MODELING AND OPTIMIZATION OF STYRENE SYNDIOTACTIC POLYMERIZATION THROUGH MULTISCALE

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MODELING AND OPTIMIZATION OF STYRENE SYNDIOTACTIC POLYMERIZATION THROUGH MULTISCALE

By

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DEDICATION

This work is lovingly and respectfully dedicated in honor of my late father and my beloved mother for her inspiration, to my wonderful wife, Nidhal Saeed for her constant encouragement and motivation, and to my forever supportive family members.

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SaadRaheem Sultan

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LIST OF ABBREVIATION

Symbol	Description
^{13}C NMR	Carbon-13 nuclear magnetic resonance spectroscopy
ANOVA	Analysis of variance
aPS	Atactic polystyrene
BET	Brunauer-Emmett-Teller
CCD	Central composite design
Cp	Cyclopentadienyl ligands
Cp*	Pentamethylcyclopentadienyl ligands
Cp_2	Bis–cyclopentadienylligands
CSTR	Continues stirred tank reactor
DBM	Data based model
DFT	Density functional theory
DLA	Diffusion limited aggregation
DNA	Deoxyribonucleic acid
DOE	Design of experiments
Dp	Degree of polymerization
DSC	Differential scanning calorimetry
FTIR	Fourier transformed infrared
GA	Genetic algorithm
GPC	Gel permission chromatography
Hf	Hafnium
ICP	Inductively coupled plasma emission spectroscopy

Ind	Indenyl
iPS	Isotactic polystyrene
KM	Kinetic model
MAO	Methylaluminoxane
MC	Monte Carlo-based methods
MD	Molecular dynamics
MEK	Methyl ethyl ketone
MGM	Multigrain model
MM	Multiscale model
MMT	Montmorillonite
Mn	Number average molecular weight
Mw	Weight average molecular weight
MWD	Molecular weight distribution
PBM	Publication balance model
PDI	Polydispersity index
PFM	Polymeric flow model
PMGM	Polymeric multigrain model
PMLM	Polymeric multilayer model
PSD	Particle size distribution
QSSA	Quasi-steady-state approximation
Re	Reynolds number
Rf	Rutherfordium
Rp	Rate of polymerization
RPPFM	Random – pore polymeric flow model

RSM	Response surface methodology
SAN	Styrene acrylonitrile copolymer
Sc	Schmidt number
SCM	Solid core model
Sh	Sherwood number
SiO_2	Silica
SPG	Single particle growth
SPGM	Single particle growth model
sPS	Syndiotactic polystyrene
St	Styrene
TBC	4-tert-Butylcatechol
TCB	Trichlorobenzene
TGA	Thermal gravimetric analysis
TIBA	Triisobutylaluminum
TMA	Trimethylaluminum
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbol	Description	Unit
$[C]_o$	Initial catalyst concentration	mol/L
$[M]_\mu$	Monomer concentration of the microparticle scale	mol/L
$[M]_b$	Monomer concentration in the bulk liquid phase	mol/L
$[M]_c$	Monomer concentration at the catalytic active sites	mol/L
$[M]_s$	Monomer concentration of the mesoparticle scale	mol/L
ΔH_c	Heat of crystallization	J/g
ΔH_m	Heat of melting	J/g
ΔH_m^o	Heat of melting of 100% crystalline polymer	J/g
A	Factor code of the initial monomer concentration in DOE	-
a	Interfacial area	m^2
A_r	Surface area of rippled surface	m^2
A_v	Area of the vortex surface	m^2
B	Factor code of the initial catalyst concentration in DOE	-
C	Factor code of the temperature in DOE	-
C*	Concentration of active catalyst sites	mol/L
C_o	Potent catalyst site	-
C^o	Unoccupied catalyst site	-
c_i	Concentration of component *i*	
D	Factor code of the polymerization time in DOE	-
D*	Deactivated catalyst site	-
$D_{ef,\mu}$	Effective diffusivity of monomer at microparticle	m^2/s
$D_{ef,M}$	Effective diffusivity of monomer at macroscale	m^2/s
$D_{ef,s}$	Effective diffusivity of monomer at mesoparticle	m^2/s
d_i	Impeller diameter	m
$D_{m,solv}$	Diffusivity of monomer in the solvent	m^2/s
D_n	Total dead polymer concentration	mol/L
Dp	Degree of polymerization	-

Dp_d	Desired values of polymerization degree	-
Dp_f	Actual values of degree of polymerization corresponding to the final reaction time	-
d_r	Reactor diameter	m
g	Gravity constant	m/s^2
h	height of the vortex	m
K_2	Polymerization rate constant	L/mol
ka	Activation rate constant	1/s
k_d	Deactivation rate constant	1/s
k_L	Mass transfer coefficient	m/s
kp	Propagation rate constant	L/mol.s
k_{tM}	Termination rate constants	L/mol.s
$k_{t\beta}$	β-hydrogen elimination rate constant	1/s
L_n	Total concentration of live polymer	mol/L
M_{solv}	Molecular weight of the solvent	g/mol
mw	Molecular weight of styrene	g/mol
n	Number of variables	-
N	Stirring rate	rpm
N_i	Number of mesoparticles in ith shell at a given macroparticle radius	-
P	Power input by stirrer	watt
PDI	Poly dispersity index	-
R_μ	Microparticle radius	µm
R_c	Radius of the catalyst core	µm
R_h	Hypothetical radius of macro particle shells	µm
R_M	Macroparticle radius	m
R_o	Initial catalyst particle radius	µm
Rp	Rate of polymerization	g sPS/g cat.hr
R_s	Mesoparticles radius	µm
T	Temperature	^oC

t	Time	min
t_f	Final reaction time	min
u_k	Kolmogorov eddy velocity scale	m/s
u_m	Macro eddy velocity scale	m/s
u_r	Radial velocity	m/s
V	Volume of the liquid phase	m^3
$V_{cc,i}$	Catalyst volume in shell i	m^3
$V_{cs,i}$	Volume of the ith shell	m^3
W	Mass of frits	g
W_1	Mass of the polymer frits	g
W_2	Mass of the sPS polymer frit after extraction	g
w_i	impeller width	m
$W_i(x)$	Weight fraction of the polymer of chain length x produced by the active site *i*	-
W_m	Weight of the monomer	g
W_p	Weight of polymer	g
X	Conversion	-
X_w	Weight chain length distribution	-
ℓ_k	Kolmogorov eddy length scale	m
ℓ_m	Macro eddy length scale	m

Greek Letters

$\emptyset_\mu$	Microparticle growth factor	-
α_μ	Microparticlethiele modulus	-
α_s	Mesoparticlethiele modulus	-
η_μ	Microparticle diffusion effectiveness factor	-
ρ_c	Catalyst density	Kg/m^3
ρ_p	Polymer density	Kg/m^3

σ^2	Variance	-
α	Factor coded level	-
α_s	Thiele modulus of the mesoparticle	-
α_μ	Thiele modulus of the microparticle	-
ε	Error	-
ϵ_d	Local energy dissipation	J/Kg/s
ε_M	Porosity of the macroparticle	-
ε_s	Porosity of the mesoparticle	-
η_s	Mesoparticle diffusion effectiveness factor	-
η_{solv}	Solvent viscosity	Kg/m.s
λ_{Dk}	Kth-moment of the dead polymer	-
Λ_f	Eulerian integral scale	m
λ_{Lk}	Kth-moment of the live polymer	-
λ_{Lo}	Total concentration of live polymer	mol/L
ν	Kinematic viscosity	m^2/s
$\nu_{m,bp}$	Molecular volume of the monomer at its boiling point	m^3/mol
ρ	Liquid desity	Kg/m^3
σ	Surface tension	Kg/s^2
τ_M	Tortuosity of the macroparticle	-
τ_s	Tortuosity of the mesoparticle	-
φ_i	Weight fraction of active site *i*	-

Subscripts

μ	Micro
a	Activation
b	Bulk
c	Catalyst, Crystallization
d	Desired, deactivation

ef	Effective
f	final
h	Hypothetical
i	Impeller, number of shell
k	Kolmogorov eddy
L	Liquid
Lk	Kth-live
m	Monomer, melting
M	Macro
p	Propagation, polymer
r	Rippled, reactor
s	Meso
solv	Solvent
tM	Termination monomer
tβ	β-hydrogen elimination
v	Vortex

PERMODELAN DAN PENGOPTIMUMAN PEMPOLIMERAN SINDIOTAKTIK STIRENA MELALUI PELBAGAI SKALA

ABSTRAK

Integrasi model, simulasi dan pengoptimuman menyediakan alat yang kuat untuk menyokong membuat keputusan dalam pasaran yang kompetitif keputusan maju. Walau bagaimanapun, apabila menggunakan alat-alat untuk pemprosesan pempolimeran, tugas yang mencabar adalah untuk menampung ramalan model matematik dan keupayaan pengoptimuman berasaskan model kerana kerumitan yang wujud itu. Dalam kajian ini, tiga pendekatan model dicadangkan, iaitu model pengkalan data, berasaskan kinetik model dan model multiskala, di mana model dimajukan untuk di iplementasikan dalam pempolimeran syndiotactic bagi stirena. Model pengkalan data telah dibangunkan berdasarkan model korelasi yang diperolehi daripada data eksperimen, di mana model linear klasik atau linear bukan klasik boleh digunakan untuk mengaitkan perubahan dalam mana-mana set data yang menggunakan rekabentuk eksperimen. Model kinetik digabungkan daripada skima kinetik pempolimeran, analisis kadar pempolimeran dan pengagihan berat molekul polimer. Model multiskala pula adalah satu rangka kerja bersepadu yang mana terdiri daripada gandingan antara model pertumbuhan zarah tunggal pada mesoskala dan model percampuran fenomena pada makroskala dengan model kinetik pada mikroskala, di mana kedua-dua pertumbuhan zarah dan percampuran fenomena yang berlaku dianggap bagi mengawal had pemindahan jisim dalam pempolimeran syndiotactic untuk stirena. Untuk mengesahkan model ini dan untuk menilai semua parameter model, pempolimeran syndiotactic untuk stirena keatas pemangkin metallocene yang disokong oleh silika telah dilakukan. Dua pemangkin yang disokong oleh metallocene telah disintesis untuk pempolimeran stirena iaitu, titanium mono siklopentadienil dan Indenyl kompleks. Kajian mendapati bahawa Indenyl kompleks memiliki aktiviti sebagai sifat pemangkin yang tinggi dengan tingkah laku syndiotacticity terpilih. Pemangkin yang telah disediakan dan sampel syndiotactic

polistiren telah dicirikan bagi sifat kimia dan fizikal menggunakan teknik analisis yang berbeza. Iaitu termasuk FTIR, 13C NMR, DSC, XRD, TGA dan SEM. Di dalam itu juga, kesan untuk keadaan operasi pempolimeran telah disiasat. Hasil keputusan pengesahan menunjukkan bahawa model multiskala meramalkan prestasi reactor pempolimeran yang terbaik. Oleh itu, model yang telah dimajukan ini telah diguna pakai dan berpotensi untuk meramalkan kondisi operasi pempolimeran yang optimum. Teknik algoritma genetik digunakan untuk mengoptimumkan operasi kondissi pempolimeran bagi model multiskala. Keputusan optimum memberikan kadar maksimum pempolimeran dan nilai yang diingini dari darjah pempolimeran dengan indeks polidispersiti minimum.

MODELING AND OPTIMIZATION OF STYRENE SYNDIOTACTIC POLYMERIZATION THROUGH MULTISCALE

ABSTRACT

The integration of modeling, simulation and optimization provides powerful tools for supporting advanced decision making in the competitive market. However, when applying the tools to polymerization processing, the challenging task is to accommodate the predictability of the mathematical model and the capability of model-based optimization due to its inherent complexities. In the present study, three model approaches are proposed, i.e. a data based model, a kinetic model and a multiscale model, whereby the developed models are implemented into the syndiotactic polymerization of styrene. The data based model was developed based on the correlation model from experimentally obtained data, where the classical linear or nonlinear models can be applied to correlate the variation in any set of data using experimental design. The kinetic model includes the polymerization kinetics scheme, polymerization rate analysis and polymer molecular weight distribution. The multiscale model is an integrated framework which consists of the coupling between the single particle growth model at mesoscale and the mixing phenomenon model at macroscale with the kinetic model at microscale, where by both particle growth and mixing phenomenon are considered to control the mass transfer limitations in the syndiotactic polymerization of styrene. To verify these models and to evaluate all model parameters, syndiotactic polymerization of styrene over a silica supported metallocene catalyst was performed. Two metallocene supported catalysts were synthesized for styrene polymerization, the titanium mono cyclopentadienyl and Indenyl complexes. It was found that the Indenyl complex possessed high catalytic activity with selective syndiotacticity behavior. The prepared catalyst and

syndiotactic polystyrene samples were characterized for their chemical and physical properties using different analytical techniques. These included FTIR, ^{13}C NMR, DSC, XRD, TGA and SEM. In context, the effect of polymerization operational conditions was investigated. The validation results demonstrated that the multiscale model predicts best polymerization reactor performance. Thus, the herein developed model has been adopted to potentially predict optimum polymerization operational conditions. The genetic algorithm (GA) technique is used to optimize the polymerization operational conditions for the multiscale model. The optimum results give the maximum rate of polymerization and the desired value of polymerization degree with minimal polydispersity index.

CHAPTER 1

INTRODUCTION

Our research was spurred on by the industry's yearning for models that would efficiently simulate to a yet reliable process via a user-friendly interface. Such developed models are universally of high importance to process engineers, who may need them to optimize the operating conditions and costs for certain products. These models could also be used to improve process efficiency and to lower the cost of process-scale experimentation.

A model of syndiotactic polymerization of styrene is presented in this work, whereby different models are developed and are implemented together in a simple and efficient way to build up an overall model of a polymerization reactor.

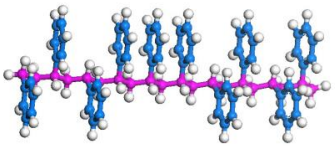
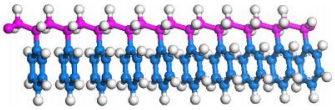
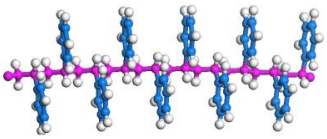
1.1. Syndiotactic Polystyrene (sPS)

Polystyrene is a common thermoplastic polymer made from the aromatic monomer styrene with good formability. The typical application of polystyrene includes: food packaging, toys, appliances and compact disc cases (Gray, 2011).

There are three different stereo-isomers of polystyrene illustrated in Table 1.1. The phenyl groups in atactic polystyrene (aPS), or general purpose polystyrene, are randomly distributed to the main polymer backbone. aPS is an amorphous polymer and one of the most widely used commodity polymers because of its good transparency, stiffness, and processibility (Pó and Cardi, 1996). In isotactic polystyrene (iPS), phenyl groups are on the same side of the backbone chain

plane. iPS is a semi-crystalline polymer with a melting point of around 240 ^{o}C, Because of very slow crystallization rate, iPS is little used to make injection moldable objects (Scheirs and Priddy, 2003). In syndiotactic polystyrene (sPS), phenyl groups alternate vertically along the backbone chain. sPS is a semi-crystalline polystyrene that can be produced using metallocene catalysts with methylaluminoxane (MAO), which has a low specific gravity, a high modulus, good electrical properties, a high melting point (270 ^{o}C), strong chemical resistance, and dimensional stability. The new property of sPS is that it is similar to those of some expensive engineering plastics. Thus, special interest needs to be shown towards it (Malanga et al., 2009; Charles and Carraher, 2012).

Table 1.1 Three different stereo-isomers of polystyrene: structures and properties (Charles and Carraher, 2012).

		T_g	T_m	Crystallinity
Atactic		100 °C	-	Amorphous
Isotactic		100 °C	240 °C	20 ~ 30 % (Slow Crystallization)
Syndiotactic		100 °C	270 °C	40 ~ 50 % (Fast Crystallization)

sPS was first synthesized by Ishihara (Ishihara et al., 1986), with cyclopentadienyl titanium trichloride catalyst. Since then, many different titanium compounds have been found active to produce sPS. In particular, half sandwiched titanium compounds (e.g. CpTi- and Cp*Ti- complexes) have high polymerization activities and high syndiospecificity (Schellenberg and Tomotsu, 2002).

1.2. Multiscale Modeling

'Multiscale' extensively refers to processes, algorithms, and data easily structured by scale, whilst the 'scales' are commonly defined by some attributive time or length of the objects and phenomena concerned. However, scales can possibly be defined based on the 'chemical resolution' of a multi-component mixture and on the rather general concept of the 'detail scale' (Lucia, 2010).

Multi-scale modeling denotes the science that connects models and phenomena seamlessly and dynamically across a variety of lengths and time scales, straddling from quantum, to macroscopic scales. The aim of this multiscale modeling is in the prediction of the macroscopic behavior of an engineering process as seen from first principles, i.e., beginning from the quantum scale and transmitting data into molecular scales and gradually reaching the process scales.

These multi-scale modeling efforts espouse the philosophy that is substantially the same models generated on the dual scales and uses two unique simulations which distribute data back and forth between both models at the correspondingly varying two scales of space and /or time. The science of studying these complex systems via multiscale methodology usually considers some essential issues, as reported elsewhere (Li et al., 2004):

1. The correlation between phenomena at various levels.
2. Compromising between variant essential mechanisms.
3. The correlation between spatial and temporal structural changes.
4. Interpreting the phenomena taking place within any complex system.

For the design and optimal operation of chemical processes that range from nano- systems to industrial-scale continuous and batch processes, the research community has dedicated some serious attention to understanding and developing typical systematic procedures that may effectively describe such systems. Figure 1.1 explains the chemical supply chain concept, starting with chemical or other products that have to be synthesized and characterized by the industry at molecule level (Grossmann and Westerberg, 2000). In the next step, the molecules aggregate into clusters, particles, and thin films that represent systems of single or multiphases. Such systems may finally be described as macro-scaled mixtures of either solids or emulsified materials. Interpreting chemical or biological changes into engineering concepts, is constituted being one step ahead of the design and analysis of the production units. These units combine to form a certain process that becomes an essential part of a plant area that is active with multiple processes. Thence, this industrial site constitutes itself as a section of the whole enterprise forced by consumer need contemplation and strictly requires the addition of product quality.

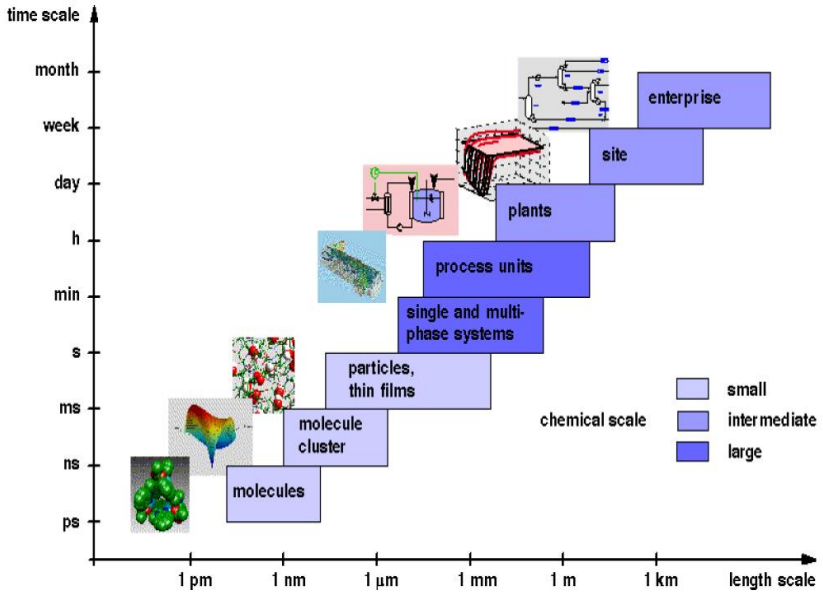


Figure 1.1 Chemical supply chain (Grossmann and Westerberg, 2000)

1.3. Multiscale Modeling of Polymerization Reactor

Multiscale modeling is considered as one of the most important issues in computational polymers-oriented work. For instance, the link between time and length scales, and the connecting of computational methods for the prediction of macroscopic traits and behavior from molecular processes (Charpentier, 2010).

A long-standing goal of physical, chemical and engineering sciences has been the development of efficient theoretical tools to understand and predict the physical properties of polymer materials from the knowledge of several input parameters (Li et al., 2004). However, the demanding nature of the development of the tools has not been refuted by fellow scholars, since in general, one is required to cope with an array of components and interactions, which would leave a dent on their structures and dynamics at a lot of different scales.

The full modeling of the polymerization process is undeniably very intricate, and understandably, the requirement is that it is handled at extensively different scales of length. Ray suggests treating this issue as three different scales: macro-, meso- and microscales (Ray, 1988). This classification is illustrated in Figure 1.2, and a general example of the phenomena at these scales is given below. The descriptions and modeling of phenomena at these scales is outlined as a road map of this thesis work.

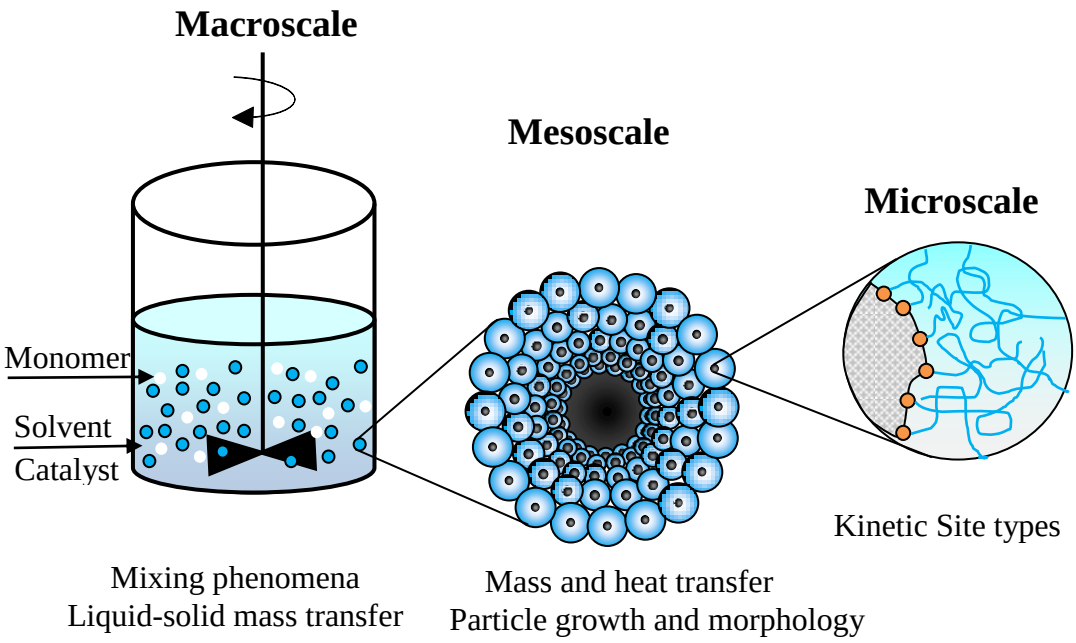


Figure 1.2 Levels of modeling polymer processes based on classification of Ray, the circles in the macroscale part symbolize polymer particle, the small magnification in the mesoscale frame represents catalyst fragments with surrounding polymer and the dots in the microscale frame symbolize the catalyst sites (Ray, 1988).

1.3.1. Microscale Modeling

It is well evidenced that the kinetic mechanisms of the polymerization reactions are studied at the microscale. If the polymerization mechanism is recognized a number of mathematical techniques will be accessible for the calculation of the molecular property distributions. By considering the reactant concentrations and the reaction rate constants, the species balance method is the most suitable approach to develop the polymerization kinetic model. Based on the mass conservation law, one can easily obtain an unlimited number of algebraic or differential equations that cling onto the reactor type to be used for different reactants. The resulting set of balance equations of species needs to be solved in order to acquire information on the preferred distributions of molecular properties.

1.3.2. Mesoscale Modeling

The modeling of mass and heat transfer limitations within interparticle and intraparticle occurs at the mesoscale. This, in turn necessitates models to be engaged in different processes like monomer adsorption and the evolution of particle morphology. The mesoscale model represents the interface between the continuum approach adopted at the macro-scale level, and the discrete approach needed at the micro-scale level.

1.3.3. Macroscale Modeling

This scale of the model compromises the overall mass and energy balances, the macro mixing phenomena within the reactor, the particle population distributions, and the mass and heat transfer rates from the reactor in conjunction with the reactor dynamics and control.

There are several benefits from a good description and understanding of the Ray proposed processes (Ray, 1988). The following possible outcomes from good process models are listed below:

- A good model helps in the interpretation of observed phenomena. Chemical effects can be discriminated from the 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 the reactor design to catalyst particle and type of active sites.

1.4. Problem Statement

An important section of the syndiotactic polymerization of styrene reactor is the metallocene catalyst that supplies the syndiotacticly of the propagation reaction at the point of polymerization. Metallocenes are very versatile catalysts, as 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.

In styrene polymerization mediated by homogeneous metallocene catalysts, the agglomeration of polymer microparticles as monomer conversion increases with reaction time. Consequently, these syndiotactic polystyrene (sPS) agglomerates become a gel, or like a piece of wet cake. As the formation of the sPS gel usually results in a thick reaction mixture which leads to a larger resistance toward agitation, such homogeneous catalysts are not industrially desirable. To avoid these drawbacks, the liquid slurry process could effectively decrease the gelation of the mixture and help to produce sPS as discrete particles; thereby acquiring a significant industrial interest. For liquid slurry process, a homogeneous catalyst must be functionalized onto a compact support material to produce a more efficient and highly stable catalytic material. At a later stage, the as-developed heterogeneous metallocene catalyst is employed for styrene liquid slurry polymerization.

The polymerization process depends mainly on the complex interaction between multi-physics such as the kinetic mechanism, physical transport phenomena, and the operational conditions, alongside the morphological properties of the product such as particle size distribution. A set of partial differential equations at a variety of

length scales are usually developed to describe a multi-physical problem system. It is well known that the solution of coupled partial differential equations (PDEs) is simultaneously implemented in correspondence with physical domains for certain physical phenomena (Dennis et al., 2006). Three major cases which establish proof of the usefulness of the multi-scale approach for processes that by nature are multiscale, when information is readily available at various resolution levels, and when inserting a standard problem in a multi-scale framework bring us to some important computational advantages. This analysis may be undertaken following three varying approaches.

i. The average without distinguishing structural difference at various scales.
ii. Discrete based on micro-mechanism scale.
iii. Multi-scale, considering the behavior discrepancy at a variety of scales.

The average approach, in spite of its being commonly used, is insufficient to formulate complicated systems as it is incapable of differentiating between scales and does not indicate the mechanism-based performance prevalent in the system. On the other hand, the micro-mechanism simulation tools, for example the molecular dynamics (MD), molecular mechanics (MM), and Monte Carlo-based methods (MC) have been widely applied for material design. In the manipulation of these tools, it seems possible to understand the molecular structure only within the scale of 0.1–10 nm. In spite of the fact that the molecular structures could be simply analyzed using these simulation tools, it is quite untrustworthy to forecast structures at the scale of 100–1000 nm. In fact, the atomistic models do not include the effect of surface diffusion, which normally falls outside their domain and influences the reaction rates and pattern formation on catalytic surfaces. In addition, early chemical models did

not consider the limitations of mass and heat transfer at all and only used the kinetic models to elucidate the polymerization process. Multi-scale approaches are currently available as simulation tools that work well in bridging the gap between micro- and macroscopic models, which include mesoscopic simulations (Lucia, 2010).

The optimization approach can have a significant effect on the polymer manufacturing process and economics. Polymer production facilities focus attention on improving the product quality and cost reductions (Alvarez and Odloak, 2012). In general, polymerization process optimization is naturally multi-objective, since it normally has several objectives that are often conflicting and non-measurable, which must be adjusting simultaneously. Therefore, solving such a problem cannot be devoid of difficulties, starting with the objective function formulating. It then proceeds with the choice of working procedure and the result selection from several options. Genetic algorithms have been successfully employed in a wide range of multi-objective problems because of their flexibility, global perspective and minimal requirements, these techniques do not need any initial guesses and converge to the global optimum even when there are several local optima present. In addition, genetic algorithms use information about the objective function and not its derivatives (such as traditional optimization techniques), nor dose they require any other auxiliary knowledge.

1.5. Research Objectives

The objectives of this work are listed as follows:-

1. To investigate the best performance of silica supported metallocene catalysts toward the formation of syndiotactic polystyrene (sPS).
2. To characterize the as-obtained sPS samples for their chemical and physical properties using different analytical techniques.
3. To study the effects of polymerization operational parameters and catalyst properties on the polymerization rate and the molecular weight distribution of the as-obtained sPS samples.
4. To model the polymerization reactor of syndiotactic polymerization of styrene by defining different models i.e. data based model, kinetics model and multiscale model.
5. To optimize the conditions of each polymerization variable for the accurate model proposed using genetic algorithm (GA) technique, toward achieving maximum polymerization reactor performance.

1.6. Scope of the Study

Syndiotactic polymerization of styrene over a silica supported metallocene catalyst was performed. Two metallocene supported catalysts were synthesized for styrene polymerization, the titanium mono cyclopentadienyl and Indenyl complexes. The prepared catalyst and syndiotactic polystyrene samples were characterized for their chemical and physical properties using different analytical techniques. In context, the effect of polymerization operational conditions and catalyst properties on the polymerization rate and molecular weight distribution of polymer was investigated.

Three modeling approaches are presented, i.e. the data based model (DBM), kinetic model (KM) and multiscale model (MM), whereby the developed models are to be implemented into the syndiotactic polymerization of styrene taking into account the effect of both polymer/catalyst single particle growth and mixing phenomena, especially in terms of mass transfer limitations.

The data based model is developed based on a correlation model from experimental data obtained. In which the classical linear or nonlinear models can be used to correlate the variation in a set of data using design of experiment. The kinetic model is the second model. It is the key to understanding and predicting the properties of the produced polymer. The model includes the polymerization kinetics scheme for syndiotactic polymerization of styrene, polymerization rate analysis and molecular weight distribution (MWD). The third model is multiscale model; it is an integrated framework consists of coupling between the single particle growth model (SPGM) at mesoscale and mixing phenomenon model at macroscale with the kinetic model at microscale. Whereby, both of particle growth and mixing phenomena are taken into account. The SPGM was developed based on the modification of the well-known multigrain model (MGM) by introducing mesoparticle scale as a third level in the description of the particle growth. On the other hand, the mixing model describes the renewal of the liquid surface, which 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. Finally, the genetic algorithm (GA) technique is used to optimize the polymerization operational conditions for the accurate model

1.7. Organization of the Thesis

The thesis consists of five chapters as listed in the table of contents. A brief introduction of polystyrene polymer, multiscale system and multiscale modeling of catalytic polymerization reactors with the polymerization phenomena at different scales is included in Chapter 1(Introduction). At the end of this chapter, problem statements that provide a basis and rationale to justify the research direction in the current study are highlighted. Based on the problem statement; the specific objectives of the research are together with the research scope.

Chapter 2 (Literature Review) A literature review of syndiotactic polystyrene (sPS) and the heterogeneous polymerization of styrene with different types of metallocene catalyst is presented in this chapter. In addition, the recent developments of the multiscale system and the multiscale modeling of the polymerization reactor, as well as polymerization phenomena at different scales, the coupling between the polymerization kinetics, single particle growth and the mixing phenomena will be discussed. The genetic algorithm (GA) technique for the optimization of polymerization reactor is also presented in this chapter.

Chapter 3 (Experimental and theoretical methods), this chapter is subdivided into two parts, the first part is experimental methods and the second part is theoretical methods. The experimental methods include the details of the materials, chemicals and equipments used in the present study. This is followed by the detailed experimental procedures, which involve the purification of styrene and solvents, synthesis silica supported metallocene catalyst and the polymerization of styrene over a silica supported metallocene catalyst. The characterization method for

syndiotactic polystyrene physicochemical properties such as polymer crystallinity and melting points, the thermogravimetric behavior, and molecular weight distribution are also outlined in the first part of this chapter. The second part include three modeling approaches of styrene syndiotactic polymerization, i.e. the data based model (DBM), the kinetic model (KM), and the multiscale model (MM). The MM consists of coupling between the single particle growth model (SPGM) at mesoscale and mixing phenomenon model at macroscale with the kinetic model at microscale. Whereby, both of particle growth and mixing phenomena are taken into account. The genetic algorithm (GA) technique for the optimization of the model is presented.

Chapter 4 (Results and Discussion) is the core of this thesis, and addresses the objectives as listed in section 1.5. The results of the experiment are subdivided into five sections. The first section discusses the performance of metallocene catalysts in syndiotactic polymerization of styrene and is followed by the characterization of syndiotactic polystyrene. The effect of polymerization operational parameters and catalyst properties on the polymerization rate and molecular weight distribution of polymer produced is presented in the third section and is followed by the validation of each model with experimental data based on statistical analyses. The final section discusses the genetic algorithm application to determine the optimum operating process variables for the accurate model presented in chapter 3.

Chapter 5 (Conclusions and Recommendations) concludes all the major findings obtained in the present study. At the end of the thesis, suggestions and recommendations to improve the present research work, as well as the future direction of the research are presented.

CHAPTER 2

LITERATURE REVIEW

This chapter addresses a literature review of polymer and the polymer industry, syndiotactic polystyrene (sPS) and the heterogeneous polymerization of styrene with different types of metallocene catalyst. This is followed by the recent developments of the multiscale system and the multiscale modeling of the polymerization reactor, as well as the polymerization phenomena at different scales, the coupling between the polymerization kinetics, single particle growth and the mixing phenomena. The optimization of polymerization reactor using genetic algorithm (GA) technique is also present in this chapter.

2.1. Polymer and the Polymer Industry

Polymers are materials characterized by large molecules which are multiples of simpler units, monomers (Roussak and Gesser 2013). Both natural and synthetic polymers exist. Natural polymer is considered to be a natural product plant or animal like cellulose, wool, natural rubber and protein. However, synthetic polymers are grouped according to the monomers from which they are formed. Examples of groups are polyesters, nylons and polyurethanes, which all have a hetero chain backbone, whereas polyethylene and polystyrene have a pure carbon backbone (Charles and Carraher, 2012).

Synthetic polymers have been categorized as modern materials. Polymer production capacity has increased dramatically from a few million tons before the Second World War to a value of more than120 million tons per annum (Figure 2.1). The annual consumption per capita has also increased over the years to a global average of about 20 kg in the year 2000 (Meyer and Keurentjes, 2005). Due to the fact that they are lightweight materials, synthetic polymers have important applications as electrical and thermal insulators. Moreover, the textural characteristics of polymeric materials cover a number of industrial applications ranging from soft packaging materials to tough fibers which are stronger than steel, with a simplicity of processing. However, this thesis will place emphasis on syndiotactic polystyrene as a synthetic polymer.

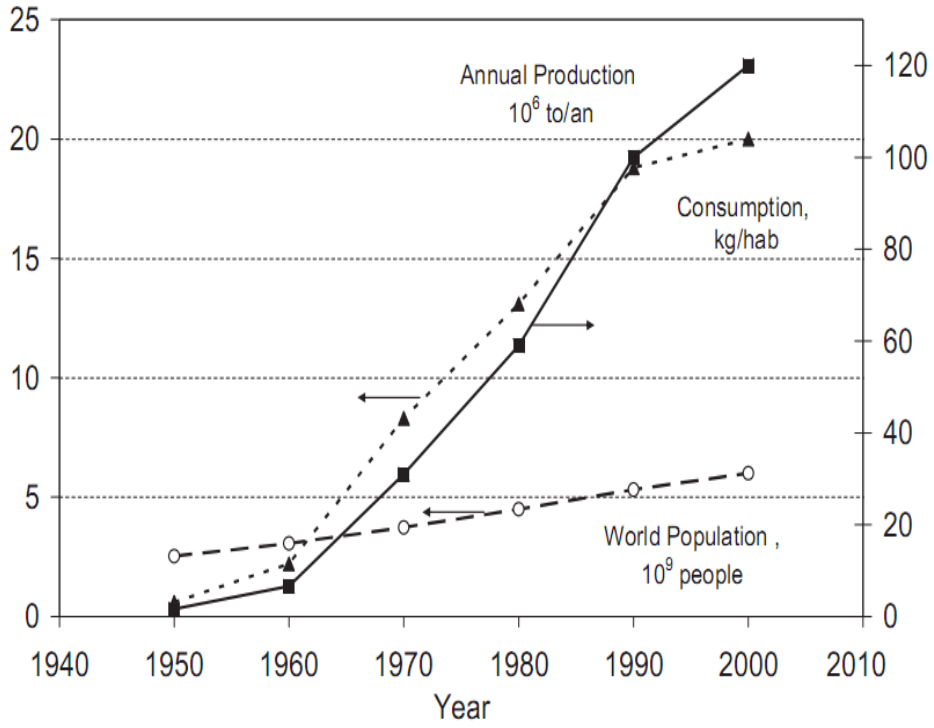


Figure 2.1 Polymer production and the evolution of the population since 1940 (Meyer and Keurentjes, 2005)

2.2. Syndiotactic Polymerization of Styrene

Syndiotactic polystyrene (sPS) is a semicrystalline thermoplastic polymer with many advantageous properties such as excellent heat resistance with a high melting point of 270-272 ^{o}C, strong chemical resistance against acids, bases, oils and water, and low dielectric constant. The relatively fast crystallization rate makes sPS a promising material for a large number of applications in the automotive, electrical and packaging industries (Charles and Carraher, 2012). Figure 2.2 shows the position of syndiotactic polystyrene and its types in the material hierarchy.

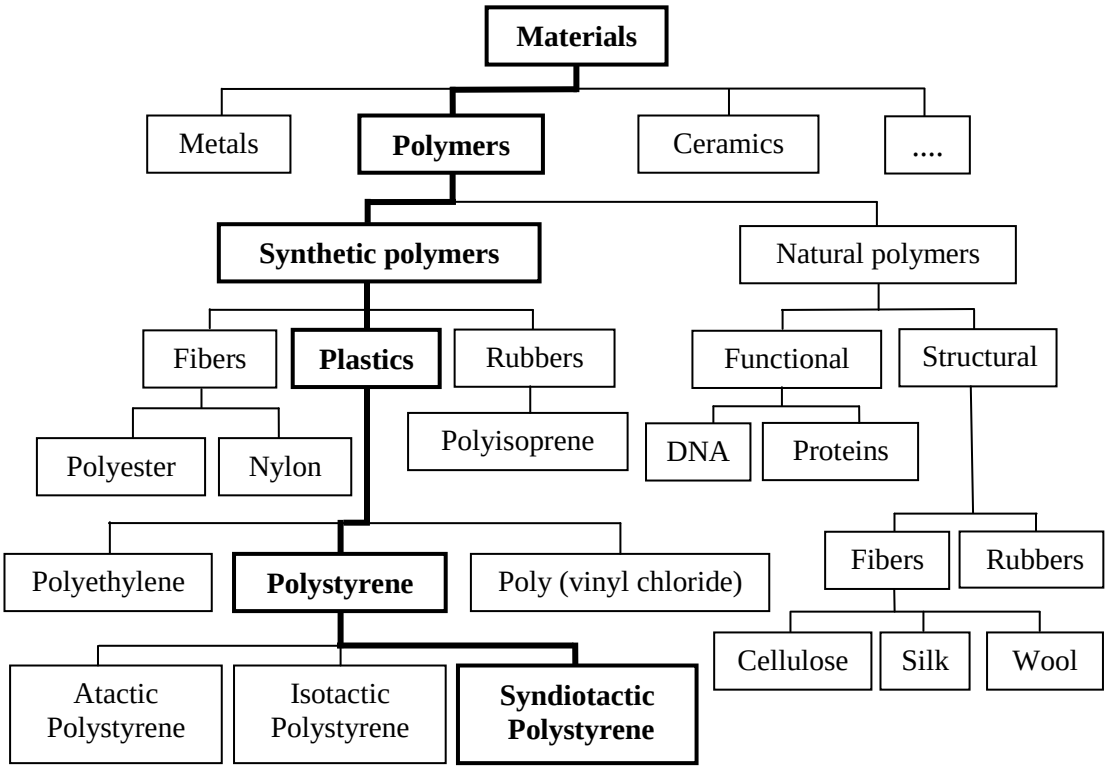


Figure 2.2 The position of syndiotactic polystyrene in the material hierarchy

In 1988, Ishihara and co-investigators were the first to synthesize sPS using cyclopentadienyl titanium trichloride ($CpTiCl_3$) catalyst with methylaluminoxanes as co-catalyst activator (Ishihara et al., 1988). Since then, serious attention has been devoted by the research community to the synthesis of sPS and as such, many review articles have mentioned with the periodical advances of metallocene catalysts for styrene polymerization (Pó and Cardi, 1996; Tomotsu et al., 1998; Schellenberg and Tomotsu, 2002; Schellenberg and Leder, 2006; Malanga et al., 2009).

Based on the transitional metal complex structure, the atactic and syndiotactic polystyrene structure can be acquired. Table 2.1 summarizes the employed transitional metal complexes, conditions of polymerization, catalytic activities and the polymer properties obtained for the syndiotactic polymerization of styrene.

2.3. Metallocene Catalyst

The term "metallocene catalyst" usually refers to organometallic coordinated compounds, whereby a transition metal atom centers on one or two cyclopentadienyl rings, or alternated cyclopentadienyl rings. In such a system, a π-bond singly binds the cyclopentadienyl ring to the central metal. As a result, the formal charge of the ring-metal bond is not placed on the center or on any one of the five carbon atoms in the ring, but is placed equally on all carbon atoms (Hamielec and Soares, 1996).

Table 2.1 Syndiotactic styrene polymerization with different types of metallocene catalysts

Catalyst	Reaction Temp. °C	Molar ratio [St]/[Me]	Molar ratio [Al]/[Me]	Syndiotacticity	Catalyst Activity	Reference
$CpTiCl_3$	50	4000	300-600	Syndiotactic	99.2%	(Huang et al., 2004)
$CpTiCl_3$	50	-	300	Syndiotactic	14.02[b]	Ghosh and Hagihara (2009)
$CpTiCl_3$/Silica	50	21800	300	87.7%	238[b]	(Yim et al., 1996)
$Cp^*Ti(OCH_3)_3$	70	3496	500	95-100	-	(Lee *et al*. 2011)
$CpTiCl_3$/MAO/Silica	50	21800	300	79.8%	38[b]	(Yim and Ihm, 2006)
$CpTiCl_3$/Silica	50	26892	940	79%	2892[c]	(Xu et al., 1997)
$Cp^*Ti(OCH_3)_3$/Silica	70	-	500	Syndiotactic	-	(Liu et al., 2008)
Cp^*TiCl_3	50	4000	100-900	Syndiotactic	75.4%	(Ishihara et al., 1988)
$Cp^*Ti(OCH_3)_3$	50	70080	300	97.2%	40[a]	(Kitiyanan and Nomura, 2006)
$Cp^*Ti(OCH_3)_3$/Silica	70	4000	500	93-95%		(Malanga et al., 2009)
Cp^*ZrCl_3	50	6880	300	Isotactic	0.08[a]	(Longo et al., 1994)
Cp^*TiF_3	50	70080	300	99.4%	940[a]	(Kaminsky, 1996)
$Cp^*Ti(OCH_3)_3$	70	233333	100	Syndiotactic	33%	(Newman and Malanga, 1997a)
$Cp^*Ti(OCH_3)_3$	50	233333	300	Syndiotactic	39.1%	(Schellenberg, 2000)
$Cp^*Ti(OCH_3)_3$	70	-	500	93-95%	-	(Han et al., 2007)
$Cp^*Ti(OCH_3)_3$	45	8775	1000	93%	30600[b]	(Liu et al., 2000)
$Cp^*Ti(OCH_3)_3$/silica	70	-	500	93-95%	-	(Han J and Choi KY, 2005)
$(CpCH_2CH_2OCH_3)TiCl_3$	50	17400	300	Syndiotactic	-	(Pragliola *et al*. 2013)
Cp_2TiCl_2	50	4020	600	Syndiotactic	1.0%	(Tomotsu and Ishihara, 1999)
$Si(CH_3)_2Cp_2TiCl_2$	50	3496	1000	47.5	1.855 g	(Longo et al., 1995)
$Cp_2Ti(OC_{10}H_{17})_2$	50	-	4000	Syndiotactic	0.32 g/h	(Grafov AV and Lopes Dias M, 1998)
Cp_2TiCl_2	50-90	100	-	atactic	-	(Patra and Bhattacharjee, 2005a)
Cp_2ZrCl_2	50-90	100	-	atactic	-	(Patra and Bhattacharjee, 2005b)
Cp^*TiF_3/MAO	50	68800	300	275[d]	690[a]	(Kaminsky et al., 1997)
Cp^*ZrF_3/MAO	50	6880	300	248[d]	0.9	(Kaminsky et al., 1997)
$IndTiCl_3$	50	17400	4000	98.2%	3700[c]	(Ready et al., 1998)
$IndTiCl_3$/silica	30	-	300-500	Syndiotactic	172[b]	(Entezami et al., 2005)
$1\text{-}(CH_3)IndTiCl_3$	50	17400	4000	89.5	51000[c]	(Ready et al., 1998)

a. kg-sPS/mol-Me.h
b. kg-sPS/mol-Me.mol-St.h
c. g-sPS/g-Ti

The catalytic performance of these organo-metallic clusters during the polymerization process toward the formation of linear and cyclic olefins is merely attributable to their composition and structure. For instance, the type of transition metal (M) and its substituents (R), the type and the number of the rings and substituents (S), the type of bridge, if there is any, and the type of co-catalyst could support this argument (Figure 2.3). Therefore, these new polymerization catalysts have been introduced to the polymer production arena, with entirely novel attributes.

Metallocene catalyst as we know them today, are new compared to the Ziegler-Natta catalysts. In the early eighties, Walter Kaminsky discovered by accident, that adding small amounts of water to the metallocene / alkylaluminium mixture, considerably increased its reactivity. This was attributed to the reaction between water and alkylaluminium to form alkylaluminiumoxane (Kaminsky, 2012).

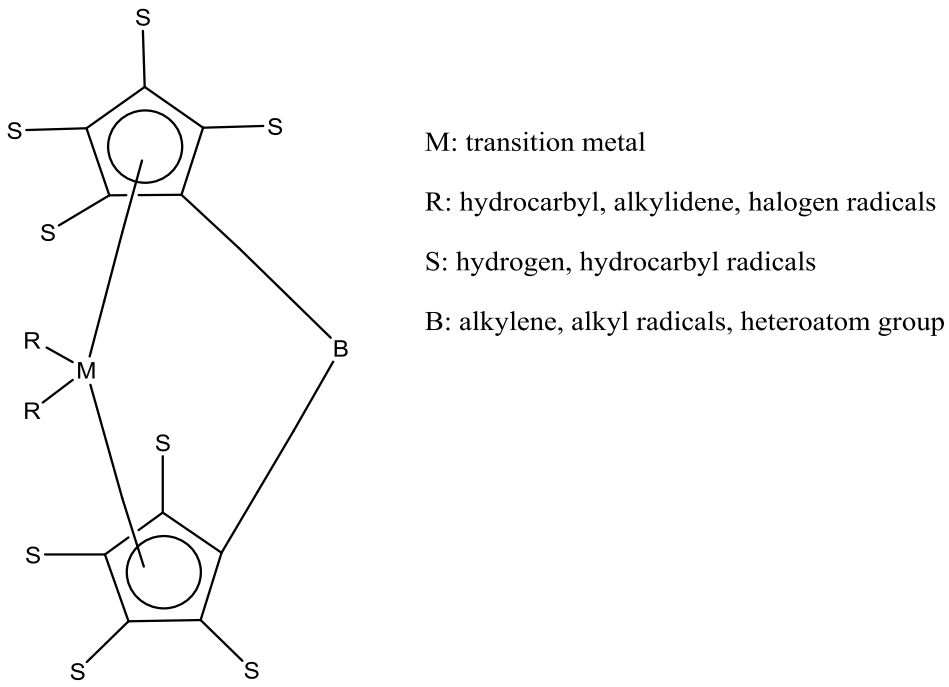


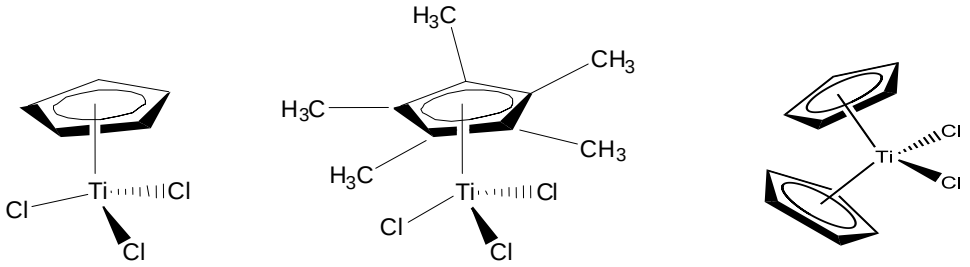
Figure 2.3 Generic structure of a metallocene catalyst

2.4. Transition Metals Complexes Catalysts for Styrene Polymerization

Since 1988, a variety of transition metal complexes has been investigated to manufacture sPS in conjunction with MAO. In addition, it has been found that the effective catalysts for sPS polymerization include cyclopentadienyl and substituted cyclopentadienyl transition metal complexes such as $CpTiCl_3$ and $Cp^*Ti(OCH_3)_3$ with methylaluminoxane (MAO) as a co-catalyst. For instance, group 4 of transition metals, (titanium (Ti), zirconium (Zr), hafnium (Hf), and rutherfordium (Rf)) and their complexes were applied as catalysts for syndiotactic styrene polymerization. These can be classified into mono-and bis–cyclopentadienyl complexes, metal complexes of other ring systems such as indenyl, fluorenyl, and other complexes.

2.4.1. Mono and Bis–cyclopentadienyl Transition Metal Complexes

Promising non-bridged half-metallocenes especially based on cyclopentadienyl ligands (Cp-Me complexes) have just recently been reviewed as catalysts for precise olefin polymerization in general (Nomura et al., 2007). With regard to syndiospecific styrene polymerization, investigations with the most often carried out using cyclopentadienyl and pentamethylcyclopentadienyl transition metal complexes of different ancillary ligands, whereas unbridged or bridged (ansa) bis–cyclopentadienyl complexes are only of minor importance. Figure 2.4 shows the structures of some types of mono and bis–transition metal complexes for syndiospecific styrene polymerization.



$CpTiCl_3$ Cp^*TiCl_3 Cp_2TiCl_2

Figure 2.4 Mono and Bis transition metal complexes structure for sPS polymerization.

Kaminsky *et al*. (1997) drew a comparison with the above-mentioned catalysts ($CpTiCl_3$, and $Cp*TiCl_3$), and their fluorinated counterparts under identical circumstances. Experiments highlight that fluorinated catalysts have not only a greater number of activities and generate polymers with more molecular weights, but also encourage the decrease of the titanium/MAO molar ratio.

A direct reaction of $CpTiCl_3$ with the co-catalyst methylaluminoxane was observed before the addition of the monomer styrene which consequently led to increased rates of polymerization, higher molecule weights and higher syndiotactic fractions compared to a pre-reaction of styrene with methylaluminoxane (Huang et al., 2004). The effects of molar ratios of catalyst components and polymerization conditions have been investigated with this complex (Jamjah et al., 2006).

Ghosh and Hagihara (2009) studied the effect of 2,6-diisopropylphenol on the catalytic activity of styrene polymerization using a titanium complex $CpTiCl_3$ and Cp^*TiCl_3 combined with methylaluminoxane (MAO) as a co-catalyst. The authors showed that the addition of the 2,6-diisopropylphenol altered the catalytic performance of the aforementioned catalytic systems, in terms of the catalytic activities of the metal complexes and microstructure, molecular weight and molecular weight distribution of polystyrene being synthesized.

In styrene polymerization at 0 and 50 ^oC using substituted bis–cyclopentadienyl complexes [$(RCp_2)\ TiCl_2$] with R = H, C_2H_5, nC_3H_7, iC_3H_7, nC_4H_9, iC_5H_{11}, cC_6H_{11}, sC_4H_9 as catalysts along with MAO as co-catalyst, maximum activity was found with R=nC_4H_9 complex toward the sPS formation (Pereira et al., 2000).

Yang and his co-workers (2004, 2006) have found that styrene monomer primary insertion is more favored than the secondary insertion at the initiation of the styrene polymerization process. They also observed that the secondary and further primary insertions might be impeded by the primary insertion product due to the stability of the formed product. This might be explained by the fact that the blocking of the primary insertion is an undesirable interaction between the phenyl groups of the pre-inserted styrene units and the oncoming styrene molecule. However, secondary insertion is more favorable in the propagation reaction than primary insertion.

Erben *et al.*(2013) described the preparation and properties of trimethylcyclopentadienes and half-sandwich titanium complexes bearing alkoxydimethylsilyl group. The alkoxylsilyl-substituted titanium compounds showed catalytic behavior in styrene polymerization, but their activity was significantly lower than that observed for corresponding trimethylsilyl-substituted titanium alkoxides.

In processes of styrene aqueous polymerizations and styrene-methyl methacrylate copolymerization, using the Cp_2TiCl_2 and Cp_2ZrCl_2 complexes with high monomer/metal molar ratio of 100:1 and at 50–90 ^oC, only tactic polymers were obtained (Patra and Bhattacharjee, 2005a; Patra and Bhattacharjee, 2005b).

The syndiotactic polymerization of styrene, substituted styrene and the copolymerization of styrene are usually catalyzed by bis-cyclopentadienyl complexes such as Cp_2TiCl_2 and $(nC_4H_9Cp)_2TiCl_2$ activated with MAO. Atactic polystyrenes formation was observed in the presence of the corresponding zirconium and hafnium complexes Cp_2ZrCl_2, $(nC_4H_9Cp)_2ZrCl_2$, $(C_6H_5CH_2Cp)_2ZrCl_2$, and $(nC_4H_9Cp)_2HfCl_2$ (Rabagliati et al., 2005; Rabagliati et al., 2008; Patra and Bhattacharjee, 2005b).

Pragliola *et al*. (2013) investigated the aqueous emulsion polymerization of styrene in the presence of half-titanocenes which $CpTiCl_3$,$(CpCH_2CH_2OCH_3)TiCl_3$, and of the titanocene $(Ph)_2C[(Cp)(Flu)Ti]Cl_2$. The polymer features are compared with those of polystyrene obtained in the same reaction conditions, by using Cp_2TiCl_2 as initiator. Titanocene $(Ph)_2C[(Cp)(Flu)Ti]Cl_2$ does not show any activity in styrene polymerization. On the contrary, by using both half-titanocenes $CpTiCl_3$ and $(CpCH_2CH_2OCH_3)TiCl_3$ and stereoirregular polystyrene is produced.