CHAPTER 4

POLYMERIZATION AND OLIGOMERIZATION OF OLEFINS AND DIENES

CHAPTER 4
OBJECTIVES

- INTRODUCTION
- α-OLEFIN POLYMERIZATION
  - Polyethylene
  - Polypropylene
  - Ethylene-Propylene-Diene Rubbers
  - Specially Polymers
- POLYBUTADIENE AND POLYISOPRENE
- OLIGOMERIZATION OF OLEFINS
  - Aluminum-Catalyzed Oligomerization of Ethylene
  - Shell Higher-Olefins Process
  - Olefin Dimerization
  - 1,4-HEXADIENE

CHAPTER 4
OBJECTIVES

- DIMERIZATION AND TRIMERIZATION OF DIENES
  - Diene Dimerization
  - Cyclododecatriene Synthesis
- FUNCTIONAL OLEFIN DIMERIZATION
- CHAIN TRANSFER CATALYSIS

INTRODUCTION

- Organometallic catalysts, both soluble and insoluble, find wide practical application in C-C bond-forming reactions of olefins and dienes.
- The largest of these are the polymerizations and copolymerizations of ethylene, propylene, butadiene, isoprene, and higher α-olefins.
- Polymerizations of these hydrocarbons with catalysts based on transition metal complexes yield ordered polymers with physical properties different from those of free-radical polymers.

INTRODUCTION

- Oligomerization of olefins and dienes with soluble metal catalysts is used extensively to produce dimers, trimers, and other low polymers.
- The major difference is that polymerization and oligomerization involve olefin insertion into a M-C bond in addition to the M-H insertion involved in hydrogenation.

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α-OLEFIN POLYMERIZATION

- The major applications of organometallic catalysts in the polymerization of olefins and dienes are listed in Table 4.1.
- Both homogeneous and heterogeneous catalysts are used commercially, but the solid catalysts are increasingly preferred because they have technical advantages in many processes.
- Even the nominally homogeneous catalysts are probably not soluble under reaction conditions.
- For example, catalytic solutions of $VOCl_3$ and i-BuAlCl are clear to the naked eye, but light-scattering experiments suggest the presence of aggregates.

α-OLEFIN POLYMERIZATION

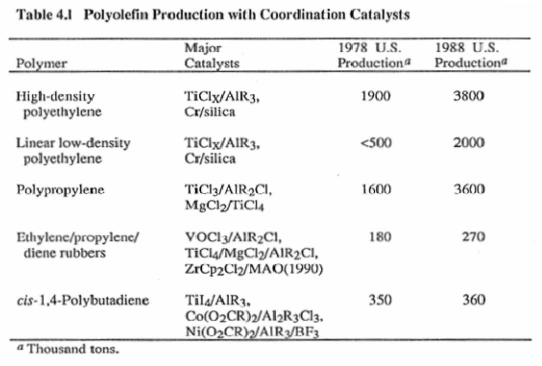


Table 4.1 Polyolefin Production with Coordination Catalysts

Polymer	Major Catalysts	1978 U.S. Production[a]	1988 U.S. Production[a]
High-density polyethylene	$TiCl_X/AlR_3$, Cr/silica	1900	3800
Linear low-density polyethylene	$TiCl_X/AlR_3$, Cr/silica	<500	2000
Polypropylene	$TiCl_3/AlR_2Cl$, $MgCl_2/TiCl_4$	1600	3600
Ethylene/propylene/ diene rubbers	$VOCl_3/AlR_2Cl$, $TiCl_4/MgCl_2/AlR_2Cl$, $ZrCp_2Cl_2$/MAO(1990)	180	270
cis-1,4-Polybutadiene	TiI_4/AlR_3, $Co(O_2CR)_2/Al_2R_3Cl_3$, $Ni(O_2CR)_2/AlR_3/BF_3$	350	360

[a] Thousand tons.

α-OLEFIN POLYMERIZATION

- The largest volume plastic in the United States is polyethylene.
- Three major varieties are produced, High Density Polyethylene (HDPE) is a linear polymer with a density approaching 0.97 and a melting point of about 136°C.
- It is made by coordination polymerization, as discussed below. Low-Density Polyethylene (LDPE), which has a density near 0.92 and a wide melting range, is a highly branched polymer prepared by free-radical polymerization of ethylene at high pressure (approximately 2000 atmospheres).
- Linear Low-Density Polyethylene (LLDPE) refers to a class of polyethylenes intermediate between high- and low- density materials prepared for specific applications by modification of the conditions used for manufacture of the high-density product.

α-OLEFIN POLYMERIZATION

- Both heterogeneous and homogeneous catalysts are discussed here because they are closely related mechanistically.
- The treatment is necessarily brief, but recent books and reviews which cover most aspects of olefin polymerization are listed at the end of the chapter.
- The references cited in these reviews represent many hundreds of research-years in the past quarter century.

α-OLEFIN POLYMERIZATION

- Curiously, despite this massive effort, there remain questions about the mechanism of coordination polymerization.
- Fundamental facts such as the oxidation state and structure of the catalytic metal site and the nature of the insertion mechanism are not well established in many cases.
- The mode of action of the many additives to these reactions is often explained only in empirical terms.

α-OLEFIN POLYMERIZATION
Polyethylene

- Two families of ethylene polymerization catalysts were developed in the early 1950s.
- Ziegler catalysts are prepared by reaction of an alkylaluminum compound with $TiCl_4$ or $TiCl_3$ to give compositions that sometimes appear to be soluble in hydrocarbon solvents.
- The Phillips catalysts are clearly insoluble materials prepared by deposition of chromium oxides on silica.

α-OLEFIN POLYMERIZATION

Polyethylene

- Despite early acceptance of the Ziegler systems, chromium-based catalysts lead the production of polyethylene in the United States.
- The chromium systems include chromacene-on-silica catalysts developed by Union Carbide.
- Colloidal Ziegler catalysts for solution-based polymerizations (like those of Dow and Du Pont Canada) are prepared by reaction of $TiCl_4$ with trialkylaluminum compounds in cyclohexane or heptane.

α-OLEFIN POLYMERIZATION

Polyethylene

- The titanium is alkylated and reduced to Ti(III).
- The catalyst can also include vanadium compounds such as $VOCl_3$. Other Ziegler catalysts which are clearly insoluble are prepared from crystalline $TiCl_3$ or $TiCl_3.1/3AlCl_3$.
- In laboratory experiments, these materials polymerize ethylene vigorously at room temperature and atmospheric pressure.
- In commercial practice, the catalyst slurry is fed to a reactor along with ethylene at pressures that vary from 10 to 160 atmospheres.

α-OLEFIN POLYMERIZATION

Polyethylene

- Rapid polymerization occurs at 130-270°C to give a viscous solution of a highly linear polymer with a relatively narrow molecular weight range.
- The combination of short reaction times and small, versatile reactors, and the desirable polymer properties, is the major advantage of this process and compensates to some extent for the need to remove the corrosive chloride-containing catalyst from the viscous polymer solution.
- New generations of these catalysts using siloxane-modified or other aluminum alkyl activators have achieved activities sufficiently high that the catalyst residues can be left in the polymer.

α-OLEFIN POLYMERIZATION

Polyethylene

- Another very significant advance has been the development of a new generation of $MgCl_2$- supported catalysts for slurry polymerizations at lower temperatures where the polyethylene is precipitated as it is produced.
- Productivities of these catalysts are very high, again allowing the catalyst residues to be left in the polymer.
- In addition, important factors such as molecular weight, molecular weight distribution, and long- and short-chain branching can be controlled by careful catalyst design.

α-OLEFIN POLYMERIZATION

Polyethylene

- The fundamental processes for chain growth and termination for the titanium- based catalysts appear to be similar to those sketched below for chromium-based catalysts.
- The titanium catalysis are discussed in more detail in connection with their use in polypropylene production where they enjoy more widespread acceptance.
- Heterogeneous chromium-containing catalysts give polyethylene with properties somewhat different from those obtained with Ziegler systems.

α-OLEFIN POLYMERIZATION

Polyethylene

- The heterogeneous catalysts are generally noncorrosive and are left in the product, affording a substantial process advantage.
- The catalysts are used in both lower-temperature slurry reactions and in ‘gas-phase” processes in which polyethylene is grown directly on the surface of the catalyst in the absence of solvent.
- Polymerization pressures are fairly low (10-30 atmospheres).

α-OLEFIN POLYMERIZATION

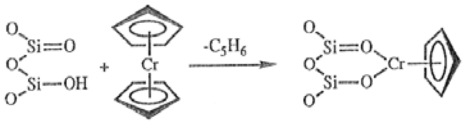
Polyethylene

- The chromium-on-silica catalysts are obtained in two very different ways.
- A silica gel may be impregnated with aqueous chromate solution or with a hydrocarbon solution of $(Ph_3SiO)_2CrO_2$ to give a dispersion of Cr(VI) oxide sites on the surface of the support.
- These catalyst sites appear to be inactive before contact with a reducing agent such as an organoaluminum compound, CO, H_2, or ethylene.

α-OLEFIN POLYMERIZATION

Polyethylene

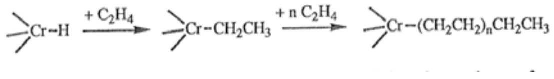
- Reduction yields Cr sites with an oxidation state of +2 to +3.
- Alternatively, in a Union Carbide process, reaction of silica with $Cr(C_5H_5)_2$ gives low valent sites in which a cyclopentadienyl ligand has been liberated by protonation by the surface OH groups:



α-OLEFIN POLYMERIZATION

Polyethylene

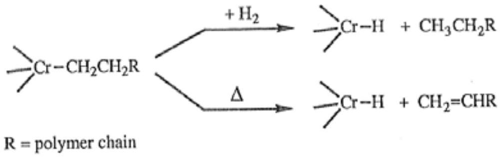
- It seems likely that chromium-on-silica catalysts prepared by both methods contain Cr-H sites which react with ethylene by a repetitive insertion process to give a high molecular weight polymer:



α-OLEFIN POLYMERIZATION

Polyethylene

- Polymer grown in this manner is chemically bonded to the catalyst surface through a labile Cr-C bond.
- The polymer molecules are released from the surface by a molecular weight control agent such as hydrogen or by thermal cleavage.
- In either situation, a metal hydride site is regenerated and can initiate growth of a new polymer chain.



α-OLEFIN POLYMERIZATION

Polyethylene

- The elimination of β-hydrogen in the thermal process generates a high molecular weight olefin.
- This olefin can copolymerize with ethylene to form a branch in a polyethylene chain.
- If olefin formation by β-elimination takes place and some of these high molecular weight α-olefins are incorporated into the growing polymer chain, a highly branched, low-density polyethylene can be produced.

α-OLEFIN POLYMERIZATION

Polyethylene

- This subsequent incorporation is generally rare because the concentration of olefinic chain ends is small in comparison with the monomer concentration and incorporation of any α-olefin is usually much slower than ethylene incorporation, but even if branching occurs only rarely, it can have an impact on end-use applications.

α-OLEFIN POLYMERIZATION

Polyethylene

- In the last decade, there has been a minor revolution in the preparation of polyethylene.
- Advances in catalysts and process conditions have allowed the customization of polymers to specific applications ranging from blow-molded bottles, injection-molded parts, and blown films.
- The vast majority of polyethylene is produced using Phillips' loop reactor technology or Union Carbide's UNIPOL fluidized-bed polymerization technology.

α-OLEFIN POLYMERIZATION

Polyethylene

- BP's fluidized-bed process provides growing competition to Carbide.
- The heart of the technology is a large, fluidized-bed reactor, represented schematically in Figure 4.1, in which supported catalysts are reacted with gas-phase ethylene.
- The process eliminates solvents and the associated recycle streams. Conversion per pass is low, allowing the considerable heat of polymerization to be removed by the fluidizing ethylene.

α-OLEFIN POLYMERIZATION

Polyethylene

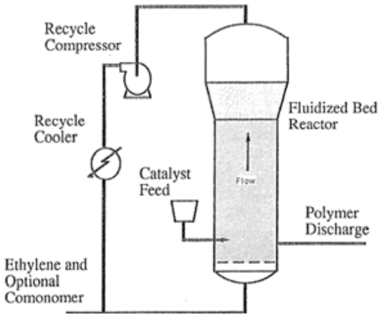


Figure 4.1 Schematic representation of Union Carbide's Unipol process

α-OLEFIN POLYMERIZATION
Polyethylene

- The catalyst is introduced in the form of small spheres of a relatively uniform size.
- Ideally, each catalyst particle grows to a single polymer particle. The polymer particles are then removed from the reactor through a rotary valve.
- Degassing and introduction of the stabilizer additives can be accomplished without pelletizing, allowing considerable savings in energy for the process.

α-OLEFIN POLYMERIZATION
Polyethylene

- Higher α-olefin monomers can be copolymerized with the ethylene to introduce short-chain branches off the main backbone of the polymer chain, thereby yielding linear low-density polyethylene.
- This LLDPE process is economically advantageous because it operates at a much lower pressure than the radical-initiated LDPE processes.
- LLDPE can often be prepared in HDPE plants, allowing the capacity to be swung from HDPE to LLDPE products as the market dictates.

α-OLEFIN POLYMERIZATION
Polyethylene

- The comonomers range from 1-butene to 1-octene.
- Incorporation of comonomer was originally limited to a few percent, but Union Carbide has been pushing densities downward through “low-density” polyethylene products (0.925-0.900) into the range (0.900-0.885) considered to be “ultralow.”
- The resulting FLEXOMER polymers have elastomeric properties between LLDPE and those of ethylene propylene rubbers.
- As densities are lowered, the tackiness of the polymers increases.

α-OLEFIN POLYMERIZATION

Polyethylene

- Maintaining fluidization becomes more difficult so temperatures and polymerization rates are lowered.
- Under some conditions, a liquid coating may form on the polymer particles and reactor walls; this condition is generally avoided in fluidization technology but seems to be essential to the currant process.
- Isolation also becomes an increasingly difficult engineering problem because the polymer particles agglomerate if allowed to remain in contact with each other.

α-OLEFIN POLYMERIZATION

Polyethylene

- Incorporation of 1-butene and higher a-olefins into the growing polymer chain can have profound impact on the properties of the polymers.
- For instance, despite the high inherent strength of high-density polyethylene, it creeps under load, resulting in rapid failure under a slight hut constant stress.
- This creep is a result of polymer chains reptating (snaking) past each other in the polymer crystal at temperatures well below the melting point.

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Polyethylene

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- This creep is a result of polymer chains reptating (snaking) past each other in the polymer crystal at temperatures well below the melting point.
- This reptation can be inhibited by incorporating a low percent of C6-side chains on the main backbone by copolymerizing ethylene with octene.

α-OLEFIN POLYMERIZATION

Polyethylene

- As copolymerization has became more sophisticated, greater control over polymer architecture has developed.
- For some applications, a homogeneous copolymer with very even and random incorporation of comonomer is desired.
- Alternatively, comonomer can be incorporated into the high or low molecular weight fraction of the polymer, can be randomly incorporated, or can be incorporated into blocks.

α-OLEFIN POLYMERIZATION

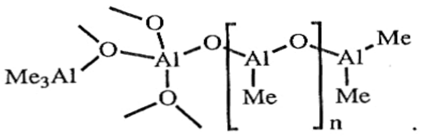
Polyethylene

- Diluents can be used to increase the randomness of incorporation.
- For some applications, specifically tailored bimodal distributions are desirable.
- With the recognition that such control was possible and desirable, catalysts and polymerization conditions have been designed to meet each of these needs.

α-OLEFIN POLYMERIZATION

Polyethylene

- A new generation of catalysts, sometimes referred to as “single-site” catalysts, is based upon modifications of $(Cp)_2ZrCl_2$ combined with methyl aluminoxanes which are complex mixtures containing the elements represented by:



α-OLEFIN POLYMERIZATION
Polyethylene

- The methyl aluminoxanes, that are the products of controlled partial hydrolysis of $AlMe_3$ with one equivalent of water, are often represented as simple linear or cyclic species with a single methyl group on each aluminum.
- In fact, they are complex mixtures of materials having many $Al(-O-)_3$ and $Al(-O-)_4$ groups, as well as $AlMe_2$ species; free $AlMe_3$ is required to keep these “homogeneous species” in solution and is probably coordinated to the bridging oxygen atoms of the aluminoxane.

α-OLEFIN POLYMERIZATION
Polyethylene

- Greatly improved control of comonomer incorporation is also possible; for instance, the comonomer can be incorporated specifically into one region of the molecular weight distribution.
- Exxon, Dow and others are bringing these custom-tailored polymers to the higher end of the polyolefin market.

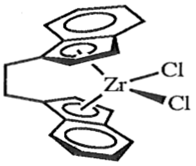
α-OLEFIN POLYMERIZATION
Polyethylene

- Polypropylene will be covered in the next section of this chapter, but single-site catalysts give interesting results when applied to propylene polymerization.
- The complex $(Cp)_2ZrCl_2$ is not chiral and as a result, gives polypropylene that is purely atactic.
- The first generation polypropylene processes described below gave more than enough atactic polymer to meet commercial needs, but with new catalysts, this byproduct has been eliminated from many processes and atactic polypropylene is now made on purpose.

α-OLEFIN POLYMERIZATION

Polyethylene

- When substituents are added to the cyclopentadienyl rings, and ring rotation is stopped by bridging the two rings, the resulting “single-site constrained-geometry” catalysts are chiral:



α-OLEFIN POLYMERIZATION

Polyethylene

- Generally, the surface of a heterogeneous catalyst is required to generate a site with suitable geometric constraints, but variations of these catalysts can produce isotactic polypropylene.
- It is even possible to resolve the optical isomers propylene and higher oligomers resulting from hydrooligomerization using the resolved catalyst are optically active.

α-OLEFIN POLYMERIZATION

Polyethylene

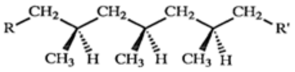
- Syndiotactic polymers have been prepared using another version of this catalyst.
- Remarkably it has been demonstrated that the methylaluminoxane is not required as a cocatalyst if a base- free or weakly ligated cationic complex can be generated compounds such as the zwitterionic $Cp^*_2Zr(C_6H_4BPh_3)$ polymerize ethylene or propylene in the absence of aluminum alkyl activators.

α-OLEFIN POLYMERIZATION
Polypropylene

- Commercial polypropylene is a very regular polymer with properties that vary with the amount of crystallization that occurs during processing.
- Densities range from about 0.85 for amorphous material to 0.93 for crystalline isotactic polymer. Other properties change correspondingly.
- The basic polymer chain is ordered with respect to placement of the methyl groups at the chiral centers in each polymer unit.

α-OLEFIN POLYMERIZATION
Polypropylene

- In the common isotactic polymer, each polymer chain will have all of the methyl groups on a single side of the extended chain:



- This selectivity for ordering all the methyls on one side of the chain rather than randomly (atactic) is related to the symmetry of the catalyst site.

α-OLEFIN POLYMERIZATION
Polypropylene

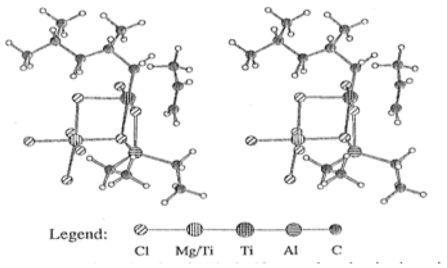


Figure 4.2 Stereo view of the active site of a Ziegler-Natta catalyst showing incoming propylene; the growing isotactic polypropylene chain; part of the support; and the residue of the AtEt$_3$ promoter.

α-OLEFIN POLYMERIZATION

Polypropylene

- Older commercial polypropylene catalysts are modifications of the $TiCl_3/AlR_3$ systems developed by Ziegler and Natta.
- In one catalyst preparation which is used in laboratory polymerizations a slurry of violet crystalline $3TiCl_3.AlCl_3$ in heptane is treated with diethylaluminum chloride in the presence of propylene.
- Rapid polymerization occurs at room temperature and 3-4 atmospheres pressure to give highly isotactic polypropylene.

α-OLEFIN POLYMERIZATION

Polypropylene

- The polymer slurry is treated with ethanol to kill the catalyst and the polymer is purified by washing.
- Similar procedures and catalysts are used in laboratory preparation of isotactic poly-i-butene and crystalline polystyrene.
- The older-generation commercial production of polypropylene resembles the laboratory preparation to some extent.
- Propylene is reacted with a hydrocarbon slurry of the alkylated $TiCl_3$ catalyst at 50-85°C and 20-40 atmospheres pressure.

α-OLEFIN POLYMERIZATION

Polypropylene

- The chemistry at the catalyst surface is not well known despite intensive study.
- The treatment with AlR is thought to alkylate surface titanium sites.
- The active site pictured in Figure 4.2 is assumed to be a monoalkylated titanium (+3) ion attached to the crystal by Ti-Cl-M (M = Mg or Ti) bridges.
- It seems likely that alkylaluminum groups are attached at or near the site by Al-Cl-Ti coordination.

α-OLEFIN POLYMERIZATION

Polypropylene

- The growing polymer chain is attached to the crystal by a Ti-C σ-bond. As shown in the figure, propylene coordinates to the titanium adjacent to the Ti-C bond.
- The polymer grows by insertion of the coordinated olefin into the Ti-C bond.
- The propylene inserts with great regularity with respect to both head-to-tail orientation and to placement of all the methyl groups on the same side of the polymer chain.

α-OLEFIN POLYMERIZATION

Polypropylene

- The regularity must arise from the stereochemistry of the coordination sphere in which the entering olefin molecule coordinates.
- To generate purely isotactic polypropylene, this coordination site must emerge unchanged from each insertion sequence.
- There is growing evidence that this process is aided by coordination of a second olefin molecule - a process which has been referred to as a “trigger” for insertion.
- The movements of atoms and repopulation of orbitals have been calculated by ab initio and other methods.

α-OLEFIN POLYMERIZATION

Polypropylene

- The new generation of catalysts uses $MgCl_2$ as a support for the $TiCl_4$ catalyst and incorporates Lewis base electron donors.
- Anhydrous $MgCl_2$ of very fine particle size is prepared by grinding $MgCl_2$ in the presence of a Lewis base, commonly ethyl benzoate, or by reacting magnesium compounds with chlorine donors in the presence of $TiCl_4$ and electron donors.

α-OLEFIN POLYMERIZATION
Polypropylene

- The catalyst is activated with aluminum alkyls in combination with additional electron donors.
- There has been a great deal of study devoted to characterization of these catalysts and the role of each of the components.
- A useful functional picture has emerged, but a molecular model remains elusive.

α-OLEFIN POLYMERIZATION
Polypropylene

- In the Himont Spheripol process polypropylene is made in a large loop reactor similar to that used in the Phillips polyethylene process, but which is completely filled with liquid propylene which serves as the reactant and the slurrying medium.
- The process schematic, pictured in Figure 4.3, indicates that the heat of polymerization is removed by cooling jackets around the loops.
- The $MgCl_2$ supported catalyst is prepared in the shape of small, uniform spheres.

α-OLEFIN POLYMERIZATION
Polypropylene

- It is impregnated with $TiCl_4$ and an internal electron donor, It is then activated with an aluminum alkyl combined with external electron donors.
- These electron donors include Lewis bases such as ethyl benzoate or related esters, silyl ethers such as phenyltrimethoxysilane, and hindered amines such as 2,2,6,6-tetramethylpiperidine-derived light stabilizers.
- The resulting catalysts have a number of advantages which make this a versatile and highly economical process.

α-OLEFIN POLYMERIZATION

Polypropylene

- Catalyst activities are very high so that catalyst residues do not have to be removed from the polymer.
- The electron donor molecules selectively poison the catalyst sites which make atactic polymer; the difficult removal of an atactic fraction is no longer required.
- Because the liquid propylene is the reaction medium, a separate solvent recycle is eliminated.

α-OLEFIN POLYMERIZATION

Polypropylene

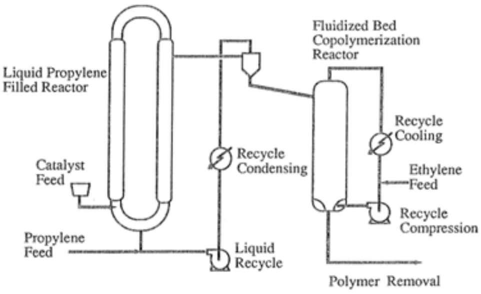


Figure 4.3 Schematic representation of the Himont Spheripol polypropylene process

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α-OLEFIN POLYMERIZATION

Polypropylene

- Finally, because the polymer is grown in the shape of uniform spheres having good bulk density, there is no need to go through a final energy-intensive pelletizing step.
- Polymer is removed from the loop reactor as a slurry in liquid propylene.
- The liquid propylene is flashed off, recondensed, and returned to the loop reactor.

α-OLEFIN POLYMERIZATION
Polypropylene

- If a simple homopolymer is desired, the residual catalyst in the polymer is deactivated and the uniform spheres are treated with the chemical stabilizers and dried, and are then ready for shipment.
- The final steps are facilitated by the small residual open- pore structure in the polymer particles.
- Alternatively, the spheres are fed to the second reactor in the figure where an ethylene-propylene copolymerization is carried out in the gas phase.

α-OLEFIN POLYMERIZATION
Polypropylene

- The rubbery EP-copolymer is formed within the pore structure of the preformed sphere, so there is no sticking problem.
- This intimate combination of polypropylene and art EP rubber is particularly useful in automotive or other applications requiring impact resistance.

α-OLEFIN POLYMERIZATION
Polypropylene

- More recent versions of the process imbibe free-radical initiators and polar comonomers such as maleic or itaconic anhydrides into the pore structure of the preformed particles.
- After wetting the internal surface structures, the particles are warmed and the resulting free-radical polymerization grafts short polar chains onto the polypropylene, providing functionality needed for specialty applications.

α-OLEFIN POLYMERIZATION
Ethylene-Propylene-Diene Rubbers

- While the homopolymers of ethylene and propylene are usually plastics, a family of ethylene-propylene copolymers are elastic and are used in place of rubber in many industrial applications.
- The simple copolymers are often blended with more crystalline polymers as toughening agents.
- More commonly, though, a small amount of an unsymmetrical diene is copolymerized with ethylene and propylene to give an elastomer which can be cured by conventional rubber technology.

α-OLEFIN POLYMERIZATION
Ethylene-Propylene-Diene Rubbers

- Common diene comonomers are ethylidenenorbornene, dicyclopentadiene, and trans-l,4-hexadiene.
- Each of these dienes has a highly reactive double bond which readily copolymerizes to affix the diene to the polymer chain.
- The less reactive C=C bond in the diene remains intact to provide a site for crosslinking polymer chains in the “cure” of the final product.

α-OLEFIN POLYMERIZATION
Ethylene-Propylene-Diene Rubbers

- The cured products are essentially saturated and any unsaturation is located in pendant groups rather than the main backbone.
- As a result, these rubbers are more ozone-resistant than natural rubber or the synthetic polydienes.

α-OLEFIN POLYMERIZATION

Ethylene-Propylene-Diene Rubbers

- Most of the ethylene-propylene copolymers and terpolymers are prepared with Ziegler catalysts based on a soluble vanadium compound such as $VOCl_3$ or VCl_4 though high-activity $MgCl_2$-supported $TiCl_4$ catalysts are being used for polymers where highly random incorporation of the monomers is not required.
- Empirically, vanadium seems unique in its ability to incorporate the comonomers into the polymer chain in a random sequence, an important characteristic to produce an amorphous, elastomeric product.

α-OLEFIN POLYMERIZATION

Ethylene-Propylene-Diene Rubbers

- In laboratory experiments that simulate commercial practice a reaction solvent such as hexane or chlorobenzene is chilled to 15°C and saturated with an ethylene-propylene mixture at one atmosphere pressure.
- The diene (e.g., dicyclopentadiene) is added, followed by the catalyst components, in this instance $Al_2Et_3Cl_3$ and $VOCl_3$.
- After a short induction period during which the active catalyst is formed, vigorous polymerization begins and the three comonomers are added at rates to maintain the desired proportion in the polymer.

α-OLEFIN POLYMERIZATION

Ethylene-Propylene-Diene Rubbers

- The relative monomer reactivity is usually ethylene>propylene>diene.
- When the polymer solution becomes too viscous for effective stirring, the catalyst is killed by addition of alcohol.
- The catalyst residues are extracted with water and the polymer is isolated by precipitation or evaporation.

α-OLEFIN POLYMERIZATION

Ethylene-Propylene-Diene Rubbers

- The chemistry of catalyst formation has been studied extensively.
- At the ratios of Al to V used commercially, VCl_4 and $VOCl_3$ are reduced to V(III) complexes which bear alkyl substituents.
- These V(III) compounds are relatively unstable and decompose to catalytically inactive V(II) species in less than an hour at 15-40°C. Fortunately, polymerizations are usually complete in minutes.

α-OLEFIN POLYMERIZATION

Ethylene-Propylene-Diene Rubbers

- The presence of extra chloride ion seems essential for the stability of the active catalyst.
- Commercial polymerizations often contain an organic compound with active chlorine atoms to regenerate the catalyst in situ.
- Useful catalyst promoters include benzotrichloride ethyl phenyldichloroacetate, butyl perchlorovinylacetate and even chloroform but these species often require the use of increased quantities of aluminum alkyls.

α-OLEFIN POLYMERIZATION

Ethylene-Propylene-Diene Rubbers

- It is believed that the catalytically active vanadium complexes (either soluble or insoluble) are very similar to the Ti-based Ziegler catalyst depicted in Figure 4.2.
- Chloride bridges to aluminum and to other vanadium ions are believed to occupy four coordination sites.
- Olefin and alkyl ligands are situated in adjacent positions to facilitate the repetitive insertion process by which the polymer chain grows.

α-OLEFIN POLYMERIZATION

Ethylene-Propylene-Diene Rubbers

- In contrast to the well-defined sites on the surface of a $TiCl_3$ crystal which constrain olefin molecules to insert in a very regular fashion, the vanadium catalyst sites must be quite flexible.
- Propylene enters the chain with random stereoregularity, random placement with respect to ethylene units, and random placement with respect to end- to-end alignment under most process conditions used commercially.

α-OLEFIN POLYMERIZATION

Ethylene-Propylene-Diene Rubbers

- While vanadium is noted for yielding very random, amorphous polymers, zirconium has also been observed to give relatively random copolymers.
- Additionally, there are some applications where it is desirable to have nonrandom distribution of the ethylene/propylene monomers to provide a low degree of crystallinity.
- This low crystallinity allows the uncured polymer to retain its shape during fabrication prior to the chemical crosslinking.
- As a result, there is a growing interest in the use of the zirconocene/aluminoxane catalysts.

α-OLEFIN POLYMERIZATION

Specially Polymers

- While polyethylene, polypropylene, and EPDM rubbers dominate the polyolefin industry, several other polymers find niche applications.
- Values-in-use of these polymers are necessarily high because they do not enjoy the economies of scale of their larger cousins.
- Poly-4-methyl-l-pentene (PMP) has the lowest density of all commercial synthetic resins, 0.83 g/cm^3. It is highly transparent, transmitting 90% of visible light; this is superior to transparent resins like polystyrene and poly(methyl methacrylate), and even glass. Its melting point is 240°C.

α-OLEFIN POLYMERIZATION

Specially Polymers

- The monomer, 4-methyl-1-pentene (4M1P), is prepared by the dimerization of propylene; this is normally carried out with a heterogeneous catalyst rather than the homogeneous species.
- As a result of these properties and others, it finds greatest application in medical instruments, laboratory ware, and industrial applications.
- PMP is synthesized in a slurry polymerization using the catalysts discussed above which give stereoregular polymers.
- Many grades of PMP include comonomers such as octene which lower melting point, but dramatically improve impact resistance.

α-OLEFIN POLYMERIZATION

Specially Polymers

- High molecular weight poly(1-butene) is used mostly in flexible plastic pipe; it will expand to accommodate the expansion of freezing water.
- It is prepared as the isotactic polymer, though atactic grades are even more elastomeric.
- The catalysts used are like those discussed for poly(propylene).
- There has been considerable work on a gas-phase process which eliminates many of the difficulties of solution processes.
- A major area of research is the development of additives such as nucleating agents to shorten the curing or crystallization time of the polymer from the melt, which can otherwise be days.

α-OLEFIN POLYMERIZATION

Specially Polymers

- Very high molecular weight poly(1-decene)s or poly(1.dodecene)s are used as flow improvers for oil pipelines.
- These remarkable, viscoelastic materials have helped push oil through the Trans-Alaska pipeline at rates in excess of 120% of design capacity.
- They function at part per million concentrations by reducing turbulence in the pipeline at high flows; the microscopic aspects of this phenomenon are unclear, Solution polymerizations are initiated using Ziegler-Natta or other catalysts at low temperatures.

α-OLEFIN POLYMERIZATION

Specially Polymers

- The temperature of the polymerization is determined by the adiabatic temperature rise because the mixtures cannot be stirred - molecular weights ate so high that stirring actually breaks the long polymer chains and lowers effectiveness.
- The polymer solutions are then removed from the reactor and shipped to the user without isolation.
- Related species having lower molecular weights are used in adhesive applications.
- Other related crosslinked species have found utility as vibration dampeners for heavy machinery and even for seismic dampening.

α-OLEFIN POLYMERIZATION

Specially Polymers

- Ultrahigh molecular weight polyethylene (UHMWPE) is a specialty product simply because it cannot be processed using the methods developed for high-density polyethylene or other thermoplastics.
- By accepted definition, the molecular weight is above 3,000,000. It is generally prepared in a low-pressure, low-temperature slurry process using modified Ziegler-Natta or Phillips catalysts.
- It generally leaves the reactor as a fine powder, which is a useful form for the processing methods required.

α-OLEFIN POLYMERIZATION

Specially Polymers

- Fabrication is normally carried out by compression molding, ram extrusion, or thermoforming and annealing.
- It is then formed into useful parts by machining. The obvious expense of fabrication is offset by the properties of UHMWPE.
- It has the highest abrasion resistance of all thermoplastics, and it has a low coefficient of friction.
- It also has excellent resistance to impact and to environmental stress cracking.

α-OLEFIN POLYMERIZATION

Specially Polymers

- As a result, it finds use in applications as diverse as artificial hip sockets and chutes for mining and mineral handling.
- It is also used for wear-resistant parts for machines and the bottom surfaces of skis and snowmobile skids.
- Although the most common propylene polymers discussed above are crystalline thermoplastics, propylene is also homopolymerized to an elastomeric material.
- Elastomeric polypropylene has a stereoblock structure with long amorphous atactic segments separated by short crystalline isotactic blocks.

α-OLEFIN POLYMERIZATION

Specially Polymers

- These isotactic blocks provide crystalline crosslinks between the flexible amorphous chains yielding a rubbery material.
- The crosslinks in normal rubbers are chemical in nature, but in this case, they are physical crosslinks which are lost during melt processing and then reappear upon cooling.
- This material can be used to compatibilize normal isotactic polypropylene with EP or EPDM rubbers, yielding materials useful in automotive and other impact-sensitive applications.
- It can also be used to replace highly plasticized poly(vinyl chloride) in medical applications where the plasticizers are of concern.

α-OLEFIN POLYMERIZATION

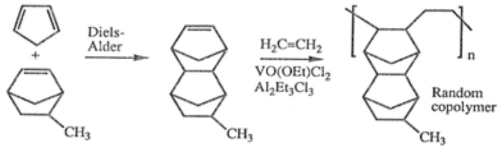
Specially Polymers

- The catalysts for this polymerization are based upon tetraalkylzirconium compounds supported on high-surface-area minerals.
- Commercial olefin polymerization has been limited to α-olefins, except in those applications where cyclic olefins are used as minor constituents in a polymer consisting primarily of α-olefins.
- An exception is Mitsui Petrochemical’s high-value, amorphous polyolefin APO” which is used in compact disk substrates and other optical applications such as aspherical lenses.

α-OLEFIN POLYMERIZATION

Specially Polymers

- It is based upon a copolymer of ethylene and a Diels-Alder adduct which are copolymerized in toluene using a vanadium catalyst to give a highly random polymer with a narrow molecular weight distribution near 10,000.



α-OLEFIN POLYMERIZATION

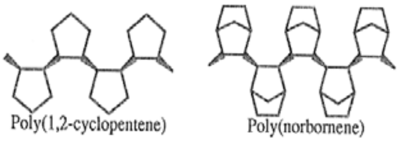
Specially Polymers

- Its polyolefin nature means that it is unaffected by humidity; it is optically clear and has low birefringence; and it has a high softening temperature for thermal resistance.
- The polymer has several clear advantages over polymethacrylates and polycarbonates used for the same purpose, but the current low volume requires a premium price.

α-OLEFIN POLYMERIZATION

Specially Polymers

- Polymerization of cyclopentene and norbornene to isotactic polymers with no ring opening has been reported.



α-OLEFIN POLYMERIZATION

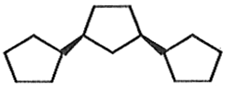
Specially Polymers

- These unusual polymers have extremely high glass transition temperatures and melting points (300-500oC).
- They exhibit the oxidative instability expected for tertiary hydrocarbons, but if this limitation can be overcome, they might find utility in a number of specialty high-temperature applications.
- Polymerization of cyclopentene in the presence of hydrogen provides oligomers as well as polymer.

α-OLEFIN POLYMERIZATION

Specially Polymers

- The trimer has been characterized as the 1,3-isomer stereoregular isomer, calling into question the proposed 1,2-structure of the cyclopentene-based polymer.



Poly(1,3-cyclopentene)

α-OLEFIN POLYMERIZATION

Specially Polymers

- Steric congestion at the metal center is relieved by the 2- to 3-isomerization before the next incoming monomer can be inserted.
- Poly(norbornene) is also obtained by polymerizations using labile Pd^{II} complexes in what is close to a living polymerization under proper conditions.
- The more usual polymerization using cyclic olefins is ring-opening olefin metathesis (ROMP), which is used in a number of specialty applications including the polymerization of dicyclopentadiene and cyclooctene.

α-OLEFIN POLYMERIZATION
Specially Polymers

- Most a-olefins polymerize by a-p-incorporation into the chain, producing polymer chains bearing alkyl branches two carbon atoms shorter than the olefin.
- One polymerization using a nickel catalyst provides 3-to-incorporation, giving only methyl branches.
- The catalyst is formed by reaction of “Ni(0)” [e.g., Ni(1,5-cyclooctadiene)$_2$], and a phosphorane ligand.

α-OLEFIN POLYMERIZATION
Specially Polymers

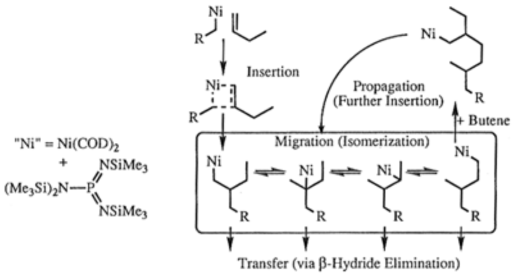


Figure 4.4 Mechanism of the β-ω-enchainment via insertion-migration polymerization of α-olefins

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α-OLEFIN POLYMERIZATION
Specially Polymers

- The polymerization shown in Figure 4.4 is accomplished by
  - (a) insertion of the olefin into the nickel-alkyl bond forming Ni-Cα and Cβ-Cω bonds;
  - (b) migration of the metal center up and down the length of the alkyl chain until it reaches the end of the polymer chain; and
  - (c) insertion of the next olefin only when the metal is at the end of the chain.

α-OLEFIN POLYMERIZATION

Specially Polymers

- Chain transfer can occur at any point during the nickel migration.
- No effect would be seen during ethylene or propene polymerizations.
- Pentene polymerization would result in a polymer equivalent to a rigorously alternating polymerization of ethylene and propylene.

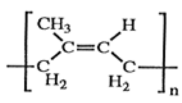
CHAPTER 4 OBJECTIVES

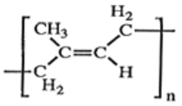
- INTRODUCTION
- α-OLEFIN POLYMERIZATION
  - Polyethylene
  - Polypropylene
  - Ethylene-Propylene-Diene Rubbers
  - Specially Polymers
- POLYBUTADIENE AND POLYISOPRENE
- OLIGOMERIZATION OF OLEFINS
  - Aluminum-Catalyzed Oligomerization of Ethylene
  - Shell Higher-Olefins Process
  - Olefin Dimerization
  - 1,4-HEXADIENE

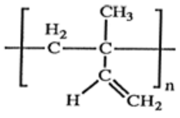
POLYBUTADIENE AND POLYISOPRENE

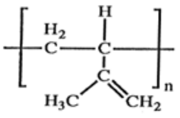
- Many of the desirable physical properties of natural rubber are due to the structure of the polymer chain which arises from a cis-1,4 polymerization of isoprene ($n \approx 20{,}000$).
- Synthetic elastomers with similar structures and physical properties are produced by coordination polymerization of butadiene and isoprene.
- As applications of these rubbers become more specialized, the control of polymer microstructure has become more important.
- Isoprene can be inserted into the growing polymer backbone in one of four different configurations:

POLYBUTADIENE AND POLYISOPRENE


cis-1,4-addition


trans-1,4-addition


1,2-addition


3,4-addition

POLYBUTADIENE AND POLYISOPRENE

- Butadiene affords only the first three of these additions, 1,2-addition being indistinguishable from 3,4-addition.
- The 1,2- and 3,4-additions can be isotactic, syndiotactic, or atactic (see description above under polypropylene), giving further control of the polymer properties.
- The two major commercial catalyst systems for the polymerization of isoprene are alkyllithiums, usually BuLi for cis-l,4-polyisoprene, and vanadium-based Ziegler catalysts for trans-1,4-polyisoprene.

POLYBUTADIENE AND POLYISOPRENE

- The butyllithium is sometimes referred to as an initiator rather than a catalyst because, discounting the effects of impurities in the system, each lithium initiates one polymer chain the resulting molecular weight distribution is very narrow.
- Titanium-centered Ziegler catalysts, and alane (aluminum hydride) with $TiCl_4$ have been used, but yield mixed microstructures.
- Commercial catalysts for polybutadiene include titanium-based Ziegler catalysts, cobalt-centered Ziegler catalysts, and allylnickel complexes.

POLYBUTADIENE AND POLYISOPRENE

- When high-vinyl- content polybutadiene is desired, butyllithium initiators combined with chelating ligands such as diglyme or tetramethylenediamine are utilized.
- Titanium-based Ziegler catalysts like those used in polymerize ethylene and propylene are also effective for the polymerization of butadiene and isoprene.
- In a preparative experiment addition of $TiCl_4$ and triisobutylaluminum to an isoprene solution in pentane produces 1,4-polyisoprene.
- The polymer has better than 80% cis conformation.

POLYBUTADIENE AND POLYISOPRENE

- The selectivity for cis-l,4-pnlybutadiene is enhanced by iodide modification of the standard Ziegler catalyst.
- Catalysts prepared by reaction of TiI_3 with an alkylaluminum compound have been studied extensively.
- Other catalysts have been formed by a three-component reaction such as $TiCl_3 + AlI_3 + AlR_3$.
- Such catalysts are suspensions of TiI3 crystals which have been surface alkylated like the polypropylene catalysts discussed earlier. They give polybutadiene which is 90-93% cis-1,4 conformer.

POLYBUTADIENE AND POLYISOPRENE

- Polymerization of isoprene with a clay-supported VCl_3 catalyst gives the thermodynamically preferred trans-l,4-polyisoprene.
- This modified selectivity with a vanadium catalyst is consistent with the flexible catalyst site suggested to explain its randomness in copolymerization of ethylene and propylene.
- With butadiene, VCl_3 yields extremely high stereospecificity polybutadiene with up to 99% trans-1,4 content.

POLYBUTADIENE AND POLYISOPRENE

- Interestingly, halogen-free cobalt catalysts can yield syndiotactic l,2-polybutadiene with high specificity.
- This material finds application as a packaging film rather than an elastomeric product.
- Organocobalt catalysts based on hydrocarbon-soluble cobalt salts seem to be true homogeneous catalysts.
- These catalysts have achieved commercial importance because they produce 96-98% cis-l,4--polybutadiene when used with a halide- containing aluminum compound.

POLYBUTADIENE AND POLYISOPRENE

- The soluble commercial catalysts are prepared by reacting a cobalt(II) carboxylate with $Al_2R_3Cl_3$.
- These conditions are nicely illustrated by a laboratory preparation of cis-l,4-polybutadiene.
- Diethyl aluminum chloride and cobalt(II) octoate react in a benzene solution of butadiene in the presence of a small amount of water to produce a very active catalyst.

POLYBUTADIENE AND POLYISOPRENE

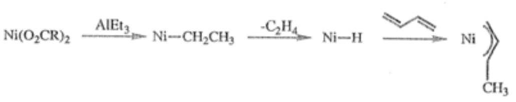
- Polymerization at 5°C gives a high molecular weight 1,4-polybutadiene with about 98% cis- 1,4 units.
- It is interesting to note that early reports of polymerizations with cobalt were often difficult to reproduce; later it was discovered that water or other ‘impurities” such as alcohols, reactive organic halides, or organic hydroperoxides were essential components of the catalyst preparation.

POLYBUTADIENE AND POLYISOPRENE

- The nickel-based catalysts are used less extensively than the cobalt systems, but much more is known about their chemistry as a result of extensive study.
- It seems likely that the intermediates in the cobalt and nickel systems are similar.
- The nickel catalysts can be prepared in several different ways, but all methods appear to give relatively stable π-allyl derivatives in the presence of butadiene.

POLYBUTADIENE AND POLYISOPRENE

- In the commercial process, alkylation of a nickel carboxylate probably proceeds through several steps.
- Similar π-crotyl derivatives are obtained by protonation of zero-valent nickel complexes in the presence of butadiene.



POLYBUTADIENE AND POLYISOPRENE

- Like cobalt, organonickel systems generally give high percentages of cts-l,4-polybutadiene.
- In the presence of iodide ion, though, the nickel catalysts give predominantly trans-l,4 product, the more stable isomer.
- This variation in product stereochemistry in butadiene polymerization closely parallels that in the codimerization of butadiene and ethylene to give cis- or trans-1,4-hexadiene.

POLYBUTADIENE AND POLYISOPRENE

- The stereochemistry of the polybutadiene can be controlled by the concentration of potential ligands in the system.
- This effect can be used to prepare a “block” polymer that is half cis- and half trans-1,4-polybutadiene.
- The polymerization is begun with π-allylnickel trifluoroacetate as the catalyst, giving rise to a segment of cis polymer.
- Before polymerization is complete, a trialkyl phosphite ligand is added; the ligand changes the course of the polymerization so that the second half of the growing polymer chain has the trans configuration.

POLYBUTADIENE AND POLYISOPRENE

- The stereoselectivity of the catalyst can be explained on the basis of chelate vs. monodentate coordination of the butadiene.
- This explanation accounts for most of the experimental observations though alternative mechanisms have been proposed.
- Figure 4.5 illustrates the chemistry involved in the preparation of a cis-trans block copolymer:

POLYBUTADIENE AND POLYISOPRENE

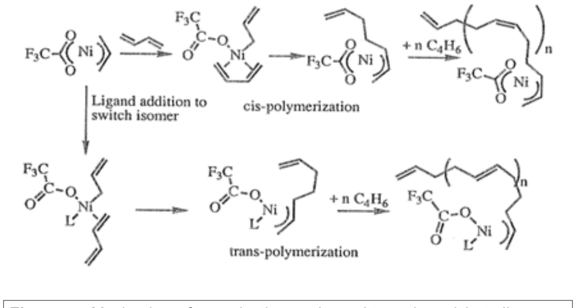


Figure 4.5 Mechanisms for production or cis- and trans-l,4-polybutadiene

POLYBUTADIENE AND POLYISOPRENE

- The π-allyl nickel catalyst coordinates a butadiene through both double bonds in chelate fashion to form an η4-complex shown in the upper pathway.
- Insertion of the diene into the Ni-C bond of the σ-allyl ligand forms a new π-allylic ligand.
- The conformation of this allylic ligand ensures that the double bonds in the growing polymer chain have the cis configuration.

POLYBUTADIENE AND POLYISOPRENE

- However, if a strongly bonding ligand such as L = P(OPh)3 is added to the system, it occupies a coordination site on nickel and forces the chemistry to follow the lower pathway.
- The butadiene complexes through only one C=C bond. Insertion of this single C=C bond gives a π-allyl which rearranges to a σ-allylic structure.
- However, the configuration of the allylic ligand formed in this way leads to a trans-C=C bond in the growing polymer chain.
- Thus the presence or absence of ligand, L, determines the stereochemistry of the growing polymer chain.

CHAPTER 4 OBJECTIVES

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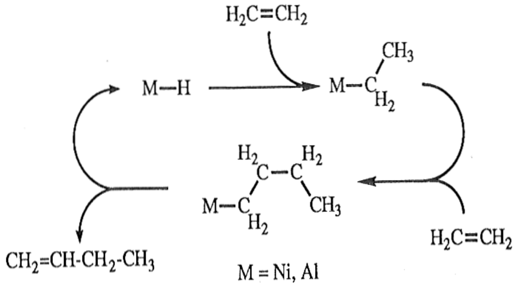
  - Olefin Dimerization
  - 1,4-HEXADIENE

OLIGOMERIZATION OF OLEFINS

- The self-addition of olefins to form dimers, trimers, and low polymers is called oligomerization.
- This process can be identical in mechanism to the ethylene polymerization described earlier except that chain termination occurs much more frequently.
- In ethylene dimerization to 1-butene, chain transfer by β-hydrogen abstraction follows every insertion into an M-C bond:

OLIGOMERIZATION OF OLEFINS



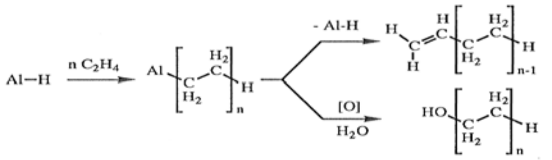
OLIGOMERIZATION OF OLEFINS

- These reactions find practical applications in
  - (a) oligomerization of ethylene by organoaluminum compounds to give linear α-olefins or α-alcohols;
  - (b) nickel- catalyzed oligomerization of ethylene to C10-C20 α-olefins by the Shell Higher Olefins Process (SHOP); and
  - (c) dimerization of propylene to branched C6 olefins useful as octane-enhancers in motor fuel.

OLIGOMERIZATION OF OLEFINS

Aluminum-Catalyzed Oligomerization of Ethylene

- Ethylene readily inserts into Al-H and Al-C bonds to form C2-C40 alkylaluminum compounds.
- These compounds are intermediates in the commercial production of linear α-olefins and α-alcohols according to the equations.



OLIGOMERIZATION OF OLEFINS

Aluminum-Catalyzed Oligomerization of Ethylene

- The synthesis of olefins is catalytic because n-hydrogen abstraction from the growing alkyl chain regenerates an Al-H bond that can start growth of a new alkyl chain.
- The linear olefins produced in this way are intermediates in the synthesis of fatty acid esters, aldehydes, and alcohols by the carbonylation reactions.

OLIGOMERIZATION OF OLEFINS

Aluminum-Catalyzed Oligomerization of Ethylene

- In contrast to the catalytic α-olefin synthesis, the alcohol synthesis uses the alkylaluminum compound stoichiometrically.
- An AlR_3 compound prepared by ethylene oligomerization is oxidized with air to $Al(OR)_3$ which is hydrolyzed to produce the linear alcohol.
- Such “fatty alcohols” are biodegradable and are used in the manufacture of detergents.
- The process competes economically with the hydroformylation of olefins even though it uses the aluminum compound stoichiometrically rather than as a catalyst.
- The coproduced alumina is of a high grade and adds value to the process.

OLIGOMERIZATION OF OLEFINS

Aluminum-Catalyzed Oligomerization of Ethylene

- The chemistry of ethylene addition to Al-C and Al-H bonds dictates the manner in which ethylene oligomerization is carried out commercially.
- Trialkylaluminum compounds catalyze the reaction of ethylene, aluminum, and hydrogen to form triethylaluminum (which is extensively dimerized in the liquid state):

$$2\,\mathrm{Al} + 3\mathrm{H}_2 + 6\,\mathrm{C}_2\mathrm{H}_4 \xrightarrow{\mathrm{AlR}_3} 2\,\mathrm{AlEt}_3 \rightleftharpoons \mathrm{Al}_2\mathrm{Et}_6$$

OLIGOMERIZATION OF OLEFINS

Aluminum-Catalyzed Oligomerization of Ethylene

- The insertion of ethylene does not stop when Al-C groups are formed.
- Continued insertion into the Al-C bonds produces alkylaluminum compounds in which the alkyl groups are polyethylene chains.
- The length of the chains is go by reaction conditions, but generally represents a statistical distribution of sizes based on the amount of ethylene available.
- Practical syntheses of terminal olefins employ reaction temperatures at which 3-hydrogen elimination is frequent.

OLIGOMERIZATION OF OLEFINS

Aluminum-Catalyzed Oligomerization of Ethylene

- Chain growth and termination occur at comparable rates.
- The reaction is carried out typically at 200-250°C and 130-250 atmospheres pressure.
- The high pressure of ethylene prevents the α-olefin products from reinserting into the growing alkyl chains by a simple mass-action effect.
- The predominance of ethylene insertion gives linear olefins with 4-8 carbon atoms as the major products.

OLIGOMERIZATION OF OLEFINS

Aluminum-Catalyzed Oligomerization of Ethylene

- The alcohol synthesis process developed by Conoco employs a temperature of only 115-130°C in the chain-growth step in order to avoid olefin formation by p abstraction.
- Ethylene and triethylaluminum are reacted at about 120°C and 135 atmospheres to form a statistical mixture of AlRR'R" compounds with most alkyl chain lengths in the C6-C14 range (all even-numbered).

OLIGOMERIZATION OF OLEFINS

Aluminum-Catalyzed Oligomerization of Ethylene

- This mixture is oxidized with dry air at about 35°C to form the corresponding Al(OR)(OR')(OR") mixture.
- Hydrolysis with sulfuric acid yields a mixture of fatty alcohols.
- In laboratory preparations of alcohols from AlR_3 compounds, trimethylamine oxide is a convenient reagent for oxidation of the Al-R bond.

OLIGOMERIZATION OF OLEFINS

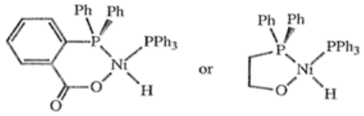
Shell Higher-Olefins Process

- Shell uses a nickel-catalyzed oligomerization of ethylene to prepare linear α-olefins on a large scale.
- Despite much research in the area, specifics of the commercial catalyst and system are still incomplete.
- As in the aluminum-catalyzed oligomerization, insertion of ethylene into M-H and M-C bonds forms metal alkyls with a statistical distribution of chain lengths.

OLIGOMERIZATION OF OLEFINS

Shell Higher-Olefins Process

- β-Hydrogen abstraction produces olefin and regenerates Ni-H species to repeat the chain-growth sequence.
- The mechanism of this process is like that discussed for olefin dimerization below.
- A nickel hydride catalyst is generated by reduction of a nickel salt in the presence of a chelating ligand such as diphenylphosphinobenzoic acid or nickel(0) is reacted with a phosphorus ylide.



OLIGOMERIZATION OF OLEFINS

Shell Higher-Olefins Process

- In practice, a catalyst of this sort is allowed to react with ethylene in a glycol solvent such as 1,4-butanediol at about 100°C and 80 atmospheres pressure, the pressure required to attain high linearity.
- A rapid reaction occurs to form a mixture of linear α-olefins.
- The α-olefin layer is immiscible in the catalyst-containing glycol layer and is decanted. The olefin layer is then washed with additional glycol to remove traces of catalyst.

OLIGOMERIZATION OF OLEFINS

Shell Higher-Olefins Process

- The olefin layer is then washed with additional glycol to remove traces of catalyst.
- The olefin chain lengths typically are distributed with about 40% in the C_4-C_8 range, 40% in the C_{10}-C_{18} range, and 20% above C_{20}.
- Originally, the C_{10}-C_{18} olefins were the more marketable fraction, but octene is now a valuable product.
- The higher and lower boiling products are then utilized in a complex sequence of catalytic reactions (Figure 4.6).
- The low- and high-boiling olefins are isomerized separately over heterogeneous catalysts to produce internal olefins.
- This step is necessary because the next step is olefin metathesis, which often does not work well with terminal olefins.

OLIGOMERIZATION OF OLEFINS

Shell Higher-Olefins Process

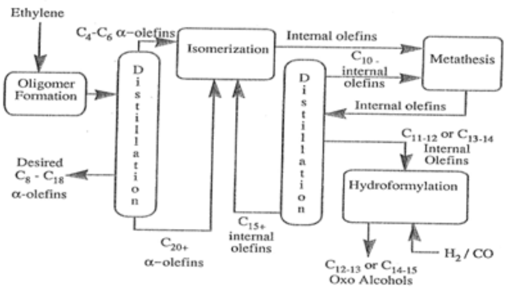
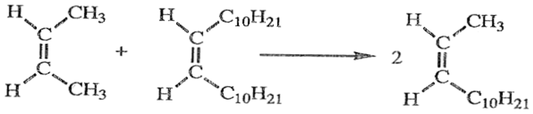


Figure 4.6 Schematic representation of the Shell Higher-Olefins Process (SHOP)

OLIGOMERIZATION OF OLEFINS

Shell Higher-Olefins Process

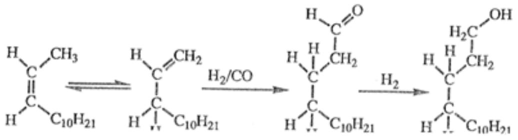
- In the process variant shown in the figure, the low- and high-boiling internal olefins react over a heterogeneous catalyst such as MoO_3 on Al_2O_3 to produce a broad range of internal olefins.
- Due to the prevalence of reactions such as much of the product is in the useful C_{10}-C_{18} range.



OLIGOMERIZATION OF OLEFINS

Shell Higher-Olefins Process

- Hydroformylation is carried out with a cobalt catalyst that converts internal olefins to terminal alcohols.
- In this way, a high proportion of the ethylene is converted to useful fatty alcohols.



OLIGOMERIZATION OF OLEFINS

Olefin Dimerization

- The dimerization of ethylene to butenes is the simplest and one of the best studied oligomerization reactions.
- Industrially, it is not very significant because butenes are generally cheaper than ethylene.
- However, in situ formation of 1-butene during ethylene polymerization may be a convenient way to produce branched polyethylene with properties approaching those of low-density polyethylene.
- Another potentially useful reaction is the dimerization of propylene in mixed C_3 streams which converts this inexpensive olefin to useful C6 compounds such as dimethylbutenes and methylpentenes.

OLIGOMERIZATION OF OLEFINS

Olefin Dimerization

- The first simple olefin dimerization was discovered in the course of Ziegler's study of ethylene oligomerization to long-chain α-olefins by alkylaluminum compounds.
- It was observed that traces of nickel from reactor corrosion diverted the ethylene oligomerization to the production of 1-butene.
- This chance discovery led to the invention of the Ziegler catalysts for polymerization, hydrogenation, and isomerization of olefins.
- As discussed above, this chemistry provides the basis for the Shell α-olefins process.

OLIGOMERIZATION OF OLEFINS

Olefin Dimerization

- The dimerization of simple olefins has been studied extensively as a model for 1,4-hexadiene synthesis.
- Greatest attention has been given to the nickel and rhodium complexes that are commercially attractive for preparation of trans-1,4-hexadiene.
- However, very effective catalysts for olefin dimerization also arise from reaction of alkylaluminum compounds with cobalt salts and with titanium(IV) complexes.

OLIGOMERIZATION OF OLEFINS
Olefin Dimerization

- The dimerization of propylene with nickel-based Ziegler catalysts has been explored extensively and provides the basis for the IFP Dimersol process discussed later in this section.
- In large-scale operations, the catalyst is prepared as it is used by mixing $NiCl_2$ triethylaluminum, and butadiene in chlorobenzene to give a π-allyl complex of nickel.
- A phosphine is added to the solution and the mixture is fed to a continuous reactor along with liquid propylene at 15 atmospheres pressure.

OLIGOMERIZATION OF OLEFINS
Olefin Dimerization

- Rapid dimerization occurs at 30-40°C to give a mixture of n-hexenes, 2-methylpentenes and 2,3-dimethylbutenes in 85-90% yield.
- The distribution of the isomeric C_6 products depends on the nature of the phosphine used in catalyst preparation.
- At low temperatures, the proportion of methylpentenes can be as high as 80% if PMe_3 or Ph is used.
- However, with sterically bulky phosphines such as $PEt(t\text{-}Bu)_2$ 70-80% of the mixture is dimethylbutenes.

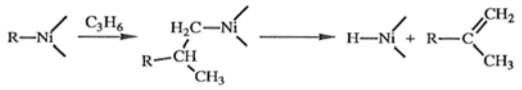
OLIGOMERIZATION OF OLEFINS
Olefin Dimerization

- Effective catalysts can be prepared from combinations of π-allylnickel halides with phosphines and Lewis acids such as $AlCl_3$ or $EtAlCl_2$.
- Similarly, zero valent nickel complexes such as bis(1,5-cyclooctadiene)nickel and $Ni[P(OPh)_3]_4$ react with Lewis acids to give catalysts for dimerization of propylene.
- The same catalyst systems also bring about the dimerization of ethylene to butenes and codimerization of ethylene and propylene to pentenes.

OLIGOMERIZATION OF OLEFINS

Olefin Dimerization

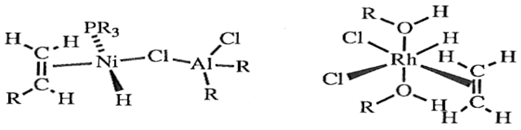
- The products are generally the thermodynamically favored internal isomers because the dimerization catalysts also catalyze double-bond migration.
- The active catalyst for olefin dimerization in all these systems is probably a nickel hydride complex.
- The Ni-H function can be formed by β-hydrogen abstraction from alkyl intermediates formed by interaction of an alkyl or allylnickel complex with propylene:



OLIGOMERIZATION OF OLEFINS

Olefin Dimerization

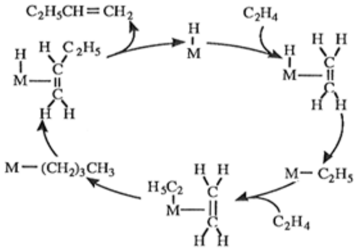
- The other coordination sites about the nickel are occupied by phosphine, olefin, and halide ligands.
- The active catalyst in the well-studied rhodium system may be similarly coordinated.
- The formation of the rhodium complex is discussed in the section on hexadiene synthesis.



OLIGOMERIZATION OF OLEFINS

Olefin Dimerization

- These complexes correspond to the olefin hydride complexes shown in the two o’clock position of the catalytic cycle.

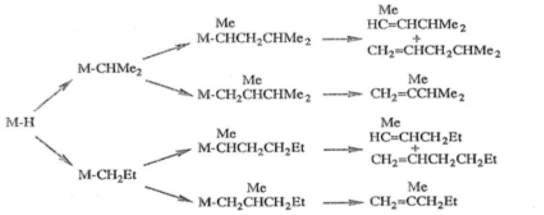


OLIGOMERIZATION OF OLEFINS
Olefin Dimerization

- This mechanism employs the familiar steps of olefin coordination to a metal hydride, insertion into the M-H bond, and subsequent insertion into an M-C bond just as in olefin polymerization catalysts.
- However, the olefin dimerization catalysts effect β-hydrogen abstraction from the growing alkyl chain after almost every M-C insertion.
- As a result, olefin dimers predominate in the product. Only small quantities of trimers and tetramers form under normal operating conditions.

OLIGOMERIZATION OF OLEFINS
Olefin Dimerization

- The ethylene dimerization shown above can produce only a single product because ethylene insertion into an M-H or M-C bond has no regioselective aspect.
- With propylene, however, both insertion steps can produce isomers:



OLIGOMERIZATION OF OLEFINS
Olefin Dimerization

- The relative frequencies of the various insertion modes determine the product distribution.
- A very crowded catalyst site produced by bulky ligands favors formation of alkyl groups with RCH_2 joined to the metal.
- This effect enhances production of the branched chain olefins.
- While 4-methyl-1-pentene is normally produced for the polyolefin industry using heterogeneous catalysts, a homogeneous catalyst shows good selectivity.

OLIGOMERIZATION OF OLEFINS
Olefin Dimerization

- BP Chemicals is commercializing a homogeneous process which yields a mixture of branched hexene isomers.
- The mixture is treated with an isomerization catalyst to yield the internal olefin, 2,3-dimethyl-2-butene.
- Extraction from the mixture by distillation is followed by a reisomerization to the desired 2,3-dimethyl-l-butene.
- This specialty product is then used by the fragrance industry to yield a synthetic musk.

OLIGOMERIZATION OF OLEFINS
Olefin Dimerization

- IFP’s Dimersol Process and variations of that process are widely used to upgrade the value of olefin-containing streams.
- Using Ziegler catalysts, a stream containing n-butenes is dimerized to isooctenes useful as plasticizer precursors.
- This reaction is often carried out on a C_4 stream from a refinery cracker after it has been depleted of isobutene by reaction with methanol to form methyl-t-butylether for a gasoline additive; saturates are unreactive and are recycled to the refinery operation.

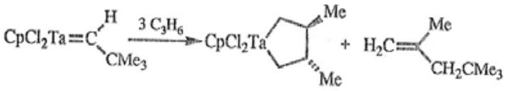
OLIGOMERIZATION OF OLEFINS
Olefin Dimerization

- This metallacyclic mechanism is probably common for olefin dimerization, hut its significance has not been appreciated until recently.
- The dimerization of ethylene to 1-butene or cyclobutane has been observed with metallacyclic nickel and titanium complexes.
- The formation of a metallacyclopentane from two moles of ethylene closely resembles the coupling of two moles of butadiene to a metallacycle, which is the first step in oligomerization of the diene by nickel or titanium catalysts.

OLIGOMERIZATION OF OLEFINS

Olefin Dimerization

- An entirely different mechanism for olefin dimerization has been proposed for catalysis by a stable alkylidenetantalum complex which is extremely selective for the dimerization of propylene to 2,3-dimethyl- 1-butene with over 90% selectivity.
- The alkylidene group is removed and an unstable metallocycle forms in the catalyst formation step.



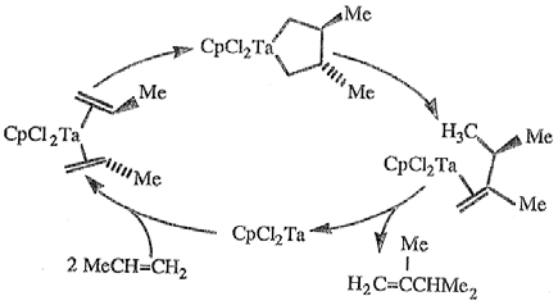
OLIGOMERIZATION OF OLEFINS

Olefin Dimerization

- In the catalyst cycle, a 1,3-hydrogen shift across the face of the ring converts the metallocycle to an olefin complex.
- Dissociation of the dimeric olefin and coordination of propylene gives the bis(propylene) complex.
- Dissociation and association of olefinic ligands may occur simultaneously.
- Reorganization of bonds regenerates the metallocycle.

OLIGOMERIZATION OF OLEFINS

Olefin Dimerization



OLIGOMERIZATION OF OLEFINS

Olefin Dimerization

- The tantalum catalyst converts ethylene to 1-butane efficiently but is less effective for dimerization of 1-butene and higher olefins.
- Because it does not involve hydride intermediates that might catalyze double-bond migration, the terminal olefin products are stable in the reaction mixture.

OLIGOMERIZATION OF OLEFINS
Olefin Dimerization

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OLIGOMERIZATION OF OLEFINS

Olefin Dimerization

- There is an interesting case where the formation of a metallacyclopentane leads to the formation of 1-hexene rather than the expected 1-butene.
- The metallacyclopentane is formed by coupling of two ethylenes as above, but this intermediate is relatively stable.
- When a third ethylene is inserted, the complex is less stable, undergoing a β-elimination on one end and then reductive elimination to yield 1-hexene with high selectivity.
- This catalytic cycle presumably involves cycling through Cr(III) and Cr(IV).

OLIGOMERIZATION OF OLEFINS

Olefin Dimerization

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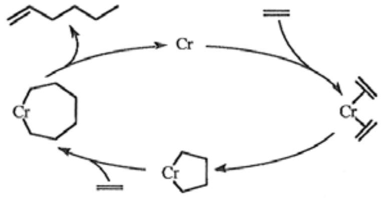


OLIGOMERIZATION OF OLEFINS

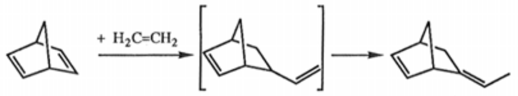
1,4-HEXADIENE

- Codimerization of ethylene and butadiene with a rhodium catalyst is used to produce trans-1,4-hexadiene, which is a comonomer in ethylene-propylene-diene (EPDM) elastomers.
- Ziegler catalysts based on nickel, cobalt, and iron salts are also very effective for this codimerization.
- The nickel catalysts produce largely the industrially interesting trans isomer while the cobalt and iron catalysts give the cis isomer cleanly.

OLIGOMERIZATION OF OLEFINS

1,4-HEXADIENE

- Since many of these catalysts also bring about olefin isomerization, care is required to remove the product from the reaction mixture before it isomerizes to the more stable conjugated 2,4-hexadiene.
- Similar nickel-based Ziegler catalysts can be used to prepare ethylidenenorbornene which is also widely used in EPDM elastomers.
- Ethylene reacts with norbornadiene in two metal-catalyzed steps:



OLIGOMERIZATION OF OLEFINS
1,4-HEXADIENE

- The industrial synthesis of trans-1,4-hexadiene is carried out under pressure, but the codimerization of ethylene and butadiene can be studied conveniently in the laboratory.
- Addition of an equimolar mixture of ethylene and butadiene to a methanol solution of commercial $RhCl_3.3H_2O$ leads to a slow reaction which accelerates with time.

OLIGOMERIZATION OF OLEFINS
1,4-HEXADIENE

- The initial induction period during which Rh(III) is reduced to Rh(I) can be eliminated by adding a preformed rhodium(I) catalyst such as $[RhCl(C_2H_4)_2]_2$.
- The product from the 1:1 mole ratio of ethylene and butadiene is a mixture of hexadienes which forms by isomerization of the initially formed trans-1,4-isomer.
- However, isomerization can be suppressed by maintaining high concentrations of butadiene that is, by operating at low conversion.

OLIGOMERIZATION OF OLEFINS
1,4-HEXADIENE

- Most hexadiene syntheses with the nickel- and cobalt-based Ziegler catalysts are carried out in metal pressure reactors.
- Typically, $NiCl_2(PBu_3)_2$ and $Al_2Cl_2(i\text{-}Bu)_4$ are mixed in tetrachloroethvlene which has been presaturated with butadiene and (mostly trans-1,4) and some 3-methyl-1,4-pentadiene, which are isolated by distillation.
- Instead of using a nickel(II) complex with a reducing agent, nickel(0) complexes can be used to codimerize ethylene and butadiene if acidic cocatalysts are supplied.

OLIGOMERIZATION OF OLEFINS
1,4-HEXADIENE

- A mixture of bis(l,5-cyclooctadiene)nickel $C_6F_5PPh_2$, $EtAlCl_2$ and Et_2AlOEt gives a high yield of trans-1,4-hexadiene.
- The aluminum cocatalyst can be replaced by a protonic acid. A solution of Ni and H in methanol effects hexadiene synthesis under conditions in which several intermediates can be observed.
- Such combinations of acid and Ni(0) generate a nickel hydride which is believed to be the true catalyst.

OLIGOMERIZATION OF OLEFINS
1,4-HEXADIENE

- All the nickel and rhodium catalysts are based on metal hydride complexes.
- In Du Pont’s rhodium system, several steps are involved in catalyst formation during the induction period:

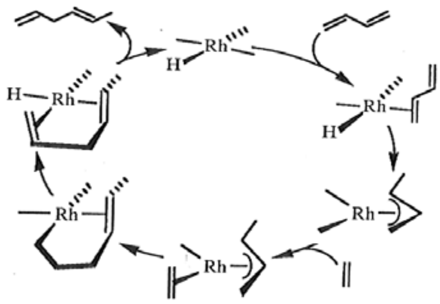
$$RhCl_3 + C_2H_5OH \longrightarrow \text{"RhCl"} + HCl + CH_3CHO$$

$$\text{"RhCl"} + HCl \longrightarrow \text{"HRhCl}_2\text{"} \xrightarrow{3L} HRhCl_2(L)_3$$

OLIGOMERIZATION OF OLEFINS
1,4-HEXADIENE

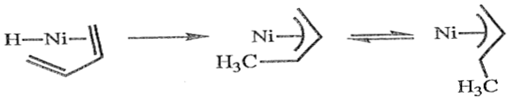
- The rhodium hydride enters the catalytic cycle at the top.
- Reaction with butadiene gives a syn-π-crotyl complex which coordinates a molecule of ethylene to form all ethylene crotyl complex.
- Insertion of ethylene at the less hindered end of the crotyl ligand forms a trans-4-hexenyl rhodium complex.
- β-Hydrogen elimination yields a transient Rh-H complex of trans-1,4-hexadiene which dissociates the product.

OLIGOMERIZATION OF OLEFINS
1,4-HEXADIENE



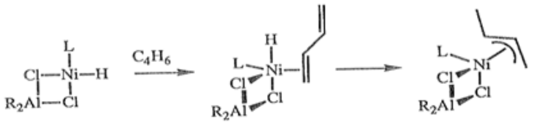
OLIGOMERIZATION OF OLEFINS
1,4-HEXADIENE

- With the rhodium and the $[HNiL_4]^+$ catalysts, it seems likely that the stereochemistry about the double bond in the product is determined by an isomerization of the π-crotyl intermediate.
- The initial insertion of butadiene into the metal-hydrogen bond is believed to give an anti-crotyl intermediate.
- This isomer would yield cis-1,4-hexadiene as the final product, but isomerization to the syn-crotyl complex is faster than ethylene insertion.



OLIGOMERIZATION OF OLEFINS
1,4-HEXADIENE

- In the Ziegler systems, product stereochemistry is believed to arise from mono- or bidentate coordination of the incoming butadiene ligand just as in butadiene polymerization.
- With nickel catalysts in the presence of excess phosphine ligand, monodentate coordination gives the syn-crotyl intermediate which yields trans-1,4-hexadiene:



OLIGOMERIZATION OF OLEFINS
1,4-HEXADIENE

- However, with a cobalt catalyst or with nickel in the absence of phosphorus ligands, the butadiene is chelated to the metal.
- The resulting anti-crotyl complex gives cis-1,4-hexadiene very cleanly with catalyst system such as $CoH(Ph_2PCH_2CH_2PPh_2)_2$.

DIMERIZATION AND TRIMERIZATION OF DIENES

- Butadiene and other conjugated dienes undergo a variety of oligomerization reactions to give both linear and cyclic products.
- Two are used commercially:
  1) cyclodimerization of butadiene with a nickel catalyst to produce 1,5-cyclooctadiene which is used in the preparation of flame retardants such as tetrabromocyclooctane and
  2) cyclotrimerization of butadiene to give 1,5,9 an intermediate in the manufacture of dodecanedioic acid, 1,13-tetradecadiene, and lauryllactam.
- Other potential industrial applications include dimerization of butadiene to linear octatrienes and cyclodimerization of isoprene to dimethylcyclooctadienes. Some of these hydrocarbons would be difficult to synthesize by conventional methods.

CHAPTER 4
OBJECTIVES

- DIMERIZATION AND TRIMERIZATION OF DIENES
  - Diene Dimerization
  - Cyclododecatriene Synthesis
- FUNCTIONAL OLEFIN DIMERIZATION
- CHAIN TRANSFER CATALYSIS

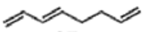
DIMERIZATION AND TRIMERIZATION OF DIENES
Diene Dimerization

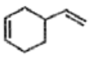
- Ziegler catalysts like those used for synthesis of polybutadiene and 1,4-hexadiene can be modified to produce both linear and cyclic dimers and trimers of butadiene.
- Nickel catalysts are the most versatile and can be used to make almost ally of the products by a suitable choice of ligands and reaction conditions.

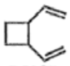
DIMERIZATION AND TRIMERIZATION OF DIENES
Diene Dimerization

- Emphasis here is centered on 1,5-cyclooctadiene (COD) and 1,3,7-octatriene (OT), Other accessible dimers include 4-vinylcyclohexene (VCH) and l,2-divinylcyclobutane (DVCB).


COD


OT


VCH


DVCB

DIMERIZATION AND TRIMERIZATION OF DIENES
Diene Dimerization

- Many substituted butadienes also dimerize to give analogous cyclooctadienes and octatrienes.
- The isoprene dimers and trimers are especially interesting for synthesis of terpenoid and sesquiterpenoid compounds of biological interest.
- The dimethylcyclooctadienes can he used as intermediates in the synthesis of fragrances.
- Low-valent palladium catalysts are often advantageous for preparation of the linear dimers such as 2,7-dimethyl-2,4,6-octatriene.

DIMERIZATION AND TRIMERIZATION OF DIENES
Diene Dimerization

- The cyclodimerization of butadiene to give 1,5-cyclooctadiene is catalyzed by a zero-valent nickel complex which contains one mole of a triaryl phosphite ligand.
- In large-scale syntheses, nickel(II) acetylacetonate is reduced with an organoaluminum compound in the presence of the phosphite.
- This catalyst differs from that used in hexadiene synthesis or butadiene polymerization in that the aluminum compound need not be a Lewis acid.

DIMERIZATION AND TRIMERIZATION OF DIENES
Diene Dimerization

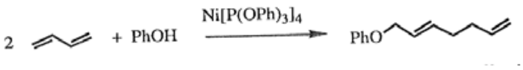
- An equally useful catalyst is obtained by reacting the triaryl phosphite with Ni(COD)$_2$ in liquid butadiene.
- The most effective catalysts are based on bulky ligands such as tris(*o*-phenylphenyl) phosphite.
- The catalyst containing this ligand rapidly dimerizes butadiene at 80°C and 1 atmosphere pressure in a hydrocarbon solvent such as cyclooctadienes.
- The product is 96% 1,5-cyclooctadiene along with small amounts of trimers and 4-vinylcyclohexene.

DIMERIZATION AND TRIMERIZATION OF DIENES
Diene Dimerization

- The latter product is the normal thermal dimer of butadiene although it is not commonly formed below 150°C.
- When the dimerization is carried out at low temperatures and low conversions, 1,2-divinylcyclobutane may be isolated in yields up to 40%.
- It readily isomerizes to COD and vinylcyclohexene in the presence of the catalyst.

DIMERIZATION AND TRIMERIZATION OF DIENES
Diene Dimerization

- The same catalysts that are used to cyclodimerize butadiene produce linear dimers when a slightly acidic coreactant is added to the reaction mixture.
- The coreactant may be ROH, R_2NH, HCN, or active methylene compounds.
- It may be incorporated in the product or it may promote formation of an octatriene.
- For example, phenols can give either octatrienes or phenoxyoctadienes as major products:

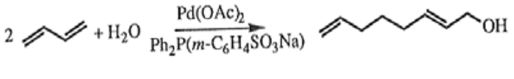


DIMERIZATION AND TRIMERIZATION OF DIENES
Diene Dimerization

- In general, however, zero-valent palladium catalysts are more effective for production of these linear dimers.
- With $Pd(PPh_3)_2$ (maleic anhydride) as a catalyst, isoprene gives 2,7 exclusively.
- Kuraray has developed a diol synthesis based upon the hydrodimerization of butadiene followed by hydroformylation.

DIMERIZATION AND TRIMERIZATION OF DIENES
Diene Dimerization

- They have started a semiworks to hydrodimerize butadiene using a homogeneous palladium catalyst which employs a monosulfonated triphenyl to solubilize the catalyst in a sulfolane/H_2O phase.
- Triethylamine is used to stabilize the catalyst, and the reaction is carried out under an atmosphere of CO_2.
- The hydrodimer is isomerized, hydroformylated and hydrogenated to yield 1,9- nonanediol.



DIMERIZATION AND TRIMERIZATION OF DIENES

Diene Dimerization

- The activity of diene dimerization catalysts is modified by the presence of carbon dioxide.
- The CO_2-promoted reaction of $Pt(PPh_3)_3$ gives octatrienes. With $Pd(diphos)_2$, it gives both octatrienes and octadiene lactones.
- The presence of CO_2 can also induce formation of octadienols from butadiene and water.
- It has been speculated that CO_2 and water combine under pressure to give carbonic acid which adds to all octatriene precursor to give a water-sensitive octadienyl carbonate.

DIMERIZATION AND TRIMERIZATION OF DIENES

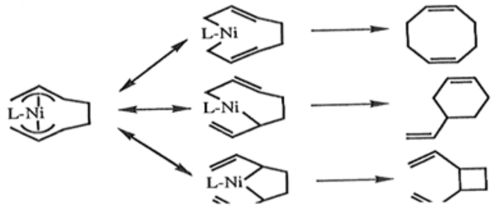
Diene Dimerization

- In the nickel system, a CO2 insertion product of an isoprene dimer complex has been characterized.
- The mechanism of butadiene dimerization has been studied thoroughly.
- It is likely that the same intermediates are involved in formation of the linear and cyclic dimers.
- Some of these intermediates also occur in the pathway to 1,5,9-cyclododecatriene, a cyclic timer of butadiene.
- It appears that two molecules of butadiene coordinate to a zero-valent nickel atom which bears one phosphorus ligand, L.

DIMERIZATION AND TRIMERIZATION OF DIENES

Diene Dimerization

- The critical step in dimer formation is coupling the two monodentate butadiene ligands to an octadienyl ligand:

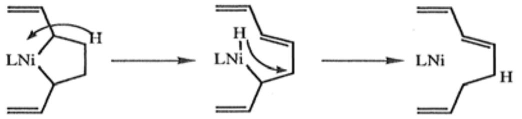


DIMERIZATION AND TRIMERIZATION OF DIENES
Diene Dimerization

- On the basis of its proton nmr spectrum, the dimer-ligand is believed to bond to the metal through a σ-allyl function as well as a π-allyl.
- However, the spectroscopically detectable σ,π-form is tautomeric with the three isomeric σ-allylic structures shown.
- Each isomer can undergo reductive elimination of two Ni-C bonds to generate a different cyclic dimer and reform the “L-Ni” catalyst.
- In practice, all three processes occur and each can predominate with proper choice of reaction conditions and the ligand, L.

DIMERIZATION AND TRIMERIZATION OF DIENES
Diene Dimerization

- The formation of 1,3,7-octatriene can be rationalized by fl-hydrogen elimination from the tautomer that ordinarily gives rise to divinylcyclobutane:

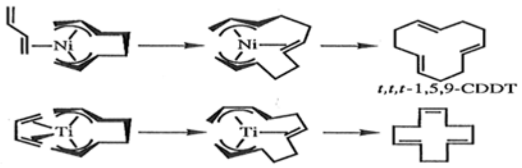


DIMERIZATION AND TRIMERIZATION OF DIENES
Cyclododecatriene Synthesis

- Butadiene and substituted dienes trimerize readily under the influence of soluble transition metal catalysts forming C_{12} molecules useful as intermediates to nylon-12’s.
- The catalyst used for commercial synthesis of cyclododecatriene is almost identical to that used for polymerization of ethylene.
- In the industrial process the catalyst is prepared by mixing $TiCl_4$ with excess $Al_2Cl_3Et_3$ in benzene.

DIMERIZATION AND TRIMERIZATION OF DIENES
Cyclododecatriene Synthesis

- After catalyst deactivation, distillation gives a 75-90% yield of 1,5,9-cyclododecatriene which is almost entirely the cis-trans-trans isomer.
- Minor amounts of the all-trans isomer, polybutadiene, 1,5-cyclooctadiene, and 4-vinylcyclohexene also form.



DIMERIZATION AND TRIMERIZATION OF DIENES
Cyclododecatriene Synthesis

- The cyclotrimerization of butadiene with nickel catalysts has been studied more thoroughly even though it is not used industrially. When nickel(II) acetylacetonate is reduced with $Al(C_2H_5)_2(OC_2H_5)$ in the presence of butadiene, a highly reactive complex is formed.
- This compound, sometimes dubbed “naked nickel”, catalyzes trimerization of butadiene to trans,trans,trans-1,5,9-cyclo- dodecatriene.
- Zero-valent nickel complexes, for example, $Ni(COD)_2$, which lack phosphorus ligands, arc also very effective for this purpose.

DIMERIZATION AND TRIMERIZATION OF DIENES
Cyclododecatriene Synthesis

- The course of the nickel-catalyzed reaction is very sensitive to the nature of the ligands on nickel since it can produce polymer or either of two butadiene dimers as major products.
- In addition, it can catalyze cotrimerization of butadiene and ethylene to form either cis, trans-l,5-cyclodecadiene or 1,4,9-decatriene.
- It seems likely that the initial steps in trimerization are identical to those in diene dimerization.
- Two butadiene ligands couple to form an open dimer in which the double bond has a trans configuration.

DIMERIZATION AND TRIMERIZATION OF DIENES

Cyclododecatriene Synthesis

- In the absence of phosphorus ligands, another molecule of butadiene inserts into an Ni-C bond to give a nickel complex which bears a bis(allylic)-Cl_2 ligand.
- On warming in the presence of butadiene, the ends of the allyl functions couple to form the cyclic triene, initially as a Ni(0) complex.
- The trans configurations of the C=C bonds in the triene derive from syn conformations of the bis(π-allyl) intermediates.
- It is tempting to speculate that the monodentate bonding of the butadiene ligand dictates for of the syn allyl intermediate.

DIMERIZATION AND TRIMERIZATION OF DIENES

Cyclododecatriene Synthesis

- In contrast, the additional vacant orbitals of a titanium catalyst permit bidentate coordination of the diene as shown, yielding an anti-allyl ligand, which in turn generates a cis double bond in the final product.
- The active species in Du Pont’s titanium catalyst system are not well characterized. Chemical evidence and analogy to olefin polymerization catalysts suggest that the Ti species are trivalent.
- However, bis(benzene)titanium(0) catalyzes the trimerization when used in combination with $Et_2Al_2Cl_4$ suggesting a Ti(0)-Ti(II) cycle exactly analogous to that observed with nickel.

DIMERIZATION AND TRIMERIZATION OF DIENES

Cyclododecatriene Synthesis

- The $Ti(C_6H_6)_2$ catalyst ordinarily gives but addition of triphenyl yields the all-trans isomer, supporting the proposal that the stereochemistry of the product is dictated by the number of orbitals available for coordination of the third butadiene molecule.

CHAPTER 4
OBJECTIVES

- DIMERIZATION AND TRIMERIZATION OF DIENES
  - Diene Dimerization
  - Cyclododecatriene Synthesis
- FUNCTIONAL OLEFIN DIMERIZATION
- CHAIN TRANSFER CATALYSIS

FUNCTIONAL OLEFIN DIMERIZATION

- The dimerization of functional olefins would be an attractive route to monomers for a variety of polymers. As a result, it has been investigated extensively.
- To date, the only functional olefin dimerization of con significance is Monsanto’s electrolytic hydrodimerization of acrylonitrile to adiponitrile, the precursor to hexamethylenediamine.

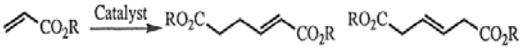
$$2\ CH_2{=}CHCN + 2e^- + 2H^+ \longrightarrow NC(CH_2)_4CN$$

FUNCTIONAL OLEFIN DIMERIZATION

- This process, originally using lead alloy cathodes, was commercialized in 1965.
- Further improvements in the process - removal of membranes, improved electrode materials, and high-conductivity electrolytes - have made this the low-cost method of producing this important nylon intermediate on a small to medium scale.

FUNCTIONAL OLEFIN DIMERIZATION

- The catalytic dimerization of acrylonitrile to l,4-dicyanobutene has been investigated as a synthetic route to hexamethylenediamine for nylon production.
- Linear dimerization of acrylates by $RuCl_3$, $RhCl_3$, or $PdCl_2$ gives unsaturated esters which can be hydrogenated directly to the corresponding ester of adipic acid.



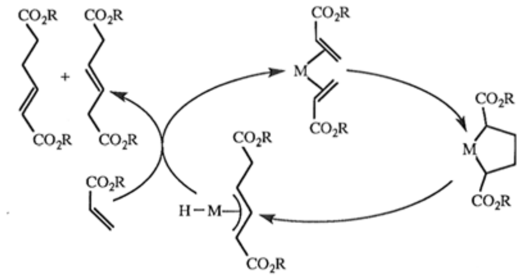
FUNCTIONAL OLEFIN DIMERIZATION

- The reaction is also useful in organic synthesis. The preformed organometallics, $[(C_2H_4)_2RhCl]_2$ and $PdCl_2(NCPh)_2$ are more tractable starting materials and the rates of dimerization are increased markedly by addition of a Lewis acid and a proton source.
- The dimerization is also catalyzed by the zero-valent species $Ru(\eta\text{-}C_6H_6)(CH_2{=}CHCO_2Me)_2$ in the presence of sodium naphthalenide or by $Ru_3(CO)_{12}$ with PPh_3.

FUNCTIONAL OLEFIN DIMERIZATION

- Several mechanisms have been proposed for functional olefin dimerization, and it is not clear that all reactions go by the same mechanism.
- The first possible mechanism is through the intermediacy of a metallacyclopentane formed by addition of the two olefins early in the process.

FUNCTIONAL OLEFIN DIMERIZATION



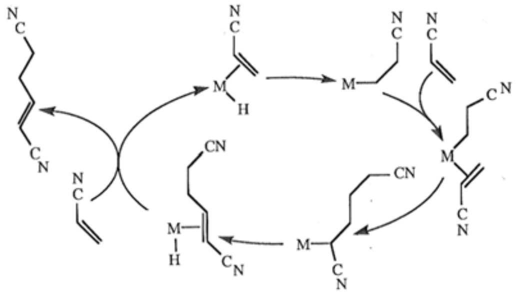
FUNCTIONAL OLEFIN DIMERIZATION

- β-Hydride elimination forms a π-allyl intermediate which transfers hydrogen back to either of two positions, giving the two products which are observed as cis or trans isomers.
- The second mechanism involves addition of a single olefin to the metal hydride, resulting in the formation of a functionalized ethyl group.
- Addition of the second olefin is followed by a second insertion to give the difunctional alkyl complex.

FUNCTIONAL OLEFIN DIMERIZATION

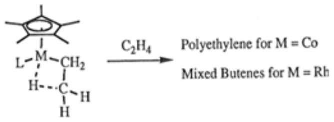
- β-Hydride elimination gives a complexed olefin which is displaced by incoming monomer.
- A deuterium-labelling study provides strong support for this second mechanism in acrylonitrile dimerization on ruthenium under hydrogen or deuterium.
- It is clear that much work remains to be done to sort out the details of these reactions with different substrates and different metal catalysts.

FUNCTIONAL OLEFIN DIMERIZATION



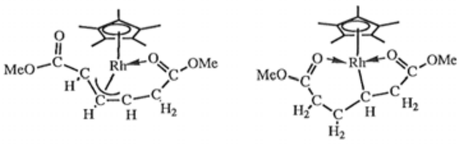
FUNCTIONAL OLEFIN DIMERIZATION

- The relationship between agostic interactions in coordinatively unsaturated metal complexes and the ability to polymerize ethylene has been pointed out.
- The agostic M-H-C interaction stabilizes the complex but is easily displaced by an incoming olefin.
- One result of this relationship was the discovery of cobalt-based catalysts for ethylene polymerization.



FUNCTIONAL OLEFIN DIMERIZATION

- The rhodium analog is active for the dimerization of ethylene to mixed butanes.
- When the rhodium analog is employed for methyl acrylate dimerization, an atmosphere of hydrogen prolongs the lifetime of the catalyst.



FUNCTIONAL OLEFIN DIMERIZATION

- The two products isolated from the reaction proved to be a degradation product which could be reactivated by the hydrogen atmosphere and an intermediate apparently on the catalytic cycle.
- Both complexes display coordination of the ester carbonyl group to decrease coordinative unsaturation at the metal center.
- This coordination serves to highlight the role that the functional group can play in these reactions and why each monomer may generate a new reaction mechanism.

CHAPTER 4 OBJECTIVES

- DIMERIZATION AND TRIMERIZATION OF DIENES
  - Diene Dimerization
  - Cyclododecatriene Synthesis
- FUNCTIONAL OLEFIN DIMERIZATION
- CHAIN TRANSFER CATALYSIS

CHAIN TRANSFER CATALYSIS

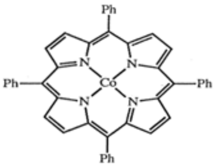
- Early in this chapter, the free-radical polymerization of olefins was mentioned.
- These reactions do not normally involve transition metal complexes except occasionally as redox couples for the generation of odd-electron species.
- Molecular weight is usually controlled by adjusting the concentration of initiator to reactant, sometimes with the addition of a thiol to terminate growing chains.

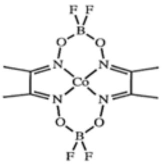
CHAIN TRANSFER CATALYSIS

- These reactions do not normally involve transition metal complexes except occasionally as redox couples for the generation of odd-electron species.
- Molecular weight is usually controlled by adjusting the concentration of initiator to reactant, sometimes with the addition of a thiol to terminate growing chains.
- For example, in methyl methacrylate polymerizations, the reaction is initiated by the thermal decomposition of azobis(isobutyronitrile) (AIBN or Vazo-57) with phenyl mercaptan to chain terminate.

CHAIN TRANSFER CATALYSIS

- To achieve the very low molecular weight polymers which are desired for high-solids automotive finishes or other applications, the high concentrations of initiator and terminator cause problems with toxicity and odor.
- Cobalt(II) complexes of tetra-aza-ligands such as porphyrins or dimethylglyoximates are extremely effective catalysts for intercepting the growing polymer chains.





CHAIN TRANSFER CATALYSIS

- The mechanism of action is shown in Figure 4.7. Because they are essentially radical species themselves, having an odd electron count, they intercept the radical end of the growing polymer chain at diffusion-controlled rates to form a cobalt(III) alkyl.
- This alkyl complex then undergoes β-elimination to generate a polymer chain having an unsaturated end-group and a Co(III)-H which initiates a new free-radical chain.

CHAIN TRANSFER CATALYSIS

- At parts per million concentrations of chain-transfer catalyst, molecular weights of the polymer are dropped from tens of thousands down to thousands.
- At higher concentrations of catalyst, the resulting products can be macromonomers incorporating just a few methacrylate units.
- The hydrogen atom eliminated from the polymer chain is almost always derived from the methyl group of the incoming monomer giving a terminal methylene group rather than an internal double bond.

CHAIN TRANSFER CATALYSIS

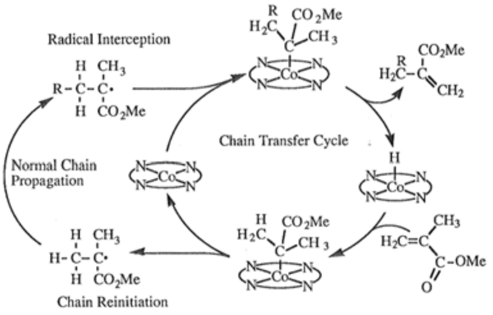


Figure 4.7 Mechanism of chain transfer catalysis in free-radical initiated methacrylate polymerizations

CHAIN TRANSFER CATALYSIS

- The catalysts are equally effective for methacrylonitrile polymers and related species, and any free-radical copolymers which incorporate these groups.
- The lower molecular weight polymers are useful in low-solvent automotive finishes.
- At higher concentrations of catalyst, the products of the reaction are oligomers which find use as macromonomers.
- These macromonomers are interesting in that they do not homopolymerize, but they will copolymerize with a variety of other monomers, giving comb-like copolymers.

CHAPTER 4
OBJECTIVES

- INTRODUCTION
- α-OLEFIN POLYMERIZATION
  - Polyethylene
  - Polypropylene
  - Ethylene-Propylene-Diene Rubbers
  - Specially Polymers
- POLYBUTADIENE AND POLYISOPRENE
- OLIGOMERIZATION OF OLEFINS
  - Aluminum-Catalyzed Oligomerization of Ethylene
  - Shell Higher-Olefins Process
  - Olefin Dimerization
  - 1,4-HEXADIENE

CHAPTER 4
OBJECTIVES

- DIMERIZATION AND TRIMERIZATION OF DIENES
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