

Table of content

1 Introduction.....	1
1.1 Polypropylene – markets and applications.....	1
1.2 A brief description of polypropylene microstructure and properties	2
1.3 Processes for the industrial production of polypropylene	4
2 Literature and scientific background	11
2.1 Catalysts for the polymerization of propylene.....	11
2.1.1 Ziegler-Natta catalysts	11
2.1.2 Metallocene catalysts.....	14
2.2 (Kinetic) Modeling of olefin polymerization with coordination catalysts.....	15
2.2.1 Multi-scale modeling approach.....	15
2.2.2 Kinetic schemes.....	16
2.2.3 Meso scale particle modeling	20
2.3 Role of hydrogen	22
2.4 Influence of prepolymerization step	24
2.5 Kinetic measurements of (coordination) polymerization reactions under gas-phase and bulk conditions	25
2.5.1 Kinetic measurements of gas-phase and slurry polymerizations	25
2.5.2 Kinetic measurements of bulk polymerizations.....	26
3 Aim of the investigations and thesis outline	30
4 Experimental investigation of the gas-phase polymerization of propylene with two different Ziegler-Natta catalysts.....	31
4.1 Experimental setup for the gas-phase polymerizations	31
4.1.1 Raw material supply and monomer purification system.....	31
4.1.2 Lab-scale polymerization reactor	32
4.1.3 Measuring principle and control units	33
4.1.4 Data acquisition system	34
4.2 Catalysts and chemicals – handling and preparation	35
4.3 Polymerization procedures	36
4.3.1 General reactor preparation	36

4.3.2	Polymerization without prepolymerization step.....	36
4.3.3	Polymerization with prepolymerization step	37
4.4	Reaction conditions and experimental plan	38
4.5	Analytical methods.....	39
4.5.1	Melt mass flow rate	39
4.5.2	Crystallinity	40
4.5.3	Porosity.....	40
4.5.4	Bulk density	40
4.5.5	Particle size distribution	41
4.5.6	Scanning electron microscopy	41
4.5.7	Sorption measurements	41
4.6	Results kinetic measurements of the gas-phase polymerization with two different Ziegler-Natta catalysts	42
4.6.1	Gained experimental data and calculation of activities	42
4.6.2	Test of reproducibility	43
4.6.3	Equilibrium monomer concentration in the polymer particle	44
4.6.4	Results catalyst A - Influence of the reaction conditions on catalyst activity	45
4.6.5	Results catalyst B - Comparison of Ziegler-Natta catalysts of different activity.....	53
4.6.6	Results polymer characterization	58
4.7	Summary experimental investigation of the gas-phase polymerization of propylene with two different Ziegler-Natta catalyst	68
5	Kinetic modeling of the gas-phase polymerization with two different Ziegler-Natta catalysts	71
5.1	Derivation of the kinetic model	71
5.1.1	Model assumptions	71
5.1.2	Derivation of the kinetic scheme	72
5.1.3	Influence of catalyst injection conditions – effect of prepolymerization	76
5.1.4	Final kinetic scheme	78
5.1.5	Mass balances of the reaction components	79
5.1.6	Particle growth and particle heat balance.....	81

5.1.7	Determination of average molecular weights using the method of moments	85
5.1.8	Calculation of equilibrium monomer concentration in the polymer particle	87
5.1.9	Model implementation and parameter estimation	88
5.2	Results kinetic modeling of the gas-phase polymerization with Ziegler-Natta catalysts	90
5.2.1	Results parameter estimation	90
5.2.2	Comparison simulated and experimentally derived data – ZN catalyst B	91
5.2.3	Comparison of simulated and experimental data – ZN catalyst A.....	96
5.3	Summary kinetic modeling of the gas-phase polymerization of propylene with Ziegler-Natta catalysts	98
6	Experimental investigation of the bulk polymerization of propylene with a supported metallocene catalyst.....	100
6.1	Scope and outline	100
6.2	Experimental setup for the bulk polymerizations	100
6.2.1	Improved raw material purification	101
6.2.2	Propylene and hydrogen feeding	102
6.2.3	Reaction calorimeter	102
6.2.4	Measuring principle.....	103
6.3	Chemicals.....	104
6.4	Polymerization procedures	105
6.4.1	General reaction preparations.....	105
6.4.2	Polymerization with in-situ prepolymerization.....	106
6.4.3	Polymerization with external prepolymerization.....	106
6.5	Reaction conditions and experimental plan.....	108
6.6	Analytics	109
6.7	Gained experimental data and calculation of activities.....	109
6.7.1	Heat flow measurements	109
6.7.2	Calculation of activity	110
6.7.3	Validation calorimetric measurements.....	111
6.7.4	Reproducibility	111

6.8	Results kinetic measurements of the bulk polymerization with a supported metallocene catalyst	112
6.8.1	Comparison of both polymerization procedures	112
6.8.2	Influence of the degree of prepolymerization on the catalyst activity	114
6.8.3	Results kinetic measurements	115
6.8.4	Results analytical measurements.....	119
6.9	Summary experimental investigation of the bulk polymerization of propylene with a supported metallocene catalyst.....	123
7	Kinetic modeling of the bulk polymerization with a supported metallocene catalyst	125
7.1	Derivation of the kinetic model for the bulk polymerization	125
7.1.1	Model assumptions	125
7.1.2	Kinetic scheme	125
7.1.3	Derivation of mass balances	126
7.1.4	Determination of the monomer concentration in the polymer particle	128
7.1.5	Determination of hydrogen concentration in liquid phase	131
7.2	Results kinetic modeling of the bulk polymerization with metallocene catalyst	132
7.2.1	Model implementation and parameter estimation	133
7.2.2	Results parameter estimation	134
7.2.3	Comparison of simulated and experimental data	135
7.3	Summary kinetic modeling of the bulk polymerization with a supported metallocene catalyst	138
8	Summary of the work	140
9	Appendix	143
9.1	Gas-phase polymerization of propylene with different Ziegler-Natta catalysts.....	143
9.1.1	Experimental results gas-phase polymerization of propylene with Ziegler-Natta catalysts A and B.....	143
9.1.2	Overview polymer characterization	144
9.1.3	Prepolymerization experiment.....	146
9.2	Bulk polymerization of propylene with a supported metallocene catalyst	147
9.2.1	Results bulk polymerization and polymer characterization	147

9.2.2 Derivation of moment equations for the calculation of average molecular weights for the bulk polymerization with metallocene catalyst.....	148
References.....	149