

Mass Transport and Kinetic Phenomena in Catalytic Polymerization of Olefins

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All models are wrong, but some are useful

George E.P. Box

Preface

More than four years of work is being finished by these lines. It is a strange feeling to end the work that has been with me every day and many nights for such a long period. A relief in one way, but also a little sad.

The reason why I choose to work with the topic that you find in this thesis is somewhat incidental. I was working with my diploma thesis when Bjørn Hafskold, my excellent supervisor at that time, came to me and said that a position as a graduate student was announced in the polymer reaction engineering field. Because I wanted to turn more practical compared to my basic studies at the Department of Physical Chemistry, I applied and luckily got the position. As I started out I did not know exactly what it would involve. The problems have more or less been formulated as I progressed. A nice way of freedom on one side, but also sometimes frustrating not knowing where to go. Anyway, when looking back at the time I have spent working in this field, I feel it has given me a lot. I have had the chance to work in many different fields and with quite different topics in this project, which has given me a wide practice in the polymer reaction engineering field. However, the main experience I will bring with me is probably the way of solving problems: There is never a real short cut, the fastest is always to be thorough the first time; all problems are more complex as you go deeper and deeper; and you have to limit your work to finish in time. I will bring this experience with me in future projects.

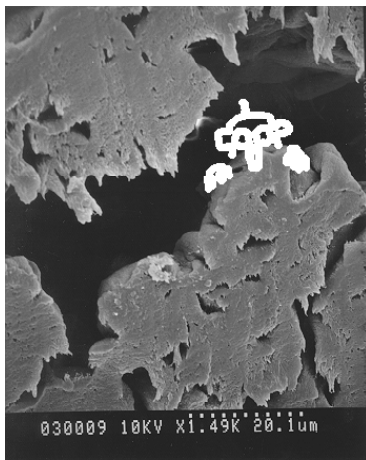
Finally I hope you as the reader of this thesis find something worth reading. I have struggled to make the models presented in this thesis more useful than wrong. Hope you agree!

Acknowledgements

I would like to express my deepest gratitude to my supervisor Hallvard Svendsen for his clear and trustworthy advice during the work with this thesis. Despite his deep engagement in many other projects, he always found time for discussions and commenting of this work.

Many thankful thoughts are sent to Tim McKenna, with whom I spent six months of this period working in Lyon, France. McKenna is a direct, critical and enthusiastic person to

cooperate with, and this work would be very different without the contact I have had with him. More than 130 e-mails the last one and a half year speaks for itself! McKenna went deeply into this material, which is illustrated by a figure he sent me one day:



Several people at NTNU has contributed to the product you see here. Erling Rytter, Hugo Jakobsen, Jon A. Støvneng, Rune Tøgersen and Thale Wester were all active partners in discussions and in the preparation of parts of this work, and are all appreciated highly. Also the other professors and graduate students associated with the Polymer Science program are thanked for their contribution. Thanks also to the other people in the reactor technology group and the rest of the employees at our department for valuable discussions and feedback and for making a nice working environment.

My second place of working was in Lyon, where I met a lot of nice people. In addition to McKenna I would especially like to thank Roger Spitz, Christine Martin and Virginie Mattioli for their inputs and help with this work.

My contact with the “real world” was through Borealis AS where I was lucky to cooperate with particularly Arild Follestad and Siw B. Fredriksen. They gave me many valuable inputs and directions from an industrial point of view.

I wish also to thank some people out of the professional groups. All my friends in the orienteering squad of NTNUI has meant a lot to me. Training is the best way to relax a tired brain! Merci à Michel Gueorgiou for all the nice trainings and trips during the stay in France. My closest relatives have been invaluable in this period. Erna and Odd supported me with many nice dinners and relaxed weekends. My mother and father always believed in me and have always kept me up. Finally, the greatest thank to Heidi for always being there and keeping life nice to live.

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Abstract

This thesis is in the field of polymer reaction engineering. The purpose of the work is to obtain tools which can be used to design catalytic systems for the production of polyolefins with new and better chemical and physical properties. This is achieved through an increased understanding of engineering related phenomena in the production of polyolefins. The thesis is divided into three parts according to the scale of the reactor at which the phenomena are taking place: macro-, meso- and microscale.

The first part treats macroscale phenomena, particularly gas-liquid mass transfer. Methods to evaluate the effect of gas-liquid mass transfer resistance in a reactor used for slurry polymerization is described. Propene was polymerized using a modern Ziegler-Natta catalyst dispersed in decane. The stirring rate was changed during polymerization, and the observed monomer feed rates were analyzed using methods based on steady state and dynamic mass balances to obtain mass transfer coefficients. A model of gas to liquid mass transfer in a stirred laboratory reactor is developed with the purpose to control mass transfer limitations in kinetic studies of olefin polymerizations. Renewal of the liquid surface is controlling the mass transfer. Generally, two different scales of eddies can be envisaged responsible for the renewal; at low stirring rates the mean liquid flow is the controlling mechanism, at high stirring rates small scale turbulence provides the renewal. The model predictions are compared with the experimental data. It is found that a small scale turbulence model is most appropriate, and fit the data within a factor 2, an accuracy which is good enough for many applications, e.g. when determining the necessary operating conditions for neglecting mass transfer resistance. The models are theoretically founded and are believed to be generally valid.

The second part treats mesoscale phenomena, particularly single particle mass transfer and morphology effects. Several more or less independent works are presented. The first work deals with the buildup and relaxation of elastic tensions inside growing particles during heterogeneous polymerization of olefins. Mass transfer resistance or inhomogeneous catalyst distribution can lead to spatial variation in the expansion rate of polymer which creates tension. This can cause the particle to break up. The focus is on the reciprocal interaction between morphology and mass transfer resistance, which is examined by applying the model to two cases where experimental data is available. It was found that the model predicts the formation of hollow particles under the most severe mass transfer

limitations, in accordance with what is found experimentally.

Another work concerns a study of the effect of changing the polymer particle morphology on the mass transfer properties in it. High impact modified polypropene was made by copolymerization of ethene and propene, making ethene-propene-rubber (EPR). It was found that above a critical copolymer content at approximately 40 wt%, it was impossible to obtain high reaction rates. This is thought to be due to a fundamental change in particle morphology and mass transfer properties due to the presence of a soft EPR copolymer phase in the micropores.

The introduction of a meso particle scale can be important in the description of mass transfer effects in the heterogeneous polymerization of olefins. E.g. the morphology-activity study referred to above, shows the presence of the described morphological level, with size on the order of some tenths of the size of the whole particle. Using traditional models, with only mass transfer effects at the macro- and microscales, gives conflicting results, as the mass transfer resistance at the mesolevel becomes significant. A new model to account for these effects is shown.

The last topic in the mesoscale part of this thesis, is a study of the effect of including convection inside growing polymer particles. Direct application of the complete mass flux equation leads to an expression that includes both molar diffusion and a molar average velocity. In cases where a highly reactive species is present in a concentrated state and is polymerized with a less reactive comonomer, this second monomer can be entrained by the convective currents and accumulate inside the particle. In a similar fashion, convective currents can also lead to the accumulation of an inert species inside the particles.

The final part concerns chemical kinetics, which are classified to be at the microscale of the reactor. Different methods for modeling kinetics are reviewed. Examples, ranging from a basic kinetic scheme to more realistic schemes, are used to demonstrate some of the methods: the use of pseudo components; the Monte Carlo method; and the continuous variable transformation method. The focus is more on the methods than the chemistry itself. It is shown that different objectives require different methods, and particularly that single site catalysts can produce nonideal MWD if the properties of the chemical reactions vary with time.

Polymer reaction engineering covers a very large field, and just a few of the problems present in a real industrial system have been examined in this thesis. All parts of this work are basically about tools for describing, optimizing and designing catalytic processes at different scales of the reactor, and important improvements have been achieved. In the field of gas-liquid mass transfer and chemical kinetics, this work has mainly shown the use of existing methods and models with small modifications. However, in the field of mass transport effects at the polymer particle level, significant improved understanding of the phenomena occurring has been obtained. This knowledge can be used for designing new catalytic systems for olefin polymerization where the benefit is better control of the polymer properties, which in turn, means new materials with improved physical and chemical properties.

Contents

Preface	iii
Abstract	v
Contents	vii
Symbols	xi
1 Introduction	1
1.1 Background	1
1.1.1 Polymers and the polymer industry	1
1.1.2 Polyolefin processes	3
1.1.3 Catalysts for polymerization of olefins	4
1.1.4 The role of polymer reaction engineering	6
1.2 Purpose	8
1.2.1 The framework of this work	8
1.2.2 Problem formulation	8
1.3 Organization of the thesis	9
I Gas-liquid mass transfer	11
2 Determination of gas-liquid mass transfer limitations	13
2.1 Introduction	13
2.2 Experimental section	15
2.3 Methods to determine the mass transfer factor	15
2.3.1 Mass balance	15
2.3.2 Steady-state method	18
2.3.3 Dynamic method	19
2.4 Results and discussion	21
2.4.1 Discussion of the methods	21
2.4.2 Kinetics of the system	21
2.4.3 Effect of stirring rate	23
2.4.4 Effect of nonideal mixing	25

2.4.5	Effects of baffles and sparging	31
2.5	Conclusions	32
2.6	Nonideal reactor models	33
2.6.1	Models	33
2.6.2	Parameter values	33
3	Modeling of gas-liquid mass transfer limitations	35
3.1	Introduction	35
3.2	Models	37
3.2.1	Contact area	37
3.2.2	Mean-flow dominated mass transfer	39
3.2.3	Small-scale turbulence-dominated mass transfer	40
3.2.4	Turbulent Reynolds number and the controlling mechanism for mass transfer	42
3.3	Results and discussion	43
3.3.1	Parameter values	43
3.3.2	Model and prediction chart for the propene-decane system	44
3.3.3	Discussion of the models	46
3.4	Conclusions	49
II	Singel particle effects	51
4	Modeling of growth-induced tension in a polymer particle	53
4.1	Introduction	53
4.2	Model	55
4.2.1	Microparticle mass balance and growth	56
4.2.2	Macroparticle mass balance and growth	56
4.2.3	Tension in a growing particle	59
4.3	Results and discussion	65
4.3.1	Cases and conditions	65
4.3.2	The effect of activity on morphology and polymer properties	65
4.3.3	How to use the model to obtain desired morphology	75
4.4	Conclusions	75
5	The effect of particle morphology on mass transfer properties	77
5.1	Introduction	77
5.2	Experimental	79
5.2.1	Chemicals	79
5.2.2	Reactor system	80
5.2.3	Procedure for the production of high impact PP	80
5.2.4	Determination of copolymerization equilibrium composition	82
5.2.5	Calculation of reaction rate	84

5.2.6	Evaluation of particle morphology	86
5.3	Results and discussion	87
5.3.1	Morphology	89
5.3.2	Polymerization activity	98
5.3.3	Modeling of the influence of morphology on observed reaction kinetics	104
5.4	Conclusions	109
5.5	List of experiments	110
6	Three-level particle model	113
6.1	Introduction	113
6.2	Three-level particle model	115
6.2.1	Basic assumptions	115
6.2.2	The model equations	116
6.2.3	Solving the set of equations	120
6.3	Simulations and discussion	121
6.3.1	Base case	121
6.3.2	Equivalent diffusivity	122
6.3.3	The path of monomer transport	124
6.3.4	The importance of the mesolevel	126
6.4	Conclusions	128
7	Intra-particle convection effects	129
7.1	Introduction	129
7.2	Mass transfer with convection	131
7.3	Simulations and discussion	132
7.3.1	Conditions	132
7.3.2	Assumptions	133
7.3.3	Simulations	135
7.4	Conclusions	141
III	Polymerization kinetics	143
8	Modeling of catalyzed olefin polymerization kinetics	145
8.1	Introduction	145
8.2	Basic kinetic scheme	148
8.2.1	Reaction scheme and mass balances	149
8.2.2	Obtaining the reaction rate	150
8.2.3	Obtaining the molecular weight distribution	152
8.3	Example I. Modeling of polymerization rate	155
8.3.1	Reaction scheme and mass balances	155
8.3.2	Results and conclusions	157
8.4	Example II. Modeling of MWD using the Monte Carlo method	160

8.4.1	The principles of the Monte Carlo method	160
8.4.2	The reaction scheme	161
8.4.3	Results and conclusions	161
8.5	Example III. Modeling of MWD using continuous variable transformation .	164
8.5.1	Reaction scheme	165
8.5.2	The continuous variable transformation method	167
8.5.3	Results and conclusions	168

Conclusions	171
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Bibliography	177
---------------------	------------

Symbols

Abbreviations

Abbrev.	Meaning
CCD	chemical composition distribution
DMA	dimethylaluminum
EOS	equation of state
EPR	ethene-propene-rubber
GC	gas chromatograph
GPC	gel permeation chromatograph
HDPE	high density polyethene
hiPP	high impact resistance polypropene
LCB	long chain branching
LDPE	low density polyethene
LLDPE	linear low density polyethene
MAO	methylaluminumoxane
MGM	multigrain model
MWD	molecular weight distribution
NMR	nuclear magnetic resonance
NTNU	Norwegian University of Science and Technology
NTNUI	Norges teknisk-naturvitenskaplige universitets idrettsforening
ODE	ordinary differential equation
PDI	polydispersity index
PE	polyethene
PFM	polymer flow model
PP	polypropene
QSSA	quasi steady state assumption
rpm	rotations per minute
SEM	scanning electron microscopy
SINTEF	The Foundation for Scientific and Industrial Research at the Norwegian Institute of Technology
SRK-EOS	Soave-Redlich-Kwong equation of state
TEM	transmission electron microscopy
TMA	trimethylaluminum

Lowercase Latin symbols

Symb.	Meaning	Unit
a	activity	$\text{kg}_{\text{pol}}/\text{g}_{\text{cat}}/\text{h}$
c	total molar concentration of molecules	mol/m^3
c_{mf}	constant in mean flow model	
c_i	concentration of component i	mol/m^3
d	reactor diameter	m
d_i	impeller diameter	m
d_r	reactor diameter	m
g	gravity constant	$9.81 \text{ m}/\text{s}^2$
h	liquid height	m
h	vortex height	m
k_{bd}	bulk to dead volume mass transfer coefficient	m^3/s
k_d	deactivation rate constant	varies
k_{eq}	equilibrium constant	m^3/mol
k_G	gas side mass transfer coefficient	m/s
k_i	initiation rate constant	$\text{m}^3/\text{mol}/\text{s}$
k_l, k_{-l}	latent site reaction rate constants	1/s
k_L	liquid side mass transfer coefficient	m/s
k_p	propagation constant, mole catalyst basis	$\text{m}^3/\text{mol}/\text{s}$
k_p^ρ	propagation constant, mass catalyst basis	$(\text{m}^3/\text{mol})^n \text{mol}/\text{kg}/\text{s}$
k_p^V	propagation constant, volume basis	1/s
k_{p0}^ρ	propagation constant at $t = 0$	$(\text{m}^3/\text{mol})^n \text{mol}/\text{kg}/\text{s}$
k_{pd}^ρ	deactivation term in propagation constant	$(\text{m}^3/\text{mol})^n \text{mol}/\text{kg}/\text{s}$
k_s	boundary layer mass transfer coefficient	m/s
k_t	termination rate constant	varies
k_{tM}	termination with monomer rate constant	$\text{m}^3/\text{mol}/\text{s}$
k_{tT}	termination with TMA rate constant	$\text{m}^3/\text{mol}/\text{s}$
l_k	Kolmogorov eddy length scale	m
l_m	macro eddy length scale	m
m_c	mass of one microparticle	kg
n	monomer reaction order	
n	number of species in the system	
n_s	number of saturated end groups	
n_u	number of unsaturated end groups	
p	pressure tensor	N/m^2
p_i	number of microparticles in shell i	
p_i	probability for incident i	
q	polydispersity index	

r	radial position in reactor/microparticle	m
r_{C_4}	relative rate of propagation of C_2 to C_4	
r_0	inner radius of a hollow particle	m
t	time	s
t_k	Kolmogorov eddy time scale	s
t_m	macro eddy time scale	s
t_p	time to peak activity	s
v^*	molar averaged velocity	m/s
v_i	average velocity of component i	m/s
v_k	Kolmogorov eddy velocity scale	m/s
v_m	macro eddy velocity scale	m/s
v_r	radial velocity	m/s
w	weight chain length distribution	
w_{skin}	width of skin	
w_i	impeller width	m
x	constant	
x_i	mole fraction of component i	

Uppercase Latin symbols

Symb.	Meaning	Unit
A	surface area	m^2
A	total gas-liquid interface area	m^2
A_r	surface area of rippled surface	m^2
A_v	surface area of vortex	m^2
C	concentration of empty, active cat. sites	mol/m^3
C	constant	
C_0	initial concentration of cat. sites	mol/m^3
C_d	concentration of empty, deactivated cat. sites	mol/m^3
D	concentration of dead polymer chains	mol/m^3
D	diffusion coefficient	m^2/s
D_{ij}	diffusion coefficient of the i - j pair in a multicom. mixture	m^2/s
D_{ij}	diffusion coefficient of the i - j pair in a binary mixture	
D_i	concentration of dead polymer chain with i monomer units	mol/m^3
D_m	effective diffusivity in meso "phase"	m^2/s
D_M^g	effective global diffusivity in macro "phase"	m^2/s
D_m^g	effective global diffusivity in meso "phase"	m^2/s
D_μ	diffusion coefficient in microparticle (i.e. in polymer)	m^2/s
E	Young's modulus	N/m^2
E'	Modified Young's modulus = $E/(3(1 - \nu))s$	$N \text{ s} /m^2$
E_q	activation energy	J/mol
E_z	dispersion coefficient	m^2/s
F	monomer feed rate over gas-liquid interface	mol/s
F_{Mm}	volum. rate of monomer transf. from macro to meso "phase"	$\text{mol}/m^3/s$
F_0	monomer feed rate at $M = M_0$	mol/s
F_i	steady state monomer feed rate at N_i	mol/s
G	Lamé's elastic coefficient	N/m^2
G	mass of catalyst	kg
J_i^*	diffusive flux	$\text{mol}/m^2/s$
L	concentration of latent sites	mol/m^3
M	monomer concentration	mol/m^3
M_0	equilibrium monomer concentration	mol/m^3
M_m	monomer concentration in meso "phase"	mol/m^3
M_M	monomer concentration in macro "phase"	mol/m^3
M_n	number averaged molecular weight	kg/mol
M_w	mass averaged molecular weight	kg/mol
N	stirring rate	rpm and s^{-1}
N_i	molar flux of component i	
N_n	number average number of monomer units per chain	
N_w	weight average number of monomer units per chain	

P	concentration of living polymer chains	mol/m ³
P	power input from agitation	J/s
P	pressure	bar = 10 ⁵ N/m ²
P	productivity	kg/g or kg/kg
P_i	conc. of living polymer chain with i monomer units	mol/m ³
P_i	partial pressure of component i	N/m ²
R	gas constant	J/mol/K
R	inner radius of reactor	m
R	radial position in polymer particle	
R	reaction rate	mol/s and g/h
R_0	catalyst initial radius	m
R_0	intrinsic reaction rate	g/h
R_c	catalyst fragment radius	m
R_i	volumetric reaction rate of component i	mol/m ³ /s
R_m	mesoparticle radius	m
R_M	macroparticle radius	m
R_p	reaction rate per microparticle	mol/s
R_μ	microparticle radius	m
R_ρ	reaction rate per mass of catalyst	mol/kg/s
Re	impeller Reynolds number, = Nd_i^2/ν	
Re_t	turbulent Reynolds number = $l_m v_m/\nu$	
Sc	Schmidt number, = ν/D	
Sh	Sherwood number, = $k_L d_r/D$	
T	temperature	K and °C
U	displacement function	m
V	liquid/polymer/catalyst volume	m ³

Greek symbols

Symb.	Meaning	Unit
α	slope	1/s
β	mass transfer factor = $k_L A$	m^3/s
ϵ	local energy dissipation	J/kg/s
ϵ	porosity	
$\bar{\epsilon}$	average energy dissipation	J/kg/s
ϵ_i	strain in direction i	
ϵ_m	mesoparticle porosity	
ϵ_M	macroparticle porosity	
η	effectiveness factor	
η_i	effectiveness factor at level i	
γ	constant	m^2/s
γ	mass fraction cat. in bulk volume	
λ	Lamé's elastic coefficient	N/m^2
λ_i	time constant	1/s
Λ_f	Eulerian integral scale	m
μ	viscosity	$\text{kg}/\text{m}/\text{s}$
ν	kinematic viscosity	m^2/s
ν	Poisson's ratio	
ν	reduced tension = τ/E'	1/s
ϕ	Thiele modulus	
Φ	expansion factor	
ρ	liquid density	kg/m^3
ρ_c	catalyst density	kg/m^3
ρ_p	density of polymer	kg/m^3
σ	surface tension	kg/s^2
σ	total stress tensor	N/m^2
τ	tortuosity	
τ_i	stress in direction i	N/m^2
τ_M	macroparticle tortuosity	
τ_m	mesoparticle tortuosity	
θ	growth factor microparticle	
ξ	volume fraction bulk volume	

Chapter 1

Introduction

1.1 Background

1.1.1 Polymers and the polymer industry

Polymers are materials characterized by large molecules which are multiples of simpler units, monomers. Both natural and synthetic polymers exist. Examples of natural polymers are hair, sugar and wood. However, this thesis will focus on polyolefins, a synthetic polymer.

Synthetic polymers are grouped according to the monomers from which they are formed. Examples of groups are polyamides, polyesters and polyurethanes which all have a heterochain backbone (different types of atoms forming the main chain), whereas acrylic polymers, fluorinated polymers and polyolefins all have a pure carbon backbone. This hierarchy of materials is illustrated in Figure 1.1.

The production of polyolefins is the concern of this thesis. Polyolefins means in practice the polymers of ethene (polyethene, PE) and propene (polypropene, PP) together with some modifications of the two, achieved by incorporating comonomers such as e.g. hexene. Polyolefins are by far the most important industrial polymer, and is the most widely produced plastic material worldwide, with an annual production of 85–95 million tonnes. This distributes into 50–60 million tonnes of PE and 35 million tonnes of PP (based on production data for 1999 and 2000 [59]). According to the statistics of Association of Plastic Manufactures in Europe (APME), about 60% of the thermoplastics are polyolefins [38]. To get a more tractable number, the annual consumption of polyolefins per inhabitant in Norway was about 35 kg in 1998. Thus, the market for polyolefins is enormous, and is still increasing, with an annual growth rate of about 4–5% [59, 74].

The reason for the popularity of polyolefins is their large variety in properties. By varying

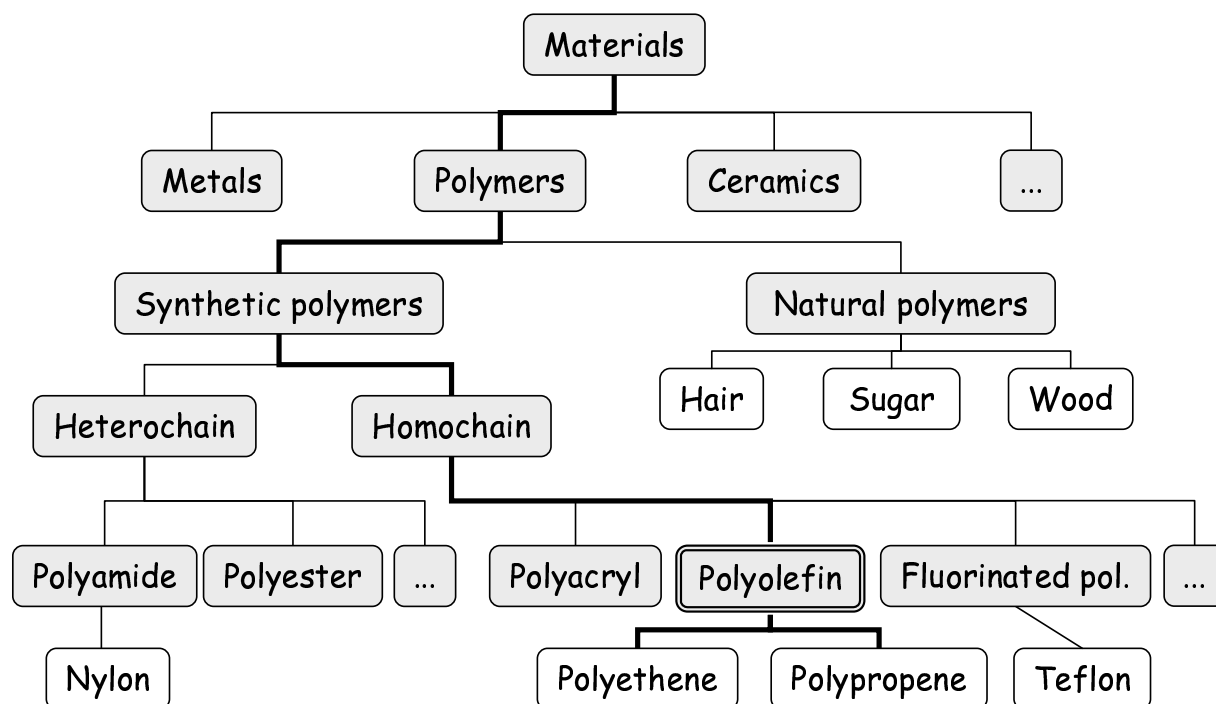


Figure 1.1: The position of polyolefins in the material hierarchy.

the chain length, the chain length distribution and the branches of the backbone, the properties of the polymer material can be tailor-made for a lot of products. Changing from polyethene to polypropene gives generally a stiffer material with higher melting point, but more sensitive to oxidation [37]. Polyolefins consist only of carbon and hydrogen atoms and are therefore harmless to humans, and only CO₂ and water are emitted by proper combustion. Another important property is the relative ease in shaping the product and to recycle it, since the olefins melt at moderate temperatures (110-180°C [37]). Many products are therefore made by molding. The products made from polyolefins are countless. According to APME the major uses of thermoplastics (polyolefins included) were packing (41%) and building/construction materials (19%). Some examples of specific products of polyolefins are listed in Table 1.1.

The raw material for polyolefins, olefinic monomers, are made from natural gas or low molecular weight constituents of petroleum. By cracking these compounds, the olefins with their “heart”, the double bond, are formed. Norway, with its rich resources in oil and gas from the North Sea, is therefore well suited for a plastic industry. Borealis AS is one of Europe’s largest polyolefin producers¹ and has a strong position in the Nordic countries.

¹Borealis is 50% owned by the Norwegian oil company Statoil, 25% by the Austrian oil and gas company OMV, and 25% by the International Petroleum Investment Company (IPIC) of Abu Dhabi. Borealis is the second largest polyolefin producer in Europe based on Borealis’ own data from 1998 [39] and the fact that Basell, a merger of Montell, Elenac and Targor in October 2000, is now the largest in Europe and

Table 1.1: Examples of products from polyolefins. From APME [38]

Type of polyolefin	Products
High density polyethene (HDPE)	Containers, toys, housewares, industrial wrappings and film, gas pipes
Low density polyethene (LDPE)	Pallet and agricultural film, bags, toys, coatings, containers, pipes
Polypropylene (PP)	Film, battery cases, microwave-proof containers, crates, automotive parts, electrical components

Borealis is an important contributor to the research in polyolefin area at NTNU. Borealis produced some 3 million tonnes of PE and PP in 1998, and had a turnover of 3 billion Euro in 1999 [39].

The polyolefin industry can be divided into three groups: those making the polymer from monomer; those processing the polymer into products; and those who produce the machinery for the polymer processing. It is only the first group of industry that will be focused on in this thesis.

1.1.2 Polyolefin processes

Mainly, four different processes exist for producing polyolefins: radical polymerization (only ethene); solution catalyzed processes; gas phase catalyzed processes; and slurry phase catalyzed processes.

Radical polymerization is done at high temperature (150–300°C) and at high pressure (1500–3500 bar) [33]. Chains are formed by chain reactions where radicals provide the chain propagation. Radical initiators are continuously fed to the reactor to keep up the reaction. Because the radicals do not only react with monomer, but also with terminated chains, there is a high probability of forming long chain branching in this process. Low density polyethene (LDPE) is made this way. If polypropene is made with this process, it will be atactic (random orientation of the methyl group), and the polymer will be useless from an industrial point of view.

In solution processes the polymer goes directly into solution. The catalyst can be soluble or solid. This type of processes are not as common as those utilizing heterogeneous catalysts where the polymer is deposited on the solid catalyst. However, some systems for producing ethene-propene and ethene-propene-dimer polymers (rubbers) are normally run in solution [34]. Solution systems are also often used in laboratory scale processes for the development of new catalyst systems. In particular, the new metallocene systems are more

one of the dominating ones in the world.

easily used in solution.

Gas phase processes are normally run in fluidized-bed reactors, but dry stirred tanks are also used. The normal temperature range for these processes is 70–100°C, and the pressure range is 5–40 bar [33]. The catalyst is supported on a carrier to form solid polymer particles that are suitable for fluidization.

Slurry processes can take on several different forms. The reactors used are stirred tanks (autoclaves) and loop reactors. The continuous fluid phase in this process can either be an inert hydrocarbon component such as e.g. isobutane, or, as in the case of propene polymerization, a liquid propene monomer². Normal operating conditions in the autoclaves are 5–20 bar and 60–90°C. A somewhat higher temperature and pressure are used in the loop reactors. When using liquid propene as the diluent, the pressure is normally 30–40 bar and the temperature about 70°C [33]. In these processes the polymer is deposited on solid catalyst particles.

The trend in the polyolefin industry today is to utilize several reactors in the same process in order to combine the properties of polymers made at different conditions by blending different polymers grades at the molecular level. In such plants it is quite common to combine several of the processes described above. Examples of such processes are the Basell's Spheripol process [33] and Borealis' Borstar process [39], both of which consist of one or more slurry loop reactors followed by one or more fluidized-bed reactors. Another new concept presented by Galli [31] and Covezzi and Mei [10] is Basell's "MultiZone Circulating Reactor Technology". The reactor is a riser-downer reactor, a sort of gas phase loop reactor, with zones where different conditions prevail. A polymer/catalyst particle will circulate in this loop and make polymer under rapidly alternating conditions. This means that a true mixing of properties on the molecular level is achieved. Such technologies theoretically expand the property and performance envelope of the polymer.

1.1.3 Catalysts for polymerization of olefins

We are now down to the core of the polymerization, the catalyst. Using catalysts for producing polyolefins allows high reactivity combined with milder reaction conditions compared to the extreme conditions used in for instance radical polymerization. Catalysts also improve the control of the stereochemistry of the polymer. Three major groups of catalysts are used for commercial olefin polymerization: the Ziegler-Natta catalysts; the metallocene catalysts; and the Phillips catalyst. Their common property is that a transition metal atom acts as the catalytic center. It is believed that the double bond of the monomer is coordinated by one free ligand of the transition metal before reacting with the

²This is understood on the basis of the thermodynamic properties of propene and ethene. Their critical temperatures and pressures are: 9°C and 50 bar for ethene; and 92°C and 46 bar for propene [65]. Thus at normal reaction temperatures (60–90°C), it is possible to operate with propene as a liquid, but pure ethene will always stay in a gas/supercritical fluid state.

growing chain which is bound to another ligand of the metal.

The first catalytic route to make polyethene was discovered by Hogan and Bank at Phillips Petroleum Company in the early fifties [7]. These type of catalyst are called Phillips catalysts, and are based on chromium oxide. These catalysts are only used for polyethene production. The difference from Ziegler-Natta catalysts, apart from the metal atom, is that Phillips catalysts do not contain an alkylmetal. About 20% of all polyethene (including radical processes) is made by Phillips catalysts [59].

A somewhat milder catalytic route (lower pressure and temperature necessary) was discovered Karl Ziegler, actually by accident³. Because Karl Ziegler's laboratory assistant did not clean the reactor properly (some traces of nickel were left), Ziegler discovered that his aluminium compound was able to polymerize ethene at low pressure and temperature [91]. This happened in 1953. The year after, Giulio Natta modified the same kind of catalyst and was able to polymerize propene to isotactic polypropene. Ziegler and Natta shared the Nobel price in chemistry in 1963 for these achievements and this type of catalyst was named after them: the Ziegler-Natta catalyst. These catalysts consist of a transition metal salt of elements of groups IV to VIII (normally titanium) and a metal alkyl of an element of groups I to III (cocatalyst/activator).

Metallocene catalysts are organometallic coordination compounds in which one or two cyclopentadienyl rings, or substituted cyclopentadienyl rings, are bound to a central transition metal atom [34]. In addition, a cocatalyst/activator is needed and normally alkylaluminiumoxane (MAO) is used. Metallocene catalysts as we know them today, are youngsters compared to the Ziegler-Natta catalysts. In the early eighties Walter Kaminsky discovered, also by accident³, that adding small amounts of water to the metallocene/alkylaluminium mixture, considerably increased their reactivity. This was attributed to the reaction between water and alkylaluminium to form alkylaluminiumoxane. Metallocenes are very versatile catalysts. By changing the geometry of the surrounding rings of the central metal, one can control the stereochemistry in new ways compared to what is possible with Ziegler-Natta catalysts. Metallocenes have also made it possible make completely new grades of polymers, such as stereospecific polystyrene. In terms of market share, metallocenes are still quite small, although their impact is expected to increase in the next years. Tattum and Potter [74] project that 4% of all PP will be made by metallocenes by 2005.

Most catalysts need to be supported on an inert material. This will ensure an effective use of the catalyst because more sites then become available for polymerization. A particle consisting of only catalyst would have many sites in unavailable places for the monomer. The use of a support also has to do with control of the morphology of the final polymer particle, and we will come back to this in the next section. Magnesium chloride (MgCl_2) and silica (SiO_2) are the most used supports. The productivity of catalysts used in the industry today is several thousands of grams of polymer per gram of catalyst. This means that polymers made with these catalysts only contain a very small fraction of catalyst

³That's why I always try to make accidents when I'm in the lab.

residue, which without problems can be left in the polymer with no detrimental effects. The costly separation stage of catalyst residue and polymer used in the early ages of the polyolefin industry can therefore be omitted.

1.1.4 The role of polymer reaction engineering

This thesis is in the field of polymer reaction engineering, which is the link between the chemistry of the polymerization and the commercial product of polyolefins. As I see it, polymer reaction engineering is the science about the surroundings of the reaction itself, making the reaction perform optimally, analogous to the service teams you find around a formula-1-driver. It is not enough to have a perfect catalyst, you must also be able to make it work the way you want.

The process of a typical polymerization starts by the injection of a catalyst particle of 15–60 μm in diameter. The monomer contained in the continuous phase must be transported by diffusion and convection from the bulk to the boundary layer of the catalyst particle, into the pores, through a polymer layer surrounding the active sites, before it finally can take its place in the growing polymer chain. Because the polymerization is exothermic, heat must be transported the other way.

Another example of a process that can be classified as part of polymer reaction engineering, is the change of structure and size of the catalyst particle as it progresses from a virgin catalyst particle, mainly consisting of an inert support material, to become a polymer particle with diameter 10–50 times larger. In the virgin catalyst particle, polymer starts to form and fill up the pores and vacancies. When there is no more room for polymer, if the support is not too strong, it ruptures and fragments, but normally does not disintegrate as the individual fragments of the support are held together by the formed polymer. However, if the support is too strong, the pores will soon be blocked with polymer and the reaction will stop. If the support is too weak, the particle will start to break before enough polymer is made to hold the fragments together, and disintegration results. Disintegrated particles can cause large problems in the operation of the process because these smaller fragments can more easily cause fouling of the reactor and cause problems downstream of the reactor with e.g. the powder handling/separation. Thus, understanding and controlling the breakup and growth of catalyst/polymer particles is essential to make the process work properly.

Polymer reaction engineering involves phenomena at different scales. The two examples above were both on the particle level. The description of the reaction kinetics is at a smaller scale, whereas for instance the description of the fluid dynamics in the reactor is at a larger scale. Harmon Ray, one of the pioneers in polymer reaction engineering, classified the different phenomena in polyolefin processes in three scales: macro-; meso- and microscale [64]. This classification is illustrated in Figure 1.2, and general examples of phenomena at these scales are given below [59, 64]. This thesis contains descriptions and modeling of phenomena at all these three scales.

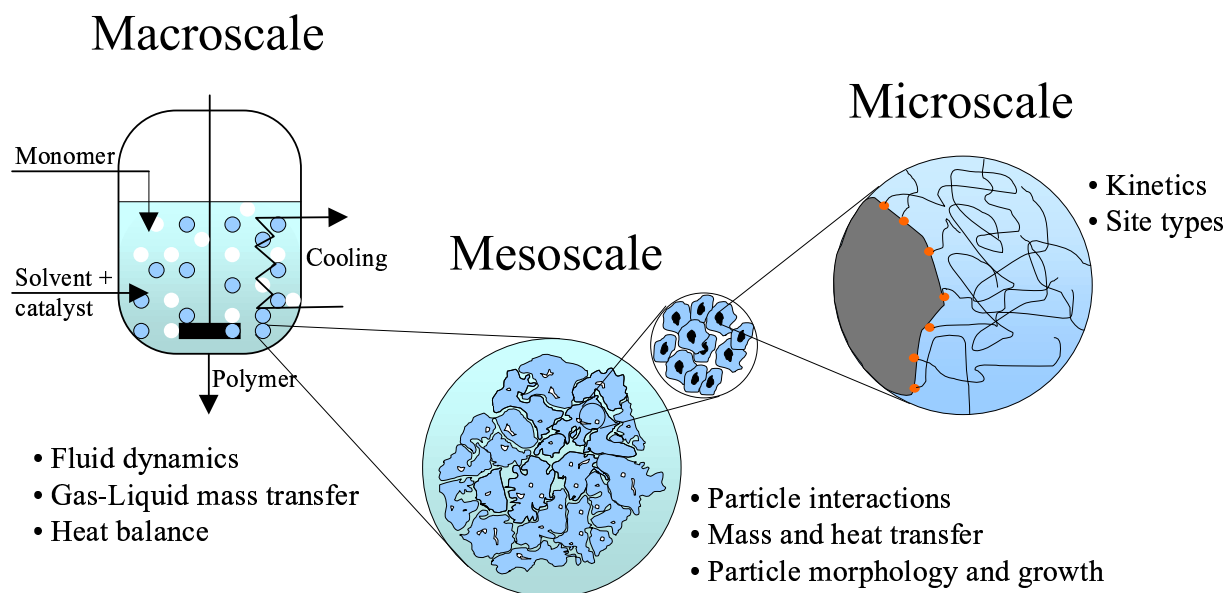


Figure 1.2: Levels of modeling polyolefin processes, based on classification by Ray [64] and a figure by Hamielec and Soares [34]. The circles in the macroscale part symbolize polymer particles and gas bubbles, the small magnification in the mesoscale frame represents catalyst fragments with surrounding polymer and the dots in the microscale frame symbolize the catalyst sites.

- **Macroscale:** Reactor fluid dynamics such as mixing properties, particle residence time distributions and entrainment, (monomer) gas-liquid mass transfer, and removal of heat.
- **Mesoscale:** Particle-particle and particle-wall interactions, particle boundary and intra-particle mass and heat transfer, particle growth and morphology development.
- **Microscale:** Reaction kinetics and nature and number of active sites. In this thesis I use the term *kinetics* for the description of the mechanisms of chemical reactions. In terms of polymerization, the kinetics describe the mechanism by which monomers are assembled to become polymer chains.

There are several benefits from a good description and understanding of the processes listed above. Ray [64], Galli [32] and Cozewith [11] list the following possible outcomes from good process models:

- The influences of reaction conditions on polymer properties can be predicted. Thus they contribute to an understanding and control of the dynamic reactor behavior.
- A good model will help to interpret observed phenomena. Chemical effects can be discriminated from physical effects.

- The model can be used to optimize the process and be a tool for scale-up, avoiding trial-and-error strategy.
- The model can be a basis for making online estimates of polymer properties.
- New processes, making polymer with new properties, can be designed. By process is meant all parts of the process, from reactor design to catalyst particle and type of active sites.

1.2 Purpose

1.2.1 The framework of this work

This thesis is a part of a Strategic University Project (SUP) on polyolefin technology at NTNU. Also SINTEF, the University of Oslo and Borealis are involved in the project. The main focus has been basic metallocene catalysis. Several other PhD projects in this field have been completed at NTNU, and others are under way. Thorshaug [78] studied the kinetics of ethene polymerization with unbridged zirconocene catalysts. The work is continued by Liu [49]. Eilertsen [18] examined the structure and role of the metallocene cocatalyst methylaluminumoxane (MAO), whereas Wigum [86] and Bruaseth [9] mainly study copolymerization reactions on different metallocenes. Other work is going on in the processing field. Tanem [73] studied the blendability of different polymers from single site catalysts and Kamfjord [42] is investigating new ways of making heterophasic PP in a post reactor process. The work closest to this thesis is the study by Seland [67], who developed an NMR method to measure the diffusion coefficients in heterogeneous polymer systems.

My role in this project has been to investigate chemical engineering aspects of the polymerization of olefins, i.e. polymer reaction engineering, particularly with metallocenes. However, we soon found out that these aspects could not be separated from polymer reaction engineering aspects of more traditional Ziegler-Natta and Phillips catalysts. Industrial metallocene catalyzed processes face the same challenges regarding heat and mass transfer, particle fragmentation, reactor mixing and so on. Thus, most of this work is general to catalyzed polyolefin processes, and the use of metallocenes as the catalyst is only one of several possibilities.

1.2.2 Problem formulation

The purpose of this work has been to obtain tools that can be used to design catalytic systems for the production of polyolefins with new and better chemical and physical properties. This is achieved through an increased understanding of different engineering related phenomena in the production of polyolefins. This thesis is especially concerned with:

- Providing methods to determine gas-liquid mass transfer limitations through experiments and through models. This topic is particularly important when doing laboratory scale reaction kinetic studies where the measured rate of monomer consumption is the measure of the reactivity. For reaction kinetic control to dominate, it is necessary (but not sufficient, because a possible resistance in the polymer particles) that the gas-liquid mass transfer rate is large enough to eliminate the gas-liquid mass transfer resistance.
- Providing increased understanding and better description of single particle mass transfer and morphology. We examine how a variation in morphology changes the mass transfer conditions, and conversely, how mass transfer resistance can change the morphology of the growing polymer particle. Further, we examine improved single particle mass transfer models, including the effects of convection and by introducing a more detailed morphology description.
- Providing an overview of methods for modeling the kinetics of catalyzed olefin polymerization. This includes showing how the methods can be used on practical examples.

1.3 Organization of the thesis

This thesis is divided into three parts according to the scale of the phenomena taking place, i.e. at the micro-, meso- and macroscales of the polymer process (see definitions above). The individual chapters are similar to journal articles in the form, but somewhat more detailed. The chapters can be read as independent work, thus the interaction effects between different phenomena have not been widely discussed. When discussing mass transfer and morphology phenomena at the single particle level, the reaction kinetics are kept simple, and when treating reaction kinetics, the effects of mass transfer resistance are not important. In this way the primary effects of the studied phenomena are clearly demonstrated, the possible interaction effects with other phenomena are left out. This was done because it gives a simpler approach, where the main effect of a phenomenon comes clearly visible. However, in practice the different phenomena will for sure interact under certain circumstances. E.g. when there is significant mass transfer resistance at the catalyst particle level, the catalyst sites will “see” different concentrations of the reactive species, which of course influences the reaction kinetics.

You will find a wide spread in processes and catalyst used in this thesis. Often, experimental results as parts of other projects were used in this thesis, in which they were analysed for chemical engineering phenomena. In this way, the discussions are founded on real problems plus it is an economical way of working. On the other hand, some of the experiments could have been differently designed to reveal more of the phenomena investigated.

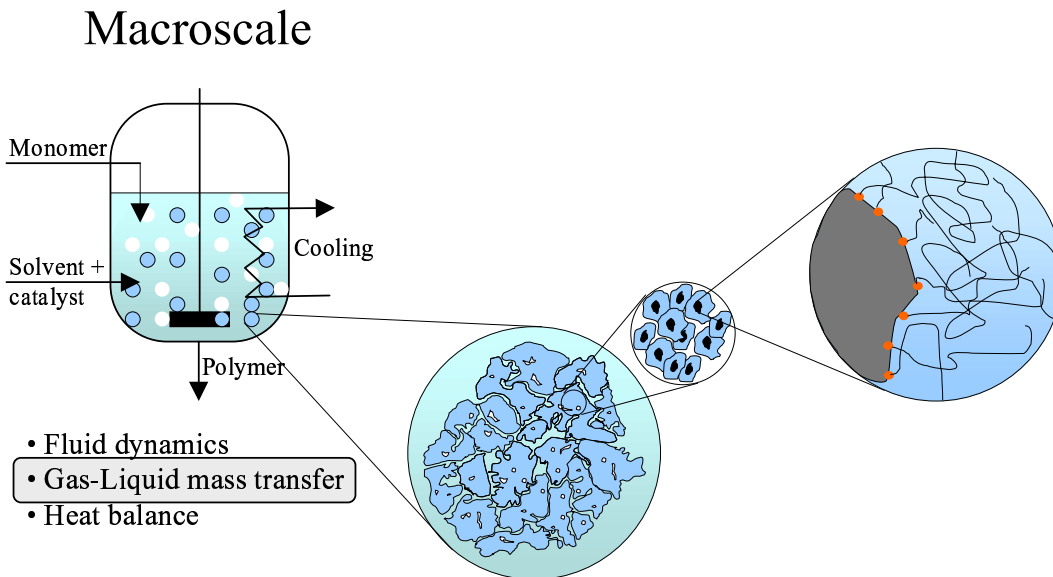
Going into more detail, the first part of the thesis concerns gas-liquid mass transfer limitations. Chapter 2 describes and discusses an experimental method to determine the gas-liquid mass transfer coefficient in a laboratory scale stirred reactor where the monomer enters the reactor as a gas and is transferred to an inert liquid hydrocarbon solvent in which the catalyst is dispersed. Chapter 3 describes and discusses models for the gas-liquid mass transfer and how to predict the importance of the mass transfer limitation. These two chapters are relevant for people doing polymerization kinetic studies with a setup as described above. A significant mass transfer resistance will often mask the kinetic study, and is therefore important to control.

The second part of this thesis concerns single particle mass transfer and morphology effects. With single particle it is meant the study of a single polymer/catalyst particle and no interaction with other particles or walls are considered. Chapter 4 describes how a spatial variation in growth rate of the catalyst/polymer particle can influence the morphology of the final polymer particle. The variation can originate from mass transfer resistance in the polymer particle or from a spatial variation in the catalyst concentration. The next three chapters are all about different aspects of mass transfer in growing polymer particles. Chapter 5 shows an experimental study of how changes in the morphology can affect the mass transfer properties. A denser particle is made by filling the smallest pores with ethene-propene-rubber (EPR), increasing the length scale of diffusion. Chapter 6 presents a new single particle mass transfer model which has three levels of morphological structure, one more than the popular multigrain model. Both the study in chapter 5 and recent published work express the need for this extra morphological information. Finally, chapter 7 describes a general mass transfer model where also the effect of self-induced convection is included. In processes where the monomer has a high mole fraction in the bulk phase, e.g. in a gas phase process, the reaction itself will set up a net convective flow towards the reactive centers. This has not been treated well in any previous literature. The topics of this part of the thesis are particularly important when designing new catalyst particles and processes, and when interpreting observed responses from experiments. Thus, people working on developing new processes and catalysts should be the target audience.

Finally, the topic of chapter 8 is catalyzed olefin polymerization kinetics. Different techniques for modeling kinetics are shown. The main focus is on how to come from reaction schemes to reaction rates and molecular weight distributions. The opposite is also important, how to interpret the reaction rate and molecular weight distribution in terms of what reactions are taking place. Three examples illustrate the use of some of these techniques. This chapter should be relevant for both people working on polymerization kinetic studies, trying to reveal the secrets of the catalysts, and to those working on modeling polymer properties in industrial processes.

Part I

Gas-liquid mass transfer



Conclusions



Conclusions

A study on mass transport and reaction kinetic phenomena in catalytic polymerization of olefins has been done. The work is divided into three parts according to the scale at which the phenomena occur. Mass transport effects at the macro- and mesoscales of the reactor, and polymerization kinetic effects at the microscale were studied. The main achievements and conclusions of this study are:

At the macroscale, the gas-liquid mass transfer in a stirred semi-batch laboratory reactor was investigated experimentally and theoretically. The objective was to find useful models for the gas-liquid mass transfer and under which operating conditions the effect of the gas-liquid mass transfer could be neglected. New experimental methods for determining mass transfer coefficients directly in a polymerizing reactor were developed. The methods are based on analyses of the dynamic and steady-state monomer feed rates as functions of the stirring rate. The results from the dynamic and steady-state methods differed significantly, and the transient responses could not be described using an ideally mixed reactor model. The discrepancy between the results can be qualitatively explained by nonideal mixing in the reactor.

Models for the mass transfer were developed and were based on the gas-liquid mass transfer being controlled by the renewal of the liquid surface. At low turbulent Reynolds numbers, the mean liquid flow provides the renewal, and at high turbulent Reynolds numbers, small-scale turbulence is the controlling mechanism. For the present system, the small-scale turbulence model was found to be most appropriate, and fitted the experimental data within a factor of 2. This accuracy is good enough for many applications, e.g. when determining the necessary operating conditions for neglecting mass transfer resistance. The models are theoretically founded and are believed to be generally valid.

At the mesoscale, mass transport phenomena in single catalyst/polymer particles were in focus. A model was developed where the stresses arising from the formation and growth of polymer were calculated and used to predict the rupture of the catalyst/polymer particle. It was shown that the largest stretch tension is normally found in the center of the particle for cases with large monomer concentration gradients or with inhomogeneous catalyst distribution. This can lead to the formation of hollow particles. It was found that the breakup of the catalyst is important when determining the final morphology.

An experimental study of the influence of polymer particle morphology on mass transfer properties was done. A three step polymerization was developed where PP was made to build a matrix, the EPR content was varied to change the morphology, and PE was made to investigate the activity with these different morphologies. It was found probable that the EPR initially forms underneath the PP produced in the first stage of the reaction, and then seeps out to partially fill the micropores of the host matrix. EPR does not change the overall particle morphology significantly. Chemical kinetic studies of the PE stage suggest that the transformation of the internal morphology can provoke mass transfer resistance at high levels of activity for a moderate to high mass fraction of rubbery polymer. This can be explained by the closing of the micropores, creating a longer diffusional path for the monomer. Models describing monomer transport by diffusion on the scale of mesoparticles of size 20–30% of the original particle agree well with the experimentally observed activity drop.

To better account for the effects of particle morphology on mass transport properties, a new mass transfer model to be used in single particle models for olefin polymerization was developed. The difference between this and traditional single particle models, is the introduction of a third level of morphology, the mesolevel, with a length scale between the size of the microparticles and the size of the whole particle. The model shows that given typical parameters, the main path for mass transport in the particles is a radial diffusion in the macropores and then diffusion in the tangential direction to the active sites at the mesoparticle level. The mesoscale level contributes only to a small fraction of the total radial mass transport. Some of the influence on the effective reaction rate with variation in morphology as found with this model cannot be explained by traditional models.

A model was developed to account for convective effects in the gas phase and liquid monomer polymerization of olefins. It was found that convective transport will be more important for higher mole fractions of the monomer and insignificant in dilute systems, where the mole fraction of monomer is low. In cases where convection is important, the less reactive or inert species will accumulate in the center of the catalyst/polymer particle. This can lead to a particle size dependent incorporation of comonomer in the polymer. Under common industrial operating conditions today, there seems to be no significant effect of accumulation of comonomers or inerts in the particles.

Three different methods for modeling of chemical kinetic phenomena, occurring at the microscale level of the reactor, were demonstrated on practical examples. The use of pseudo-components was found appropriate for modeling and description of polymerization rates, the Monte Carlo method was useful in cases where a very complex kinetics scheme makes it difficult to set up mass balances, and the use of the continuous variable transformation was one possible way of calculating the complete molecular weight distribution. The choice of which technique to use, should be determined by the purpose of the study.

Important improvements have been achieved through this study. In the fields of gas-liquid mass transfer and in reaction kinetics, the work has mainly shown the use of existing

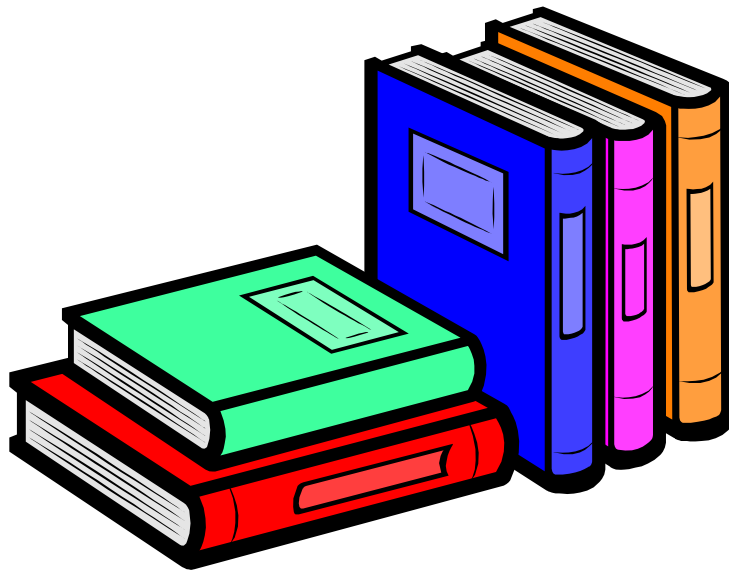
methods and models with small modifications. However, in the field of mass transport effects at the polymer particle level, significant improved understanding of the phenomena occurring has been achieved. The models presented can be used as tools for designing new catalytic systems for olefin polymerization with the results of better control of the polymer properties, which in turn means new materials with improved physical and chemical properties.

I think for a chemical engineer, among the topics covered in this work, the main focus of future work should be placed on single particle modeling. Gas-liquid mass transfer is well covered in literature, and is well understood. Moreover, it is seldom a dominating effect in industrial processes. The field of reaction kinetics is a very important aspect of olefin polymerization, but I would say that most work to be done is for chemists; to develop new catalysts and understand which mechanisms are controlling the kinetics. The methods to describe and model the rates, MWD and other properties, once the individual reactions are known, are in place. In the field of single particle modeling, much work is still to be done. New, more efficient and selective catalysts, will call for accurate control of the transport processes and the particle morphology. Existing models, partly working well with less reactive catalysts, often fail at the conditions used today as was shown in this thesis. I think some problems that lack good answers are:

- What controls the formation of the particle morphology?
- How is the coupling between particle morphology and mass transfer effects?
- How does the particle morphology affect the polymer properties?

I think the starting point for answering these questions is to examine the early stages of the “life” of a catalyst particle, get an estimate of which forces that are involved in the particle breakup, and to incorporate the necessary detailed description of the particle morphology to get a reliable mass transfer model. This model must necessarily be quite complex, so much experimental validation will be needed to achieve reliable conclusions.

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