

Chapter 9

Coordination Polymerization

The coordination polymerization is invented by two Italian scientists: Karl Ziegler and Giulio Natta. They shared the nobel prize in chemistry in 1963 using Ziegler–Natta catalysts to polymerize nonpolar monomers: 1-alkene, cycloalkenes, dienes, and alkynes through coordination mechanism instead of common chain or step polymerization [1]. The polymers can exhibit stereo specificity if the monomer contains unsymmetrical carbon. Since the 1960s, both heterogeneous and homogeneous Ziegler–Natta catalysts have been developed. The heterogeneous catalysts consist of transition metal compound (e.g., titanium chloride) and organometallic compounds (e.g., aluminum alkyl halide) as cocatalyst. The homogeneous catalysts are made from transition metal metallocene and aluminum alkyl halide. The metallocene is a compound typically consisting of two cyclopentadienyl anions (Cp , which is C_5H_5^-) bound to a metal center (M) in the oxidation state II, with the resulting general formula $(\text{C}_5\text{H}_5)_2\text{M}$. However, the homogeneous catalysts exhibit low activity, not until 1980, W. Kaminsky found that the catalytical effects of homogeneous Ziegler–Natta catalysts can be greatly enhanced by the addition of cocatalysts derived from the reaction of aluminum alkyl with water (e.g., methylalumoxanes (MAO)) [2]. The cyclopentadienyl group of metallocenes in the homogeneous catalysts provides defined space that can control the stereo specificity of the polymer better than that of heterogeneous catalysts. Table 9.1 shows some of commercial polymers synthesized by coordination catalysts.

9.1 Heterogeneous Ziegler–Natta Polymerization

9.1.1 Catalysts

The Ziegler–Natta initiators are the only initiators that polymerize α -olefins such as propene and 1-butene which can not be polymerized by either radical or ionic initiators. Thousands of different combinations of transition and Group I-III metal

Table 9.1 Commercially available polymers synthesized with complex coordination catalysts [3]

Polymer	Principal stereochemistry	Typical uses
Polyethylene, high density (HDPE)	–	Bottles, drums, pipe, conduit, sheet, film, wire and cable insulation
Polyethylene, ultrahigh molecular weight (UHMWPE)	–	Surgical prostheses, machine parts, heavy-duty liners
Polypropylene	Isotactic	Automobile and appliance parts, rope, cordage, webbing, carpeting, film
Poly(1-butene)	Isotactic	Film, pipe
Poly(4-methyl-1-pentene) ^a	Isotactic	Packaging, medical supplies, lighting
Polystyrene	Syndiotactic	Specialty plastics
1,4-Polybutadiene	trans	Metal can coatings, potting compounds for transformers
1,4-Polyisoprene	trans	Golf ball covers, orthopedic devices
Ethylene-1-alkene ^b copolymer (linear low density polyethylene, LLDPE)	–	Blending with LDPE, packaging film, bottles
Ethylene-propylene block copolymers (polyallomers)	Isotactic	Food packaging, automotive trim, toys, bottles, film, heat-sterilizable containers
Polydicyclopentadiene ^c	–	Reaction injection molding(RIM) structural plastics
1,4-Polybutadiene	cis	Tires, conveyer belts, wire and cable insulation, foot-ware
1,4-Polyisoprene	cis	Tires, foot-ware, adhesives, coated fabrics
Poly(1-octenylene) (polyoctenamer) ^c	trans	Blending with other elastomers
Poly(1,3-cyclopentenylenevinylene) (norbornene polymer) ^c	trans	Molding compounds, engine mounts, car bumper guards
Polypropylene(amorphous)	–	Asphalt blends, sealants, adhesives, cable coatings
Ethylene-propylene copolymer (EPM,EPR)	–	Impact modifier for polypropylene, car bumper guards
Ethylene-propylene-diene copolymer (EPDM)	–	Wire and cable insulation, weather stripping, tire side walls, hose, seals

^a Usually copolymerized with small amounts of 1-pentene

^b 1-Butene, 1-hexene, and 1-octene

^c Synthesized by ring-opening metathesis polymerization of the corresponding cycloalkene

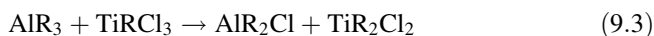
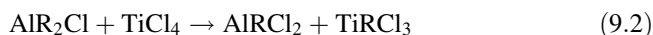
components, often together with other compounds such as electron donors, studied for use in alkene polymerizations [4].

Catalysts are prepared by mixing the compounds in a dry, inert solvent in the absence of oxygen usually at a low temperature. The mixture of aluminum compound with titanium compound is to form radical, the first of this kind catalyst being used as shown below.

Table 9.2 Variation of polypropylene isotacticity with catalyst [3]

Catalyst ^a	Stereoregularity (%)
AlEt ₃ + TiCl ₄	35
AlEt ₃ + β-TiCl ₃	45
AlEt ₃ + α-TiCl ₃	85
AlEt ₃ + ZrCl ₄	55
AlEt ₃ + VCl ₃	73
AlEt ₃ + TiCl ₄ + P,As or Sb compounds	35
AlEt ₂ X + TiCl ₃	90–99
AlEtX ₂ + γ-TiCl ₃ + amine	99

^a Et = ethyl; X = halogen



Further reduction may also occur:



In addition, TiCl₃ may be formed by the equilibrium



The stereo regularity of the polymers depends on the type of catalysts used as shown in Table 9.2 which indicates the isotacticity of polypropylene is varied by different catalyst. Syndiotactic polypropylene has been prepared under both heterogeneous and homogeneous conditions, but only under homogeneous condition a high degree of syndiotactic placement has been achieved.

With the appropriate choice of catalyst, specific stereochemical arrangements of polymerization of diene monomer can be obtained as shown in Tables 9.3, and 9.4. The 1,3-butadiene monomer will obtain *cis*-1,4; *trans*-1,4; isotactic 1,2-, and syndiotactic 1,2-polymers. The isoprene monomer will obtain *cis*- and *trans*-1,4; 1,2-; and 3,4-polymers.

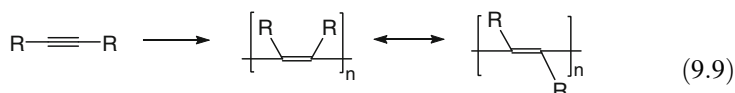
The *cis* polymer is usually formed at relative low temperature, for instance, polymerization of acetylene using an Al(C₂H₅)₃–Ti(OC₄H₉ – n)₄ catalyst yields *cis* polymer at temperatures below –78°C, but *trans* polyacetylene is formed at 150°C. The result may be due to thermal isomerization of the initially formed *cis* polymer.

Table 9.3 Catalysts for the stereospecific polymerization of butadiene [3]

Catalyst ^a	Yield (%)	Polymer structure ^b
R ₃ Al + VCl ₄	97–98	trans-1,4
R ₃ Al + VCl ₃	99	trans-1,4
R ₃ Al + VOCl ₃	97–98	trans-1,4
R ₃ Al + TiI ₄	93–94	cis-1,4
R ₂ AlCl + CoCl ₂	96–97	cis-1,4
R ₃ Al + Ti(OC ₄ H ₉) ₄	90–100	1,2
Et ₃ Al + Cr(C ₆ H ₅ CN) ₆ ; Al/Cr = 2	~ 100	st-1,2
Et ₃ Al + Cr(C ₆ H ₅ CN) ₆ ; Al/Cr = 10	~ 100	it-1,2

^a Et = ethyl^b st = syndiotactic, it = isotactic**Table 9.4** Catalysts for the stereospecific polymerization of isoprene [3]

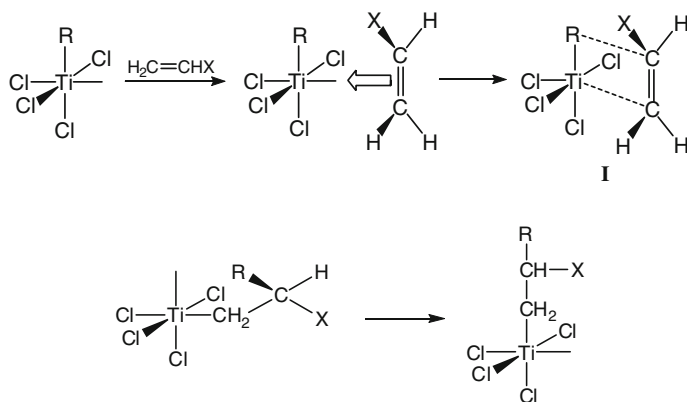
Catalyst ^a	Yield (%)	Polymer Structure
R ₃ Al + α -TiCl ₃	91	trans-1,4
Et ₃ Al + VCl ₃	99	trans-1,4
Et ₃ Al + TiCl ₄ ; Al/Ti < 1	95	trans-1,4
Et ₃ Al + TiCl ₄ ; Al/Ti > 1	96	cis-1,4
Et ₃ Al + Ti(OR) ₄	95	3,4

^a Et = ethyl

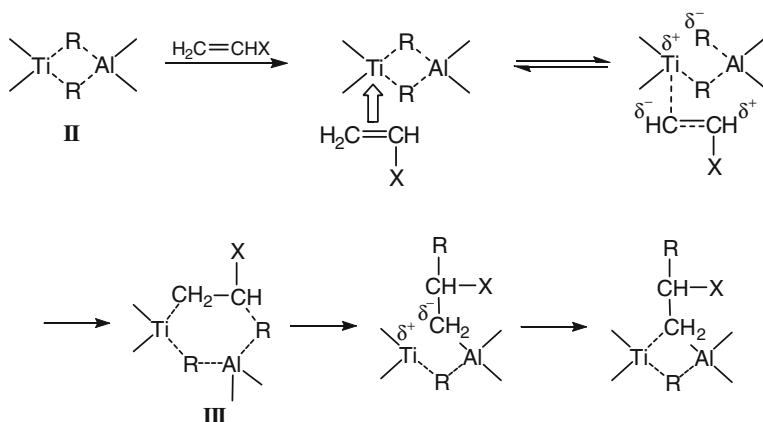
9.1.2 Reaction Mechanisms

The coordination polymerization of alkene can be preceded either by monometallic mechanism or bimetallic mechanism depending on the catalyst. Scheme 9.1 shows the reaction mechanism of substituted alkene being polymerized by using titanium compound catalyst. The double bond of alkene will undergo *cis* addition and coordinate with the empty orbital of titanium compound to form four membered ring coordinate intermediate **I**. The stereo specificity of substituted alkene is preserved via intermediate **I**. Then the bond is formed on the Ti compound catalyst. If the catalyst is made from aluminum compound and titanium compound, the polymerization will proceed through bimetallic mechanism as shown in Scheme 9.2. A bridge structure **II** is formed between two metal compounds first. Then the substituted alkene is coordinated with Ti compound to form six-membered ring coordination **III**. The stereo specificity of substituted alkene is preserved via intermediate **III**.

The polymer chain grows from the catalyst surface by successive insertion reactions of complexed monomer and the R group originally present in the

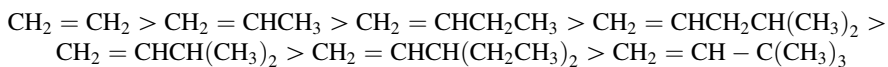


Scheme 9.1 Monometallic mechanism of Ziegler–Natta polymerization of substituted alkene



Scheme 9.2 Bimetallic mechanism of Ziegler–Natta polymerization of substituted alkene

organometallic cocatalyst ends up as the terminal group of the chain. Monomer activity decreases with increasing steric hindrance about the double bond as shown below:



The reaction has the characteristic of living anionic polymerization. The reaction is usually terminated by active hydrogen as shown in the following Eqs. 9.10–9.15. Hydrogen is the preferred transfer agent for controlling molecular weight due to low cost and clean reaction but the termination reaction is usually carried out by hydrogen containing compounds as shown in Eq. 9.15 [3].

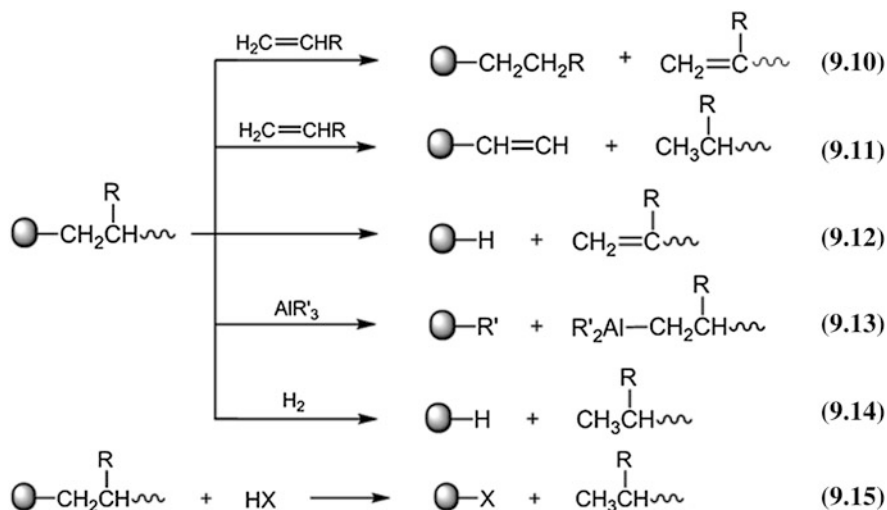
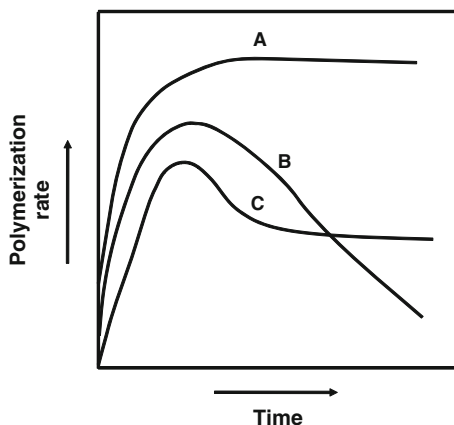


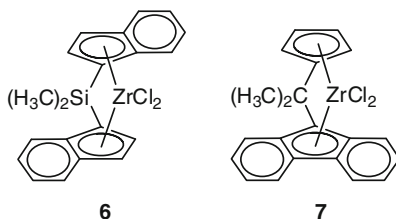
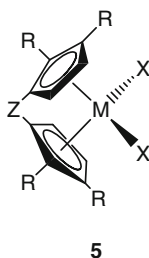
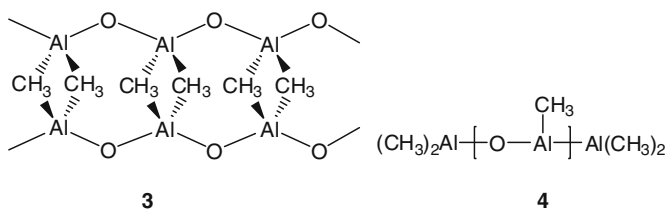
Fig. 9.1 Three types of polymerization rate observed in Ziegler-Natta polymerization: **a** constant, **b** decaying, and **c** decaying to constant [3]



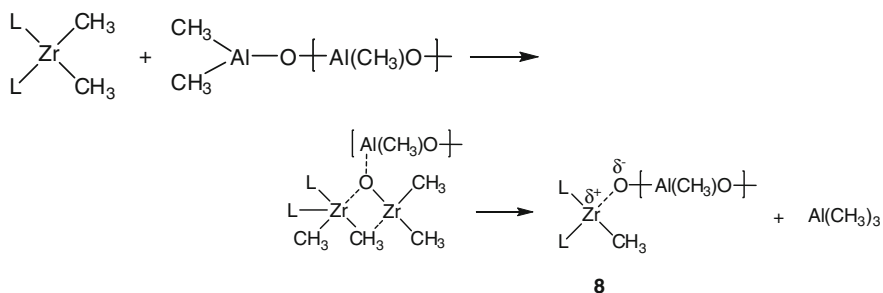
The relationship between the polymerization rate and time is shown in Fig. 9.1. The decaying rate type is most common. That is due to structural changes from the reducing the number or activity of active centers. It is also due to the encapsulation of active centers by polymer which prevents approach by monomer.

Molecular weight distributions are generally broad when insoluble catalysts are used and much narrower with soluble catalysts. The broad distribution may arise from the decay of catalyst activity or from the presence of sites of variable activity.

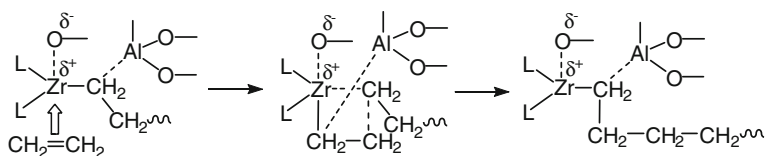
There are two theories to explain the reaction mechanisms of coordination of dienes. One theory is based on whether the catalyst coordinates one or both double bonds of the diene. Coordination of one would thus lead to 1,2-polymerization and coordination of both to 1,4-polymerization. Another theory is based on the



Metallocene has well-defined molecular structure and polymerization occurs at one position in the molecule, the transition metal atoms. Thus, the metallocene is also called *single-site catalyst* in contrast to the multi active site of heterogeneous catalyst. Scheme 9.4 shows an example of the formation of active site in a zirconium catalyst, L_2ZrCl_2 (where L represents the π ligands) which involves initial complexation between MAO and the catalyst, is followed by Cl-CH₃ exchange to



Scheme 9.4 Formation of the active site in a zirconocene catalyst

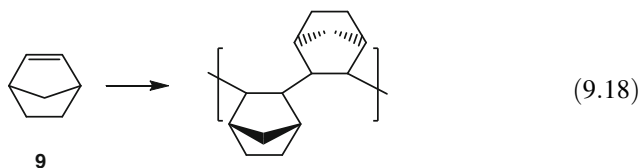


Scheme 9.5 Possible polymerization mechanism for ethylene using zirconocene catalyst

form $L_2Zr(CH_3)_2$. The methylated zirconocene reacts further with MAO to form the active species of **8**.

Scheme 9.5 shows the possible polymerization mechanisms of ethylene using zirconocene catalyst. The ethylene is *cis* added to the empty orbital of Zr site to form transition site, then is further on to precede polymerization.

The comparison between metallocene catalysts and heterogeneous catalysts for alkene polymerization is shown in Table 9.5. The metallocene out performs over the heterogeneous catalysts. Heterogeneous catalysts contain sites of variable activity that accounts for the large PDI. Metallocene catalysts differ from heterogeneous catalysts is that they are capable of polymerizing strained cycloalkenes such as cyclobutene or norbornene **9** through the double bond to yield crystalline stereoregular polymers (Eq. 9.18). Ring-opening polymerization of cycloalkene monomers is more common with heterogeneous Ziegler–Natta catalysts.



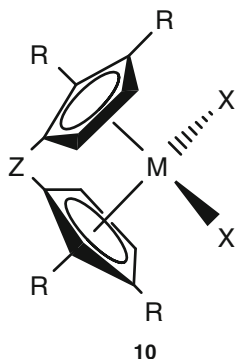
The molecular weight decreases with increasing polymerization temperature, with increasing catalyst concentration, with the addition of hydrogen to the monomer feed.

The reactivity of metallocene catalyst **10** depends on its chemical structure. The M of metallocene can be Zr, Ti or Hf. The X is Cl or alkyl; Z is an optional bridging group, $C(CH_3)_2$, $Si(CH_3)_2$, or CH_2CH_2 ; R is H or alkyl. For the group 4B metals, the order of activity is $Zr > Ti > Hf$. Alkyl groups on the cyclopentadiene rings increase catalyst activity if they are not too bulky. Large, bulky alkyl groups and electron-withdrawing groups decrease the activity. Increasing the size of the

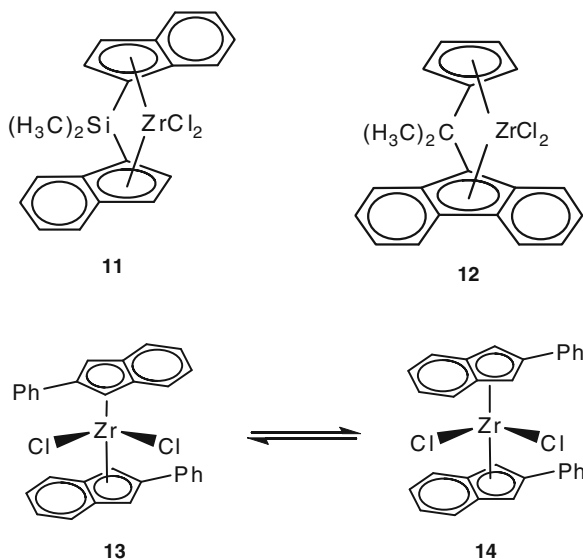
Table 9.5 Comparison between metallocene catalysts and heterogeneous catalysts for alkene polymerization

Catalyst	PDI	Catalyst activity	Strained cycloalkene type
Metallocene	2–2.5	10–100	Yes
Heterogeneous	5–6	1	No

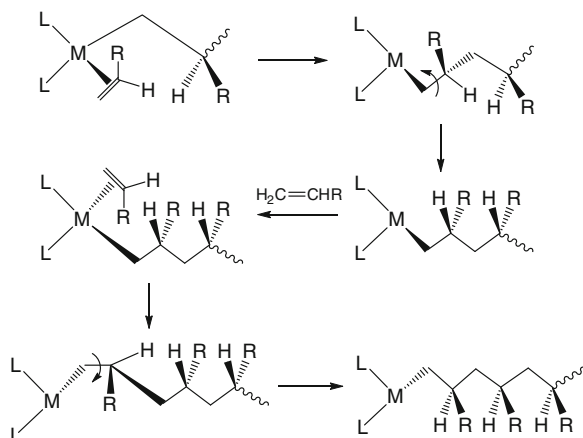
groups attached to the atom bridging, the cyclopentadiene rings (C or Si) reduces the activity. MAO affords much higher catalyst activities than ethyl or higher alkyl alumoxane cocatalyst.



Achiral catalysts of CpZrCl_2 , bridged or unbridged yield atactic polymer. Catalyst **11**(chiral) yields isotactic; **12**(achiral) yields syndiotactic polymer. The much different size of the two π ligands of **12** is assumed to play a role in the formation of syndiotactic polymer. Substitution of a methyl group on the cyclopentadiene ring of **12** results in hemi isotactic polypropylene (mixture of isotactic and atactic). Catalyst **13** can rotate between chiral and achiral geometries, with the chiral form being responsible for the isotactic blocks and the achiral form for the atactic blocks. The isotactic blocks form crystalline microdomains in the polymer matrix, the stereoblock copolymers exhibit elastomeric properties. The degree of isotacticity is sensitive to propylene pressure and reaction temperature.



Scheme 9.6 A mechanism for isotactic placement with a metallocene catalyst [3]



What are the reaction mechanisms for the stereospecificity of metallocene catalyzed polymerization? Most models take into account steric interactions involving the π ligands attached to the metal atom and the last inserted monomer unit of the polymer chain, as the incoming monomer inserts itself into the constrained active site. Scheme 9.6 describes the isotactic placement for **11**. Optically active isotactic polymer will form from pure enantiomer of **11**. The larger fluorenyl group restricts the approach of the propylene molecule such that one side of the coordination site is enantioselective to one face of the monomer, and the other side of the coordination site shows the opposite enantioselectivity. Thus as the coordination site moves from side to side, syndiotactic polymer is formed. A methyl group on the cyclopentadiene ring presumably interferes with the selectivity on one side only. Since only one side of the coordination site is then stereoselective, a hemi-isotactic polymer forms.

Dow Chemical Company is using metallocene catalysis to produce its new Questra syndiotactic polystyrene (SPS). Dow has transformed polystyrene—an amorphous, low melting point, relatively brittle plastic—into a tough crystalline material with a melting point of 270°C (conventional is 250°C) for electronics, automotive under-the-hood, engineered films, and medical applications. Therefore polystyrene can be either low cost common plastic or high performance engineering plastics.

9.3 Ziegler–Natta Copolymerization

Random copolymers of ethylene and 1-alkenes are obtainable with Ziegler–Natta catalyst. The most important ones are ethylene with 1-alkene (LLDPE) and ethylene with ethylene propylene monomer (EPM) or ethylene-propylene-diene monomer (EPDM). Table 9.6 summarizes the reactivity ratio of Ziegler–Natta

Table 9.6 Representative reactivity ratios of Ziegler–Natta copolymerization [3]

Monomer 1	Monomer 2	Catalyst ^a	r_1	r_2
Heterogeneous				
Ethylene	Propylene	TiCl ₃ /AlR ₃	15.72	0.110
Ethylene	Propylene	VCl ₃ /AlR ₃	5.61	0.145
Ethylene	1-Butene	VCl ₃ /AlR ₃	26.90	0.043
Propylene	1-Butene	VCl ₃ /AlR ₃	4.04	0.252
Homogeneous				
Ethylene	Propylene	Cp ₂ ZrMe ₂	31	0.005
Ethylene	Propylene	[Z(Ind) ₂]ZrCl ₂	6.6	0.060
Ethylene	1-Butene	Cp ₂ ZrMe ₂	55	0.017
Ethylene	1-Hexene	Cp ₂ ZrMe ₂	69	0.020

^a R = C₆H₁₃; Cp = cyclopentadiene; Me = methyl; Z = CH₂CH₂; Ind = indene

copolymerization. The reactivity ratio is the rate constant ratio of monomer toward itself and toward other monomer and expressed as $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. The determination of reactivity ratio will be discussed in [Chap. 10](#).

Ethylene is more reactive than higher alkenes with both heterogeneous and homogeneous catalysts. In most instances, $r_1 r_2$ is close to unity. With heterogeneous catalysts, a wide range of compositions is generally obtained, possible because different active sites may give rise to different reactivity ratios, or because of decay of activity. A more homogeneous polymer composition is obtained with soluble catalysts, particularly if monomer composition is carefully controlled to remain relatively constant during polymerization.

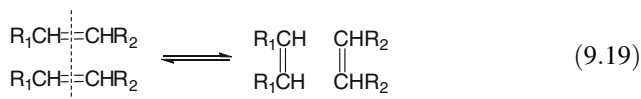
There is serious question as to whether the compositions also include significant amounts of homopolymer. The problem arises with uncertainties over the lifetimes of propagating chains, which may become detached from catalyst by chain transfer, thereby leaving the catalyst still active to initiate homopolymerization of a second monomer. Thus Ziegler–Natta method is inferior to anionic polymerization for synthesizing carefully tailored block copolymers.

Kodak's polyallomers and Uniroyla's TPR are block copolymer of ethylene and propylene. They are high impact plastics exhibiting crystallinity characteristics of both isotactic polypropylene and linear polyethylene. They contain homopolymers in addition to block copolymers. The conventional random copolymers of ethylene and propylene are elastomeric nature.

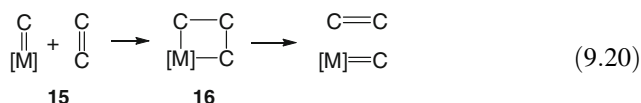
9.4 Metathesis Polymerization

Alkenes undergo a double bond redistribution reaction (Eq. 9.19) called olefin metathesis in the presence of certain complex coordination catalysts. Bond redistribution involves cleavage of the double bonds (trans-alkylidenation). Scission of the single bonds adjacent to the double bonds (trans-alkylation) has been

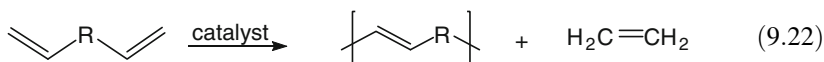
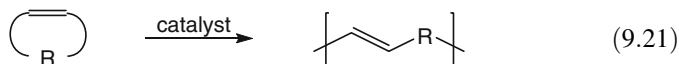
ruled out as a possibility from deuterated alkene experiments. Tungsten compounds are particularly effective for olefin metathesis. The catalysts are formed by the reaction of tungsten hexachloride (WCl_6) with alcohol and ethylaluminum dichloride ($\text{C}_2\text{H}_5\text{AlCl}_2$). Other transition metals, notably Ru, Mo, Rh, and Ti are also effective.



The reaction mechanisms of metathesis polymerization are shown in Eq. 9.20.



Equations 9.21 and 9.22 show two examples of metathesis polymerization. A double bond containing polymer can be obtained through metathesis polymerization. The method developed in 1970, now it is recognized as a particularly convenient way to make polymers containing precisely spaced carbon-carbon double bonds in the polymer backbone.



The Grignard metathesis reaction has been used to synthesize conducting polymer extensively such as poly(3-hexyl thiophene) as shown in Fig. 5.6 where the catalyst of $\text{Ni}(\text{dppp})\text{Cl}_2$ was used [5, 6].

9.5 Problems

1. Explain (a) how sites of variable activity in a heterogeneous catalyst might result in a polymer of high polydispersity, (b) why molecular hydrogen is useful for controlling molecular weight in Ziegler-Natta polymerization, and (c) why only coordination catalysts are effective for polymerizing propylene and higher 1-alkenes. They cannot be polymerized by free radical polymerization.
2. Explain how LDPE and LLDPE differ in terms of structure, synthesis, and properties.

3. Assuming only head-to-tail polymerization and *cis* double-bond opening occurs, give the structure and stereochemical designation of all stereoregular polymers obtainable in principle by stereospecific polymerization of (a) 2-methyl-1-butene, (b) trans-2-pentene, (c) isoprene, and (d) propyne.
4. What are the mechanisms for syndiotactic and isotactic placement in propene polymerization? Please describe the reaction conditions which are favored either syndiotactic placement or isotactic placement.
5. Please discuss the use of homogeneous versus heterogeneous reaction conditions for the coordination polymerizations of propene, isoprene, styrene, methyl methacrylate, and n-butyl vinyl ether.
6. Crystalline-crystalline block copolymer of regioregular poly(3-hexyl thiophene) and polyethylene can be prepared by ring-opening metathesis polymerization (Eq. 9.21). Please write out the reaction mechanism to show how the copolymer is being synthesized [7].

References

1. J. Boor Jr, *Ziegler–Natta Catalysts and Polymerizations* (Academic Press, New York, 1979)
2. H. Sinn, W. Kaminsky, H.J. Vollmer, R. Woldt, *Angew. Chem. Int. Ed.* **19**, 390 (1980)
3. M. P. Stevens, *Polymer chemistry* (3rd edn., Chapter 8). (Oxford University Press, New York, 1999)
4. Odian, G. (2004). *Principles of polymerization* (4th edn., Chapter 8). (Wiley, New York, 2004)
5. M.C. Iovu, E.E. Sheina, R.R. Gil, R.D. McCullough, *Macromolecules* **38**, 8649 (2005)
6. M. Jeffries, G. Sauve, R.D. McCullough, *Macromolecules* **38**, 10346 (2005)
7. R.A.J. Janssen et al., *J. Am. Chem. Soc.* **127**, 12502–12503 (2005)