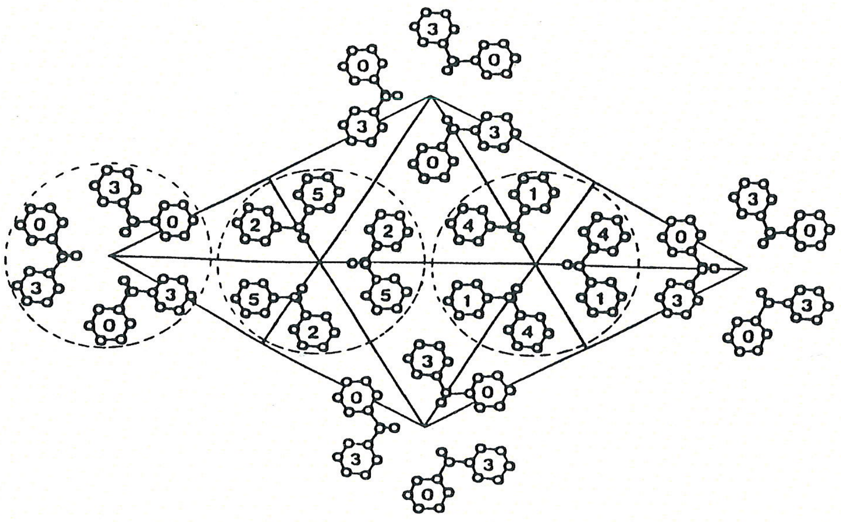
HANDBOOK OF THERMOPLASTICS



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HANDBOOK OF THERMOPLASTICS

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To the memory of my mother
Maria Ọlapade Ọlabisi
and my father
Joseph Ọnaọlapọ Ọlabisi
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Preface

The global thermoplastics market, representing approximately 10% of the worldwide chemical industry, is the fastest growing segment of the world economy. This growth is being driven by several forces, among which are the following: (a) the widening sphere as well as the demanding requirements of the emerging thermoplastics applications; (b) the need to conserve the dwindling natural resources and the environment; (c) competitive basic, mission-oriented, and applied R&D (corporate, national, or international); and (d) the revolutionary and evolutionary scientific and technological innovations that indicate that scientists and engineers, in a paradigm shift, are making a fundamental break from the past. ''Tailor-made'' materials with controlled microstructures are beginning to emerge not only in polyolefins and other commodity thermoplastics, but also in polar thermoplastics, thermoplastics elastomers, synthetic water soluble thermoplastics, high performance thermoplastics, high temperature thermoplastics, specialty thermoplastics for super-function membranes, conducting thermoplastics, polymeric nonlinear optical (NLO) materials systems, liquid crystalline polymers, and advanced thermoplastics composites for structural applications.

This *Handbook of Thermoplastics* underscores these emerging developments and serves as an authoritative source for a worldwide audience in industry, academia, government and nongovernment organizations. It provides comprehensive, up-to-date coverage for each thermoplastic in terms of the following:

- History, development, and commercialization milestones
- Polymer formation mechanisms and process technologies
- Structural and phase characteristics as they affect use properties
- Blends, alloys, copolymers, composites and their commercial relevance
- Processing, performance properties, and applications
- Any other issue that relates to current and prospective developments in science, technology, environmental impact, and commercial viability

These points were regarded as guidelines and every contributor was urged to choose a polymer-specific format that would make the handbook a timeless reference. A thorny element for each author, and indeed a most important issue that will continue to challenge the thermoplastics industry into the next century, relates to environmental waste. The industry has worked long and hard to develop products capable of withstanding extreme and/or aggressive conditions and having a long life. The rapid proliferation of thermoplastics in an impressive array of applications is evidence of the success of the thermoplastics industry, but this very success implies that many thermoplastics, discarded after they have fulfilled their purposes, will pose a formidable disposal challenge.

The *Handbook of Thermoplastics* is composed of 42 chapters prepared by 70 contributors from 18 countries. It contains more than 4000 bibliographic citations plus over 500 tables and figures. Each chapter includes full references at the end of each chapter. Each chapter has been edited, reviewed and revised where necessary, but the authors are responsible for the content. Although no attempt was made to rigorously group the chapters into subsections, there are some subtle groupings as well as grouping overlaps. This is inspired by the reality of the changing thermoplastics industry with its overlapping product families, flexible output, and thermoplastics applications. A pragmatic approach was taken, based on the conventional wisdom embodied in the broad classification of thermoplastics in terms of their applications loosely superimposed on their general spectrum of performance properties, namely, *commodity*, *transitional*, *engineering*, *high performance*, and *high temperature*. The final outcome, representing a cohesive treatment premised on this particular perspective, illustrates the phenomenal progress and the still evolving panoply of thermoplastics.

The first 12 chapters focus on polymeric materials that are essentially ethenoid in origin. Chapters 1 and 2 are devoted to polyolefins; Chapters 2, 3, and 4 treat stereoregular nonpolar and polar thermoplastics; and Chapters 4, 6, and 7 relate to styrenic thermoplastics. Water-soluble polymers (Chapters 12 and 13) are discussed prior to the thermoplastics based on cellulose (Chapter 14), the most abundant organic substances found in nature. Elastomeric materials are discussed in Chapters 15, 16, and 17. The polyester-based polymers are covered in Chapters 17–20, while polyarylates (Chapter 25), which are wholly aromatic polyesters, and the liquid crystalline polymers (Chapter 41), which include a significant percentage of polyester-based materials, appear independently because of their uniqueness.

The compatibilized thermoplastic blends (Chapter 21) are intimately related to, and indeed form the basis for, some of the key methods used in the toughening of thermoplastics (Chapter 22). The current and emerging engineering, high performance, and high temperature thermoplastics are contiguous to each other (Chapters 18–20, 23–33, and 36–41), interspersed with a few general but related chapters. To achieve some dovetailing, the chapters on conducting thermoplastics (Chapter 34) and conducting thermoplastics composites (Chapter 35) are placed after polyphenylene sulfide [PPS] (Chapter 32) and polyphenylene vinylene [PPV] (Chapter 33). This is because PPV, even without a doping agent, possesses a good measure of intrinsic conductivity, and PPS, upon doping with selected agents, is capable of significant electron conductivity. The advanced thermoplastics composites (Chapter 42) are discussed last to permit the prerequisite discussion of the relevant matrix materials on which the various composites are based.

It is hoped that this single-volume collective work will serve its intended purposes, contributing to the dialogue on questions that will continue to arise: What should be the priorities and targets for future development and future investments in the thermoplastics industry? What are the prospective developmental patterns? What will be the available opportunities and the prevailing threats? What are the possible strategic approaches? What, in short, are the new sets of thermoplastics products that are likely to be produced and what process technologies are likely to be used to manufacture them in the 21st century and beyond?

The efforts of the contributors in preparing and revising their manuscripts for the handbook are deeply appreciated. During the course of preparing her manuscript, the author of Chapter 4, Vittoria Vittoria, lost her husband, Francesco de Candia, who made outstanding contributions to the study of syndiotactic polystyrene. I commend her fortitude; her contribution is an essential memorial essay. Life, they say, is intimately entwined with death. I congratulate Emilia Di Pace on the birth of a child during the course of preparing her co-authored manuscript. I am delighted to thank M. Jamal El-Hibri for his support and for relaying information to some specific contributors. I acknowledge the support of the Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia. As always, I am indebted to my wife and friend, Juliet Enakeme Olabisi, for a considerable amount of assistance, and to the youngest members of the family—Toyosi, Wande, and Simisola—who, though apparently unimpressed by the handbook project, diligently handled the attendant volume of fax messages.

Olagoke Olabisi

Contents

1

Conventional Polyolefins

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I. INTRODUCTION

The global thermoplastics market, representing approximately 10% of the global chemical industry [1], was about 90 million tons in 1995, 60% of which is accounted for by polyolefins. This percentage is made up of 16% low-density polyethylene (LDPE), 16% high-density polyethylene (HDPE), 9% linear low-density polyethylene (LLDPE), and 19% polypropylene (PP) homo- and copolymers [2]. It was in 1933 that polyethylene was discovered by the ICI research scientists Fawcett and Gibson [3] who polymerized ethylene using less than 0.2% oxygen as an initiator, at 200°C and pressures of 0.1–0.3 GN/m^2. The first commercial plant was in operation in September 1939 and by the early 1940s LDPE production was already based on two high-pressure technologies, namely, autoclave reactor and tubular reactor, yielding two significantly different product streams primarily for extrusion coatings and film production, respectively. These two parallel developments have persisted until today with overlapping product range and, since the late 1970s, both technologies have been adapted for the production of HDPE, LLDPE, and medium-density polyethylene (MDPE).

The first solution phase process for the production of linear HDPE, at 100–250°C and pressures of 3–5 MN/m^2, was carried out independently, in 1951–1952, by the Standard Oil of Indiana (now AMOCO) and Phillips Petroleum Company with the use of transition metal oxide catalysts [4,5], i.e., molybdenum oxide and chromium oxide, respectively. Polymer recovery was effected by vaporizing the solvent. By the 1960s, catalyst development efforts enabled the low-temperature production of linear HDPE solid using a slurry phase reactor with an inert solvent. High-activity catalyst developed by the middle of 1960 finally enabled the introduction of gas phase ethylene polymerization and today several variants of these processes are in operation in different parts of the world. High-

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activity chromium oxide catalysts are used today in the production of LLDPE in the new-generation solution and gas phase processes, and the medium-density version is made in slurry phase processes. The production of polypropylene followed a similar trend except that it normally lags behind.

The other type of ionic polymerization process for the production of linear HDPE became a reality in 1953 when Karl Ziegler discovered [6] the revolutionary first-generation transition metal halide catalyst with its aluminum alkyl cocatalyst. Guilio Natta's major contribution [7] was the use of the Ziegler catalyst, namely $TiCl_4$-$AlEt_3$, for the isospecific polymerization of propylene in 1954 and the resulting family of catalysts are now collectively called the Ziegler–Natta catalysts. Stereoregularity is an important practical property in the polymerization of vinyl monomers, CH2═CHR, which is capable of yielding polymers that are atactic, characterized by a random arrangement of R; isotactic, characterized by an arrangement of R uniformly on one side of the polymer backbone; and syndiotactic, characterized by an arrangement of R on alternate side of the polymer backbone plane.

The second-generation $MgCl_2$ and/or donor-supported Ziegler–Natta catalyst system, which was at least 100 times more active, led to the development of the low-pressure polymerization processes for polyolefins and synthetic elastomers. This revolutionary development resulted in the simplified gas phase low-pressure polymerization plant operation without the need for the removal of residual trace catalyst from the polymer, making nonpelletized PE and PP the industry standard. Simonazzi et al. [8] provided an impressive array of the accomplishments in the science, engineering, and technology of the Ziegler–Natta catalysis since its discovery. Although the review sought to highlight the significant role of the Montecatini Research Center (now Montell), it does provide an insight into the worldwide effort as it relates to the simplification of the polyolefin process technologies in terms of economics, versatility, safety, and environmental efficiency.

Basically, both the heterogeneous transition metal halide and oxides catalyst systems are characterized by the following common features: (1) a solid surface for monomer adsorption; (2) a transition metal that is easily converted from one to the other of its several valence states; and (3) a propensity for the formation of organometallic compound with another organometallic or a monomer. Stereospecific polymerization of butene-1 or propylene (small, nonpolar, volatile monomers) requires the presence of a strong complexing active center adsorbed on a solid surface [9–12].

This chapter is devoted principally to the conventional polyolefins prepared with the following conventional catalyst systems: (1) free radical polymerization catalysts such as peroxides and peroxyesters; (2) anionic coordinated chromium-based Phillips catalysts; and (3) anionic coordinated transition metal compounds/aluminum alkyl–based Ziegler–Natta catalyst systems. The global annual market size is 6000 tons for free radical initiators, 5000 tons for Phillips catalysts, and 1500 tons for Ziegler–Natta catalysts. However, more than 60% of the global polyolefin production is due to the Ziegler–Natta catalyst systems [2].

II. POLYMER FORMATION

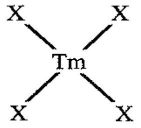
The 1933 ICI method [3] was a free radical polymerization process that includes the following reaction steps: initiation, propagation, termination, and chain transfer. Chain transfer incorporates disproportionation, hydrogen abstraction, scission reactions, and intermolecular as well as intramolecular hydrogen transfer. The ionic polymerization processes of the transition metal halides and the transition metal oxide catalysts also involve initiation, propagation, and termination steps. In the production of linear polyethylenes, the reactivity of the commercially significant ionic polymerization catalysts decrease in the order Ti > Cr > V, whereas in propylene copolymerization the reactivity of the catalysts decreases in the order V > Cr > Ti. Overall, the most crucial differences could be found in the microstructure of the polymers resulting from each of the catalysts. For example, titanium-based catalyst normally yields narrow molecular weight and/or comonomer distributions, compared to the vanadium- and chromium-based catalysts, which yield intermediate or broad distributions.

The ionic polymerization catalysts could be homogeneous or heterogeneous. A typical heterogeneous olefin polymerization catalyst system may consist of (1) a support, (2) a surface-modifying reductant such as trialkylaluminum, (3) a catalyst precursor, and (4) a cocatalyst that activates the catalyst. The order of addition of components has an effect on the overall nature of the catalyst system. The support normally has to be pretreated either by physical dehydroxylation (calcination), chemical dehydroxylation, thermal degassing, or surface modification using a reductant [13]. The factors affecting the overall performance of a supported catalyst include (1) dispersion of the catalyst precursor, (2) transformation characteristics during support pretreatment, (3) interaction of the catalyst precursor with the support, (4) possible agglomeration of the catalyst precursor, and (5) catalyst impurities and poisoning. An important element of catalyst design is the prevention of dangerous runaway reactions, particularly in gas phase polymerization where explosion could be especially devastating.

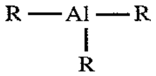
A. Ziegler–Nata Catalyst Systems

The Ziegler–Natta [6,7] catalyst system consists of two components that are schematically represented below. The transition metal compound is customarily called the catalyst and the alkylaluminum compound the cocatalyst. Some typical examples of these compounds are presented in Table 1.

- Catalyst:



- Cocatalyst:



$$R-\underset{\displaystyle R}{\underset{|}{Al}}-R$$

where Tm is a transition metal from group IV to VIII; Ti, V, Zr, and Hf are normally used but metal carbonyls of low valency states transition metals, such as Mn and Fe, have been used in cocrystallization with titanium compounds [14]. X is chlorine or other halogen; Al is aluminum; and R is an alkyl group.

The reactions of the various catalysts and cocatalysts have been studied extensively and the product derived from the reaction between, for example, $TiCl_4$ and $AlEt_3$ is known to consist of a partial colloidal mixture of the titanium halides at various oxidation states [8]. No complex compound was found that includes the two metal atoms such as titanium and aluminum [9–12,15]. The preferred Ziegler–Natta titanium catalyst compounds are the high-surface-area violet crystalline forms of $TiCl_3$ and the commercially utilized titanium trichlorides are normally activated by hydrogen or by organometallic compounds such as organoaluminum, organozinc, or organomagnesium compounds. Complete reduc-

Table 1 Examples of Two-Component Ziegler–Natta Catalyst Systems

Transition metal salt	Organometallic compounds	
$TiCl_4$	Et_3Al	
$Zr(OC_3H_7)_4$	Et_3Al	
$Zr[OCHEt_2]_4$	Et_3Al	
VCl_3	Et_2AlCl	
$V(acac)_3$[a]	Et_2AlCl	
$Cr(acac)_3$[a]	Et_2AlCl	
$CoCl_2 \cdot 2$ pyridine	Et_2AlCl	
$Zr(OC_3H_7)_4$	Et_2AlCl	
$Zr[OCHEt_2]_4$	Et_2AlCl	
$TiCl_4$	BuLi	
$TiCl_3$	Bu_2Mg	
Cp_2[b]$TiCl_2$	$EtAlCl_2$	
$TiCl_4$, VCl_3, or $TiCl_3$	Et_2AlCl	DEAC
$TiCl_4$, VCl_3, or $TiCl_3$	$(i\text{-}C_4H_9)_xAl_y(C_5H_{10})_z$[c]	Isoprenyl
$TiCl_4$, VCl_3, or $TiCl_3$	$Et_3Al_2Cl_3$	EASC[d]
$TiCl_4$, VCl_3, or $TiCl_3$	Et_3Al	TEAL
$TiCl_4$, VCl_3, or $TiCl_3$	$(i\text{-}C_4H_9)_3Al$	TIBAL
$TiCl_4$, VCl_3, or $TiCl_3$	$(i\text{-}C_4H_9)_2AlH$	DIBAL-

[a] acac, acetylacetonate anion.
[b] Cp_2, cyclopentadienyl.
[c] Where $z \approx 2x$, made by reacting TIBAL or DIBAL-H with isoprene.
[d] Ethyl aluminum sesquichloride; $Zr(OC_3H_7)_4$ and $Zr[OCH(CH_2CH_3)_2]_4$ react with Et_3Al and Et_2AlCl.
Source: Refs. 8, 74–76.

tion of $TiCl_4$ to $TiCl_3$ could be accomplished with $EtAlCl_2$ or Et_2AlCl at 1:1 or 2:1 ratios, respectively [16–19].

The activity and yield of the catalyst largely depends on the nature of the cocatalyst (activator) and on the catalyst/cocatalyst ratio. The effects of additional organic adjuncts attached to the aluminum cocatalyst underscore the fact that the activity of a catalyst system depends strongly on the cocatalyst type [20–23]. Dual functional titanium catalysts and benzyl derivatives of titanium, which are active in the absence of aluminum trialkyl, also exist [24–26].

A variety of Ziegler–Natta catalysts, based on zirconium and vanadium, are as follows: (1) $Zr(OC_3H_7)_4$ and $Zr[OCH(CH_2CH_3)_2]_4$; (2) $Zr(OC_4H_9)_2Cl_2$, $Zr(OC_6H_{13})_2Cl_2$, $Zr(OC_8H_{17})_2Cl_2$; (3) VCl_3 [26], VCl_4 [28,29], $VCl_3(THF)_3$ [29,30]; (4) $VOCl_3$ [31–34], $VO(OBu)_3$ [35], and $VO(OC_2H_5)_3$; (5) vanadyl acetate [36]; and (6) mixtures. Unlike titanium or the other transition metal catalysts, vanadium catalysts need promoters such as chloroform [27,30], Freon-11 [29], dichloromethane or methylene dichloride [29–31], trichlorofluoromethane [27,29,30], 1,1,1-trichloroethane [27,29,39], hexachloropropane, heptachloropropane, or octachloropropane [37]. Because of the structural and chemical homogeneity of its active center, the homogeneous vanadium-based catalysts are traditionally used for the production of ethylene-propylene rubber (EPR) copolymer and ethylene-propylene-diene monomer (EPDM) terpolymers. The preferred cocatalyst is halogenated aluminum alkyls and the preferred promoters include ethyl trichloroacetate, *n*-butyl perchlorocrotonate, and benzotrichloride. In the production of LLDPE, silica-supported vanadium catalysts are particularly active in the presence of halocarbon promoters resulting in a higher α-olefin comonomer incorporation rate and better comonomer distribution along the polymer chain. However, the vanadium-based catalysts are less capable of effecting a strong control over the molecular weight distribution yielding intermediate or broad molecular weight distribution compared with those based on titanium, zirconium, or hafnium. Calcium carbonate-mixed silica support could also be used for the vanadium based catalysts.

Several methods exist for the preparation of the varieties of supported Ziegler–Natta catalysts. Some of these are impregnation, milling, comilling [38], or solution methods. Cocrystallization using low-valency transition metal carbonyls [14] such as $Mn_2(CO)_{10}$, $Mn(CO)_5Cl$, $V(CO)_6$, and $Fe(CO)_8$ result in solid solutions, such as $FeCl_2 \cdot 2TiCl_3$ and $MnCl_2 \cdot 2TiCl_3$, which are known to be quite active. Dialkyl magnesium compounds have also been used as reducing agents and include the following: dimethyl magnesium, diethyl magnesium, di-*n*-butyl magnesium, *n*-butyl-*s*-butyl magnesium, ethyl-*n*-butyl magnesium, ethyl-*n*-hexyl magnesium, dihexyl magnesium, and butyloctyl magnesium [14,17,18,22]. Metal chloride reducing agents, such as $SiCl_4$ [39] and BCl_3 [23,40], have also been used.

Generally, the most active catalyst is based on titanium, and the high-activity, high-yield $MgCl_2$-supported titanium chloride catalyst is produced either by dry comilling of $MgCl_2$ and titanium halides or by cocondensing $MgCl_2$ vapor with the vaporized toluene/$TiCl_4$ or heptane/$TiCl_4$ or diisopropylbenzene/$TiCl_4$ substrates [20] or by solution. The solubility of $MgCl_2$ in the electron donor solvent, such as tetrahydrofuran (THF), increases in the presence of the reducing Lewis acid such as aluminum chloride, ethyl aluminum, and boron trichloride. This enables a good technique for activating the magnesium halide–based titanium or vanadium catalysts [40]. However, the catalyst reactivity and stereospecificity of the $MgCl_2$-supported titanium chloride is related to the structure of α-$TiCl_3$, γ-$TiCl_3$ and δ-$TiCl_3$ vis-à-vis that of the $MgCl_2$ support [8]. The crystalline layer structure of the violet $TiCl_3$ is similar to that of $MgCl_2$ and dry comilling of the two results in favorable epitaxial placement of the active dimeric titanium chloride on the (100) lateral planes of $MgCl_2$ exposing a larger number of stereospecific sites, and hence the propagation rate. While the lateral (100) surfaces are known to be stereospecific, the (110) planes are known to be aspecific.

In addition, the chemical nature and porosity of the $MgCl_2$ are said to play more effective roles than the specific surface area [19,42]. Indeed, complexes containing titanium and magnesium bonded by double-chloride bridges have been observed, exposing the titanium atoms on the catalyst surface where they are more accessible [8]. Silica, silica-alumina, modified or unmodified, as well as MgO supports have been used with mixed results [16,18,19,22,38,40,43–45]. Catalyst modifiers such as $NdCl_3$, $BaCl_2$, $ZnCl_2$, $ZnEt_2$, and Grignard reagents (C_6H_5MgCl) have been used. Magnesium alkoxides modifiers that have been used include magnesium methoxide and magnesium ethoxide [16,38,43,46–49]. For the $MgCl_2/TiX_4/Al(iBu)_3$ system, the nonchloride ligands impart decreased activities although the resulting polyolefins might have improved properties [50]. With nonchloride ligands, the activity of the titanium-based catalysts increases with the decreasing electron-releasing capability of the ligand [51] in the following order: $Ti(OC_6H_5)_4 > Ti(O(CH_2)_3CH_3)_4 > Ti(N(C_2H_5)_2)_4$. This is further illustrated by another study where the catalyst activity is in accordance with the following order [52]: $TiCl_4 > TiCl_2(OBu)_2 > TiCl(OBu)_3$.

The high-yield, high-stereospecificity $MgCl_2$ donor-supported titanium chloride catalyst was first developed by using a Lewis base modifier like the esters of aromatic monocarboxylic or phthalic acids as the internal donor. Later development led to the use of an additional external modifier, a bifunctional Lewis base like polyalkoxysilane, as a cocatalyst along with the aluminum trialkyl, which is a strong Lewis acid. The use of the

Table 2 Traditional and High-Yield Catalyst Systems for Propylene Polymerization

Catalyst system	Activity [kg PP/(mol Ti) MPa h]	Isotactic index[a] (%)
$TiCl_3$-Et_2AlCl	76	90–95
$MgCl_2$ supported $TiCl_4$-Et_3Al	9,000	30–50
$MgCl_2$ supported $TiCl_4/LB_1$[b]-Et_3Al	7,000	50–60
$MgCl_2$ supported $TiCl_4/LB_1$[b]-Et_3Al/LB_2[c]	6,000	92–95
$MgCl_2$ supported $TiCl_4/LB_3$[d]-Et_3Al/LB_4[e]	15,000	98–99
$MgCl_2$ supported $TiCl_4/LB_5$[f]-Et_3Al	20,000	97–99

[a] Weight percent of polymer insoluble in boiling *n*-heptane.
[b] LB_1, ethyl benzoate.
[c] LB_2, methyl 4-methylbenzoate.
[d] LB_3, diisobutyl phthalate.
[e] LB_4, dicyclopentyldimethoxysilane.
[f] LB_5, 2,2-diisobutyl-1,3-dimethoxypropane.
Source: Ref. 8.

internal and external donors led to the possibility of controlling the morphology of the catalyst granules. The catalyst morphology (size, shape, and porosity) is important and there are significant differences in the polymerization rate pattern between granular versus powdered catalyst or between spherical powder versus granular powder [23,53,54]. Indeed, the morphology of the resulting polymer particle replicates that of the catalyst, which essentially acts as a template for the polymer growth, justifying the trend toward spherical catalyst particles [8,53,54]. The polymer particle size distribution is also similar to that of the catalyst. This similarity has made it possible to control the polymer granule size, its porosity, and its stereoregularity. Additionally, the polymer molecular weight distribution could be similarly controlled by changing the structure of the external donor.

A further advance has made it possible to use a single donor, such as 1,3 diethers, eliminating the need for the external donor. The mechanism of the Lewis base donors is presumed to be related to the selective poisoning and/or modification of the aspecific catalyst sites through complexation with the base. The 1,3 diether is characterized by the desired oxygen–oxygen distance, which is crucial for chelating to the tetracoordinate magnesium atoms located on the (110) aspecific plane of $MgCl_2$.

This line of catalyst development has made it possible to exploit the living polymerization capability of each catalyst granule whereby each granule contains a ''living polymer'' whose growth could be spontaneously continued by the addition of the same or different sets of monomers resulting in block or multimonomer copolymers. Thus, not only does this emerging technology facilitate the synthesis of homopolymers whose molecular weight ranges from very low to extremely high, but heterophase polyolefin copolymers, blends, and alloys incorporating nonolefinic comonomers could also be made in situ with each catalyst granule serving as a self-contained reactor. The traditional and high yield–unsupported and $MgCl_2$-supported catalyst systems for polypropylene polymerization appear in Table 2 and those for polyethylenes appear in Table 3.

B. Chromium-Based Catalysts

1. Phillips Catalysts

The chromium oxide ethylene polymerization catalyst was a product of serendipity at the Phillips Petroleum Company in 1950 when it was discovered by He, Lanning, Hogan, and

Table 3 Traditional and High-Yield Catalyst Systems for Ethylene Polymerization

Catalyst system	Activity [kg polym/(mol Ti) MPa h]
$TiCl_3$-Et_2AlCl	320
$TiCl_3$-Et_3Al	710
$MgCl_2$ supported $TiCl_4$-Et_3Al	17,000

Source: Ref. 8.

Banks. Chromium oxide was supposed to aid the conversion of refinery stack gases into motor fuel; however, it converted the ethylene in the stack gases into polyethylenes. The chromium oxide catalyst consists of a refractory support and an oxide of Cr(II), Cr(III), Cr(VI), or any inorganic chromium compounds that could be calcined to chromium oxide such as chromic nitrate, chromium sulfate, ammonium chromate, chromium carbonate, chromyl chloride, and *t*-butyl chromate [55–58].

The Phillips catalyst has been modified using a variety of inorganic and organic compounds including boron trichloride, boron phosphate, boron ester, isopropyl borate, trimethyl borate, ammonium tetrafluoroborate, ammonium hexafluorosilicate, α,ω-aliphatic diene, isoprene/nickel oxide, isoprene/nickel nitrate, isoprene/nickel acetate, isoprene/nickel chloride, titanium/tetraisopropyl titanate, magnesium ethoxide/tetraisopropyl titanate, dibutyl magnesium/tetraisopropyl titanate, trialkyl dialkyl phosphate-titanate, or benzene. The supports that have been used include silica, alumina (could be fluorided or phosphated), silica-alumina, zirconia, zirconia-silica cogel, thoria, germania, or mixtures thereof. Triisobutyl aluminum, 1,5-hexadiene/triethyl aluminum, 1,7-octadieneand/triethyl aluminum, and triethyl borane have been used as cocatalysts for chromium oxide catalysts [55–67].

The SiO_2-supported chromium oxide catalyst could be activated at 750°–1500°C in a stream of nonreducing moisture-free gas containing oxygen or in vacuo at temperatures between 400 and 900°C. Photoreduction with a mercury lamp light source, in the presence of carbon monoxide, was also found to be just as effective and it could be done at temperatures as low as 200°C. Generally, activation with carbon monoxide, as with triethyl borane, reduces the oxidation state of chromium. On the other hand, molybdenum oxide (or cobalt molybdate) on γ-alumina titania or zirconia support needs a reducing gas such as hydrogen or carbon monoxide.

The effects of metal oxide loading on reactivity and kinetic profile have been studied. Ethylene polymerization is presumed to occur through the reaction of an adsorbed monomer with an adjacent monomer or a polymer similarly adsorbed on the solid surface. In the case of $Cr/AlPO_4$ catalyst, the P/Al ratio has an effect on the catalyst activity as well as the tendency towards bimodality of the polymer molecular weight distribution. In general, however, chromium-based catalysts yield linear HDPE with intermediate or broad molecular weight distribution.

2. Organochromium Catalysts

The organochromium family of catalysts, due to Union Carbide, consists of the closed ring bis(cyclopentadienyl)chromate (chromocene) [68] and/or bis(triphenylsilyl)chromate [69]. The latter is the reaction product of triphenylsilanol and chromium trioxide, which when supported on silica-alumina is very active particularly for the gas phase ethylene polymerization process. The former, when supported on high-surface area silica, liberates a cyclopentadienyl group and polymerizes ethylene via a coordinated anionic mechanism. Other organochromium catalysts with π-bonded ligands include open ring chromocene [64], namely, dimethylpentadienyl chromate [$Cr(DMPD)_2$], mixed open/closed ring chromocene, namely, Cr(Cp)DMPD [70], biscumene [Cr(0)] [71], $Cr(neopentyl)_4$, bismesitylene [Cr(0)] [63], as well as those with σ-bonded ligands such as $Cr_4(trimethylsilyl)_8$, $Cr(trimethylsilyl)_4$, chromium acetyl acetonate, chromium acetate, chromium stearate, $Cr(benzene)_2$, $Cr(octate)_3$, as well as organophosphoryl chromium compounds. The supports normally used are silica, aluminophosphate, alumina, and fluorided and phosphated alumina.

The organochromium catalysts are not as thermally stable as the chromium oxide family of catalysts but a calcined chromium oxide catalyst could be modified by impregnation with organochromium compound in order to form a highly active mixed Cr-Cr catalyst. This is exemplified by the modification of hexavalent *t*-butyl chromate with zerovalent organochromium dicumene Cr(0) as well as that of divalent Cr(II) or hexavalent Cr(VI) oxide with the divalent alkyl chromium $Cr_4(trimethylsilyl)_8$ [71]. Similarly, organochromium esters could form bimetallic complexes with metal chlorides. The hydrated chromium acetate [$Cr(CH_3COO)_3 \cdot H_2O$]/magnesium chloride and anhydride chromium stearate [$Cr(C_{17}H_{35}COO)_3$]/magnesium chloride systems have been extensively investigated [72,73] with the cocatalysts $AlEt_2Cl$, $Al_2Et_3Cl_3$, $AlEtCl_2$, and $AlEt_3$. The effects of chromium loading on reactivity and kinetic profile have also been studied for organochromium catalysts [65].

III. PRODUCTION TECHNOLOGY

The 14 basic types of commercial olefin polymerization processes could be loosely classified as low- or high-pressure processes. The properties of the manufactured polyolefins resins depend on the polymerization process used. Consequently, the choice of catalyst and the appropriate control of reactor conditions normally determine the polyolefin molecular weight, molecular weight distribution, density, and other properties [74,76].

A. High-Pressure Processes for Branched LDPE

Branched low-density polyethylene (LDPE) was first commercialized [3,77] in 1939 by ICI using its high-pressure technology that is based on free radical polymerization at temperatures of 200–300°C and pressures of 0.1–0.3 GN/m^2. Commercially available high-pressure processes use tubular or stirred autoclave reactors at pressures higher than 0.2 GN/m^2 and recent developments have enabled the use of ionic polymerization catalyst systems as well.

1. Autoclave Reactor Process

The high-pressure autoclave reactor process operates at pressures of about 0.2 GN/m^2 at temperatures of 150–315°C. The commercial high-pressure autoclave technology available for the production of branched LDPE generally use oxygen or peroxide initiators. They are proprietary to the following companies: ICI, Cities Services/ICI, CdF Chimie, Dow Chemical, DuPont, El Paso, Gulf, National Distillers/ICI, and Sumitomo. The LDPE is produced at 15–20% conversion and the density range falls within 0.915–0.925 gm/cm^3. A telogen, such as butane, is normally added to the feed stream for molecular weight control. The LDPE are generally used for injection molding, extrusion coating, heavy-duty film, wire and cable covering. The autoclave reactor is also used in the production of ethylene–vinyl acetate (EVA) copolymers.

The control of the LDPE density, chain branching, crystallinity, molecular weight and its distribution require a judicious adjustment of pressure, temperature profile, initiator type and concentration, telogen type, and concentration. For example, low temperatures are used for the production of injection molding grades requiring broad molecular weight distribution; uniform high temperature and high initiator concentration results in narrow molecular weight distribution. Long-chain branching is favored by high temperature, low pressure, and high initiator concentration. An increase in temperature also leads to an increase in chain transfer reaction (decrease in molecular weight) whereas an increase in pressure leads to an increase in chain growth reaction resulting in an increase in density. Initiator and telogen type and concentration could affect the LDPE chain length by a factor of 2–4. Density, which depends on the extent of chain branching vis-à-vis the polymer molecular weight, is also sensitive to temperature and pressure to a much lesser extent.

2. Tubular Reactor Process

The flow chart for the tubular and autoclave reactor processes are similar except for the reactor section where the heavy-walled reactor tubing replaces the autoclave. The reactor tubing is 1000–2000 m long, 25–50 mm internal diameter, and the process operates at pressures of about 0.3 GN/m^2 with temperatures ranging between 170°C and 330°C. The commercial high-pressure tubular technology available for the production of branched LDPE generally uses oxygen or peroxide initiators. They are proprietary to the following companies: ICI, ANIC, Arco, ATO Chimie, BASF, Exxon, El Paso, Imhausen, Distillers/ICI, Stemicarbon, Sumitomo, Union Carbide, and VEB-Leuna Werke.

The molten LDPE is produced at a conversion of 25–35%, which is higher than that of the autoclave processes principally because of the easier method of heat removal through cooling jackets. As with the autoclave reactor, polymer density, chain branching, crystallinity, molecular weight and its distribution are controlled during the polymerization process. A telogen is normally added to the feed stream for molecular weight control and the density of the resulting LDPE ranges between 0.918 and 0.93 g/cm^3. The polymers find applications in tough, stiff clarity film and packaging, as industrial liners, heavy-duty bags, shrink film, lamination film, wire, and cable. The tubular reactor is also used in the production of EVA co- and terpolymers characterized by high-environmental-stress cracking resistance useful in frozen food packaging and other high-clarity and high-gloss applications.

Certain specific operating conditions of the tubular reactor process could be related to the following structure–property differences:

- The higher operating pressure results in higher reaction propagation rate, higher density, lower degree of branches, higher molecular weight, stiffer polymers.
- The plug flow character leads to elongated as opposed to the near-spherical structure of the polymer made in the autoclave.
- The variability of the temperatures and pressures somewhat results in the production of polymers characterized by a relatively wide molecular weight distribution.

B. Polymerization Processes for Linear HDPE, MDPE, LLDPE, and Copolymers

The advent of the Phillips and Ziegler catalysts gave birth to the low-pressure olefin polymerization processes operating at pressures of about 2–10 MN/m^2 and temperatures of about 100°C. In most modern commercial polymerization processes, the supported catalyst system is conveyed to the reactor either in the form of a powdery solid or a Bingham fluid composition [78,79]. While pressure is a key variable for density control in the high-pressure branched LDPE polymerization, the amount and type of α-olefin comonomer in the feed composition is the key density-controlling variable for the low-pressure LLDPE processes. In addition, the average molecular weight of the polymer is responsive to the polymerization temperature whereas the molecular weight distribution is responsive to the catalyst system. Hydrogen is used as a molecular weight modifier.

1. High-Pressure Processes

Although the high-pressure autoclave and tubular processes were developed for branched LDPE, contemporary catalyst developments have resulted in several adapted high-pressure technology for linear MDPE, HDPE, and LLDPE. The high-pressure technology available with their corresponding catalyst systems are proprietary to the following companies [75–77]:

1. High-pressure autoclave reactor
    - ARCO technology using Ziegler catalyst system produces LLDPE.
    - Bayer technology using silyl ester catalyst system produces linear MDPE.
    - Dow Chemical technology using Ziegler catalyst system produces linear MDPE, HDPE, and LLDPE.
    - CdF Chimie technology using Ziegler catalyst system produces linear MDPE, HDPE, and LLDPE.
2. High-pressure tubular reactor
    - ATO Chimie technology using Ziegler catalyst system produces LLDPE.
    - Dow Chemical technology using Ziegler catalyst system produces linear MDPE, HDPE, and LLDPE.
    - El Paso/Montedison technology using Ziegler catalyst system produces LLDPE.
    - Imhausen technology using Ziegler catalyst system produces linear MDPE, HDPE, and LLDPE.
    - Mitsubishi Petrochemical technology using Ziegler catalyst system produces linear MDPE, HDPE, and LLDPE.

2. Low-Pressure Liquid Slurry Processes

The first low-pressure linear HDPE slurry technology to utilize the Ziegler catalyst was commercialized in 1955 by Hoechst. The process is based on a stirred-tank reactor containing a heavy hydrocarbon diluent with a continuous ethylene feed. The reactor is operated at a pressure of about 0.8 MN/m^2, a temperature of about 85°C, and an average residence time of 2.7 hr. The concentration of the solid polymer particles in the reactor discharge stream range between 13 and 45 wt %, depending on the particular polymer grade, and the overall ethylene conversion is generally about 98 wt % [75–77,80]. The more recent catalyst system consist of a reaction product of magnesium tetrachloride, titanium tetrachloride, titanium tetraisopropylate, with aluminum isopropylate as the cocatalyst.

The Mitsubishi continuous stirred-tank reactor process, utilizing either chromium oxide or titanium-vanadium catalyst system, operates at a pressure of about 3.5 MN/m^2, a temperature of 80–90°C, an average residence time of 2 hr with an overall ethylene conversion of about 95 wt %. The Montedison stirred-tank reactor technology is essentially similar to the Mitsubishi process [74–76]. However, a more recent stirred-tank reactor technology has been developed by R. G. C. Jenkins and Company [81], whereas a multiple cascade reactor technology is due to BP Chemicals Ltd. [82].

The liquid pool slurry process technology for polypropylene, developed by El Paso Polyolefins Company, could also be used for linear polyethylene provided isobutane or propane is used as the liquid hydrocarbon diluent for the ethylene monomer feed and the catalyst is appropriately modified [75–77,80]. It is based on a jacket reactor with a transition metal catalyst system that is proprietary to Mitsui Petrochemical/Montedison. It operates at a pressure of about 2.6 MN/m^2, temperatures of about 60°C, and an average residence time of 1–2 hr. The polymerization takes place in the presence of the diluent and the average spherical particle size of the polymer formed is about 1200 μm. The concentration of the solid polymer particles in the product stream is 30–43 wt %.

The first low-pressure linear polyethylene slurry loop reactor technology, using supported chromium oxide catalyst in a light hydrocarbon diluent, was commercialized in 1961 by Phillips Petroleum Company [55]. Isobutane was used as the diluent in a continuous path double-loop reactor operating at a pressure of about 3.5 MN/m^2, temperature range of 85–110°C, and an average residence time of 1.5 hr. The modified chromium/titanium catalyst system enables the production of a broad range of polymer products which, as with the original Phillips catalyst, do not have to be deashed but are normally stabilized and pelletized. The polymer is formed inside the pores of the catalyst that it eventually pulverizes, distributing the microscopic catalyst particles uniformly. The concentration of the solid polymer particles in the reactor discharge stream range between 18 and 50 wt %, depending on the particular polymer grade, and the overall ethylene conversion is generally about 98 wt %. A more recent process, developed by Phillips Petroleum Company [83], uses chromium-based catalyst on high silica-titania cogel support with a cocatalyst of triethyl borane or diethyl aluminum ethoxide. The polymers produced are characterized by a range of density between 0.915 and 0.965 g/cm^3.

The Solvay heavy hydrocarbon diluent slurry technology, based also on loop reactors, uses a supported Ziegler–Natta catalyst system consisting normally of magnesium ethylate, titanium butylate, and butyl aluminum dichloride, with aluminum as the cocatalyst. The hydrocarbon diluent is *n*-hexane and the continuous path double-loop reactor operates at a pressure of about 3 MN/m^2, temperatures of about 85°C, and an average residence time of 2.5 hr. The concentration of the solid polymer particles in the reactor discharge stream range between 16 and 50 wt %, depending on the particular polymer grade, and the overall ethylene conversion is generally about 97 wt %. The liquid slurry technology available for the production of linear polyethylenes and the corresponding catalyst systems are proprietary to the following companies [75–77,80]:

1. Slurry phase heavy-diluent stirred-tank reactor
    - Asahi Chemical technology using Ziegler catalyst system
    - Chisso technology using Ti/Mg/V catalyst system
    - Dow Chemical technology using Ziegler catalyst system
    - DuPont technology using Ziegler catalyst system
    - Hoechst technology using Ziegler catalyst system
    - Hüls technology using Ziegler catalyst system
    - Idemitsu technology using Ziegler catalyst system
    - Mitsubishi Chemical technology using Ti, Cr, V, Ti/V catalyst system
    - Mitsubishi Petrochemical technology using Ziegler catalyst system
    - Mitsui Petrochemical technology using Ziegler catalyst system

  - Montedison technology using Ziegler catalyst system
  - Stamicarbon technology using Ziegler catalyst system
2. Slurry phase light-diluent stirred-tank reactor
   - Mitsui Toatsu technology using Ziegler catalyst system
3. Slurry phase light-diluent loop reactor
   - Chemplex technology using Cr/Sn/Al/Ti catalyst system
   - Phillips technology using Ziegler Cr/Ti, Cr/P, Cr, Ti/Mg, V, Ti/V catalyst system
4. Slurry phase heavy-diluent loop reactor
   - National Distillers/USI technology using Ziegler catalyst system
   - Solvay technology using Ziegler catalyst system
5. Slurry phase liquid pool reactor
   - El Paso/Montedison technology using Ziegler catalyst system

3. Low- and Medium-Pressure Solution Processes

Solution polymerization processes predate but are now superceded by the slurry processes [75–77,80]. As opposed to the slurry processes, polymerization was effected in a solvent at high pressure and above the melting point of the polymer. The polymer formed dissolves in the solvent resulting in a homogeneous single-phase liquid product stream that is subsequently devolatilized. The major advantage of the solution processes is the wide operating temperature range limited only by the polymer solubility and the polymer degradation temperatures. This enables a more efficient control of the polymer molecular weight distribution. The need for the energy-intensive solvent vaporization is its major disadvantage. The modern solution processes have been improved and are in use by Dow, DuPont of Canada, Mitsui, Phillips, Stamicarbon/DSM, and Eastman Kodak.

The DuPont solution process technology, based on a stirred-tank reactor system, uses soluble Ziegler–Natta catalyst system such as titanium or vanadium tetrachloride with triisobutyl aluminum as the cocatalyst in a solvent such as cyclohexane. It is an adiabatic medium pressure process operating at a pressure of about 10 MN/m^2, temperature of 200°C, average residence time of 2 min with an overall ethylene conversion of about 88 wt %. Another process due to DuPont [82] operates at a temperature range of 105–320°C and a pressure of 1.7 MN/m^2. The Stamicarbon technology is an adiabatic low-pressure stirred-reactor process operating at a pressure of about 3 MN/m^2, temperatures of 130–175°C, an average residence time of 5 min with an overall ethylene conversion of about 95 wt %. The Dow technology is a cooled low-pressure twin stirred-reactor process based on conventional soluble Ziegler catalyst. The reactors operate at a pressure range of about 1.9–2.6 MN/m^2, a temperature of 160°C, an overall residence time of 30 min with an overall ethylene conversion of about 94 wt %. The solution phase technology available for the production of linear polyethylenes and the corresponding catalyst systems are proprietary to the following companies [75–77,80]:

1. Solution phase medium-pressure adiabatic reactor
   - Amoco technology using Mo oxide catalyst system
   - DuPont technology using Ziegler catalyst system
   - Mitsui Petrochemical technology using Mo oxide catalyst system
   - Phillips technology using Cr, Cr/Ti catalyst system
   - Stamicarbon technology using Ziegler catalyst system
2. Solution phase low-pressure cooled reactor
   - Dow technology using Ziegler catalyst system

4. Low-Pressure Gas Phase Processes

The gas phase, fluidized bed ethylene polymerization technology, first described by Union Carbide in 1957, was commercialized in 1968. The Union Carbide low-pressure Unipol process, introduced in 1975, was based on silica-supported titanium-modified chromium oxide catalysts [85–87], although high-activity Mg-Ti catalysts and a variety of process modifications have since been developed by Union Carbide [87–91] and British Petroleum [93–96]. The reactor is operated at a pressure of 2 MN/m^2, a fluidized bed temperature of 75–100°C, depending on the particular polymer grade, and an average residence time of 3–5 hr with an overall ethylene conversion of about 97 wt %. The reactor is operated at 85–100°C for HDPE or 75–100°C for LLDPE, the polyethylene product range is broad, and the particle size could be as high as 15–20 times the size of the original catalyst particle. The product withdrawal rate is used in ensuring a constant fluidized bed volume. UCC has licensed the Unipol process in the United States, Japan, Europe, Australia, and Saudi Arabia. It remains the single largest technology for LLDPE production at present. The process is characterized by simplicity, reaction uniformity, and suitability for large-scale production.

The BP Chimie/Napthachimie process is similar to the Unipol technology except for the use of a proprietary highly active titanium/alkylaluminum catalyst system. It is operated at a pressure range of 0.5–3.3 MN/m^2 and a fluidized bed temperature of 60–100°C. The vertical continuous stirred (mechanical) bed gas phase polyolefin technology developed by BASF came on stream in 1976 as Novolen process [75–77,80,97]. It is operated at a pressure of 3.4 MN/m^2, a temperature of 100–110°C, depending on the particular polymer grade, and an average residence time of 4 hr with either a magnesium-supported two-component Ziegler catalyst or a silica-supported modified chromium oxide catalyst. The horizontal continuous stirred-bed gas phase polyolefin technology, developed by Amoco [98–100], is based on a compartmentalized cylindrical vessel stirred by a series of axially mounted longitudinal paddles. It is operated at a pressure of 2 MN/m^2, a temperature of 82–88°C, depending on the particular polymer grade, and an average residence time of 4.3 hr with either a magnesium-supported two-component Ziegler catalyst or a silica-supported Phillips catalyst.

The Spherilene process, the most recent commercial gas phase technology developed by Montell [2,8], is a hybrid process for the production of linear polyethylenes, in a spherical granular shape, whose molecular weight ranges from very low to very high. The process consists of a loop reactor followed by a fluidized bed gas phase reactor and it is equipped with a stripping unit so effective that the final polymer contains no monomer residue. It is characterized by high productivity, rapid and low-cost changeover of polymer grades, and excellent product quality.

The gas phase technology available for the production of linear polyethylenes and the corresponding catalyst systems are proprietary to the following companies [75–77,80]:

1. Gas phase fluidized bed reactor
    - Union Carbide technology using proprietary Cr, Cr/Ti, Ti/Mg catalyst systems
    - Cities Services/ICI technology using proprietary Ziegler catalyst systems
    - ICI technology using proprietary Ziegler catalyst systems
    - Mitsubishi Petrochemical technology using proprietary Ziegler catalyst systems
    - Mitsui Petrochemical technology using proprietary Ziegler catalyst systems
    - Nippon Oil technology using proprietary Ziegler catalyst systems

- Shell technology using proprietary Ziegler catalyst systems
- BP Chimie/Napthachimie technology using proprietary Ziegler catalyst systems

2. Gas phase horizontal stirred-bed reactor
   - Amoco technology using proprietary Ti/Mg catalyst systems
3. Gas phase vertical stirred-bed reactor
   - BASF technology using proprietary Cr, Ti/Mg catalyst systems
4. Hybrid slurry-phase loop reactor/gas phase fluidized bed reactor
   - Montell technology using proprietary Ti/Mg catalyst systems

C. Polymerization Processes for PP and Propylene Copolymers

Practically all of the above processes have been used in the production of PP primarily because of contemporary catalyst developments. The special process technologies for PP and propylene copolymers include two variants of the liquid pool slurry process, the Eastman Kodak solution process, the Novolen gas phase process jointly developed by BASF, ICI, and Quantum, as well as the Catalloy modular gas phase process of Montell.

1. Low-Pressure Liquid Pool Slurry Phase Processes

The liquid pool slurry process technology for polypropylene, developed by El Paso Polyolefins Company [77,80], uses liquid propylene as the diluent as well as the feed. It is based on a jacket reactor with a highly active, highly stereospecific transition metal Ziegler catalyst system that is proprietary to Mitsui Petrochemical/Montedison. It operates at a pressure of about 2.6 MN/m^2, temperatures of about 60°C, an average residence time of 1.3 hr, and the concentration of the solid polymer particles in the product stream is 43 wt %. The removal of atactic PP or catalyst residue is not required because of the high productivity and stereospecificity of the catalyst.

The Spheripol process, developed by Montell [2,8], is based on a proprietary high-yield, high-stereospecificity donor/$MgCl_2$–supported titanium-based Ziegler–Natta catalyst systems. The process operates without wastewater, no solid waste, minimal steam requirement, and significantly low-power requirement. More than 60% of the global production of PP is based on the Spheripol process.

2. Low-Pressure Modular Gas Phase Reactor

The Catalloy gas phase technology, developed by Montell [2,8], consists of three mutually independent gas phase reactors in series. It is based on a high-yield, high-stereospecificity, high-surface-area catalyst system whose morphology ranges from a dense spherical shape to a sponge-like structure. The process is capable of producing PP with higher polydispersity, higher stereoregularity, random copolymers containing up to 15 wt % comonomers, and multiphase alloys containing up to 70 wt % multimonomer copolymers. It operates with no byproduct, no liquid waste, and no solid waste.

3. Other Processes

Contemporary and emerging catalyst developments have resulted in several adapted technologies for polypropylene. For example, the following technologies and the corresponding catalyst systems are proprietary to the following companies [75–77,80]:

1. Slurry phase heavy-diluent stirred-tank reactor

    - Amoco technology using proprietary catalyst system
    - Asahi Chemical technology using Ziegler catalyst system
    - Chisso technology using Ti/Mg catalyst system
    - Hercules technology using Ziegler catalyst system
    - Exxon technology using Ziegler catalyst system
    - Hoechst technology using Ziegler catalyst system
    - ICI technology using Ziegler catalyst system
    - Idemitsu technology using Ziegler catalyst system
    - Mitsubishi Petrochemical technology using Ziegler catalyst system
    - Mitsui Petrochemical technology using Ziegler catalyst system
    - Mitsui Toatsu technology using Ziegler catalyst system
    - Montedison technology using Ziegler catalyst system
    - Shell technology using Ziegler catalyst system
    - Sumitomo technology using Ziegler catalyst system
2. Slurry phase light-diluent loop reactor (bulk)
    - Phillips technology using Ziegler catalyst system
    - Solvay technology using Ziegler catalyst system
3. Slurry phase stirred-tank bulk reactor
    - Mitsui Toatsu technology using Ziegler catalyst system
4. Slurry phase liquid pool reactor
    - El Paso technology using Ziegler catalyst system
5. Slurry phase liquid pool loop reactor
    - Montell technology using Ti/Mg Ziegler–Natta catalyst systems
6. Slurry phase light-diluent stirred-tank reactor
    - Sumitomo technology using Ziegler catalyst system
7. Slurry phase heavy-diluent loop reactor
    - Solvay technology using Ziegler catalyst system
8. Gas phase fluidized bed reactor
    - Union Carbide technology using proprietary Cr, Cr/Ti, Ti/Mg catalyst systems
    - Shell technology using Ziegler catalyst system
    - Mitsui Petrochemical technology using Ziegler catalyst system
    - BP Chimie/Napthachimie technology using proprietary Ziegler catalyst systems
    - Cities Services/ICI technology using proprietary Ziegler catalyst systems
    - Nippon Oil technology using proprietary Ziegler catalyst systems
    - Sumitomo technology using Ziegler catalyst system
9. Modular gas phase fluidized bed reactor
    - Montell technology using proprietary Ti/Mg Ziegler–Natta catalyst systems
10. Gas phase horizontal stirred-bed reactor
    - Amoco-Chisso technology using proprietary Ti/Mg, Cr catalyst systems
11. Gas phase vertical stirred-bed reactor
    - BASF technology using proprietary Cr/Ti/Mg/Sn/Al catalyst systems
12. Solution phase medium-pressure adiabatic reactor
    - Eastman technology using Ziegler catalyst system

D. Polymerization Processes for Other Polyolefins

The processes discussed above were developed for the large-volume polyolefins but have also been adapted for other olefin polymers on account of the contemporary catalyst developments. Ultrahigh molecular weight polyethylene (UHMWPE) is produced in the slurry phase heavy-diluent stirred-tank reactor by Hercules and Hoechst based on the proprietary Ziegler catalyst system. Polybutene-1 (PB-1) and copolymers are made in slurry phase light-diluent stirred-tank reactor by Hüls and in the solution phase medium-pressure adiabatic reactor by Hüls and Shell using the Ziegler catalyst system. In addition, PB-1 is made by Mitsui Petrochemical, which also manufactures poly(4-methylpentene-1) based on stereospecific Ziegler–Natta catalysts. The tubular high-pressure process is used in the production of ethylene–vinyl acetate (EVA) co- and terpolymers.

IV. POLYOLEFIN STRUCTURE–PROPERTY RELATIONSHIPS

A classification of polyolefins and their corresponding densities appears in Table 4. A list of possible polyolefin structural characteristics and properties is presented in Table 5. Density is generally a reflection of polyolefin linearity. The higher the density, the higher the following polymer characteristics and performance properties: (1) chain linearity; (2) stiffness; (3) tensile strength; (4) tear strength; (5) softening temperature; and (6) brittleness [101]. On the other hand, polyolefin failure properties such as impact strength, flexural strength, and environmental stress crack resistance (ESCR) decrease as the polyolefin density increases. A simplified synopsis of polyolefin catalyst/technology–structure–property interdependence [8] is presented in Fig. 1.

Polyolefins are used in several different applications primarily because of their wide range of resin characteristics and endproduct properties. These properties, particularly processability and the physical and mechanical properties, are highly dependent on the average molecular weights and molecular weight distribution. For example, injection molding requires resins with low melt viscosity and elasticity, whereas blow molding requires resins characterized by high molecular weights and molecular weight distribution that possess high melt viscosity and elasticity. These molecular weight characteristics are also the determinants of such properties as molded part warpage, failure, and ESCR. In particular, as the high molecular weight species increase, the positive salutary effects on the ESCR

Table 4 Classification and Density of Polyolefins

Polyethylene type	Macromolecular classification	Density range (g/cm^3)
Low-density polyethylene (LDPE)	Homopolymer	0.910–0.925
Medium-density polyethylene (MDPE)	Homopolymer	0.926–0.940
Linear low-density polyethylene (LLDPE)	Copolymer	0.910–0.940
Very-low-density polyethylene (VLDPE)	Copolymer	0.890–0.915
High-density polyethylene (HDPE)	Copolymer	0.941–0.959
High-density polyethylene (HDPE)	Homopolymer	0.960 and higher
HMW polyethylene (HMWPE)	Homopolymer	0.947–0.955
UHMW polyethylene (UHMWPE)	Homopolymer	0.940
Polypropylene	Homopolymer	0.904–0.906
Ethylene-propylene copolymer	Copolymer	0.904–0.907
Polybutene-1	Homopolymer	0.910
Poly(4-methyl pentene-1)	Homopolymer	0.830

Table 5 Possible Polyolefin Structural Characteristics and Properties

Structural characteristics
Molecular weights
Molecular weight distribution
Polydispersity
Short-chain branching
Long-chain branching
Unsaturation
Crystallinity
Morphology
Stereoregularity
Randomness
Chain linearity

Processing properties
Shear viscosity
Extensional viscosity
Intrinsic viscosity
Formability, malleability
Melt flow (index,rate)
Melt strength
P-V-T relation

Physical properties
Density
Average particle size
Particle density
Surface texture, gloss
Film clarity, haze
Thermal expansion
Specific heat
Thermal conductivity
Electrical conductivity
Glass transition temperature, T_g
Melting temperature, T_m
Crystallization temperature, T_c
Softening temperature
Heat distortion temperature
Permeability (gas, water vapor)

Degradation properties
Thermal degradation
Oxidative degradation
Photodegradation
Biodegradation
Shear degradation
Environmental stress cracking

Mechanical properties
Tensile strength
Impact strength (tensile, Izod, dart)
Flexural strength
Tear strength
Tensile strength, at yield
Ultimate tensile strength
Tensile modulus
Flexural modulus
Stiffness, rigidity
Toughness, ductility
Brittleness
Notch sensitivity
Elongation at yield
Elongation at break
Orientation factor
Creep resistance
Strain hardening
Resilience
Hardness
Compressive strength
Shear yield strength
Shear ultimate strength
Puncture resistance
Lubricity
Abrasion resistance

properties would be counterbalanced by the negative effects such as part warpage, surface roughness, and opacity.

The use temperatures of the different polyolefins are limited by the glass transition temperature (T_g) at the low end and the crystalline melting point (T_m) at the upper end. However, the degree of mechanical property retention is better related to either the heat deflection temperatures or the Vicat softening points. Of all the polyolefins, only the poly(4-methylpentene-1) copolymer has a Vicat softening point (179°C), which is higher than that of PP (145–150°C), and a melting point of 240°C compared to 165–179°C for PP. The specific heat of polyolefins are in the order polyethylenes > polypropylene > polybutene-1, but polypropylene has about the lowest thermal conductivity and thermal expansion coefficient. Polyolefins generally have good environmental stress crack resistance, with PP being better than PE, but all polyolefins require a degree of stabilization against all forms of degradation.

A. Polyethylenes

The density of commercially available polyethylenes ranges between 0.890 and 0.980 g/cm^3, with the density of polymethylene being 0.98 g/cm^3 and that of the amorphous phase of polyethylene being 0.85 g/cm^3. The density of polyethylene depends on its relative content of long- and short-chain branching [102]. The long-chain branching (LCB) may vary from 20 to thousands of carbons and the short-chain branching (SCB) may have 5–

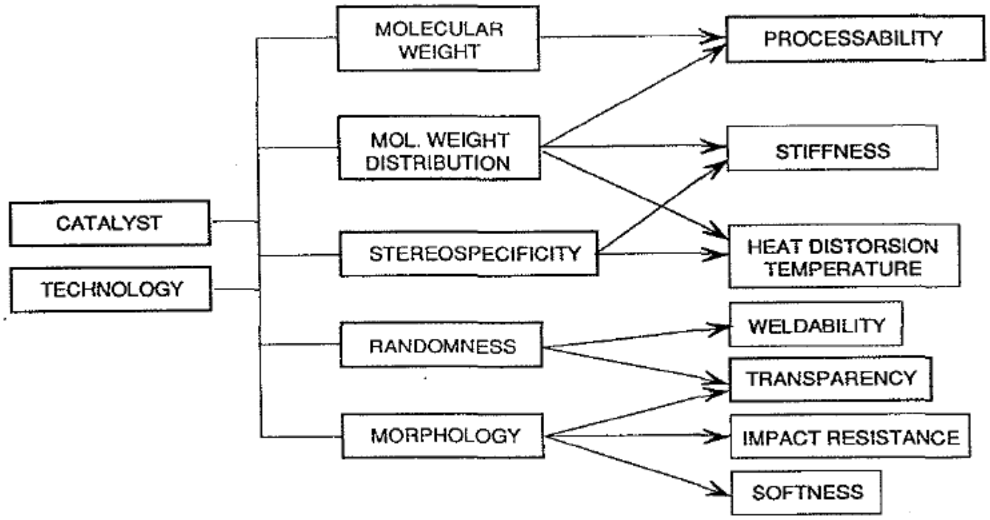


Figure 1 Catalyst/technology–structure–property relationship of polyolefins. (From Ref. 8.)

10 carbons depending on the α-olefin comonomer used. SCB could be attached either to the main polymer backbone or to the LCB.

The degree and type of chain branching strongly influences the molecular weight distribution, degree of crystallinity, lamellar morphology, density, and rheology of the polyethylenes. SCB is expressed as methyl groups per 1000 carbon atoms and is measured by infrared absorption techniques and empirical relations exist for comparing the degree of LCB of different polymers [74]. LCB is normally irrelevant for polymer properties below the melting point but is quite relevant in determining the rheological and processing properties, which are highly dependent on the molecular weight distribution. LDPE have LCB and, consequently, have much broader molecular weight distributions [102] compared to the others. Because of the existence of molecular weight distributions, polyethylenes do not melt at a single temperature but have a rather broad melting range.

For linear polyethylenes, there is a reasonable consensus that the melt flow index, an industrially important empirical flow property, is inversely related to the melt viscosity, impact strength, notch sensitivity, creep resistance, heat resistance, toughness, melt strength, and average molecular weight. It is directly related to clarity and mold shrinkage. This apparent relationship is utilized in down-gauging molded parts, extruded films, and profiles but no hard correlation can be inferred. The melt index is influenced by molecular weight, its distribution, chain branching, branch length, and many other molecular structural parameters. Indeed, it has been shown that the molecular weights of two LDPEs having similar melt indexes but different LCBs could differ by a factor of 2. That is, melt index is a poor indicator of molecular structure for LDPE. The comparative processing and performance property profiles of LDPE, HDPE, and LLDPE appear on Table 6 [103].

All polyethylenes are non-Newtonian, but LDPE is less so than HDPE, LLDPE, PP, and PB-1, in that order, and could therefore be more easily compounded with colorants and additives. Its melt viscosity is far more temperature-sensitive and shear-sensitive and it has an enhanced extentional viscosity. On the other hand, the more non-Newtonian polyolefins have a more plug-like velocity profile with a corresponding higher pumping efficiency. Their viscosities are less temperature- or shear-sensitive and they have considerably less extentional viscosities.

1. Branched Low-Density Polyethylenes (LDPE)

Branched low-density polyethylene is not closely packed as it contains a substantial amount of LCB much like a tree. It has a density of 0.910–0.930 g/cm^3, a 45–60% crystallinity and a respectable flexibility. LDPE is characterized by a broad molecular weight distribution with a polydispersity index as high as 20; a broad molecular weight ranging between 17,000 and 30,000; and a broad melting temperature range that depends on the degree and randomness of branching [101] but is normally centered around 110°C. Its molecular weight is skewed toward the higher molecular weight components.

LDPE made in a highly backmixed autoclave reactor tends to branch equally in all directions giving rise to somewhat spherical molecules as opposed to the commercial products of tubular reactor which contain fewer, longer branches on an elongated main backbone. LDPE also contains short-chain branches consisting of ethyl and butyl groups whose frequency distribution is quite narrow. For a given melt index, higher LCB implies higher mechanical properties, broader molecular weight distribution, higher flow resistance, and enhanced possibility of entanglement with the concomitant effects on processability and the other performance properties of the finished products. The degree of LCB, rather than melt index, is the indicator of LDPE molecular structure and properties. It is because of the enhanced melt strength and melt elasticity imparted by the high degree of LCB that LDPE is a preferred material for blown film, shrink film, and extrusion coatings.

Table 6 Processing and Performance Properties of LDPE, HDPE, and LLDPE

Property	LDPE	HDPE	LLDPE relative to LDPE	LLDPE relative to HDPE
Tensile strength (MN/m^2)	6.9–15.9	21.4–38	Higher	Lower
Elongation (%)	90–650	50–800	Higher	Higher
Impact strength (J/12.7 mm)	No break	1.02–8.15	Better	Similar
Environmental stress cracking resistance	—	—	Better	Same
Heat distortion temperature (°C)	40–50	60–82	15°C higher	Lower
Stiffness (4.5 MN/m^2)	1.18–2.42	5.53–10.4	Higher	Lower
Warpage			Less	Similar
Processability	Excellent	Good		Easier
Haze (%)	40	—	Worse	Better
Gloss (45° %)	83	—	Worse	Better
Clarity	Near transparent to opaque	Translucent to opaque	Worse	Better
Melt strength	—	—	Lower	Lower
Softening point range (°C)	85–87	120–130	Narrower	Narrower
Permeability (ml cm^{-2} g^{-1} mil^{-1} cm)				
H_g^{-1} at 25°C $\times 10^{-8}$				
(a) H_2O vapor	420	55	Better	Worse
(b) CO_2	60	13	Better	Worse

Source: Ref. 103.

The negative aspect of its high sensitivity to extension is that its melt strength could be exceeded during blown film processing unless adequate allowance is made in die design.

The individual crystallite dimensions in LDPE films are about 10–30 nm and an agglomerate of these results in a spherulite whose dimension is larger than the wavelength of light. The morphology of LDPE solid depends on the relative magnitude of the rates of crystallite nucleation and spherulite growth. In all polyethylenes including LDPE, the two rates are sufficiently significant [104]. The translucence of LDPE-blown film is due partly to the film surface unevenness and partly to the presence of spherulites whose size is a function of the degree of branching and the material thermal history. The presence of LCB implies smaller polymer molecular size and therefore higher clarity if the formation of aggregates is minimized. Because of this, melt elasticity, viscosity, temperature, and their effects on surface texture are, in the final analysis, the primary determinants of film clarity in commercial LDPE.

2. Linear Low-Density Polyethylenes (LLDPE)

Linear low-density polyethylene is a copolymer of ethylene and a linear α-olefin comonomer such as propylene, butene-1, pentene-1, hexene-1, heptene-1, octene-1, decene-1, tetradecene-1, or methyl-4-pentene-1 [104–107]. Commercially available conventional LLDPE normally contains 8–12% of butene-1, hexene-1, or octene-1, and it has a nonrandom broad comonomer distribution with density ranges between 0.900 and 0.945 g/cm^3. The situation is of course different for the LLDPE produced with the emerging single-site catalyst technology. The very-low-density polyethylene (VLDPE) has a density between 0.890 and 0.915 g/cm^3 and is structurally similar to LLDPE [108]. There is an inverse relationship between comonomer content and LLDPE density and between the molecular weight and density. The SCBs of the low molecular weight fractions are 2–4 times those for the high molecular weight chains. This catalyst-specific heterogeneity derives from the production technology used [109]. A homogeneous LLDPE with random and narrow comonomer sequence distribution as well as narrow molecular weight distribution is characterized by lower density, lower melting point, higher impact strength, significantly lower film haze, and improved film properties in the machine and transverse directions. This type of LLDPE essentially belongs with the next chapter on single-site polyolefins.

In spite of the shortcomings of conventional LLDPE, it still has much improved properties over LDPE of the same density, molecular weight, and molecular weight distribution. The primary advantages of LLDPE, arising from its backbone linearity and the presence of SCB, are as follows: higher tensile strength, impact strength, toughness, stiffness, film gloss, puncture resistance, tear strength, ESCR, permeability of water vapor and carbon dioxide. Up to a point, the extent of the property improvement is directly related to the amount and chain length of the oligomeric comonomer [102,110]. For equally the same reasons, its optical properties, melt strength, and rheological properties are not necessarily optimum. For the same density, LLDPE is about 5% more crystalline and has a melting point that is about 14°C higher than that of LDPE [111].

The α-olefin comonomer forms the SCBs on the linear ethylene chain backbone of LLDPE disrupting the crystallization process and limiting the crystalline size structure, thus increasing the percentage of the amorphous phase at the expense of the crystalline phase and lowering the density [74,104]. In conventional LLDPE, the SCB frequency distribution is uneven and, combined with the highly linear character of the polymer, the nonuniformity increases the relative magnitude of both the rate of crystallite nucleation and that of spherulite growth resulting in higher haze values. The haziness of LLDPE-blown film is due partly to the film surface unevenness and partly to the presence of spherulites whose size is a function of the nonuniformity of SCB and the material thermal history. Higher density LLDPE has lower SCB and higher nonuniform frequency distribution with a corresponding larger spherulite and higher haze. Because of this, melt elasticity, viscosity, temperature, and their effects on surface texture are not as important in determining film clarity as they are for LDPE.

LLDPE is more non-Newtonian than LDPE but its higher melt viscosity is not as temperature-sensitive or as shear-sensitive as LDPE. Because of its higher non-Newtonian character, its velocity profile in a channel is more plug-like with a corresponding higher pumping efficiency. But the absence of LCB and the narrower polydispersity imply a lower melt strength and a lower shear thinning behavior which, when combined with the higher viscosity, makes LLDPE more prone to melt fracture given the higher pressure and screw torque required for commercial extrusion. Because of the absence of LCB and the narrower polydispersity, LLDPE melt does strain-harden; it is soft in extension but stiff in shear. It therefore has to be processed at a higher melt temperature with a wider die gap to permit the use of a lower pressure and a higher draw-down ratio in blown films [74]. For the same melt index and density, LLDPE-cast film properties are superior to those of LDPE; consequently, a higher melt index LLDPE could easily yield a lower film thickness and a higher productivity.

Generally, LLDPE has penetrated the market normally dominated by other polyethylenes principally because of the high optical quality of its film and its corresponding performance properties even at rather low film thickness. The best LLDPE would be characterized by uniform inter- and intramolecular comonomer SCB distribution with a variety of comonomers such as betene-1, hexene-1, octene-1, 4-methylpentene-1 etc. The super random copolymer of Dow Chemical made in the proprietary solution process is based on octene-1 and it has a high compositional uniformity and film performance. On the other hand, the LLDPEs produced in the gas phase process using supported titanium chloride catalysts are characterized by nonuniform composition distribution and high hexane extractables. So are the LLDPEs made with the high-pressure retrofitted-LDPE processes based on butene-1. The estimated annual growth rate for LLDPE is 7–8%.

3. High-Density Polyethylenes (HDPE)

High-density polyethylene is closely packed with a density of 0.960–0.980 g/cm^3, a crystallinity as high as 95%, and a melting point as high as 138.5°C, with the highest values in all cases corresponding to those of polymethylene. Commercially available conventional HDPE normally contains 1–3 wt % of butene-1, hexene-1, or octene-1; it has a few SCBs with a polydispersity index in the range 5–15 although its molecular weight distribution is generally sharper than that of a corresponding LDPE. The situation is of course different for the HDPE produced with the emerging single-site catalyst technology. The homopolymer medium-density polyethylene (MDPE) has a density ranging between 0.926 and 0.940. Quenched HDPE could have a density as low as 0.945 g/cm^3 because of the reduced crystallinity [101,104]. However, the morphology of HDPE solid is determined by the relative magnitude of the rates of crystallite nucleation and spherulite growth, both of which are so high that it is nearly impossible to quench HDPE fast enough to obtain spherulites small enough to give high optical quality. Film clarity could only be improved through the use of heterogeneous nucleating agents.

Nonetheless the longer the molecular weight of HDPE, the more the crystallization process is inhibited, limiting the crystalline size structure and increasing the percentage of the amorphous phase at the expense of the crystalline phase resulting in reduced density.

The increased amorphous phase enhances the impact properties and lowers the yield properties, hardness, as well as stiffness up to a point. The ultimate tensile properties and elongation are increasing functions of molecular weight up to the point where chain entanglement becomes important. There is an inverse relationship between the melt index and the molecular weight but the intrinsic viscosity is related to the viscosity average molecular weight through the Mark–Houwink equation. The HDPE molecular weight has an effect on the following properties: density, tensile strength, tensile elongation, impact strength, toughness, stiffness, and permeation characteristics. Up to a point, the HDPE molecular weight is inversely related to its hardness and flexural stiffness, whereas it is directly related to Vicat softening point and Izod impact strength. On balance, however, it is the molecular weight distribution that determines the endproduct physical, mechanical, rheological, and processing properties.

HDPE is non-Newtonian and its velocity profile in a channel is plug-like with a high pumping efficiency, but this is more true for the polymer with the narrow molecular weight distribution. The melt viscosity of the HDPE with the narrow molecular weight distribution is not particularly temperature-sensitive or shear-sensitive making it more amenable to higher drawdowns when used as fibers and monofilaments. The HDPE with a broader molecular weight distribution has a higher melt index, a higher melt strength, and an enhanced shear thinning ability which facilitate processing in blow molding of large containers, extrusion of parts with large cross-sectional areas, and blow extrusion of thin crisp films used as replacements for paper. On the other hand, for a given melt index, the HDPE with the narrower molecular weight distribution has the higher impact strength. Generally, HDPE has an excellent low-temperature flexibility and its brittleness temperature is almost independent of its melt index. The high molecular weight HDPE [weight average molecular weight (M_w) of $3–4 \times 10^5$] with fractional melt indices are used in the manufacture of carrier bag, garbage bag, drum, and pipe whereas the medium molecular weight varieties ($M_w \approx 2.5 \times 10^5$) find applications as wrapping paper, grease-proof paper for meat, and flower packaging.

The specialty grade remains the high molecular weight HDPE with the best performance–processibility balance for blow molding and extrusion applications such as thin film, pipes, and heavy drums. A judicious choice of catalyst and polymerization process enables the production of HDPE with the best combination of structural molecular parameters vis-à-vis the required properties. For this premium grade of HDPE, the stirred-tank slurry processes are the best suited. The commodity large-volume HDPE is dominated by the cost-effective gas phase processes that have essentially surpassed the most licensed light diluent slurry loop reactor process. The HDPE includes the narrow molecular weight injection molding grades as well as the medium molecular weight extrusion grade for film and pipe. The Unipol gas phase process is able to produce bimodal HDPE grades and the new polymerization technology from Mitsui Petrochemical produces what has been called ''super-polyethylene.'' Of all the available processes, the new Spherilene process developed by Montell is the most versatile as it is able to produce HDPE with molecular weights ranging from very low to very high [2,8]. It could therefore supply both the specialty and the commodity market. The expected annual growth rate of HDPE is 4% and about 40–50% of the annual global market size for the Phillips catalysts is used for the production of HDPE.

4. Ultrahigh Molecular Weight Polyethylenes (UHMWPE)

The ultrahigh molecular weight polyethylene (UHMWPE) [111] with M_w in excess of 3.1×10^6 and a density of 0.94 g/cm^3 is structurally similar to HDPE with folded zigzag crystalline conformations having fold spacings between 10 and 50 nm. The chemical properties, electrical properties, tensile impact strength, and elastic modulus are similar except that UHMWPE is characterized by exceptional self-lubricating properties, low-temperature performance properties, and its abrasion resistance is superior to that of abrasion-resistant steel. It normally decomposes before it melts and some of its processing techniques mimic those of powder metallurgy.

The UHMWPE prepared under exceedingly high pressures between 0.2 and 0.7 GN, christened RT UHMWPE by DuPont, is tough, malleable, permanently deformable without breaking, and processable by solid phase extrusion or other solid phase–forming technique [111]. Its impact strength and elastic modulus are comparable to those of polycarbonate. The RT UHMWPE has an extended chain crystal structure fold spacings of about 1000 nm compared to about 250 nm for the extended chain crystal structure of conventional HDPE, produced under high-pressure crystallization, which is brittle at ordinary temperatures. The RT UHMWPE is used as machined parts for prosthetic devices, small gears, automotive parts that ordinarily would have required ABS or polyacetal, and many other applications requiring its outstanding combination of properties. Like other polyethylenes, its upper use temperature is below 100°C.

B. Polypropylene

There are basically three forms of polypropylene homopolymers: crystalline, amorphous, and elastomeric polypropylenes [2,8,74,114,115]. The short-chain branching of PP interferes with its polymer crystallization, limiting the size and formation of the crystallites, increasing the proportion of amorphous polymer, and decreasing the density. The syndiotactic crystalline form has a calculated density of 0.90 g/cm^3. The isotactic crystalline form has a measured density of 0.90–0.91 g/cm^3, a degree of crystallinity 60–80%, T_m 165–179°C, Vicat softening point 145–150°C, and it is capable of significant supercooling. Aside from being dependent on the method of measurement, the measured crystallinity depends on the molecular weight, the molecular weight distribution, crystallization conditions, and annealing. The atactic amorphous PP is soft and gummy, it has a measured density of 0.86–0.89 g/cm^3, its mechanical properties are significantly lower than those of the crystalline forms, and it finds application primarily as hot melt adhesives and bitumen binders.

The crystalline form of PP depends on the relative magnitude of the rates of crystallite nucleation and spherulite growth, both of which are determined by the cooling rate as well as the relative nearness of the crystallization temperature (T_c) to the crystalline melting point (T_m). When T_c is slightly below T_m and the cooling rate is slow, spherulite growth prodominates and the resulting material is highly crystalline. For this material, the higher the crystallinity, the higher the density, tensile yield strength, and elastic modulus; the lower the impact strength, toughness, and elongation. With high cooling rates, the T_c decreases fast. Nucleation becomes predominant, smaller spherulites are formed, and the degree of crystallinity is diminished. For this material, impact strength, toughness, and elongation are high but density, tensile yield strength, and elastic modulus are low. If the cooling rate is fast enough, small enough spherulites could be formed to obtain high optical quality [116]. Film clarity could be further improved through the use of heterogeneous nucleating agents [117], which would also enhance the crystallinity, density, tensile yield strength, and elastic modulus.

The weight-average molecular weight of polypropylenes strongly influences the physical, mechanical, rheological, and processing characteristics. Polypropylene melt is non-Newtonian at high shear rates but approaches Newtonian behavior when the shear rates are very low. Its shear rate dependence is a function of the polydispersity index and the PP with the broad molecular weight characteristics has a better processability, particularly for injection molding and extrusion applications where PP competes with amorphous polymers such as impact modified polystyrene and polycarbonates. Because of its crystalline nature, its significant shrinkage represents its disadvantage relative to its amorphous competition, but its high T_m and the consequent high heat distortion temperature compensate adequately. The broad molecular weight distribution polymer could also be obtained by blending polymers of different polydispersity indices and those with good enough melt strength are used in thermoforming, pipe extrusion, blown film, and blow molding.

There is an inverse relationship between the melt flow index and the molecular weight but the intrinsic viscosity is related to the viscosity average molecular weight through the Mark–Houwink equation. Commercial PP could have a narrow or a broad range of polydispersity index between 5 and 15. The narrow polydispersity index PPs with high melt flow index are used in injection molding of thin-walled containers, cast film production, and fiber spinning and are characterized by high strength, toughness, ductility, elasticity, resilience, and orientation. Oriented polypropylene films find applications in food packaging, graphics, solar control, and the film tapes are used as primary carpet backing fabric, sacks, ropes, twine, and nets for seedlings [118]. Until recently, the PP with controlled rheology and narrow polydispersity index (3.0) could only be obtained by the controlled chemical or thermal degradation of high molecular grades (visbreaking). This grade of PP could now be produced by the Montell technology using donor-assisted Ti/Mg catalyst systems [2,8].

Other PPs that could now be made include (1) high-modulus homopolymers, random and block copolymers for solid state pressure-forming applications requiring superior clarity, stiffness, impact strength, and heat distortion; (2) high-melt-strength PPs with enhanced elongational viscosity for application as extrusion coating, foaming, blow molding, melt phase thermoforming, and a host of others that have eluded PP [2,8].

C. Poly(butene-1)

There are primarily three crystalline polymorphs of poly(butene-1) (PB-1) classified as follows [119–124]: (1) the hexagonal or rhombohedral polymorph (a) form I (T_m 136°C) and (b) form I′ (T_m = 98–103°C); (2) tetragonal form II (T_m 124°C); and (3) orthorhombic form III (T_m 106°C). Although each polymorph has different properties with form I having the highest density, crystallinity, hardness, rigidity, stiffness, and tensile yield strength, the commercially available PB-1 is 98–99.5% isotactic, 50–55% crystalline, and its weight-average molecular weight is $2.5–6.5 \times 10^5$. Structurally, PB-1 is similar to PP except that it has ethyl chain branches rather than methyl. The commercially available PB-1 exists first in the form II polymorph structure, which has 11 monomer units in 3 turns or 40 units in 11 turns of its helical molecular structure, before it transforms irreversibly to the form I polymorph with 3 monomer units per turn in its helix. The phase transformation occurs within seconds, days, or weeks depending on the prevailing pressure, temperature, state of strain, molecular weight, tacticity, catalyst residue, nucleating agents, additives content, comonomer composition and distribution. The addition of about 10% of polypropylene has been known to shorten the transformation half-time by as much as 70%.

The physical properties of PB-1 cut across all other polyolefins and its general characteristics is a cross between polyethylenes and polypropylene. Its T_g is −25°C, in-between that of polyethylenes (−60°C) and polypropylene (≈0°C); its T_m is much like that of HDPE, i.e., 124–136°C; and it has a measured density of 0.91 g/cm^3, which is essentially identical to that of PP. Its tensile yield strength is about the same as that of medium-density polyethylene; its flexibility is much like that of LDPE having a density of 0.92 g/cm^3; its high-temperature mechanical property retention is much like that of HDPE; its non-Newtonian character is much like that of LDPE and it could therefore be easily compounded with colorants, additives, and high filler loading. The relative magnitude of its specific heat compares as follows: polyethylenes > polypropylene > polybutene-1. The tear strength of its film is about 6 times that of LDPE and about 3 times that of LLDPE [125,126]. Compared to PP and PEs, PB-1 has a good electrical properties, moisture barrier properties, an excellent environmental stress crack resistance, as well as an outstanding abrasion, impact, and creep resistance. While polyethylenes and polypropylene do not strain-harden, PB-1 strain-hardens as its chain orientation and the corresponding material state of stress are a strong function of strain.

In the melt, PB-1 has an excellent melt strength and it finds applications in pipe extrusion for hot water pipes, blown film, laboratory/medical ware, food/meat packaging, agricultural packaging, compression wraps, and hot-fill containers. The blown film is characterized by high strength, toughness, ductility, elasticity, resilience, and orientation potential.

D. Poly(4-methylpentene-1)

The principally isotactic poly(4-methylpentene-1) has a tetragonal crystalline form whose helical molecular conformation has seven monomer units in two turns of its helix. The polymer has a high T_m between 235°C and 250°C and a low density of about 0.83 g/cm^3—the lowest density of all polyolefins. Its helical conformation is presumed to be retained even within the amorphous phase; consequently its crystalline and amorphous phases have a similar density and this is responsible for its exceptional transparency with a light transmission value of 90–93% [127]. Its monomer, unlike that of other polyolefins, is not a byproduct of steam-cracking operations; it results from propylene dimerization. The monomer confers on poly(4-methylpentene-1) a crowded side chain branching which in turn confers a rigid backbone to the stereoregular variety. Of all of the polyolefins, the commercial poly(4-methylpentene-1) copolymer variety, with a trade name of TPX, has the best high-temperature mechanical property retention up to 205°C [128]. For this reason, it is capable of hundreds of sterilization cycles with high-pressure steam (150°C) in laboratory and medical applications. Because of the bulky and crowded side groups, poly(4-methylpentene-1) has a significant free volume that is responsible for its high water vapor permeability, high gas permeability, high oxygen uptake, and a high susceptibility to photooxidation.

The physical properties of poly(4-methylpentene-1) are generally close to those of polypropylene; the tensile strength, flexural modulus, hardness, and impact strength are similar. It is transparent while PP is translucent at best. Poly(4-methylpentene-1) is thixotropic and could easily be compounded with colorants, additives, and fillers. Its melt viscosity is far more temperature-sensitive than that of all the other polyolefins and could be processed in injection molding, blow molding, and extrusion. Its market includes laboratory/medical ware, lighting, automotive, appliances, electronics and electrical parts. It has superior electrical properties.

E. Polyolefins Elastomers

Commercially available polyolefin elastomers include the following: (1) poly(transisoprene); (2) poly(chloroprene); (3) poly(1,2 butadiene); (4) poly(styrene-co-butadiene);

(5) nitrile rubber; (6) butyl rubber; (7) ethylene-propylene rubber (EPR); (8) ethylene-propylene-diene monomer rubber (EPDM), etc. The estimated global consumption of polyolefins elastomers in 1995 is 8 million tons [2]. EPR and EPDM are discussed briefly with propylene copolymers in the next section, but no others will be discussed further as the subject of thermoplastic elastomers forms the basis of another chapter in this book.

F. Polyolefins Blends, Copolymers, and Composites

1. Polyolefins Blends

Polymer blends (PBs) are mixtures of structurally different homopolymers, copolymers, terpolymers, and the like. The copolymers, terpolymers, etc., may be random, alternating, graft, block, star-like, or comb-like, as long as the constituent materials exist at the polymeric level. The strongest reason for blending polymers is the cost–performance ratio. An expensive polymer whose property spectrum is much higher than is needed for a new application may be blended with an inexpensive polymer whose property spectrum is such that the resulting PB has a cost–performance ratio that makes it very attractive for the given application. Thus, the standard of performance demanded by the new application is satisfied by a mixture of commercially available polymers without the need to develop a new polymer or to invest in a new plant. The situation is even more attractive if, by a judicious choice of compatibilizers, a significant degree of synergy, rather than additivity, is achieved in the polyblends and a new material is essentially created [129–132].

PBs could be classified in terms of the technology of manufacture. For polyolefins, mechanical PB is probably the most relevant, and is made by melt-blending the polymers either on an open roll or in an extruder or any other suitable intensive mixer at a processing temperature well above the T_m. Depending on the state of thermal stability of the polymers being mixed, the high-intensity processing shear could initiate degradation, resulting in free radicals that could cause polymeric reactions and possible crosslinking of the constituent polymers. This may or may not be desirable. PBs could also be classified in terms of the polymer–polymer phase behavior. Most of the commercially important polyolefin PBs presented on Table 7 are multiphase and would be characterized by low ductility and elongation [74,75,132,133]. This is why the blends normally must be compatibilized to ensure a very effective interfacial stress transfer between the constituent polymers and the resulting materials could in some cases be referred to as polyolefin alloys.

Generally, a block copolymer could operate as a dispersing agent (emulsifier), reducing the interfacial tension and the particle size of the dispersed phase. It could significantly contribute to the dispersion of the constituent polymers and improve elongation, tensile strength, and impact strength of the PB. In effect, an A-co-B nonreactive compatibilizer would increase the compatibility of a normally immiscible mixture of A and B homopolymers. The impact properties of the blends of poly(ethylene-b-propylene)/HDPE, poly(ethylene-b-propylene)/EP (rubber), and PP/EP (rubber) are enhanced because the ethylene or the propylene components of the copolymer provide the needed compatibilization effects. Pendant reactive chemical groups, namely, the A–X reactive compatibilizers, and ionomer-reactive compatibilizers have also been used to enhance polymer compatibility. Polybutene-1 is compatible with PP and HDPE and the PB-1/PP films find applications where the required toughness, creep, ESCR, memory, and heat sealability properties would have precluded the use of either PP or PB-1. HDPE enhances the heat distortion temperature and the T_m of PB-1 [124].

2. Polyolefin Copolymers

Inasmuch as most polyolefins blends are incompatible, copolymerization is one method of creating new commercially viable polyolefin materials such as random, block, and graft copolymers from the wide range of olefin monomers. LLDPE is a copolymer of ethylene and α-olefins. Other commercially important polyolefins copolymers are as follows: (1) those based on LDPE such as ethylene–vinyl acetate (EVA) copolymer; (2) those based on PP such as ethylene-propylene (EP) copolymer; (3) those based on PB-1 such as copolymers of butene-1 with ethylene, propylene, pentene-1, 3-methylbutene-1, 4-methylpentene-1, and/or octene-1; and (4) those based on poly(4-methylpentene-1) such as the copolymers of 4-methylpentene-1 with pentene-1 and hexene-1.

Ethylene–Vinyl Acetate (EVA) Copolymers

EVA, a random statistical copolymer that normally contains up to 40% vinyl acetate, is usually made in a free radical LDPE at pressures higher than 0.1 GN/m^2. The vinyl acetate–ethylene (VAE) copolymers containing above 40% and up to 100 wt % vinyl acetate are made either in a medium-pressure solution phase process or in a low-pressure emulsion polymerization process. It is the EVA rather than the VAE that is generally predominant and is considered a variant of LDPE with lower crystallinity but higher density. When the vinyl acetate content approaches 50 wt %, the crystallinity decreases to zero as the density approaches 1.0 g/cm^3. The property advantages of EVA could be

Table 7 Commercially Important Polyolefin Blends

HMW PP/PP
PP/LDPE
PP/HDPE
PP/EPDM
PP/PIB/LDPE
PP/EPDM/HDPE
PP-EP/HDPE
PP/EPR or EBR/LDPE or EVA
HDPE/EPR or EBR/LDPE or EVA
PB-1/EPR or EBR/LDPE or EVA
LDPE/LLDPE
LDPE/LLDPE/EVA
HMW HDPE/HDPE
HMW MDPE/MDPE
HMW HDPE/LLDPE
PB-1/PP
PB-1/HDPE
Polyolefins/S-EB-S/engineering thermoplastics
PP/S-EB-S/PBT
PP/S-EB-S/polyamides
Polyolefins/S-EP-S/engineering thermoplastics
Polyolefin/S-EP-S/polyphenylene ether
Polyolefin/S-EP-S/thermoplastic polyurethane

Source: Refs. 74–76, 132–133.

appreciated by comparing the stretch wrap film, containing 9–12 wt % vinyl acetate, with LDPE or plasticized PVC. The EVA has superior stretchability, puncture resistance, retained wrap force, and tear resistance—all of the properties that are *sine qua non* for stretch-wrap films [134]. EVAs containing 2–40% vinyl acetate find applications as high-clarity films for packaging, heavy-duty stretch-wrap films, agricultural films, injection molding, profile extrusion, shoe soles, and hot melt adhesives.

Polypropylene Copolymers

The conventional poly(ethylene-co-propylene), or EP, copolymer is available primarily in two forms, namely, random or block copolymers. The *raison d'être* for EP copolymer is to increase the low-temperature impact properties as well as the amorphous phase of the crystalline PP. Random EP copolymers have good melt strength and are used in thermoforming and for blow molding of bottles requiring high contact clarity. The thin film of the single-phase random copolymer is transparent as the material has a significantly reduced crystallinity. The random copolymerization of propylene with as much as 20 wt % α-olefins such as decene-1 or longer yields a tough polymer whose density is 0.896 g/cm^3 with significantly improved low-temperature properties and polymer rheology.

On the other hand, the film of the block copolymer is essentially opaque, reflecting the presence of the two types of crystallite that render the EP block copolymer multiphase. In comparison with PP homopolymer, EP block copolymer exhibits lower density, lower brittleness temperature, higher impact strength, higher toughness, higher elongation, lower notch sensitivity, plus the characteristic hinge effect of PP homopolymer [2,8,74,135,136]. The environmental stress crack resistance of EP block copolymer is outstanding and the effect of the weight-average molecular weight is similar to that of the PP homopolymer. It finds applications where its property profile makes it superior to PP.

The emerging $MgCl_2$ catalyst technology has also made it possible to produce, in one reactor, a tough, high-impact, multiphase polypropylene alloy containing a blend of isotactic polypropylene homopolymer as the continuous phase and EP rubber as a uniformly dispersed phase [2,8]. Ordinarily, this sort of material would have had to be made by blending the component polymers in an intensive mixer such as an extruder. In addition, random copolymers containing up to 15% comonomers and multiphase alloys containing up to 70% multimonomer are now available through the emerging catalyst technology. The ability to combine olefinic and nonolefinic monomers has made it possible to produce polymers that combine the desirable properties of olefins with the desirable characteristics of amorphous engineering thermoplastics [2,8].

Ethylene-propylene rubber (EPR) copolymer containing 25–70 wt % propylene is amorphous and elastomeric. When made in the presence of a small amount of nonconjugated diene, such as 1,4-hexadiene, dicyclopentadiene, or 5-ethylidene-2-norbornene, ethylene-propylene-diene monomer (EPDM) rubber is obtained. Because the only remaining double bond is pendant to the backbone, EPDM, like natural rubber, is less sensitive to oxygen and oxone. EPDM is characterized by excellent low-temperature performance properties, good dielectric properties, and excellent resistance to chemicals. It is commercially produced in solution and suspension processes. Its unique structural molecular parameters include the possible presence of random/alternating/block comonomer distributions, variable block sequence lengths, a measure of tail-to-tail enchainment, absence or presence of crystallinity and of gels. There are observable relationships between these structural parameters and the elastomeric performance properties such as cure ability, processability, wear resistance, elasticity, mechanical properties, etc.

Poly(butene-1) Copolymers

Copolymers [119] of butene-1 with ethylene, propylene, pentene-1, 3-methylbutene-1, 4-methylpentene-1, and octene-1 have been investigated. Of these, 3-methylbutene-1, 4-methylpentene-1, and octene-1 are easily incorporated into the PB-1 lattice structure and they significantly retard the phase transformation of polymorph form II to that of polymorph form I. On the contrary, the ethylene and propylene are not well incorporated into the PB-1 lattice structure and, even at very low quantities, they significantly accelerate the phase transformation to such an extent that the form I polymorph precipitates directly from the melt. Although poly(ethylene-co-butene-1) with more than 20 mol % ethylene comonomer is virtually amorphous with a T_g less than −40°C, the random copolymer, poly(propylene-co-pentene-1) retains a small measure of crystallinity and its 50:50 block copolymer actually contains both the PP crystalline structure and the form I structure of PB-1 with the respective melting points. The poly(1-pentene-co-butene-1) exists in the form I polymorph with up to 84 mol % pentene-1 comonomer. The injection molding processability of PB-1 is enhanced by the incorporation of ethylene or propylene comonomer, and at very low comonomer concentrations propylene has been known to increase the isotacticity of the polymer.

Poly(4-methylpentene-1) Copolymers

The commercially available variety of poly(4-methylpentene-1), manufactured by Mitsui Petrochemical, is christened TPX and contains pentene-1 or hexene-1 comonomer. It is more crystalline than the homopolymer with a melting range of 230–240°C, a Vicat softening temperature of 179°C, and a heat distortion temperature of 100°C. The corresponding values for the homopolymer are 100°C, 245°C, and 58°C, respectively [127,128]. TPX has higher elongation, impact, and softening temperature than the homopolymer; it has a higher melting and softening temperature than PP. Like its homopolymer, its film is exceptionally transparent whereas the PP film is translucent at best. It could be processed in injection molding, blow molding, and extrusion processes; its major applications are identical to those of the homopolymer. It is also used in polyolefin composites.

3. Polyolefin Composites

The birth of composite, as a material containing polymers plus particulate fillers and fiber reinforcements, could be traced to the first truly synthetic plastic, a phenolic resin, christened ''Bakelite,'' after Dr. Leo Hendrick Baekeland [137] who founded the Bakelite Corporation which later became the Union Carbide Corporation. The pressure vessel used to commercialize Bakelite, called the Bakelizer, was in November 1993 designated the first National Historic Chemical Landmark and is housed at the Smithsonian Institution's National Museum of American History in Washington, D.C. In the 1910s, the addition of wood flour to Bakelite gave rise to the first synthetic composite. By the 1950s, the field had included the glass fiber–reinforced plastics and this preceded the era, in the late 1960s, of intense interest in composites beginning with the development of the high-performance carbon and aramid fibers.

Fibers that could be used in polyolefin composites include acicular particulates, alumina, aramid, boron, ceramic, glass, carbon, polyolefins, modern rigid rod polymer fibers, and knitted reinforcements. The desired features of fibers are as follows: high aspect ratio, chemical stability, thermal stability, low cost, low health hazard, minimum grain size, minimum porosity, minimum surface flaws, minimum surface roughness, high specific strength, high specific stiffness, and high toughness. No single fiber is characterized by the best combination of all of these properties and a significant body of knowledge exists pertaining to the dependence of the polyolefins–fiber composite performance on the interplay between the individual fiber component, matrix, interface, nature of damage, and failure mechanisms. The key applications of polymer–fiber composites are in simple primary structures and macromechanics has been used to elucidate the paramount issues dictating the design requirements for polymer–fiber composites in structural applications [138].

Particulate fillers that have been used as polyolefins additives or extenders are as follows: wood powder, glass spheres, hollow silicates, calcium silicate (wollastonite, $CaSiO_3$), silica minerals (diatomaceous earth, kaolin clays), magnesium silicates (talc, mica, asbestos), calcium sulfate whiskers, barium sulfate, calcium carbonate, and carbon black. Fillers or fibers are used either to lower the cost or to improve the physical properties of the polymeric materials. In general, however, fibers have the strongest effects on polyolefin properties followed by plate-like and particulate fillers, in that order.

Flexural modulus, tensile modulus, stiffness, abrasion resistance, antistatic behavior, and heat distortion temperature are almost always improved and the coefficient of thermal expansion is considerably reduced by the addition of fibers or fillers. The same cannot be said for impact strength (toughness) and elongation to break (ductility) unless an appropriate interfacial agent is used. Toughness and ductility are low in filled polymers because of strain magnification as the rigid inclusions constitute stress concentration flaws and all of the strains are imposed on the diminished quantity of ductile matrix. This is why polyolefin composites are weak and brittle if the interfacial agent is not effective. Coupling agents improve adhesion and thereby enhance the composite toughness with little or no increase in ductility, resulting in a strong but brittle material. On the contrary, a decoupling agent decreases adhesion but facilitates microcavitation, which significantly increases ductility with little or no increase in toughness, resulting in a ductile but weak material.

The most desired interfacial agent is that which significantly increases both toughness and ductility through enhanced particle-to-matrix adhesion and the formation of a discernible tough interface. This implies diminished interface stress concentration and uniform microcavitation so as to obtain an overall reduced stress even if a moderate triaxial state of stress exists throughout the composite. Synergism is an ultimate goal. The search for such reinforcement promoters [139,140] constitutes a dynamic ongoing research area in industry, universities, and research institutes interested in composites materials. So far, there is a loose consensus that shear banding, crazing, and/or microcavitation are the essential mechanisms for toughness and ductility as they are largely responsible for creating the desired new surfaces that are capable of absorbing large amounts of energy during deformation.

In preparing polyolefin composites, the interfacial agents are first deposited on the fillers and/or fibers before the melt compounding and/or interfacial reaction is effected. The interfacial agents that have been used with polyolefins include organosilanes, organotitanates, other organometallic compounds, crosslinking agents, and polymerization catalysts. The various aspects of the methods are well documented. Composite materials could be processed in one or more of the following: autoclave molding, filament winding, hand lay, injection molding, and pultrusion.

Under the influence of an adverse environmental agent, the ultimate properties of polyolefin composites are susceptible to degradation. Such an adverse environment could be something as innocuous as moisture. The effect of adsorbed moisture is to degrade the matrix-dependent properties with a resultant effect on the load-bearing performance. In a less friendly environment, plasticization and possibly environmental stress cracking could occur.

V. PROCESSING METHODS FOR POLYOLEFINS

The six most important processing methods for polyolefins are injection molding, rotational molding, blow molding, extrusion, blown film extrusion, and cast film extrusion [102]. In injection molding, the polyolefin granules or pellets are placed in a hopper that continuously feeds the heated barrel of an extruder. The polymer is plasticated, melted, and the molten material is injected, under a very high pressure, into a relatively cold mold where the material solidifies replicating the shape of the mold cavity. Aside from the independent variables of time, temperature, and pressure, the choice of an appropriate injection machine for a given polyolefin is critical for successful processing. It is essential for the melt viscosity to be sufficiently low to ensure that the mold cavity is filled in a minimum possible cycle time. Injection molding is a cyclic process.

In rotational molding (rotomolding or rotoforming), finely ground thermoplastic powders are heated inside a rotating mold where the polymer melts and uniformly coats the inner surface of the mold. The mold is cooled in a special chamber just prior to part removal. The process is used for the production of large complex polyolefin parts such as large containers, storage tanks, water tanks, and portable sanitary facilities. Rotational molding is a cyclic process.

The injection or extrusion blow molding makes hollow parts through the formation of a parison that is expanded, with a gas, against a mold cavity. Smaller containers (<1 liter) are produced with the injection blow molding, whereas extrusion blow molding is suitable for larger containers and for containers with handles. Melt strength, rather than melt viscosity, is the key controlling resin characteristic and large containers require high molecular weight polyolefins with broad molecular weight distribution that are easier to process and less likely to exhibit parison sag. Blow molding is a cyclic process.

In extrusion, polyolefin granules or pellets are placed into a hopper that continuously feeds the heated barrel of an extruder. The polymer is plasticated, melted, and the molten material pumped through a die of roughly the same shape as the final product such as sheets, pipes, films, wire and cable coatings. The extruded product is drawn by some type of takeoff equipment, sized, and cooled until solidified. Extrusion is a continuous process.

In blown film extrusion, molten polyolefin is extruded through a circular die whereby the die mandrel introduces an internal air pressure that expands the extruded tube from 1.5 to 2.5 times the die diameter. Melt strength, rather than melt viscosity, is the key controlling resin characteristic; die swell and melt fracture are unwanted. Blown film extrusion is a continuous process.

In cast film extrusion process, molten polyolefin is extruded, as a thin sheet on a mirror-surfaced chill roll, through a large die whose size is equal to the width of the film to be cast. The extruded thin sheet is then drawn down by other rolls. Cast films are used as diaper liners, pallet stretch wrap, household cling wrap, and overwrap. Cast film extrusion is a continuous process.

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2

New Polyolefins

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I. INTRODUCTION

Polyolefins have established themselves among the most widely used commodity polymers during the last four decades. They are economically and, even more important, ecologically attractive materials. Modern gas phase and liquid pool technologies do not require solvents and polymer purification. Polyolefins are known for their low energy demand during polymerization and melt processing. Sometimes referred to as ''solid crude oil,'' they offer advantages over other plastics in recycling. They may be degraded by catalytic hydrogenation, cracked, or used as a source for incineration. These properties are the driving forces in development of new polyolefins; trying to broaden the properties envelope of polyolefins, expanding their boundaries toward the areas traditionally occupied by more sophisticated, expensive, and sometimes hazardous materials.

Initially, research was mainly devoted to catalyst improvement in terms of activity and stereospecificity. Today catalysts should also allow for the creation of diversified molecular structures in synthesis, reproducible molecular and morphological structures for homo- and copolymers and for alloys, as well as the control of the molecular weight and the molecular weight distribution, of the configuration of monomeric units as well as chain configuration, and, last but not least, of the size and shape of polymer particles [1].

Development of new catalysts allows the synthesis of new polymers and polymer blends. Single-site metallocene catalysts are capable of producing new polyolefin types with tailor-made microstructures and properties. Due to the fact that this new breed of Ziegler–Natta catalysts has been known for only 15 years, developments in morphology control as well as those in polymer particle size and shape are only at the beginning, whereas for Ti-based catalyst very sophisticated developments have already led to new types of polyolefins, namely, polymer blends generated within the process of polymerization. This chapter will focus on these as well as on single-site catalysts for the polymerization of olefins.

II. POLYETHYLENE

A. Catalyst Development

In the last decade homogeneous catalysts based on group 4 metallocenes and an aluminoxane, especially methylaluminoxane (MAO), as cocatalysts have gained widespread industrial and scientific interest (for reviews, see Refs. 2–6). The catalyst components, as well as the active species generated from them, are soluble in hydrocarbons; thus they are sometimes referred to as homogeneous Ziegler–Natta catalysts or, due to the uniformity of the active sites, as single-site catalysts.

MAO is a mixture of oligomers formed by the controlled reaction of trimethylaluminum and water under elimination of methane. Its structure has been a riddle since the first synthesis but recent research by Barron [7–9] and Sinn [10] draw some light onto it. Association/dissociation phenomena, as well as condensation and cleavage by trimethylaluminum, characterize the dynamic behavior of MAO in solution (see Fig. 1). The molecular mass of MAO measured cryoscopically in benzene depends on the degree of hydrolysis; in polymerization experiments MAO having a mass of 1000–1500 g/mol is most widely used. Usually an excess of MAO is needed covering an Al/metallocene ratio of 50:100 for supported systems and 400:20,000 in solution. The optimum Al/metallocene ratio depends on the metallocene used and the experimental conditions [11,12].

The role of MAO in these catalysts is manifold. The generation of the active species involves alkylation of the metallocene by the MAO and as a second-step abstraction of a methyl group from the dimethyl metallocene. The resulting active species is discussed as a 14-valence electron cationic alkylmetallocenium ion [13] formed by dissociation of the

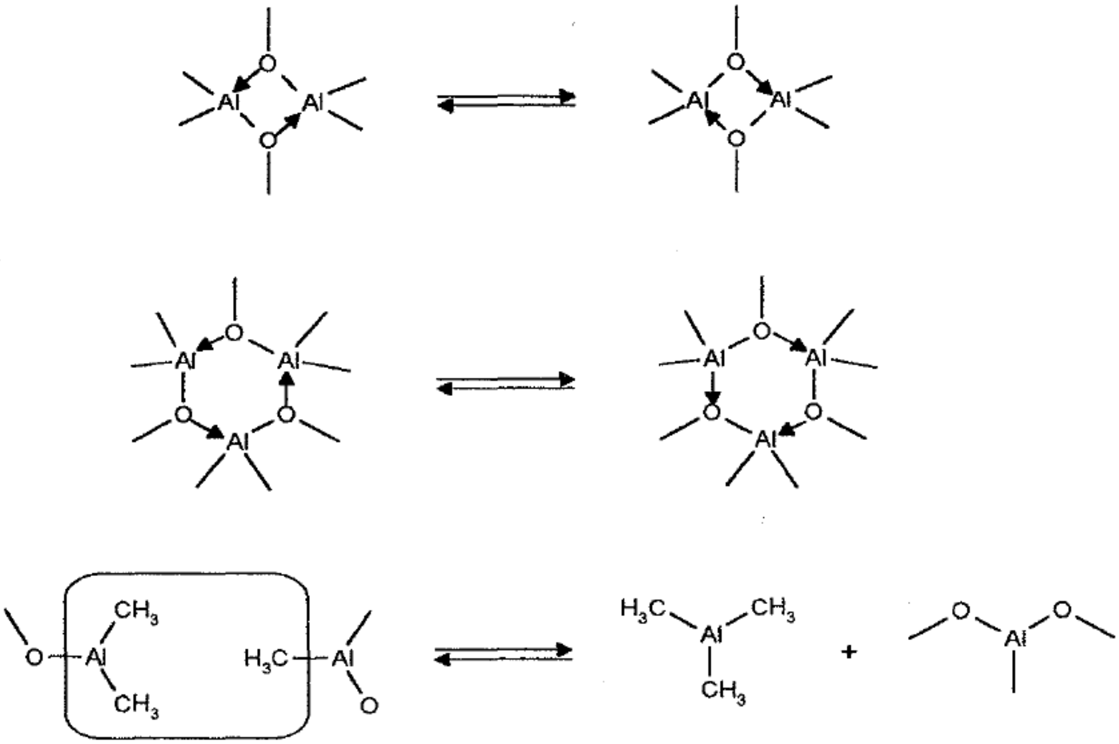

Figure 1 Dynamic processes of methylaluminoxane in solution.

metallocene–aluminoxane complex. The $[\text{MAO Me}]^-$ anion is regarded as non- or weakly coordinating (see Fig. 2). MAO may be replaced using Me_2AlF [14], $[B(C_6H_5)_4]^-$ [15], $[C_2B_9H_{12}]^{2-}$ [16], $B(C_6F_5)$ [17], $[Ph_3C][B(C_6F_5)_4]$ [18,19], $[R_2R'NH][B(C_6F_5)_4]$ [20], or $[Ph_3C][B(C_6F_4(SiR_3)]$ [21], in combination with trialkylaluminum compounds as alkylating agent and dichlorometallocenes or simply in combination with dialkylmetallocenes. In most of these systems, the following two problems arise: (1) There is a need for a scavenger (usually trialkylaluminum) due to the highly unsaturated character of the active species. (2) Most of the Lewis acids used show some interaction with the active species; thus they may not be regarded as noncoordinating [22]. Especially systems based on $[Ph_3C][B(C_6F_5)_4]$, $[R_3NH][B(C_6F_5)_4]$, or $[Ph_3C][B(C_6F_4(SiR_3)]$ seem to fulfill the requirements for good cocatalysts.

Polyethylenes produced by metallocene catalysts are characterized by narrow molecular weight distributions of $M_w/M_n = 2-2.5$ reflecting the single-site character of the catalyst. They are highly linear and usually contain a vinyl end group in each polymer chain. The molecular weight may be controlled by the choice of the metallocene, by the experimental conditions (monomer/metallocene ratio, temperature), or by addition of small amounts of hydrogen. Generally, zirconium catalysts are more active than their hafnium or titanium analogs, whereas in the case of the hafnocenes a lower number of active species is detected. As for the titanium systems, rapid decomposition decreases the activity [23].

Metallocenes have been used most successfully in the production of linear low-density polyethylenes (LLDPEs). The uniformity of the active species in metallocene catalysts enables the producer to maximize the uniformity of the physical properties of the polymers. Advantages over conventional Ziegler–Natta catalysts include higher activity, uniform comonomer incorporation, narrow molecular weight distribution, high ability to incorporate sterically demanding comonomers, and the possibility to design the comonomer distribution in the polymer chain from alternating to random or blocky structures by the choice of the metallocene.

The higher activity is reflected in the amount of ash and metal found after incineration of the polymer, which is much higher for conventional catalysts (30 ppm Al, 7–8 ppm Ti, 330 ppm total ash) than for metallocene catalysts (<20 ppm Al, <0.5 ppm Zr, <20 ppm total ash) [24], making metallocene catalyst quite attractive from an ecological point of view.

The absence of low-molecular-weight, high-comonomer-content molecules of LLDPE leads to low extractables (offering applications in food packaging and medical

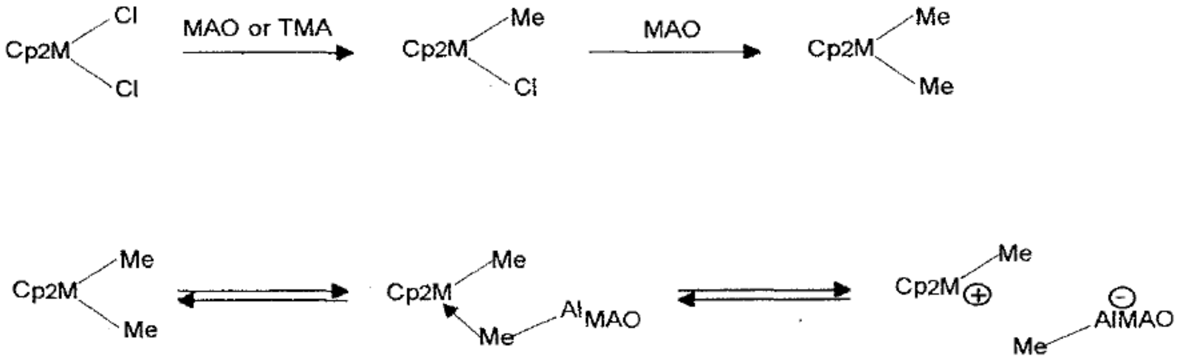

Figure 2 Generation of the active sites in metallocene/MAO catalysis by alkylation of the metallocene and abstraction of an Me^- by the aluminoxane.

sectors), low film blocking, and a better flow of pellets. In the conventional LLDPE the high-molecular-weight, low-comonomer-content fraction has a crystallization temperature significantly higher than that of the fractions containing more comonomer units and these latter chains form the nuclei for crystallization. This heterogeneous nucleation leads to the formation of thick lamellae with a low number of tie molecules. On the contrary, the nucleation in the copolymers produced by metallocene catalysts is almost homogeneous due to the narrow comonomer distribution resulting in thinner lamellae and more tie molecules [25–27]. As a result of the homogeneous nucleation, the melting point of metallocene LLDPE is lower than that of the conventional LLDPE and it decreases as the density decreases. The lower melting point allows lower heat seal temperatures whereas the increased number of tie molecules enhances the dart impact strength. Another advantage of the homogeneous composition is the higher clarity of the products; in conventional LLDPE the crystallites formed by the low-monomer-content chain scatter light and give rise to haze. The major drawback of the metallocene LLDPE is the more viscous nature of the product because of the absence of the low-molecular-weight fraction and the absence of long-chain branching. This may be overcome using mixtures of metallocenes to produce bimodal distributed polymers, blending of copolymers of different molecular weight distribution, or catalysts allowing a small amount of long-chain branching (see Table 1).

The better incorporation of the comonomer leads to a lower amount of comonomer consumed and a better recovery efficiency. The combination of two metallocenes also allows the combination of the toughness of high-molecular-weight polymers with the processability of lower molecular weight polymers. While the copolymerization of ethylene and α-olefins using conventional Ziegler–Natta catalysts results in an isotactic arrangement of the α-olefin blocks, in the case of metallocene catalysis, the stereochemistry can be varied over the whole range of the possible microstructures (see Table 2). The potential of these new polyolefins has not even been touched up to now.

Especially for the copolymerization of ethylene and higher α-olefins like octene, Dow [28] and Exxon have introduced new half-sandwich metallocenes (constrained geometry catalysts; see Fig. 3). Materials containing up to 20 wt % of α-olefin are called plastomers. They are flexible and thermoplastic; thus they match the properties of conventional LLDPEs and very-low-density polyethylenes (VLDPEs) at much lower densities. Copolymers containing more than 20 wt % of comonomer are called polyolefin elastomers; their flexibility, clarity, and tensile strength enable them to replace flexible thermoplastics like polyvinyl chloride (PVC), EVA, EMA, and styrene block copolymers as well as ethylene-propylene rubber (EPR) and EPDM [29].

Table 1 Comparison of Linear Low-Density Polyethylenes (LLDPEs) Produced by Conventional and Metallocene Catalysts

	Conventional LLDPE	Metallocene LLDPE
Density (g/cm^3)	0.922	0.923
Melt index (g/10 min)	1.0	1.1
Melting point DSC (°C)	123	117
Crystallinity (%)	54.7	55.5
Long period (Å)	278	235
Probability of forming tie molecules (%)	1	3

Source: Ref. 64.

Table 2 Comparison of Ti, V, and Metallocene Catalysts for Production of Linear Low-Density Polyethylene

Property	Ti catalyst	V catalysts	Metallocene
Molecular weight distribution	Narrow 4–6	Medium to broad	Very narrow ($M_w/M_n = 2$)
α-Olefin incorporation	Moderate	High	Low to very high
Composition distribution	Heterogeneous	Homogeneous	Homogeneous
Microstructure of α-olefin blocks	Isotactic	Atactic to isotactic	Syndiotactic to atactic to isotactic
Polymer Unsaturation	Low	Very low	0.1–1 vinyl group per chain

Using constrained geometry catalysts, the incorporation of octene as well as the incorporation of vinyl-terminated polymers formed during the polymerization leads to a product containing long-chain branches. Long-chain branching in this case differs from long-chain branching in LLDPE for the following reasons: (1) the long-chain branches are fewer and longer; (2) the level of long-chain branching is controlled by the catalyst used; (3) the long-chain branches are almost linear [30]. The low level of long-chain branching significantly improves the processability to a level superior to that of conventional PE types, despite the narrow molecular weight distribution, without affecting the polymer properties. They are extruded up to 2.5 times faster than conventional LLDPEs and their melt tensions, which are correlatable to melt strength and bubble stability, can be twice as high—which is important for film blowing applications.

B. Process Innovations

The technology for producing high-density polyethylenes (HDPEs) and LLDPEs is marked by problems in versatility and flexibility. Thus different processes ranging from slurry polymerization for HDPE production to solution processes for LLDPE and gas phase processes for commodity polyethenes are applied for different grades. New technologies with improved flexibility have been developed based on the developments in catalyst design.

Himont introduced the Spherilene process as a low-cost gas phase technology for polyethylene using a spherical $MgCl_2$-supported catalyst to control the polymer morphology on a level similar to the polypropylene gas phase processes [31]. The polyethylene

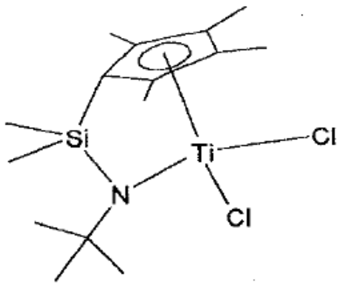

Figure 3 Structure of a constrained geometry metallocene, which if combined with a suitable cocatalysts enables the production of ethylene/α-olefin copolymers.

produced has a spherical morphology and a high bulk density. A combination of two gas phase reactors in series allows the synthesis of polymer blends within the production process, making new products available, as well as blends having the properties of polymers produced by another technology. The catalyst and cocatalyst are reacted in a prepolymerization loop in a diluent slurry to achieve morphology and mileage control. Two gas phase reactors separated by a hook loop are used for the production of the polymer, which is stabilized and bagged downstream; pelletization is optional but not necessary due to the spherical form of the polymer.

Another new technology that improves the capacity of the existing plants has been introduced by Exxon [32] utilizing the following advantages of metallocene catalysts: (1) good comonomer incorporation; (2) homogeneous composition; and (3) high activity of the copolymerization. In gas phase polymerization, the reactor capacity is mainly determined by the heat removal capability of the gas stream circulated. Thus, capacity is dependent on the recycle gas composition and the physical properties of the reactant determine the following: (1) gas phase density (the higher the density, the more gas is circulated); (2) gas dew point (control is necessary to keep the fluidized bed free of liquid); and (3) reactor temperature (higher temperature allows higher dew points, increasing the heat removal capacity). Hence by injecting the reactants as condensed phase it is possible to utilize their heat of vaporization to increase the plant capacity. By controlling the density of the fluidized bed, it is possible to increase the amount of liquid above 10 wt % per cycle without the formation of hot spots, lumps, or instabilities of the reactor (supercondensed mode technology). The capacity of the plant, as well as the product range, may be improved further by using a metallocene catalysts. The better comonomer incorporation allows lower comonomer concentrations, and the better response to molecular weight regulation by hydrogen leads to a decrease in hydrogen concentration by a factor of 100. Thus more condensing agent may be added improving the density as well as the heat removal capacity. The narrow molecular weight distribution and the uniform composition of the copolymer allow higher temperatures because of the absence of a low-molecular-weight, high-comonomer-content fraction that would become sticky at elevated temperatures. It is possible to increase the capacity of a plant by a factor of up to 2 with this technology and at the same time broaden the product envelope significantly by incorporating additional comonomer and utilizing comonomers like hexene and octene for the gas phase processes.

III. POLYPROPYLENE

A. Catalyst Development

Metallocene catalysts for the production of LLDPEs have been commercially operational since 1991, whereas the commercialization of polypropylene produced by metallocene catalysts began in 1995 (see Table 3). The fact that production of LLDPEs was a little ahead of that of polypropylene (PP) may be attributed to the difficulties metallocene catalysts had in the beginning in competing with high mileage Ziegler–Natta catalysts. Today the catalytic properties of metallocene catalysts in terms of isospecificity, molecular mass, productivity, as well as the possibility to tailor the polymer products microstructure within a broad range, promises to be a positive market for metallocene iPP grades. The tailoring of the microstructure by choosing the appropriate metallocene will enhance the use of metallocenes for the production of special iPPs, syndiotactic polypropylene (sPP), and high-molecular-weight atactic polypropylene (aPP).

Table 3 Status of Commercialization of Metallocene-Based Products in 1995

Company	Capacity (kt/y)	Location
	Ethylene/α-olefin copolymers	
Dow	112	USA
	56	Spain
Exxon	100	USA
	15	USA
Mitsubishi Yuka	100	Japan
Nippon Petrochemical	100	Japan
Ube Industries	20	Japan
Total	453	
	Isotactic polypropylene	
BASF	12	Germany
Chisso	20	Japan
Exxon	100	USA
Hoechst	100	Germany
Mitsui	75	Japan
Total	307	

Source: Catalyst Consultants.

Achiral metallocenes like $C_{p2}ZrCl_2$ or $[Me_2Si(Flu)_2]ZrCl_2$ produce aPPs. The polymerization is not stereo- but regioselective due to the bent structure of the tetrahedral active complex favoring 1,2 insertions (2,1 misinsertions are barely detectable). Up to now, only low-molecular-weight aPP wax was known and it was used as additive in bitumen and adhesives. This aPP has a broad molecular weight distribution and is produced by solvent extraction of the iPP, which is normally prepared by Ziegler–Natta catalysts. Using metallocene catalysts, aPPs, which cover the whole range of molecular weights of technical interest with narrow molecular weight distributions, can be produced. The main characteristics of the high-molecular-weight aPP produced by $[Me_2Si(Flu)_2]ZrCl_2$ are low density, high transparency, softness, low modulus, and high elongation occasioned by the totally amorphous state of the polymer [33]. High-molecular-weight aPP has potential applications in blends with other polyolefins for upgrading transparency, softness, elastic recovery, and elongation (see Table 4).

For stereospecific polymerization of α-olefins like propylene, a chiral active center is needed, giving rise to diastereotopic transition states when combined with the prochiral monomer. This results in a different set of activation energies for the insertion. Stereospecificity may arise from the chiral β-carbon atom at the terminal monomer unit of the growing chain (chain and control) or from a chiral catalyst site (enantiomorphic site control). The microstructure of the polymer produced depends on the mechanism of stereocontrol as well as on the metallocene used.

The first chiral-bridged zirconocene synthesized in 1984 by Brintzinger and used as an isospecific polymerization catalyst by Kaminsky was racemic ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride [34–36]. Ewen showed that the analogous ethylenebis(1-indenyl)titanium dichloride (a mixture of the meso form and racemate) produces a mixture of isotactic and atactic polypropylene [37]. The chiral titanocene as well as the zirconocene were shown to work by enantiomorphic site control. As for the titanocene, the achiral meso structure causes the formation of atactic polymer (see Fig. 4).

Table 4 Comparison of Low-Molecular-Weight Atactic Polypropene from Solvent Extraction of a Polymer Produced Using a Conventional $TiCl_4/MgCl_2$ Catalyst with Two High-Molecular-Weight Atactic Polypropenes of Different Molecular Weight Prepared by Using $[Me_2Si(Flu)_2]ZrCl_2/MAO$[a]

Property	Low-molecular-weight aPP	High-molecular-weight aPP		iPP
Intrinsic viscosity (dl/g)	0.4	1.4	2.7	2.3
Melt index (dg/min)	670	7	0.1	1.8
$M_w \times 10^{-3}$ (g/mol)	29	200	490	520
M_w/M_n	6	3.3	2.3	8
Density (g/cm^3)	0.8626	0.8606	0.8550	0.9031
Shore A hardness (°shore)	67	50	55	—
Haze (%)	58	20	18	85
Modulus (MPa)	10	8	5	1650
Strength at break (MPa)	1	1	2	20
Elongation at break (%)	110	1400	2000	300

[a] For comparison, the typical data of an isotactic polypropene prepared by using a conventional catalyst are also given.

Due to the fact that the polymer chain migrates during insertion, the symmetry of the metallocene is of fundamental importance to the tacticity of the polymer produced. C_2-symmetrical metallocenes like the bridged bis(indenyl) compounds mentioned above have homotopic coordination sites and thereby always favor the same orientation of the prochiral monomer during the approach. This leads to the formation of an isotactic polymer (see Fig. 5).

The properties and melting point of isotactic polypropenes prepared by metallocene catalysts are determined by the amount of irregularities (stereo and regioerrors) randomly distributed along the polymer chain. Thus the term *stereospecificity* does not refer to the extractable aPP, which contributes to the fact that conventional iPP always has a melting point of 160–165°C. Depending on their substitution pattern, metallocene catalysts can give a wide range of homopolymers having melting points between 125°C and 165°C (see Table 5).

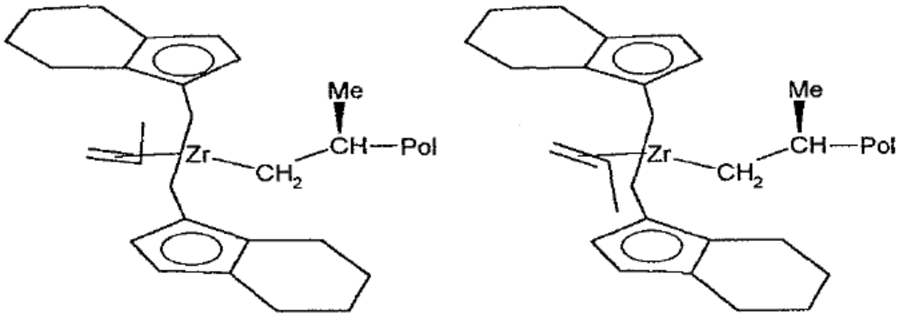

Figure 4 Origin of the stereospecificity of C_2-symmetrical bis(indenyl)zirconocene catalysts. The orientation shown on the right is favored over the one shown left due to nonbonding interaction of the approaching monomer and the ligand.

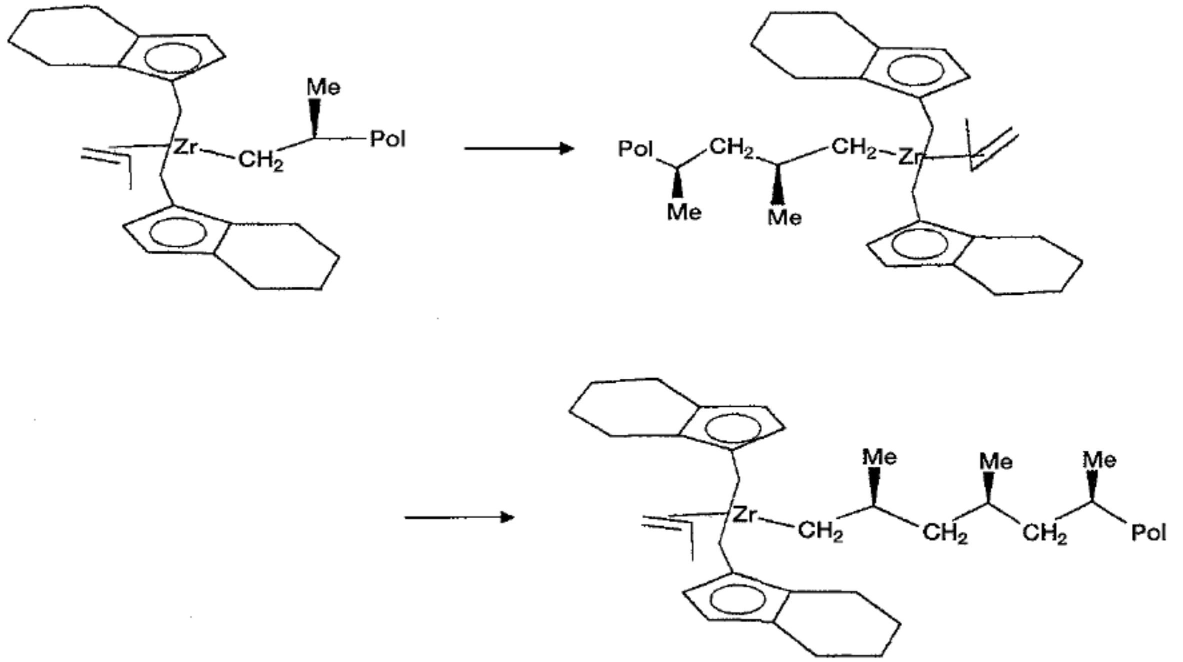

Figure 5 Mechanism of the isotactic polymerization of propylene using an alkylzirconocenium ion generated from a C_2-symmetrical bis(indenyl)zirconocene.

The molecular weight distribution of these iPPs (M_w/M_n = 2–2.5) is still lower than that of conventional controlled rheology grade obtained by peroxide degradation (M_w/M_n = 3–4). Its processing performance by thin-wall molding or fiber spinning is good. For applications demanding broader molecular weight distributions, two or more metallocenes may be combined to give a tailor-made molecular weight distribution. Compared with the conventional iPP grades metallocene products possess enhanced mechanical strength, which could be further improved by tailoring the molecular weight distribution.

The state-of-the-art metallocenes are supported on silica treated with MAO [38,39]. They operate at low Al/Zr ratios and are used in gas phase processes [40]. These catalysts are free-floating powders. With these catalysts polymer particle morphology control is possible and could match conventional systems with particle diameters of several hundred millimeters with narrow particle size distribution and bulk densities above 0.45 g/cm^3 (see Table 6).

The low melting points obtained with some metallocene catalysts even at high pentad isotacticities are caused by the 2,1 and 1,3 misinsertions [41,42]. Low-melting-point polymers with conventional catalysts are obtained by copolymerization with small amounts of ethylene. A comparison of a conventionally produced polymer having the same melt flow rate and low melting point as a metallocene copolymer and a metallocene homopolymer illustrates the enhanced stiffness and transparency of the metallocene product (see Table 7). The most important feature is the low amount of extractables, which makes it possible for the polypropylenes to be used for food wrapping and other applications even at cooking temperature.

The excellent performance of metallocenes in copolymerizations also offers improvements in impact copolymers. Among the wide variety of properties of impact copolymers,

Table 5 Comparison of the Productivity, Molecular Weight, Melting Point, and Isotacticity Obtained in Polymerization Experiments with Various Metallocene/MAO Catalysts Showing Broad Range of Product Properties[a]

Metallocene	Productivity [kgPP/(mmolZr*h)]	$M_w \times 10^{-3}$ (g/mol)	m.p. (°C)	Isotacticity (% mmmm)
$[En(Ind)_2]ZrCl_2$	188	24	132	78.5
$[Me_2Si(Ind)_2]ZrCl_2$	190	36	137	81.7
$[Me_2Si(IndH_4)_2]ZrCl_2$	48	24	141	84.5
$[Me_2Si(2Me\text{-}Ind)_2]ZrCl_2$	99	195	145	88.5
$[Me_2Si(2Me\text{-}4iPr\text{-}Ind)_2]ZrCl_2$	245	213	150	88.6
$[Me_2Si(2,4Me_2\text{-}Cp)_2]ZrCl_2$	97	31	149	89.2
$[Me_2Si(2Me\text{-}4tBu\text{-}Cp)_2]ZrCl_2$	10	19	155	94.3
$[Me_2Si(2Me\text{-}4,5BenzInd)_2]ZrCl_2$	403	330	146	88.7
$[Me_2Si(2Me\text{-}4Ph\text{-}Ind)_2]ZrCl_2$	755	729	157	95.2
$[Me_2Ge(2Me\text{-}4Ph\text{-}Ind)_2]ZrCl_2$	750	1135	158	—
$[Me_2Si(2Me\text{-}4Naph\text{-}Ind)_2]ZrCl_2$	875	920	161	99.1

[a]Conditions: Bulk polymerization in liquid propylene at 70°C, Al/Zr ratio 15,000.
Source: Ref. 65.

it is safe to say that the stiffness of the material is determined by the matrix material, whereas the impact resistance depends largely on the elastomeric ethylene/propylene rubber (EPR) phase. While conventional catalysts have some inhomogeneities in the EPR phase due to crystalline ethylene–rich sequences, the more homogeneous comonomer distribution obtained with metallocene catalysts results in a totally amorphous EPR phase [43].

Metallocenes are also of interest for the production of new iPP waxes for use as pigment dispersants, toner, or laquer surfaces [44]. With an appropriate choice of metallocene, it is possible to prepare iPP with molecular weights ranging between 10,000 and 70,000 g/mol and with melting points ranging between 140°C and 160°C. With conventional catalysts, hydrogen or polymer degradation is used to control the molecular weight while the melting point is controlled by the addition of a comonomer. As illustrated in Table 8, metallocene catalyst offers property combinations not accessible with conven-

Table 6 Comparison of Isotactic Polypropylenes Prepared by Different Metallocene/MAO Catalysts — $[En(IndH_4)_2]ZrCl_2$ (I), $[Me_2Si(4,5BenzInd)_2]ZrCl_2$ (II), $[Me_2Si(4,6iPrInd)_2]ZrCl_2$ (III) — at 70°C in a 1l Bulk Polymerization at Al/Zr = 15,000 to Conventional Isotactic PP Prepared by a $TiCl_4/MgCl_2$ Catalysts (IV)

Property	(I)	(II)	(III)	(IV)
Melting point (°C)	139	151	160	162
M_w/M_n	2.2	2.3	2.5	5.8
Tensile modulus (N/mm^2)	1060	1440	1620	1190
Hardness (N/mm^2)	59	78	86	76
Impact resistance Izod (mJ/mm^2)	128	86	100	103
Light transmission (% 1-mm plate)	56	44	35	34
Melt flow rate (°/min)	2	2	2	2

Source: Ref. 47.

Table 7 Comparison of Low-Melting-Point Polymers Obtained by Copolymerization Using a Conventional Catalyst, a Metallocene Catalyst, and by Homopolymerization Using a Metallocene Catalyst

Property	Conv. copolymer	Metallocene copolymer	Metallocene homopolymer
Melting point (°C)	141	140	142
Tensile modulus (N/mm^2)	620	940	1120
Hardness (N/mm^2)	41	59	65
Impact resistance Izod (mJ/mm^2)	23.1	11.3	7.3
Light transmission (% 1-mm plate)	57	65	48
Extracables (% hexane, 69°C)	7.9	1.1	0.7

Source: Ref. 43.

tional systems. For example, the vinyl end groups of the metallocene products may be utilized for functionalization whereas with conventional catalysts only saturated end groups are formed due to the high amount of hydrogen used for molecular weight regulation. With conventional catalysts, the reactor normally has to be run under nonoptimal conditions (high temperature, high hydrogen pressure → lower productivity) to obtain the desired product. There is also the problem of decreased output rate, which is necessitated by the difficulty of condensing the hydrogen/propylene feed with its large amount of hydrogen coupled with the low heat removal capacity of these mixtures. If run at optimum conditions, polymer degradation with expensive peroxides must be used to control the molecular weight. Metallocenes avoid these difficulties and thereby enable process simplification (see Table 8).

Table 8 Isotactic Polypropylene Waxes Prepared by $[Me_2Si(2Me\text{-}4tBuCp)_2]ZrCl_2/MAO$ (I), $[Me_2Si(IndH_4)_2]ZrCl_2/MAO$ (II) Compared to Waxes Produced by Conventional Catalysts via Molecular Weight Regulation by Hydrogen (III) or Visbreaking of PP Random Copolymers (IV) or Homopolymers (V)

Property	(I)	(II)	(III)	(IV)	(V)
$M_w \times 10^{-3}$ (g/mol)	68	50	40	44	36
M_w/M_n	1.8	2.0	3.8	2.2	1.9
C_2/C_4 (%)	—	—	—	4.0/2.4	—
m.p. (°C)	163	133	159	133	155
Crystallinity (%)	69	50	60	30	59
Isotacticity (mmmm %)	96	85	91	80	91
Double bonds/chain	0.5–1	1	0	4	5
Misinsertions/1000 C	1.7 1,3 0.2 2,1	4.7 1,3 0.3 2.1	0.3 2.1	19 C_2 7 C_4	n.d.
Melt viscosity (200°C) (mm^2/s)	2800	2521	900	1684	1040
Hardness (bar)	2000	874	1800	423	1870
Yellowness index	0.5	0.8	1	5–6	1–2
Dropping point (°C)	168	147	160	149	169
Congealing temp. (°C)	n.d.	113	117	102	124

Source: Ref. 47.

Table 9 Syndiotactic Polypropylenes Prepared by Different Metallocene Catalysts

Metallocene	Productivity [kgPP/(mmolZr*h)]	Intrinsic viscosity (dl/g)	m.p. (°C)	Syndiotacticity (rrrr %)
$[Me_2C(Flu)(Cp)]ZrCl_2$	81	0.82	137	—
$[Ph_2C(Flu)(Cp)]ZrCl_2$	37	2.35	132	0.895
$Me_2C(2,7tBu_2\text{-}Flu)(Cp)]ZrCl_2$	45	0.81	134	—

Source: Ref. 47.

Using C_s-symmetrical metallocenes, the production of syndiotactic polymers is possible due to enantiotopic vacancies formed by the chain migratory insertion [45,46,47] during polymerization (see Table 9).

Syndiotactic polypropylenes produced by metallocene catalysts show a higher level of irregularities than isotactic ones. Comparing samples of the same degree of tacticity the syndiotactic polymer exhibits a lower melting point, lower density (strongly depending on the tacticity, ranging from 0.87 to 0.89 g/cm^3), lower crystallinity, and a lower crystallization rate [48]. The smaller crystal size in syndiotactic polypropylene enables a higher clarity of the material but is also responsible for its inferior gas barrier properties preventing applications in food packaging. On the other hand, its strong resistance to radiation allows medical applications. Other advantages of sPP are the higher viscous and elastic modulus at high shear rates and its outstanding impact strength which disappears at low temperatures because of the independence of the glass transition temperature from tacticity (see Table 10).

Commercial production of syndiotactic polypropylene utilizes a silica supported metallocene in a bulk suspension process at 50 to 70°C and a pressure of 30 kg/cm^2 [49].

The combination of flexibility, clarity, and tensile strength as well as the low heat seal temperatures enables syndiotactic polypropylenes to be used instead of PVC, EVA, and LLDPE in films, foils, and extruder products [30] (see Table 11).

B. Product Development

Reactor granules of spherical morphology were introduced in the 1980s. These products do not need to be melt-extruded [50,51]. Using two reactors in series facilitates the production of reactor blends by transferring the homopolymer-containing active catalyst to a second reactor where an EPR phase is produced. Combination of the products of different

Table 10 Comparison of Isotactic and Syndiotactic Polypropylenes of the Same Stereoregularities Prepared by Metallocene Catalysts

Property	$[Me_2Si(Ind)_2]ZrCl_2$	$[Me_2C(Flu)(CP)]ZrCl_2$
Tacticity	Iso	Syndio
mmmm%/rrrr%	83.1	83.6
Niso/nsyn	33	25
m.p. (°C)	138.4	133.2
Crystallinity DSC (%)	41.6	27.2
MFI 230/5	16.4	21.1
Density	0.899	0.885

Table 11 Mechanical Properties of Syndiotactic Polypropylene Compared to a Random Ethylene-Propylene Copolymer

Property	Syndiotactic PP	Random copolymer
Melt index (g/10 min)	3.0	8.0
Haze (%)	1.7	3.0
Tensile modulus (MPa)	61	60
Impact strength (kJ/m^2)	80	90
Heat seal temp. at 120 g/cm (°C)	135	138
Heat seal temp. at 200 g/cm (°C)	137	143

Source: Ref. 30.

composition in the two reactors allows the synthesis of a broad range of products having medium to ''superhigh'' impact strength. By replacing the polypropylene homopolymer of these blends with a random copolymer matrix the flexibility and tensile strength at low temperatures are enhanced but the melting point and stiffness are decreased. Blending of these copolymers with the soft LLDPE results in a soft polypropylene with tensile-modulus less than 100 MPa, which may replace thermoplastic elastomers like EVA, PVC, and SEBS [52].

Using highly stereoselective catalysts (heterogeneous high-mileage Ziegler–Natta types or metallocenes), highly crystalline and stiff polypropylenes are produced. These polymers exhibit a stiffness that is 25–30% above that of conventional polypropylene, resembling that of polypropylenes filled with talc or other minerals [53]. Packages made from these polypropylenes may have reduced wall thicknesses, are easier to recycle, and show enhanced impact strength, heat resistance, lower density, and lifetime stability (see Table 12).

IV. POLY(CYCLOOLEFINS)

A. Homopolymers

Strained cyclic olefins like cyclobutene, cyclopentene, and norbornene can be used as monomers and comonomers in a wide variety of polymers. Generally they can be polymerized by ring-opening polymerization (ROMP) featuring elastomeric materials or by double-bond opening (vinyl polymerization). Homopolymerization of cyclic olefins by

Table 12 Mechanical Properties of Highly Stiff Polypropylene Compared to Normal Materials

Property	pp homopolymer		pp-block copolymer	
Stiffness	High	Normal	High	Normal
Application	Thermoforming		Thin wall injection molding	
MFR 230/2.16	3.5	3.5	58	45
e Modulus (MPa)	1950	1500	1550	1350
Tensile strength (MPa)	38	35	29	26
Izod impact strength at 23°C/−30°C (kJ/m)	85/10	80/15	70/25	110/30
HDT A/B (°C)	60/108	55/85	57/98	53/90

Source: Ref. 56.

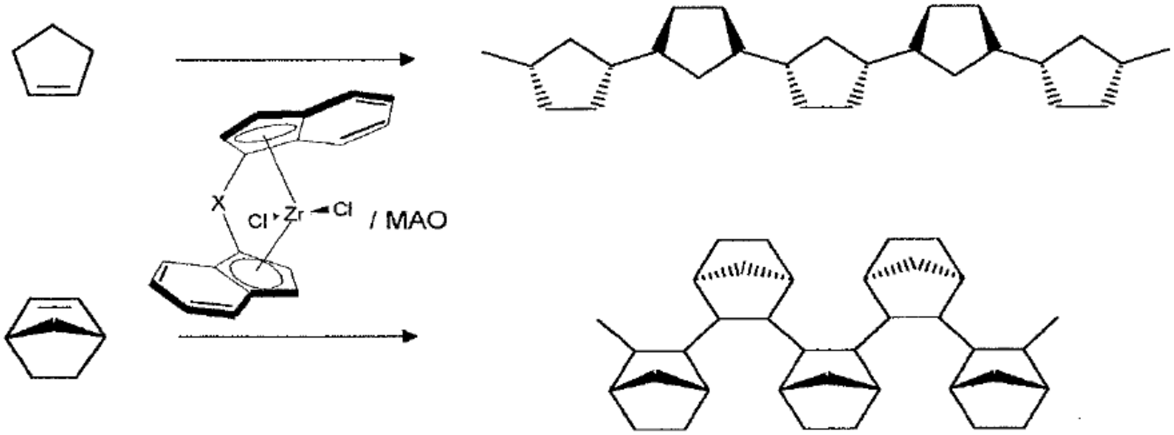

Figure 6 Polymerization of cyclopentene and norbornene to erythrodiisotactic polymers by using *rac*-[En(Ind)$_2$]ZrCl$_2$/MAO.

double-bond opening is achieved by several transition metal catalysts, i.e., palladium catalysts and metallocene catalysts (see Fig. 6).

The polymers feature two chiral centers per monomer unit and therefore are ditactic. While polymers produced by achiral palladium catalysts seem to be atactic using chiral metallocene catalysts, highly tactic, crystalline materials could be produced featuring extraordinary high melting points (in some cases above the decomposition temperature) and extreme chemical resistance. The microstructures of those polymers have been investigated using oligomers as models. Norbornene was shown to polymerize via cis-exo insertion [54,55], whereas in the case of cyclopentene quite unusual cis- and trans-1,3 enchainment of the monomer units is observed [55–58].

B. Cycloolefin Copolymers (COCs)

The homopolymers of cycloolefins like norbornene or tetracyclododecene are barely processable due to their high glass transition temperatures and their insolubility in common organic solvents. By copolymerizing these cyclic olefins with ethylene or α-olefins, cycloolefin copolymers (COCs) are produced representing a new class of thermoplastic amorphous materials [59–61]. Early attempts to produce such copolymers were made using heterogeneous $TiCl_4/AlEt_2Cl$ catalysts. In the 1980s vanadium catalysts were used for the copolymerization, but real progress was made utilizing metallocene catalysts for this purpose. Metallocenes are about 10 times more active than vanadium systems and, by judicious choice of the metallocene, the comonomer distribution may be varied from statistical to alternating. Statistical copolymers are amorphous if more than 15 mol % of cycloolefin is incorporated in the polymer chain. The glass transition temperature can be varied over a wide range by appropriate choice of the cycloolefin with the amount of cycloolefin incorporated in the polymer chain. As for the ethylene/norbornene copolymerization, it is possible to produce copolymers showing molecular weight distributions of M_w/M_n = 1.1–1.4 by controlling the polymerization conditions [62]. This ''pseudo–living polymerization'' enables the production of block copolymers by changing the feed composition. Statistical copolymers are transparent due to their amorphous character; they are colorless and show a high optical anisotropy. Because of their high carbon/hydrogen ratio, these polymers have a high refractive index (1.53 for an ethylene/norbornene co-

Table 13 Properties of a Random Ethylene Norbornene Copolymer Containing 52 mol % of Norbornene

Mechanical Properties	
Density (g/cm^3)	1.02
Glass transition temperature (°C)	150
Tensile modulus, ISO 527 (MPa)	3100
Tensile strength, ISO 527 (MPa)	66
Elongation at break, ISO 527 (%)	2–3
Optical Properties	
Clarity	White, clear
Anisotropy	Very low
Refractive index	1.53

Source: Ref. 66.

polymer at 50 mol % incorporation; see Table 13). Their stability against hydrolysis and chemical degradation in combination with their stiffness and very good processability makes them potential materials for optical applications for example in compact disks, lenses, and optical fibers [63].

The ethylene/norbornene alternating copolymer has a glass transition temperature of 130°C and a melting point of 295°C, and thermoplastic processing is possible at 300–330°C. Its melting point as well as its crystallinity may be influenced by the choice of the metallocene and polymerization conditions. Compared to the statistical copolymers, the alternating structures are characterized by better heat resistance and are unaffected by nonpolar solvents. The diameter of the crystallites is about 0.05–1 mm; thus these copolymers are transparent. Similar alternating structures could be obtained by the ring-opening polymerization of multicyclic polyolefins followed by hydrogenation of the unsaturated polymer.

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