UNIVERSITY OF KWAZULU-NATAL

GAS-PHASE ETHYLENE POLYMERIZATION STUDIES USING A MAGNESIUM CHLORIDE-SUPPORTED ZIEGLER-NATTA CATALYST

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OMASHA NAICKER

Gas-Phase Ethylene Polymerization Studies Using a Magnesium Chloride-Supported Ziegler-Natta Catalyst

Omasha Naicker
BScEng (Chemical)

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Abstract

The gas phase polyethylene production process is the most recently developed and boasts many distinct advantages when compared with the commercial slurry and solution processes. However, in the public literature on ethylene polymerization with $MgCl_2$-supported Ziegler-Natta catalysts there is a general lack of kinetic data that can be used for reactor design and control of polymer properties. This is in spite of intensive research efforts and the successful application of these catalyst systems in industry. The reason is that olefin polymerization on a small scale is rather difficult to execute and the lack of fundamental kinetic models is therefore related to the difficulty in obtaining high-precision kinetic data. For kinetic studies, control of temperature and pressure is important and high precision in experiments demands close control of these parameters. In addressing the issues mentioned above, the solution lies in firstly designing and constructing competent reactor systems.

A 0.7 L stainless steel gas-phase semi-batch reactor system was therefore designed and constructed and was equipped with both temperature and pressure control systems. The reactor was also fitted with a specially designed catalyst injection system which was used to inject the solid catalyst and liquid co-catalyst into a porous catalyst basket. The catalyst remained in the basket where it catalyzed the formation of solid polymer from the gas phase monomer. The injection system safeguarded inert conditions and was essential since both the catalyst and co-catalyst were air and moisture sensitive. The catalyst basket was employed to provide gas and solid phase agitation while not mechanically destroying the catalyst and growing polymer, as would be the case if an impeller was used. Polymer melting and agglomeration was however observed and was attributed to inadequate agitation of the growing particles. With enough mixing energy the contents of the basket can be sufficiently mixed and it is therefore necessary that a higher power motor and magnetic drive replace the motor used in this work.

For the polymerization experiments, a spherical $MgCl_2$-supported Ziegler-Natta catalyst was synthesized. The re-crystallization method for active $MgCl_2$ preparation was preferred to the ball milling method and two of the three implementations of this method were tested. Both the quick cooling and the solvent evaporation techniques were unsuccessful and a variation of the latter was therefore proposed. In the original solvent evaporation method a magnetic stirrer was used and the ethanol was eliminated by evaporation under vacuum. In the method employed in this work, the reaction emulsion was more vigorously stirred with a mechanical stirrer and a vacuum was not required. Instead, the reaction emulsion was stirred under a high, continuous flow of nitrogen which together with the evaporated ethanol passed through an opening in the reaction flask. For polymerization reactions the final catalyst system was $MgCl_2/TiCl_4$/dibutyl phthalate, activated by the co-catalyst triethylaluminium. Scanning electron microscopy verified that the produced support and catalyst particles were both spherical. Further characterization of the catalyst by inductively coupled plasma analysis showed that the two catalysts prepared contained 3.69 wt% Ti and 6.48 wt% Ti, respectively.

The gas-phase ethylene polymerization experiments were aimed at determining the effect of the co-catalyst/catalyst (Al/Ti) molar ratio, the reaction pressure, and the reaction temperature on the product yield. To determine the effect of pressure, experiments were conducted at 1 and 2 barg, at 50°C, and with Al/Ti = 33 and 50. For Al/Ti = 33 an increase in the pressure from 1 to 2 barg led to an increase in the yield from 11.3 to 12 g PE/g cat. h. while for Al/Ti = 50, the same increase in the pressure led to an increase in the yield from 14.2 to 17 g PE/g cat. h. The effect of Al/Ti was determined at 10, 33, and 60 and the yields obtained were 0.8, 8.5, and 14.2 g PE/g cat. h., respectively. These runs were undertaken at 1 barg and 50°C. It was found that an increase in Al/Ti led to an increase in the yield while an optimum Al/Ti between 60 and 100 is generally observed in the literature. The effect of temperature was assessed at 50, 60 and 70°C and the yields obtained were 8.5, 24.4 and 8 g PE/g cat. h., respectively. A pressure of 1 barg and Al/Ti = 33 was used. The yield was found to increase as the temperature was increased from 50 to 60°C, but decreased when the temperature was further increased to 70°C. This optimum temperature is generally observed in the literature but is different for different types of catalyst systems.

The molar masses of the products of two experiments, carried out at 1 bar and 50°C, were determined by gel permeation chromatography. For Al/Ti = 26 and 60, the number average molecular weight (M_n) was found to be 227 000 and 330 400, respectively, and the weight average molecular weight (M_w) was found to be 1 260 600 and 1 516 400, respectively. The polymer produced with Al/Ti = 26 and 60 were found to have a polydispersity index of 5.6 and 4.6, respectively. These are within the expected range for supported catalysts. Scanning electron micrographs confirmed that the polymer particles had the same spherical morphology as the catalyst particles and one of the objectives of preparing the supported catalyst was realized.

The yields obtained in this work were found to be lower than those presented in the literature. The first explanation for this is the inadequate agitation of the growing polymer particles. The melting and agglomeration which resulted led to active site deactivation and therefore to the low yields observed. The second reason could be that the prepared catalyst had a much lower specific surface area than those used in the literature. This is possible even though much effort had been made in this work to increase the specific surface area of the catalyst, firstly by dealcoholation of the support and secondly by repeating the treatment of the catalyst with $TiCl_4$.

With the exception of the inadequate mixing, the rest of the reactor system was successfully used to carry out the necessary polymerization reactions. The temperature and pressure control systems worked accurately and the catalyst injection system made it possible to inject the catalyst without contamination. Also, although product yields were not optimised, the difficulties associated with synthesizing an air and moisture sensitive Ziegler-Natta catalyst have been overcome. The synthesized catalyst was capable of polymerizing ethylene and of replicating its morphology into the morphology of the polymer.

I, Omasha Naicker, declare that to the best of my knowledge, the work contained in this document is my own, unless stated to the contrary in the text. This thesis has not been submitted for degree purposes, in part or in whole, to any other university.

O. Naicker

As the candidate's supervisor, I, Prof. M. Starzak, have approved this thesis for submission.

Prof. M. Starzak

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List of Abbreviations

Abbreviation	Description
ccp	cubic close packed
CSTR	continuous stirred tank reactor
DBP	dibutyl phthalate
DIBP	diisobutyl phthalate
DIOP	diisooctyl phthalate
EB	ethyl benzoate
ED	external electron donor
FBR	fluidized bed reactor
FTIR	Fourier transform infrared
GPC	gel permeation chromatography
hcp	hexagonal close packed
HDPE	high density polyethylene
ICP	inductively coupled plasma
ID	internal electron donor
IR	infrared
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
MAO	methyl aluminoxane
MFI	melt flow index
M_n	number average molecular weight
M_w	weight average molecular weight
MWD	molecular weigh distribution
PDI	polydispersity index
PE	polyethylene
PP	polypropylene
PSD	particle size distribution
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SSC	single-site catalysts
TEA	triethylaluminium
UHP	ultra high purity
XRD	X-ray diffraction

Chapter 1

Preliminaries

In this chapter a general introduction to the polymerization of ethylene with heterogeneous Ziegler-Natta catalysts is given. Since the discovery of these catalysts there have been significant improvements in the catalyst system and the historical development is briefly outlined here. An explanation of the mechanism of Ziegler-Natta catalysis and of the physical and mechanical properties of polyethylene, such as polymer density, chain length, and molecular weight, then follows. Polyethylene is produced commercially by a number of diverse processes but the gas phase process is of sole interest in this work and only the commercial gas phase processes are elaborated on. The advantages and disadvantages of these gas phase processes are also highlighted. An overview of a typical polymerization process then follows and the chapter is concluded by highlighting objectives of this study and by a brief overview of each of the chapters that follow.

1.1 Introduction

Although both the science and technology of polymers had advanced remarkably by the early 1950s formidable challenges remained to be surmounted. The abundant supply and low cost of hydrocarbons meant that hydrocarbon polymers represented a highly useful class of substances. Particularly attractive targets were polymers which could be made from the smallest and most abundant such hydrocarbons, ethylene and propylene, containing two and three carbon atoms respectively. The general ability of hydrocarbon molecules to join together to form long chains had long been recognized; however, in the case of ethylene and propylene this presented a significant challenge. The polymerization of ethylene had been accomplished but only at uneconomically high temperatures and pressures and yielding polymers whose properties left much to be desired. The polymerization of propylene remained to be achieved.

In 1953, while engaged in basic research on the reactions of compounds containing aluminium-carbon bonds German chemist Karl Ziegler, working at the Max Planck Institute for Coal Research in Mulheim, discovered that by adding salts of certain metals (e.g. Ti or Zr) these compounds resulted in highly active catalysts for the polymerization of ethylene under relatively mild conditions. Furthermore, the polymers formed in this way had chains that were longer and more linear, and these polymers therefore had superior properties such as strength, hardness and chemical inertness, making them useful in many applications.

Building on Ziegler's discovery, Italian chemist Giulio Natta, working at the Milan Polytechnic Institute, demonstrated that similar catalysts were effective for the polymerization of propylene. With such catalysts it became possible to achieve exquisite control of the chain length and structures of the resulting polypropylene polymers and therefore also of their properties. In 1963, the Nobel Prize in Chemistry was awarded to both Ziegler and Natta for their discoveries in the field of the Chemistry and Technology of Polymers.

Industrial applications of Ziegler-Natta catalysts were realized almost immediately and, with various subsequent refinements, continue to expand. The uses of polyethylene and polypropylene extend to virtually every facet of industry and daily life, including construction and building materials, containers, toys, sporting goods, electronic appliances, textiles, carpets and medical products. In many of these applications polymers replace other materials, such as glass and metals, but their distinctive properties have also given rise to entirely new applications. The billions of tons of polyolefins (essentially homopolymers and copolymers of ethylene and propylene) which are manufactured each year clearly indicate the commercial significance of Ziegler-Natta catalyzed polymerization processes. Also, the thousands of patents and articles describing numerous variations of the Ziegler-Natta catalyst system make polyolefin production technology a very active area of research.

1.2 Ziegler-Natta catalysts

A Ziegler-Natta catalyst is comprised of at least two parts: a transition metal component and a main group metal alkyl compound. The transition metal component is usually either titanium or vanadium and the metal alkyl compound is usually an aluminium alkyl. In common practice, the titanium component is called the "catalyst" and the aluminium alkyl is called the "co-catalyst" and it is the combination of the two that make up the active catalyst. The importance of these catalysts lies in their ability to produce stereoregular polymers from ethylene, and isotactic (methyl groups oriented uniformly) polymers from propylene. Improvements in the catalyst system since their discovery have been significant, and a brief summary of their evolution is outlined here.

1.2.1 The first generation - titanium trichloride catalysts

The first commercial catalysts resulted from the industrial extensions of Natta's work on the relationship between the crystal structure of titanium chlorides and the overall activity and selectivity of the catalysts. $TiCl_3$ was prepared from $TiCl_4$ by many different routes including reduction with hydrogen, irradiation and reduction with alkylaluminiums. Natta found that four structural modifications existed (named α, β, γ, and δ). The brown β-$TiCl_3$ had a chain like structure and had moderate activity and low stereoselectivity and was therefore not economically attractive. More stereospecific $TiCl_3$ (α, γ, δ) were formed upon thermal treatment of the β-phase and had a deep purple colour and a layer lattice structure. These catalysts, however, were economically infeasible and attempts were made to include a third component (electron donors such as triethylaluminium, TEA) to improve stereoselectivity. Another attempt to improve catalyst performance was ball-milling which resulted in an activity increase due to the reduction in size of the primary crystallites. The addition of a Lewis base to the catalyst was later attempted, essentially in order to improve the stereospecificity of the polymers, however, the higher stereospecificity did not correspond to an increase in activity.

1.2.2 The second generation – elimination of catalyst poisons

In the case of the second generation catalysts, it became apparent that the presence of co-precipitated $AlCl_3$ led to the formation of the catalyst poison $AlEtCl_2$, and that the large size of the catalyst ($TiCl_3$) crystallites resulted in a low proportion of active Ti sites. The removal of the co-precipitated $AlCl_3$, by washing with hydrocarbons at elevated temperatures, resulted in an approximate 30% increase in activity. It was also noted that by transforming the brown β-$TiCl_3$ into the stereoselective δ-$TiCl_3$ at low temperatures (<100 °C) in the presence of $TiCl_4$, which acted as a catalyst for the change of phase, resulted in smaller primary crystallites. The success of the second generation catalysts was due to the new morphology of the catalyst particles, which were highly porous active catalysts with high surface areas.

1.2.3 The third generation – supported catalysts

The prehistory of the third generation catalysts began in 1960, when Shell patented a catalyst for propylene polymerization that used $TiCl_4$ supported on $MgCl_2$. In 1968, Montecatini and Mitsui independently patented catalysts prepared from $TiCl_4$, $MgCl_2$ and an electron donor, and activated by a mixture of trialkylaluminium with another electron donor. These catalysts were formed by physically or chemically supporting catalyst molecules on the surface of a solid support. Since only the sites located at the surface of the support were available for polymerization, supports with high specific surface areas such as silica and magnesium dichloride ($MgCl_2$) were preferred. This generation of catalysts brought about a 50-fold increase in activity.

1.2.4 The fourth generation – homogenous catalysts

The fourth generation of catalysts, based on metallocene compounds, is now evolving towards industrial success. In 1986 Kaminsky and Sinn discovered that methyl aluminoxane (MAO)-activated homogeneous metallocene catalysts were capable of polymerizing propylene and higher olefins. Practical applications of metallocene catalysts require their pre-adsorption onto solid supports such as alumina or silica gels.

Although the metallocene-based single-site catalysts (SSC's) have recently been shown to have the ability to produce precisely tailored polymers, the high activity supported Ziegler-Natta catalysts are set to dominate polyolefin production for at least the next few decades.

1.3 Polymerization chemistry

Ethylene is the smallest α-olefin and because steric demand is minimal the aspect of stereoregularity does not play a role. Three types of polymerization mechanisms have been found to result in polymer:

- radical polymerization
- true anionic polymerization, and
- co-ordination polymerization

Ziegler-Natta type catalysts, such as the first generation $TiCl_3$ catalysts, supported catalysts such as the $MgCl_2$ supported catalysts and homogenous catalysts all polymerize by co-ordination polymerization. The repeating structural unit of polyethylene is demonstrated in Figure 1-1 and the resulting linear polymer is referred to as high-density polyethylene (HDPE).

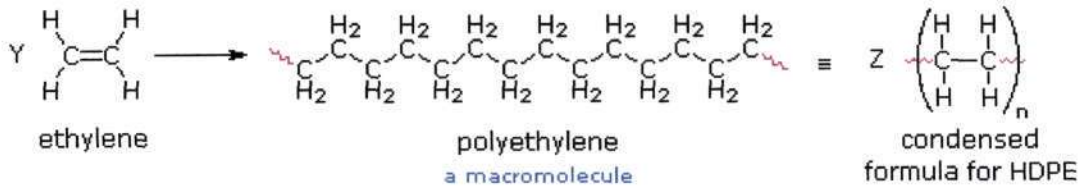

Figure 1-1 Polyethylene Polymerization

Ziegler-Natta catalysts are a combination of a transition metal catalyst like $TiCl_4$ and a co-catalyst which is usually based on group III metals like aluminium. Most often the catalyst/co-catalyst pair is $TiCl_4$ with Al $(C_2H_5)_3$. In the interior of a $TiCl_4$ crystal each titanium is surrounded by six chlorines, but on the surface a titanium atom is surrounded by only five chlorine atoms, making it reactive. The co-catalyst donates one of its ethyl groups to titanium, but removes one of the chlorines in the process. The Al remains co-ordinated to one of the carbon atoms of the ethyl group that it has just transferred to the titanium, and also to one of the adjacent chlorine atoms. *The now active titanium still has one empty orbital to be filled and this is where* polymerization occurs.

A polymer chain is initiated when a monomer molecule attacks an active titanium centre. There are two electrons in the π-system of a carbon-carbon double bond, and these electrons are used to fill the empty orbital of the titanium. The atoms then rearrange themselves to form a slightly different structure, once again leaving the titanium atom with one empty orbital (Figure 1-2). The polymer chain grows as monomer is inserted between the chain and the active site, thus increasing the chain length. The polymer bulk accumulated around the catalyst particle is an agglomeration of numerous polymer chains.

A chain will grow at a catalytic site until it reacts with a terminating agent which causes a scission from the site. When a polymer chain is terminated, it joins the bulk polymer material accumulated around the catalyst. This frees the catalytic site for chain initiation and subsequent propagation. The chief terminating agent is considered to be hydrogen and it is deliberately added to the reaction mixture for this purpose. However, chains may also be terminated by the co-catalyst and the monomer.

The reactions discussed above may be classified as series and parallel reactions. The growth of a polymer chain occurs sequentially; only one monomer unit can be inserted between the catalytic site and the polymer chain at a time. However, other reactions (catalytic site and chain termination reactions) can occur simultaneously.

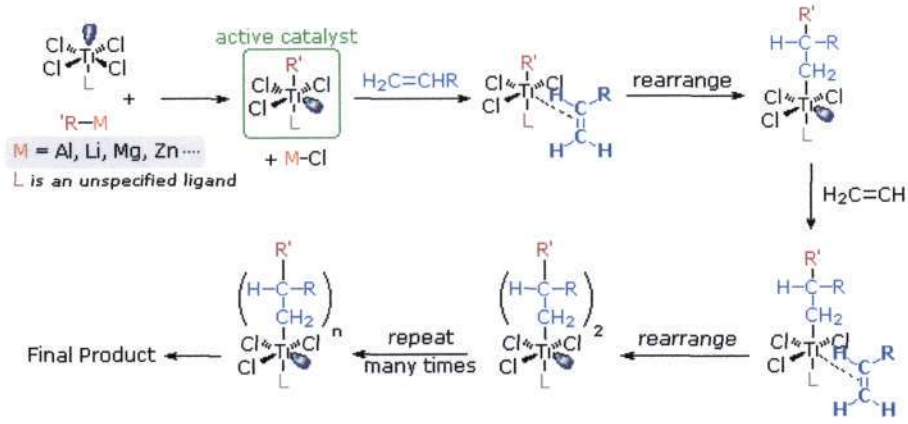

Figure 1-2 Mechanism of Ziegler-Natta Catalysis

1.4 Physical and mechanical properties of polyethylene

Although polyethylene (PE) is the simplest of the polyolefins it has been and remains to be the most extensively studied polymer. This is due to the fact that the term "polyethylene" can no longer be used to refer to a single polymer. Instead, it encompasses an array of ethylene-based materials that differ from each other in several respects, which include molecular weight and distribution, chain length and the presence/absence of branches.

Physical and mechanical properties of polyethylene depend on density, crystallinity, molecular weight and distribution, chemical composition, and other characteristics. These variables are controlled by polymerization conditions and are not mutually independent. The essential variable which affects all the physical properties is the chain microstructure of the polyethylene. Backbone linearity contributes to improve tensile strength and tear properties, while branching increases the toughness of the material. Commercial resins are mainly specified by density, molecular weight (melt index) and molecular weight distribution (melt flow ratio). The processing and end-use properties are mainly governed by these variables.

1.4.1 Polymer density

Polyethylene is normally classified as low density (LDPE) at 0.910-0.930 g/cm^3 and high density (HDPE) at 0.931-0.970 g/cm^3 (Figure 1-3). Low density polyethylene is further classified as low-density polyethylene (LDPE) and linear low density polyethylene (LLDPE) based on polymer chain microstructure and synthesis process. The density of polyethylene depends largely on the following factors: the number of branches, branch chain length, branch frequency distribution, chemical composition distribution and molecular weight and distribution. In general, the density of polyethylene decreases with an increase of branch numbers and the crystallinity of polyethylene decreases significantly with an increase in branch frequency and size. Therefore any physical properties related to crystallinity, such as stiffness and yield stress will be affected by branching. Also, density decreases with an increase in molecular weight, this is due to the inhibition of crystallization by longer molecular chains.

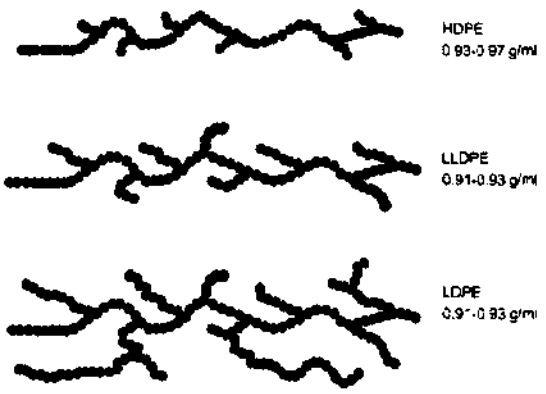

Figure 1-3 Schematic of Molecular Structures of Polyethylene

1.4.2 Chain length

Polymerization occurs by the sequential addition of monomer to the polymer chain. The termination reaction occurs in parallel, with hydrogen being the chief terminating agent. It is generally accepted (Long Chain Assumption) that the length of the polymer chain growing at a catalytic site does not affect the termination reaction, which proceeds at a rate determined solely by the temperature and the concentration of the terminating agent. Chains are continuously terminated and the probability of a chain growing to a certain length decreases with increasing chain length. Also, shorter chains have a smaller molecular weight and therefore constitute a smaller mass fraction than the longer chains. These factors together contribute to the overall shape of the chain length distribution, as is depicted in Figure 1-4. The chain length distribution is characterized by two measurable indices, known as the Melt Flow Index (MFI) and Polydispersity Index (PDI). These are related to the viscosity of the molten polymer and correspond to the average chain length and statistical spread respectively.

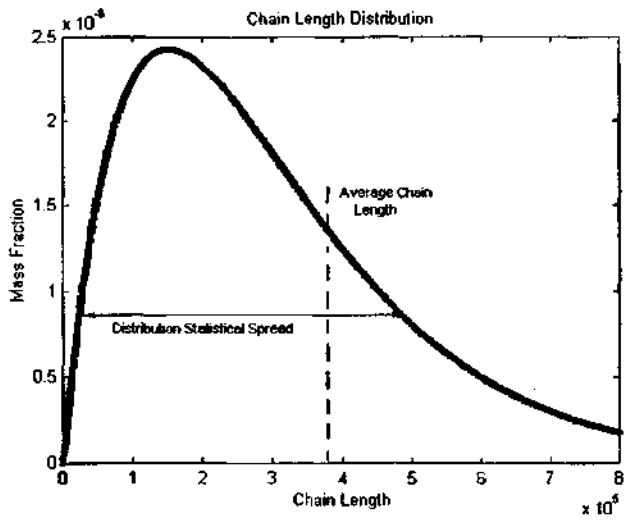

Figure 1-4 Typical Chain Length Distribution

1.4.3 Molecular weight and distribution

Unlike simple pure compounds, most polymers are not composed of identical molecules. The high density polyethylene (HDPE) molecules, for example, are all long carbon chains, but the lengths may vary by thousands of monomer units. Because of this, polymer molecular weights are usually given as averages. Two experimentally determined values are common: M_n ($M_n = \Sigma n_i M_i$), the number average molecular weight is calculated from the mole fraction distribution of different sized molecules in a sample, and M_w($M_w = \Sigma w_i M_i$), the weight average molecular weight is calculated from the weight fraction distribution of different sized molecules. Since larger molecules in a sample weigh more than smaller molecules, M_w is necessarily skewed to higher values, and is always greater than M_n.

1.4.4 Tacticity

Symmetrical monomers such as ethylene and tetrafluoroethylene can join together in only one way. Monosubstituted monomers, on the other hand, may join together in two organized ways, illustrated in Figure 1-5, or in a third random manner. Most monomers of this kind, including propylene, join in a head-to-tail fashion, with some randomness occurring from time to time.

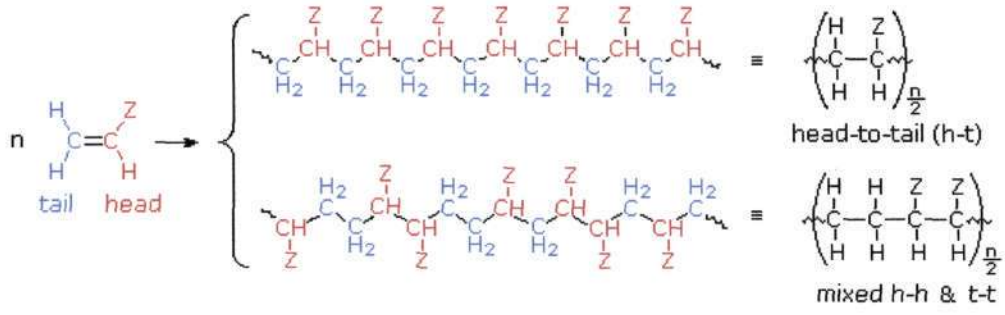

Figure 1-5 Regioisomeric Polymers from Substituted Monomers

If the polymer chain is drawn in a zig-zag fashion, as shown above, each of the substituent groups (Z) will necessarily be located above or below the plane defined by the carbon chain. Consequently three configurational isomers of such polymers can be identified. If all the substituents lie on one side of the chain the configuration is called isotactic. If the substituents alternate from one side to another in a regular manner the configuration is termed syndiotactic. Finally, a random arrangement of substituent groups is referred to as atactic. Examples of these configurations are shown in Figure 1-6.