2.2.1	Ligand Design for Increasing Molecular Weight	116
2.2.2.2	Ligand Design for Increasing Isospecificity	116
2.2.2.3	Influence of Polymerization Conditions	118
2.2.3	Beyond Ziegler–Natta Catalysis: Fine-Tuning Stereoregularity	121
2.2.3.1	Syndiotactic Crystalline and Elastomeric Polypropylene ...	121
2.2.3.2	Amorphous Polypropylene	124
2.2.3.3	Low Isotacticity: From Elastomeric to Flexible Isotactic Polypropylene	126
2.2.3.4	Propylene–Ethylene Copolymers	131
2.2.3.5	Propylene– α -Olefin Copolymers	134
2.2.4	The Industrial Development of Metallocene Catalysts	135
2.2.5	Polypropylene Industrial Production with Metallocene Catalysts: Facts and Expectations	139
2.2.6	Conclusions and Outlook	141

3 Polypropylene Morphology	147
<i>Roger A. Phillips, Michael D. Wolkowicz</i>	
3.1 Introduction	147
3.1.1 Building Blocks of PP Morphology	147
3.1.2 Crystallinity and Stereoregularity	148
3.1.3 Relationship of Morphology to Structure, Processing, and Properties	151
3.2 Morphology of α -Form Isotactic PP	153
3.2.1 Crystallographic Symmetry	153
3.2.2 Lamellar Morphology	155
3.2.3 Spherulitic Morphology	158
3.2.4 Melting Behavior	160
3.2.4.1 Equilibrium Melting Point	160
3.2.4.2 Copolymer Melting	168
3.2.4.3 Cocrystallization	170
3.2.4.4 Multiple Endotherms	173
3.2.4.5 Elastomeric Polypropylene (ELiPP)	176
3.2.4.6 Summary	178
3.2.5 Kinetics	179
3.2.5.1 Isothermal Crystallization: Regime Analysis	179
3.2.5.2 Cocrystallization	184
3.2.6 Physical and Thermodynamic "Phase Separation" in Semicrystalline Blends	186
3.2.6.1 Tacticity Mixtures of Poly(propylene)	188
3.2.6.2 <i>i</i> PP/Rubber Blend Thermodynamics and Morphology Development	192
3.3 Polymorphic Forms of Isotactic Poly(propylene)	195
3.3.1 The β -Form	196
3.3.1.1 Crystallographic Symmetry	196
3.3.1.2 Lamellar Morphology	197
3.3.1.3 Spherulitic Morphology	197
3.3.1.4 Melting Behavior	197
3.3.1.5 Crystallization Kinetics/Morphology Development	199
3.3.2 The γ -Form	200
3.3.2.1 Crystallographic Symmetry	200
3.3.2.2 Lamellar/Spherulitic Morphology	202
3.3.2.3 Melting Behavior	202
3.3.2.4 Crystallization Kinetics and Morphology Development	204
3.3.3 Mesomorphic (Smectic) Form	205
3.3.3.1 Crystallographic Symmetry	206
3.3.3.2 Lamellar Morphology	209
3.3.3.3 Melting Behavior	209
3.3.3.4 Morphology Development	210
3.4 Syndiotactic Polypropylene	210
3.4.1 Crystallographic Symmetry	211

3.4.2	Lamellar Morphology	215
3.4.3	Spherulitic Morphology	216
3.4.4	Melting Behavior	217
3.4.5	Crystallization Kinetics	222
3.5	Morphology of Rubber-Modified Polypropylene	223
3.5.1	Rubber Modification	224
3.5.2	Morphology	224
3.5.3	Viscosity Ratio	226
3.5.4	Processing	228
3.5.5	Crystallinity in the Rubber Phase	231
3.5.6	High Alloy Copolymers	233
3.5.7	Rubber-Modified PP from Single-Site Catalyst Technology	235
3.6	Injection Molded Homopolymer	238
3.6.1	Injection Molding Process	238
3.6.2	Macromorphology	238
3.6.3	Morphology Hierarchy	240
3.6.4	Structure/Processing/Morphology/Property Relations	241
3.7	Concluding Comments and Future	243
4	Additives	265
	<i>Ronald F. Becker, E. Burgin, Lester P. J. Burton, Stephen E. Amos</i>	
4.1	Introduction	265
4.1.1	Background	265
4.2	Role of Additives in Polypropylene	266
4.3	Mechanism of Polypropylene Oxidation and Degradation	267
4.3.1	Initiation	267
4.3.2	Propagation	268
4.3.3	Chain Transfer or Branching	268
4.3.4	Self-Termination	268
4.4	Stabilizing Polypropylene	271
4.4.1	Primary Antioxidants	272
4.4.1.1	Hindered Phenols	272
4.4.1.2	Hindered Amines	274
4.4.2	Secondary Stabilizers	275
4.4.3	Effects of Flame Retardants	278
4.4.4	Fillers	278
4.5	Other Additives Used in Polypropylene	279
4.5.1	Acid Scavengers	279
4.5.2	Nucleating Agents	280
4.5.3	Peroxides	283
4.5.4	Slip Agents	285
4.5.5	Antiblocks	286
4.5.6	Antistats	286
4.5.6.1	Internal Antistats	286
4.5.6.2	External Antistats	288

4.5.7	Mold Release Agents	288
4.5.8	Pigments	289
4.5.9	Fluorescent Whitening Agents	289
4.5.10	Metal Chelators	290
4.5.11	Lubricants	290
4.5.12	Biocides	290
4.6	Additive Requirements for Resin Suppliers	291
4.7	Additive Requirements for Specific Markets	291
4.7.1	Fibers	291
4.7.1.1	Disposable Items	292
4.7.1.2	Carpet and Upholstery	292
4.7.2	Packaging	293
4.7.2.1	Flexible Packaging – Film	293
4.7.2.2	Rigid Packaging – Sheet Extrusion and Thermoforming ...	294
4.7.3	Medical Applications	296
4.7.3.1	Chemistry and Stabilization of Irradiated PP	296
4.7.4	Automotive	298
4.7.4.1	Under the Hood	299
4.7.4.2	Exterior	299
4.7.4.3	Interior	300
4.7.5	Housewares	300
4.7.6	Construction	301
4.7.6.1	Roofing and Geomembranes	301
4.7.6.2	Pipes	301
4.8	Testing	302
4.8.1	Process or Melt Stability	302
4.8.2	Long-Term Heat Aging (LTHA)	303
4.8.3	UV Stability	303
4.8.4	Radiation Resistance	304
5	Product Mix and Properties	307
	<i>D. Del Duca, D. Malucelli, G. Pellegatti, D. Romanini</i>	
5.1	Introduction	307
5.2	Homopolymers	308
5.3	Random Copolymers	312
5.4	Heterophasic Copolymers	314
5.5	New Multiphase Structures	317
5.6	Compounded Polypropylene Products	320
5.6.1	The Compounding Process	320
5.6.2	Compounding Technologies	321
5.6.2.1	Single Screw Extruders	322
5.6.2.2	Rotating and Continuous Reciprocating Single Screw Mixers	323
5.6.2.3	Fully Intermeshing Co-Rotating Twin Screw Extruders	324
5.6.2.4	High-Intensity Internal Batch and Continuous Mixers	325
5.6.3	Traditional Filled and Reinforced PP	326

5.6.3.1	Calcium Carbonate Filled PP	327
5.6.3.2	Talc Filled PP	327
5.6.3.3	Mica Reinforced PP	329
5.6.3.4	Wollastonite Reinforced PP	329
5.6.3.5	Glass Fiber Reinforced PP	330
5.6.3.6	Wood/PP Composites	331
5.6.4	PP-Nanocomposites	332
5.6.4.1	Nanofiller Preparation	333
5.6.4.2	Nanofiller Dispersion	334
5.6.4.3	Dimensional Stability/Isotropy	336
5.6.5	Thermoplastic Vulcanizates	336
5.6.5.1	Dynamic Vulcanization	337
5.6.5.2	Morphology	340
5.6.5.3	Rheology	341
5.6.5.4	Performance	342
5.6.6	Other Specialty Products	345
5.6.6.1	Flame Retardant PP	345
5.6.6.2	High Melt Strength PP	347
5.7	Eco-Balance and Recycling	351
5.7.1	Life Cycle Analysis (LCA)	351
5.7.2	Energy Recovery	352
5.7.3	PP Recycling	353
5.7.4	Final Remarks	354
II	Polypropylene – The Technology	359
6	Manufacturing	361
	<i>D. Bigiavi, M. Covezzi, M. Dorini, Richard T. LeNoir, Richard B. Lieberman,</i> <i>D. Malucelli, G. Mei, G. Penzo</i>	
6.1	Early Processes	361
6.2	Current Processes	368
6.3	Monomer	376
6.4	Polymer Finishing	377
6.5	Process Environmental Issues	378
7	Fabrication Processes	381
	<i>A. Addeo, Edward P. Moore, Jr.</i>	
7.1	Introduction	381
7.1.1	Introduction to Extrusion Processes	382
7.1.1.1	Extrusion	382
7.1.1.2	Quenching	384
7.1.1.3	Reheating	384
7.1.1.4	Coextrusion	385

7.1.1.5	Health, Safety, and Environmental Issues	386
7.1.2	Introduction to Orientation	387
7.1.2.1	Types of Orientation	388
7.1.2.2	The Orientation Process	389
7.1.2.3	Properties of Oriented Articles	390
7.1.2.4	Measurement of Orientation	391
7.2	Extrusion Processes	393
7.2.1	Fibers	393
7.2.1.1	Melt-Blown Fibers	393
7.2.1.2	Spunbonded Fabric	395
7.2.1.3	Conventional Fine Denier PP Fibers	397
7.2.1.4	Continuous Filament Fibers	398
7.2.1.5	Bulked Continuous Filament	399
7.2.1.6	Staple Fibers	401
7.2.1.7	Monofilaments	402
7.2.1.8	Slit Tape	403
7.2.1.9	Strapping	404
7.2.1.10	Decorative Ribbon	405
7.2.2	Oriented Films	405
7.2.2.1	Tubular Biaxially Oriented Film	405
7.2.2.2	Tentered Biaxially Oriented Film	407
7.2.2.3	Polymer Selection	409
7.2.3	Unoriented Products	409
7.2.3.1	Chill Roll Cast Film	409
7.2.3.2	Water-Quenched Blown Film	412
7.2.3.3	Air-Quenched Blown Film	413
7.2.3.4	Sheet	414
7.2.3.5	Extrusion Coating	417
7.2.3.6	Other Extrusion Operations	418
7.3	Injection Molding	422
7.3.1	Product Design	423
7.3.1.1	Mechanical Loads (Static and Impact)	424
7.3.1.2	Wall Thickness – Effect on Shrinkage	424
7.3.1.3	Ribs	425
7.3.1.4	Radii	426
7.3.1.5	Draft Angles	426
7.3.1.6	Undercuts	427
7.3.1.7	Living Hinges	427
7.3.1.8	Bosses	427
7.3.1.9	Holes	428
7.3.2	Mold Design	429
7.3.2.1	Gate Design	430
7.3.2.2	Gate Location	432
7.3.2.3	Vent Location	432
7.3.2.4	Cooling Requirements	433
7.3.2.5	Ejection System Requirements	433

7.3.2.6	Multicavity Mold Design	434
7.3.3	Molding Cycle	434
7.3.3.1	Mold Fill	435
7.3.3.2	Mold Pack	435
7.3.3.3	Hold	435
7.3.3.4	Cooling	435
7.3.3.5	Screw Recovery	435
7.3.3.6	Ejection	436
7.3.3.7	Molding Process Setup and Optimization	436
7.3.3.8	Common Molding Problems	439
7.3.4	Resin Selection	441
7.3.5	Special Molding Processes	441
7.3.5.1	Thin Wall Injection Molding	441
7.3.5.2	Sequential Injection Molding	442
7.3.5.3	Co-Injection-Gas Assist Molding	443
7.3.5.4	Structural Foam Molding	443
7.4	Blow Molding	444
7.4.1	Extrusion Blow Molding	445
7.4.2	Injection Blow Molding	445
7.4.3	Injection Stretch Blow Molding	446
7.5	Other Processes	447
7.5.1	Compression Molding	447
7.5.2	Foamed Bead Molding	447
8	Regulations and Approvals	451
	<i>Patrizia Busi, Richard T. LeNoir, George J. Ouellette</i>	
8.1	Introduction	451
8.2	Hazard Communication	452
8.2.1	Material Safety Data Sheets (MSDSs)	452
8.2.2	PP and PP Copolymers	452
8.3	Chemical Registration	453
8.3.1	Toxic Substances Control Act (TSCA) – United States	454
8.3.2	European Inventory of Existing Chemical Substances (EINECS)/ European List of New Chemical Substances (ELINCS)	455
8.3.3	Domestic Substances List (DSL) and Non-Domestic Substances List (NDSL) – Canada	456
8.4	Food Contact	456
8.4.1	United States: Food and Drug Administration (FDA)	457
8.4.1.1	FDA Petitions	457
8.4.1.2	FDA Food Contact Notifications (FCN)	457
8.4.1.3	FDA Regulations for PP Homopolymers and Copolymers ..	458
8.4.1.4	Title 21, Part 177.1520 – Olefin Polymers Regulation	458
8.4.1.5	Food Types	460
8.4.2	Canada: Health and Welfare Department – Health Protection and Food Branch (HPFB)	461

8.4.3	European Union	462
8.4.3.1	PP and PP Copolymers and Additives	462
8.4.3.2	Other Components	463
8.4.3.3	Certifications for Food Contact Compliance	463
8.4.4	Japan: Japan Hygienic Olefin and Styrene Plastics Association (JHOSPA)	463
8.5	Potable Water	464
8.6	Medical Applications	465
8.7	Fire and Electrical Safety Certifications	466
8.7.1	Flammability	467
8.7.1.1	Horizontal Burn (94 HB)	467
8.7.1.2	20-mm Vertical Burn (V0, V1, V2)	467
8.7.1.3	125-mm Vertical Burn (94-5VA, 94-5VB)	468
8.7.2	Short-Term Property Evaluations	468
8.7.3	Long-Term Property Evaluations	469
8.8	Customer Specifications	470
III	Polypropylene – The Market	473
9	Polypropylene: The Market	475
	<i>N. Pasquini, P. Sgarzi</i>	
9.1	The Thermoplastics Market	475
9.2	Demand for Polypropylene	478
9.3	Polypropylene Capacity	479
9.4	Monomer Supply	481
9.5	Economics	483
9.5.1	Price Cyclicity	483
9.5.2	Inter-Polymer Competition	485
9.5.3	Main Remarks	486
IV	Polypropylene – The Business	489
10	Polypropylene – The Business	491
	<i>N. Pasquini</i>	
10.1	Introduction	491
10.2	Phase 1: 1957–1982/1983	491
10.2.1	The Early Commercialization of PP	491
10.2.2	Film and Fiber Applications	492
10.2.3	Injection Molding Applications	495
10.2.4	Downstream Integration	496
10.3	Phase 2: 1982/1983–2004	498
10.3.1	The New Technologies	498

10.3.2	Expanded Product Property Profile	498
10.3.3	Marketing Opportunities in Packaging and Consumer Segments	501
10.3.4	New Generation Copolymer Resins	501
10.3.4.1	High Stiffness – Impact Resistance	501
10.3.4.2	High Fluidity Resins	502
10.3.4.3	Clyrell: High Clarity Super-Tough Resins	503
10.3.5	Marketing Opportunities in the Textile Segment	505
10.3.5.1	New Generation of Homopolymer Resins	505
10.3.6	Catalloy: A Revolutionary Process for Advanced Products	507
10.3.7	The Marketing Era and PP Growth	509
10.3.7.1	Value Selling	509
10.3.7.2	Market Segmentation	510
10.3.7.3	Inter-Polymer Competition	511
10.3.7.4	Innovation Through Technology Push	513
	Invention and commercial phase	513
10.4	Applications	517
<i>Charles G. Oertel, T. Zwygers, P. Sgarzi</i>		
10.4.1	The Evolution	517
10.4.2	Fibers	518
10.4.2.1	Carpets	518
10.4.2.2	Slit Tape	519
10.4.2.3	Nonwoven Fabrics	521
10.4.2.4	Apparel	524
10.4.2.5	Cordage	525
10.4.2.6	Netting	526
10.4.3	Injection Molded Consumer Products	526
10.4.3.1	Appliances	526
10.4.3.2	General Consumer Products	528
10.4.3.3	Medical Applications	531
10.4.3.4	Rigid Packaging	533
10.4.4	Industrial Applications	537
10.4.5	Transportation	538
10.4.5.1	Interior Uses	538
10.4.5.2	Exterior Uses	540
10.4.5.3	Under the Hood	542
10.4.6	Film	542
10.4.6.1	Biaxially Oriented Film	543
10.4.6.2	Unoriented Film	545
10.4.7	Miscellaneous Applications	546
10.5	The Future	549
<i>N. Pasquini</i>		
10.5.1	The Challenge for the Polypropylene Industry	549
10.5.1.1	PP's Future in a Global Environment	549
10.5.1.2	The PP Supplier Profile	557

10.5.1.3	Price Cyclicity	557
10.5.2	Strategies for the Future	560
10.5.2.1	Resilient and Effective Businesses	560
10.5.2.2	Progressive Strategies	561
10.5.2.3	The Suppliers	562
10.5.2.4	Innovation	564
10.5.2.5	Customer Satisfaction	565
Index		571