POLYPROPYLENE

1. Introduction

Polypropylene is one of the most important of all plastic materials. Its use has grown rapidly since its discovery in 1954 by Nobel Prize winner, G. Natta, at the Politecnico di Milano University. Today, polypropylene demand is about 40 milion t/y with a market share, among all the thermoplastic material, of about 26%, second only to polyethylene, which represents 39% of the market share. The expected annual growth in the next ten years is about 6%.

The high molecular weight of the polymers and their chain structure was discovered around 1920. During the 1930s several plastics reached commercial status, and consequently, the characterization tools were developed and improved greatly. The concept of a stereoregular polymer chain was largely ignored and discussion of stereoregularity occurred only among a few of the more theoretical chemists. In 1942, Bunn predicted the helical form of crystalline polypropylene (PP), but this theory remained unknown until Natta's publication on crystalline PP 13 years later. In 1930, low level of crystallinity was observed in several polymers, but no thorough investigation was done. By 1950, chemists were familiar with crystalline polyethylene, and high branched LDPE had sufficient linear sections for a moderate level of crystallinity Crystalline PP was never observed on any scale.

Polymerization of propylene proceeded without any specific order and high molecular weight material could not be achieved.

Ethylene is symmetrical, and the orientation of the monomer entering the growing macromolecule to produce a crystalline material does not need regulation. Only branching affects the crystallizability of the high molecular weight ethylene homopolymer. In contrast, the observation of the isotactic PP chain in the PP crystal obtained from the asymmetric polypropylene molecule was a demonstration of stereoregular polymerization with no branching.

In 1950, Ziegler worked on the growth of alkyl chains by the insertion of ethylene into the Al–C bond of trialkyl aluminium. Several people were interested in the results of this research and took out early licenses based on the Ziegler discoveries.

One of these people was Giulio Natta of the Politecnico di Milano University who was sponsored by Montecatini.

While Ziegler mainly focused in the field of polyethylene, Natta tried to polymerize propylene from the start and succeeded in March 1954. Natta's reaserch group fractionated the polymer obtained and found that 40% of the material obtained was a hard, high melting insoluble fraction. The separated fraction was characterized very high crystallinity. They identified the helical chain crystal structure and recognized the role of stereoregular polymerization in achieving this structure. In 1963, Ziegler and Natta shared the Nobel Prize for chemistry, Ziegler for having discovered the basic catalyst system for the polymerization of ethylene and Natta for having discovered the catalyst to control the propylene polymerization.

Soon after Natta's discovery, the first industrial plant was set up by Montecatini in Ferrara and production of polypropylene started in 1956.

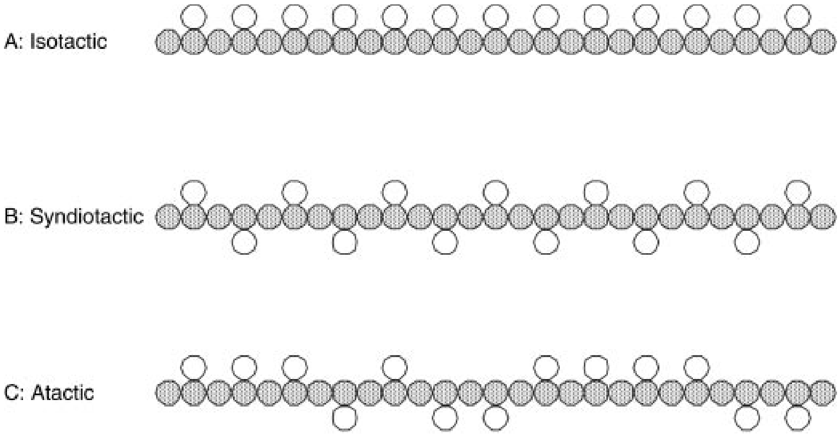


Fig. 1. Polypropylene structural chain: Isotactic, syndiotactic and atactic.

2. Properties

The polymerization of propylene ($CH_2 = CH - CH_3$) generates polymers with different characteristics according to the position of the methyl group in the long polymer chain.

Other monomers do not show such behavior, for example, ethylene ($CH_2=CH_2$), is symmetrical and there is no difference in the way each monomer unit links to the other.

Propylene can polymerize into three distinct structural chains: isotactic, syndiotactic, and atactic (Fig. 1).

Isotactic PP occurs when all of the methyl groups are arranged on the same side of the carbon chain and attached to every other carbon atom.

Syndiotactic PP occurs when the methyl groups are attached to every other carbon atom in the chain, but are located on alternating sides of the chain.

Atactic PP occurs when the methyl groups are *randomly* dispersed along the carbon chain. Properties of various propylene forms are given in Tables 1–4.

3. Process Chemistry and Thermodynamics

3.1. Homopolymer.

The polymerization of propylene with various heterogeneous catalyst systems in hydrocarbon diluent, bulk liquid phase or gas phase may result in isotactic polypropylene.

In polypropylene homopolymers, the balance between atactic and isotactic fractions directly impacts several critical properties such as stiffness and resistance to impact, and these properties are of primary interest when discussing polymer chemistry. Production of syndiotactic polypropylene requires a specialized catalyst and donor systems, and are not yet fully used commercially.

Table 1. **Properties of Homopolymers**[a]

Properties	Test	Extrusion, sheet	General-purpose injection molding		Injection molding thin complex parts	
melt flow, g/10 min	ISO1133	0.7	3.2	12	20	35
density, g/cm^3	ISO1183	0.9	0.9	0.9	0.9	0.905
tensile strength,[b] MPa[c]	ISO527-1-2	33	34	35	41	36
elongation,[b] %	ISOR527	14	13	13	7	
flexural modulus 1% secant, MPa[c]	ISO178	1400	1450	1550	2300	1600
Rockwell hardness, R scale	ASTM785	100	102	102	111	102
deflection temperature at 455 kPa,[d] °C	ISO75/B	100	110	117	110	95
notched Izod impact at 23°C, kJ/m^2[e]	ISO179/1A	6	5	3.5	2	2

[a] Ref. 1.

[b] At yield.

[c] To convert MPa to psi, multiply by 145.

[d] To convert kPa to psi, multiply by 0.145.

[e] To convert J/m to ft·lb/in., divide by 53.38.

Catalyst Systems. The catalyst systems are composed of three basic parts: (*1*) a solid catalyst, generally $TiCl_4$ supported on $MgCl_2$ or silica, (*2*) stereoregulating agents, an internal and external Lewis base, and (*3*) an aluminium alkyl.

The catalyst is composed of two main elements: a transition metal salt and an inert support structure.

The $MgCl_2$ support structure of the catalyst has several roles. It creates a highly disorganized crystalline structure. Thus, the active centers where polymerization takes place are greater in number and reactivity than those of other conventional catalysts. This explains the high activity of these catalyst systems. $MgCl_2$ contributes indirectly to the stereospecificity due to interactions with the donor. Finally, due to its chemical-physical properties, $MgCl_2$ can be converted into particles with controlled shapes and sizes. These characteristics are also transferred to the catalyst and to the polymer.

The active part of the catalyst is titanium tetrachloride ($TiCl_4$). In this form, the catalyst will not polymerize and requires "activation" by an aluminium alkyl and a Lewis Base.

The rapid and successful commercialization of polypropylene manufacturing is primarily due to the continuous development of new and improved catalysts. Each evolution or generation of catalysts both reduced the complexity of the manufacturing process and expanded the control over resin morphology. A brief summary of PP catalyst evolution is shown in Table 5.

Table 2. **Properties of Impact-Resistant Copolymers**[a]

	Medium impact			High impact	
Properties	Extrusion, sheet	Injection molding	Injection molding, thin parts	Injection molding	Blush resistance
melt flow, g/10 min	0.8	3.5	100	3.5	22
density, g/cm^3	0.9	0.9	0.9	0.901	0.902
tensile strength,[b] MPa[c]	26	29	30	29	23
elongation,[b] %	16	10	4	11	7
flexural modulus 1% secant, MPa[c]	110	1400	1750	950	1000
Rockwell hardness, R scale	80	94	105	80	75
deflection temperature at 455 kPa,[d] °C	88	93	100	75	83
notched Izod impact at 23°C, kJ/m^2[e]	50	11	2.5	60	8

See Table 1 for what test was used.

[a] Ref. 1.

[b] At yield.

[c] To convert MPa to psi, multiply by 145.

[d] To convert kPa to psi, multiply by 0.145.

[e] To convert J/m to ft·lb/in., divide by 53.38.

The polymer flake size and shape is a large copy of the size and shape of the catalyst particle. Average diameter of the polymer particles depends on the average diameter of the catalyst and on the polymerization mileage.

Mileage. While catalyst performance or yield has been clearly and precisely defined, the unit "Zieglers" is generally not used in manufacturing plants. The more generic and slightly less precise term—mileage—is commonly accepted as the unit for measuring and comparing performance. Mileage is defined as the kilograms of PP produced per gram of catalyst.

Propane concentration has an effect on catalyst mileage. Increasing propane concentration reduces mileage as the concentration of propylene at the catalyst's active sites is decreased. Comparison of mileage results must always be made based on results using the same polymerization basis.

The activity of a catalyst is its tendency and capability to polymerize propylene (and other comonomers) under standard conditions. Activity is measured in units called Zieglers. One Ziegler is defined as one gram of polymer per millimole of $TiCl_3$ per atmosphere of propylene pressure per hour.

Several catalysts can be used in the Spheripol technology, each tailored according the final application of the polymer. Catalyst can be granular or spherical form (Fig. 2). It can be tailored to have very high isotactic index, very high mileage, and quite broad or narrow molecular weight distribution

Table 3. **Properties of Filled Polypropylenes**[a]

		Talc filled				Calcium carbonate filled			
Properties	ASTM test	Homopolymer		Copolymer		Homopolymer		Copolymer	
filler, wt %		20	40	20	40	20	40	20	40
melt flow, g/10 min	D1238L	4	4	4	4	4	4	4	4
density, g/cm^3	D792A-2	1.05	1.22	1.04	1.22	1.05	1.22	1.03	1.20
tensile strength,[b] MPa[c]	D638	34.5	32	27	25	32	25.5	25.5	21
flexural modulus 1% secant, MPa[c]	D790B	2550	3400	2100	2700	2300	2750	1800	2200
Rockwell hardness, R scale	D785A	98	97	90	85	98	97	88	87
deflection temperature at 455 kPa,[d] °C	D648	125	134	117	127	113	113	98	104
notched Izod impact at 23°C, J/m[e]	D256A	37	37	80	37	48	43	91	69

[a] Ref. 2.

[b] At yield.

[c] To convert MPa to psi, multiply by 145.

[d] To convert kPa to psi, multiply by 0.145.

[e] To convert J/m to ft·lb/in., divide by 53.38.

Table 4. **Properties of Random Copolymer**[a]

Properties	Blow molding	Injection molding[b]	Film
melt flow, g/10 min	1.8	25	9
density, g/cm^3	0.901	0.905	0.9
tensile strength,[c] MPa[d]	25	29	27
elongation,[c] %	14	12	12
flexural modulus 1% secant, MPa[d]	1000	1150	950
Rockwell hardness, R scale	85	94	
deflection temperature at 455 kPa,[e] °C	90	80	73
notched Izod impact at 23°C, kJ/m^2[f]	11	4	4

See Table 1 for what test was used.

[a] Ref. 1.

[b] High clarity resin.

[c] At yield.

[d] To convert MPa to psi, multiply by 145.

[e] To convert kPa to psi, multiply by 0.145.

[f] To convert J/m to ft·lb/in., divide by 53.38.

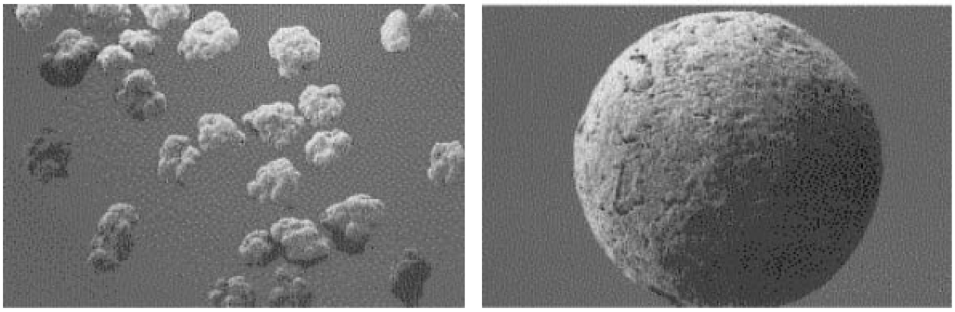
Table 5. **Performance of Different Catalyst Generations**

Generation	Catalyst composition[a]	Yield (kg PP/g Cat)	I.I. wt%	Morphology control	Process requirements
1st	$TiCl_3/AlCl_3 + DEAC$	1	90–94	not possible	deashing + atactic removal
2nd	$TiCl_3 + DEAC$	10–15	94–97	possible	deashing
3rd	$TiCl_4$/ester/$MgCl_2$ + AlR_3/ester	15–30	90–95	possible	atactic removal
4th	$TiCl_4$/diester/$MgCl_2$ + TEA/silane (HY/HS)	30–60	95–99	possible	
5th	$TiCl_4$/diether/ $MgCl_2$ + TEA	70–120	95–99	possible	
	$TiCl_4$/succinate/ $MgCl_2$ + TEA	40–70	90–99	possible	
6th	Zirconocene + MAO		90–99		

[a] DEAC = diethyl aluminium chloride, TEA = triethyl aluminium, MAO = methylaluminoxane.

etc. Microscopic photos of granular and spherical catalyst particles are depicted in Figure 2.

Replication Factor. The particle size distribution of the PP flake is a replica of the particle size distribution of the catalyst. In the industrial process, a broader PSD flake is obtained than the batch polymerization. More fine particles are produced because of friction in the reactors, flash line, and other processing equipment. Also fines are produced due to a residence time distribution which is different in the batch polymerization compared to the continuous plant process. In the batch polymerization, all the catalyst particles have the same time to grow and make polymer. In the continuous reactor, there is a distribution of residence times. There are particles that stay in the reactor for only few minutes, while others stay for few hours. The ratio between the average diameter of the flake and the diameter of the catalyst is called the replication factor. The replication factor is proportional to the cube root mileage. The higher the



(a) (b)

Fig. 2. Morphology control of the catalyst. (**a**) catalyst for flake, (**b**) spherical catalyst.

mileage, the larger the particle of polymer produced. The replication factor is generally calculated by the formula:

$$[(\mathrm{g\,PP/g\,cat}) \times (2/0.9)]^{1/3}$$

Aluminium Alkyl. Polymerization of olefins with Ziegler-Natta catalyst involves a stepwise insertion of the monomer into a transition metal-carbon bond as follows:

$$\mathrm{Mt} - \mathrm{R} + n\,\mathrm{C{=}C} \rightarrow \mathrm{Mt} - (\mathrm{C} - \mathrm{C})_n - \mathrm{R}$$

Catalysis of propylene requires the presence of an aluminum alkyl. For the polymerization of propylene the most widely used alkyl is triethyl aluminum, $(C_2H_5)_3Al$ or TEAL for short. The activation reaction is as follows:

$$\mathrm{TiCl_4} + (\mathrm{C_2H_5})_3\mathrm{Al}- \rightarrow \mathrm{TiCl_3} + (\mathrm{C_2H_5})_2\mathrm{AlCl} + (\mathrm{C_2H_5})^{\bullet}$$

The reaction is exothermic with a $\Delta H = 131.6$ kcal/kg $TiCl_4$.

In addition to assisting in the polymerization reaction, TEAL acts as a scavenger for certain monomer poisons, most notably water, which would seriously impair or completely stop the reaction. Therefore, TEAL is added to the reaction in amounts greater than the stoichiometric amount required to activate the catalyst. The amount of excess TEAL depends mainly by monomer purity.

Stereoregulation and Isotacticity–Donor Function. During polymerization, olefins can be inserted into the carbon-metal bond in two different orientations. Random insertion will produce a material with high irregularity or atactic structure. Atactic PP is soft and sticky and of little value as a material. The inclusion of a Lewis Base or electron donor into the polymerization reaction greatly increases the regularity at which the olefin molecules are inserted into the polymer chain, producing a highly usable, stereoregular (isotactic) polymer. The electron donors are called “donor” for short. Along with the evolution of catalysts, there has been a parallel evolution of donors.

The degree to which propylene is polymerized in an orderly or stereoregular manner is measured by the amount of crystalline material produced. This is called the isotactic index and is measured as % by weight. In general, homopolymer PP is produced in with isotactic index in the range of 92–99%. The amount of donor controls the isotactic index of the polymer.

Measurement of isotactic index is a fairly complex test, utilizing extraction with boiling heptane. This test has generally been replaced with the measurement of the atactic portion, which uses xylene. More recently magnetic resonance technology has been used. Most plants refer to the atactic portion of the polymer as xylene solubles (XS). While not exactly the same, xylene solubles and isotactic index have been used interchangeably.

Polymer Chain Length Control. The length of the polymer chain has a significant impact on its performance, particularly its flowability. This is a critical parameter for downstream use of the resin. Direct measurement of the polymer chain is difficult and not suited to plant laboratories. Instead, polymer chain length is measured indirectly in several ways. For many years, the intrinsic viscosity (IV) of the polymer was measured. IV results were directly proportional to polymer chain length. That is, the higher the IV, the longer the average chain length.

While still used to some extent during the production of impact copolymers, intrinsic viscosity has been replaced with the much quicker and more repeatable melt flow rate (MFR). As the term implies, MFR is the weight of melted polymer that can flow through a specific orifice, under a standard load, at a given temperature and time.

Standard load = 2.16 kg

Standard temperature = 230°C (for very high MFR products, a lower temperature is used)

Standard time = 10 minutes

As would be expected, MFR results are the inverse of chain length. That is, polymers with long chain length will have a low MFR.

With the development of automated testing machines in the late 1970's, polymer MFR can be measured quickly with high accuracy and repeatability.

Hydrogen is added to the polymerization reaction to control the molecular weight (ie, chain length) of the polymer by acting as a chain-transfer agent. Hydrogen increases the activity of the catalyst. More hydrogen imply shorter chain and higher MFR.

Molecular Weight. *Polymer vs. MFR.* Polymer chain length (or molecular weight) is directly related to MFR. Laboratory work has shown the relationship to be closely approximated by the following formula:

$$\log \mathrm{MW} = -0.2773 \times \log \mathrm{MFR} + 5.7243 (r^2 = 0.9780)$$

MWD of the Polymer. As with all reactions the polymer chain lengths produced are not equal. However, for a given catalyst/donor system, the distribution of chain lengths is constant. Changing reaction temperature, residence time, etc, will not significantly affect the distribution.

A fundamental measurement of the molecular weight distribution (MWD) is gel-permeation chromatography, currently known as size exclusion chromatography, which responds to the physical size of the different molecules in dilute solution. In this technique, the polymer solution is passed over a porous medium from which the different sized molecules elute at different times. The curve of eluted material versus time becomes the molecular weight distribution. From that curve, it is possible to calculate the weight-average molecular MW (M_w) and the number-average MN (M_n). The ratio of these two, M_w/M_n, gives the polydispersity that is a widely used term to describe MWD.

Mathematically:

$$M_n = \frac{\sum n_i M_i}{\sum n_i} \qquad \text{and} \qquad M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

where:

n_i = N° of moles of fraction i
M_i = molecular weight of molecules in fraction i

Because the rheology of PP responds strongly to the MWD, a correlation between the polydispersity from GPC and a rheological parameter, called the polydispersity index (PI), has been established. The PI is considerably easier to determine and is consequently growing in use. Die swell (from the melt flow rate measuring instrument) also corresponds directly to PI, providing a plant a relatively simple method for measuring PI.

The MWD of the polymer plays an important role in the performance of the resin. A narrow MWD is beneficial for fiber applications while a broad MWD improves resin performance in oriented films.

In a multistage process, such as Spheripol, broadening of the MW may be obtained by polymerizing widely different MWs (ie, different melt flow rates) in separate reactor stages, but this approach is limited by the degree to which the different viscosity may be homogenized in the extrusion process. This method of polymerization is called bimodal. In bimodal polymerization it is important that the high molecular weight component be at least 50% of the total. Low molecular weight material can be blended into the high molecular weight material without problem.

Conversely, the addition of alkyl peroxides to the polymer during the extrusion process will cause breaking of longer chain molecules, thus narrowing the MWD. This process is called visbreaking or cracking.

Catalyst Yield. Impact of Residence Time. Catalyst mileage is directly affected by residence time – the period of time in which the catalyst is in the reactors. From its kinetics, the long life of the catalyst allows for a higher residence time and thus the possibility for higher mileage.

All other things being equal, in the Spheripol technology, slurry density in loop reactors shall be maintained as high as possible to maximise the residence time; hence the catalyst mileage. However, there is an upper limit. To have good processability of the slurry, the proper amount of unreacted monomer is needed to keep the polymer well suspended.

The parameter that defines the limit of slurry concentration is the power consumption of the reactor circulating pumps.

Impact of MFR. As discussed previously, the melt flow rate of the polymer is proportional to the amount of hydrogen added to the reaction. As hydrogen acts to increase the reactivity of the catalyst, catalyst mileage is therefore proportional to melt flow rate. When comparing catalyst mileage, it must be done at the same MFR.

In processes polymerizing in gas phase, reactivity increases with hydrogen concentration up to a maximum, then, being hydrogen concentration very high, the partial pressure of propylene is reduced thus reducing the catalyst mileage.

Impact of Propane Concentration. Another important factor affecting catalyst performance is the propane concentration in the reactors. A small amount of propane enters the reactors as part of the propylene feed stream entering the plant battery limits. Obviously, the higher the propane concentration in the reactor, the lower the propylene concentration. Since polymerization rate is a direct function of the active center concentration of the catalyst and the monomer concentration, the higher the propane concentration the lower the reactivity.

Propane entering with the feed monomer does not react. In Spheripol technology, approximately 60% of the monomer entering the reactors is polymerized, with the remaining being separated, recovered and recycled. Thus propane concentration in the reactor builds up with time. The increasing propane level reduces catalyst mileage. In order to prevent a significant loss in mileage, a small stream of propane must be continuously purged. Increasing propane concentration reduces the cost of purged monomer but increases catalyst cost (ie, lower mileage). As such, there is an economic balance point between catalyst mileage and propane level in the reactors. This balance is dependent upon the cost of monomer and the cost of catalyst.

Monomer Quality. The quality of the monomer in the reactors has a great impact on both catalyst mileage and resin quality. Monomer contaminants fall into several general categories, depending upon how they affect the reaction:

The first group of contaminants reacts with the aluminium alkyl co-catalyst and greatly reduces catalyst yield when present at the ppm level. Examples of these materials would be: CO_2, alcohols and H_2O. Water is by far the most common poison of the group.

The second group of contaminants reacts with the active sites of the catalyst and seriously reduces catalyst yield when present at the ppb level. Examples of these poisons are CO, arsine, phosphine, carbonyloxysulfide etc.

The third type of contaminants are hydrogenating compounds, which have a strong effect on the MFR of the polymer and, consequently, on the yield. Some of these will also affect the stereospecificity of the polymer, generally increasing the atactic level.

3.2. Random Copolymers. *Random Factor.* Adding ethylene directly into to the polymerization reactor(s) produces random copolymers. Ethylene molecules are added to the polymer chain at random locations. The higher the concentration of ethylene in the feed, the higher the chance of having two or more ethylene molecules bound between the propylene molecules. The random factor is the ratio between the percentage of single-bound ethylene and the total percentage of bound ethylene. The higher the ethylene concentration in the feed, the lower is the random factor. In other words, increasing the ethylene concentration in the copolymerization reaction increases the probability of having short chain polyethylene between two molecules of propylene. There are no parameters developed to control the random factor. The catalyst inherently produces the random factor. Random copolymers with 1-butene or random terpolymer using 1-butene and ethylene are included in this reaction type.

Polymerization Reaction. To produce random copolymers, ethylene is added directly to the polymerization reactors. The addition of ethylene increases the polymerization rate significantly. This behavior may be accounted for by assuming that propylene insertion in the Ti-carbon bond is easier when an ethylene unit is bonded to the transition metal or that the ethylene insertion after a regio-irregular propylene insertion reactivates a "dormant" site. The reactivity ratio is the ethylene/propylene mole ratio in the polymer divided by the ethylene/propylene ratio in the liquid monomer circulating in the reactor.

Polymer Tacticity. Adding ethylene to the polymer increases the xylene soluble fraction. On average, having 1% ethylene bound in the copolymer gives an increase in xylene soluble fraction of about 1%. Therefore, when making a homopolymer with a 3% xylene soluble fraction, the corresponding 3.5% random copolymer (RACO) would have a total xylene soluble level of 6.5%. This increases the stickiness of the polymer and causes handling and processing problems.

Ethylene does not affect the hydrogen-propylene relationship. That is, the same amount of hydrogen is required to meet a specific MFR for both homopolymer and random copolymer.

The addition of ethylene to the polymer chain lowers the melting point significantly. With 3–4% atactic fraction, homopolymer polypropylene has a melting point of approximately 165°C, while a random copolymer with 2% ethylene bonded has a melting point of about 150°C.

Physical Characteristics of RACO's. The addition of ethylene to the homopolymer chain modifies the physical properties of the resin as follows: increases clarity (beneficial for injection molded applications, such as the type of resins used in food containers); reduces melt temperature (beneficial for some film applications); reduced stiffness; and increased impact resistance (at moderate temperatures).

3.3. Heterophasic Copolymers. *Polymer Structure.* Heterophasic copolymers (commonly called impact copolymer or HECO) are an intimate mixture of homopolymer and bipolymers. Bipolymers are mainly amorphous materials produced through polymerizing ethylene and propylene in the gas-phase reactor (GPR) installed downstream of the homoreactors. A homopolymer is produced in the first stage of polymerization. The flake flows to the GPR, where ethylene and propylene are fed in a predetermined ratio. In the GPR, bipolymerization occurs and the bipolymer grows inside the homopolymer sphere. The result is a semicrystalline matrix (homopolymer) with a nearly amorphous elastomeric component (bipolymer) dispersed within it. The final product is "heterophasic" in that it is a mixture of two different products: homopolymer and bipolymer. By fractionation, it is possible to separate the two materials from each other.

Catalyst Requirement. To produce a polymer with the desired characteristics, a proper amount of rubber must be produced in the copolymerization step and, consequently, a long-life catalyst structure showing a high residual activity after the homopolymerization step is needed. Furthermore, the rubber must be retained inside the flake granule and homogeneously dispersed in the homopolymer matrix to prevent undesired reactor fouling. Consequently, a proper catalyst architecture is required. This polymerization technique, in fact, behaves in such a way that the rubber grows around the homopolymer microgranules. The internal voids of the homopolymer granule are occupied by the growing rubber, which, after the pores are filled, migrates to the particle surface. A high porosity is thus required to bear the desired amount of rubber inside the granule and prevent its migration to the surface with consequent reactor fouling and operation problems.

Reactivity Ratio. The bipolymer that is produced with gas of a certain composition of ethylene and propylene will have a different composition than the gas because of the different reactivities of the monomer with the catalyst. Ethylene is more reactive than propylene in the gas phase. Knowing the reactivity ratio and the gas composition, it is possible to calculate the composition of the bipolymer. As a result, a specific bipolymer composition can be produced by controlling the gas ratio in the GPR.

The gas ratio $\frac{(C_2^=)}{(C_2^= + C_3^=)}$ is carefully controlled in order to produce the correct bipolymer composition. Bipolymers have good elastomeric properties, thus, improving the impact resistance of the copolymer, a highly desirable characteristic property.

Control of Physical Properties. With homopolymers, where physical properties play a less important role, only the molecular weight of the polymer (ie MFR) and the amount of atactic material (xylene soluble) are controlled. Hydrogen is used to control the MFR and the Teal/Donor ratio is used to control the level of xylene soluble.

With heterophasic copolymers, the amount and composition of the bipolymer fraction play critical roles in determining the physical properties of the polymer. Physical properties are controlled as shown in Table 6.

Balance of Physical Properties. The critical physical properties of copolymers are MFR, flexural modulus, tensile strength, IZOD impact and dropped weight impact and HDT. In polymeric materials there is a balance between stiffness and resistance to impact. Stiffness must generally be reduced in order to gain impact strength. This relationship holds true within any given copolymer structure. However, it may be possible to somewhat increase both the impact and stiffness by changing either or both the catalyst and donor systems.

Table 7 shows how physical properties are affected by changes in polymer structure. This table should be used as a general guideline only, as the additive package used can influence the final properties of the resin.

Table 6. **Control of Physical Properties of Heterophasic Copolymers**

Physical property/parameter	Is controlled by adjusting
catalyst mileage/activity	slurry density in reactor
MFR of homopolymer	hydrogen concentration in (loop) reactor
XS of homopolymer	T/D ratio in the (loop) reactor
$C_2^=$ content of the copolymer	total $C_2^=$ fed to the GPR
$C_2^=$ content in bipolymer	gas ratio $(C_2/C_2 + C_3)$ in the GPR
I.V. of the bipolymer	hydrogen ratio (H_2/C_2) in the GPR
final MFR of the copolymer	hydrogen ratio (H_2/C_2) in the GPR

Table 7. **Standard Parameters vs. Mechanical and Optical Characteristics**[a,b]

	Action ↑	Unit	Flex modulus	Ball drop			Stress whitening	Tensile yield	Gloss	Hardness	HDT
				Izod	Trans. temp	Enerty					
Homopolymer	melt flow rate	g/10”	↑	↓	↑	↓	↓	↑	↓	↑	↑
	molecular Weight distribution	–	↑	↓	×						
	isotactic index	%	↑	×		×		↑		↑	↑
Ethylene / Propylene Bipolymer	total amount of bipolymer C_3-C_2	%wt	↓	↑	↓	↓	↓	↓	↓	↓	↓
	xylene soluble of bipolymer	%wt	↓	↑	↓	↑	↓	↓	×	↓	↓
	intrinsic viscosity of xylene soluble	dl/g	↓	↑	↓	↑	↑	↓		↓	
	ethylene content in xylene soluble	%wt	↓	↑	↓*	↑					
	xylene insoluble (crystalline bipolymer)	%wt	↓*	↑*	↓*	↑	↑*	↓*	↓*	↓*	↓*
	intrinsic viscosity of xylene insoluble	dl/g	↓	↑	↓	↑	↑		↓		
	ethylene content in xylene insoluble	%wt					↑		↓		
	Polyethylene	%wt	↓*	↑*	↓*	↑*	↑*	↓*	↓*	↓*	

[a] When the Action increases (↑) the parameters of the center column, the mechanical and optical properties increase (↑), decrease (↓), or remain unchanged (x).

[b] At constant amorphous fraction content. If the increase of this fraction means a reduction of the amorphous one, these correlations are inverted.

4. Manufacturing

The history of PP manufacturing processes is strictly connected to the evolution of the history of the catalytic system.

In the 1960s, polypropylene processes, batchwise operated, employed first generation low yield catalysts ($<$ 1,000 kg PP/kg catalyst) in mechanically stirred reactors filled with an inert hydrocarbon diluent. Polymer produced with these catalysts had unacceptably high residual metals and contained 10% atactic polypropylene, which required separation. Removal of catalyst residues and atactic PP involved treatment of the polymer with alcohol, multiple organic and/or water washings, multistage drying and elaborate solvent, amorphous and catalyst separation systems. These processes were costly and difficult to operate, and also required extensive water treatment facilities, and catalyst residue disposal systems.

An intermediate step was reached with the second-generation catalyst increasing yield (6,000–15,000 kg PP/kg catalyst) and isotacticity, but not yet at a level that allowed to simplify the production process. In these phase several different processes had been developed, slurry, solution, bulk, gas phase. Slurry processes replaced the batch reactors with continuous-stirred vessel operated in series that run full or under level control. Operating pressure depended on the selected solvent. The most common solvent used was hexane, but also heptane, kerosene, and butane were used. Bulk processes (liquid monomer), were operated at higher pressure and have the advantages of higher reaction rate because of the high monomer concentration, and the absence of diluent. The solution process was complex and expensive. The product range was somewhat restricted because a special, high temperature catalyst was required.

The gas phase process was a simple one, and even with the second generation catalyst, atactic PP and catalyst residuals were left in the final polymer and, because of that, the product quality suffered the presence of atactic and catalyst residuals (stiffness, color, resistance to oxidation).

In the 1970s, the discovery of the milled, active $MgCl_2$ support for PE, the extension to PP with the use of electron donors, and of the combination of internal and external electron donors to promote the iso-index without renouncing to the catalyst yield, brought the catalyst to the third-generation high yield catalysts (15,000–30,000 kg PP/kg catalyst), eliminating the need for catalyst residue removal, (Ti level below 5 ppm), but atactic was still unacceptably high. This simplified the washing, but did not eliminate the atactic recovery steps.

In the 1980s, fourth generation high yield, high selectivity (HY/HS) catalysts (30,000 kg PP/kg catalyst, Isotactic index 95÷99%) eliminated the need for catalyst and atactic removal. This further simplified the process and improved product quality. Other breakthroughs occurred in the process design, through the refinement of gas-phase and bulk polymerization reactors that led to the development of Spheripol technology in 1982.

Today, the capabilities of the Spheripol process are further enhanced by the current catalyst generation, which has the ability to produce new families of

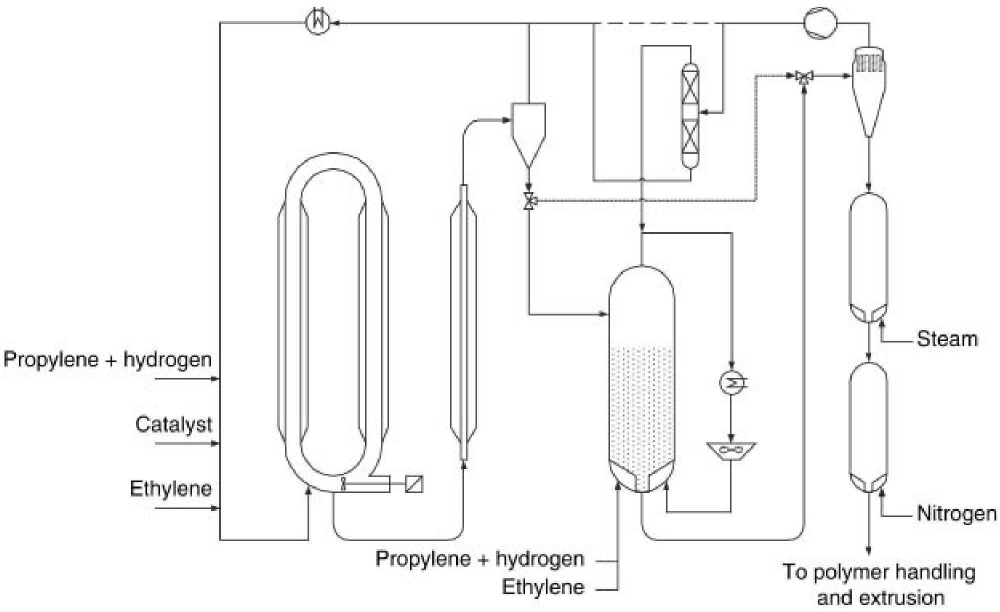


Fig. 3. Spheripol technology process flow diagram.

reactor-based products with improved properties. They offer even greater control over morphology, isotacticity and molecular weight, and continually challenge new frontiers in the development of propylene polymers.

In 2005, 95 Spheripol PP lines have been licensed for a capacity of over 16.8 million ton/y. Spheripol technology accounts for more then 50% of all high yield/ high selectivity PP technologies available.

4.1. Spheripol Technology. The Spheripol process (Fig. 3), using HY/ HS catalysts supplied by Basell, has the unique ability to produce polymer spheres directly in the reactor. Spherical polypropylene differs considerably from the small, irregularly shaped, granular particles produced with some other technologies and provides significant advantages in terms of process reliability.

The Spheripol process is a modular technology. In its most widely adopted configuration the polymerisation section involves the following main units: Catalyst feeding; polymerization includes bulk polymerization (homopolymer/ random copolymer and terpolymer); gas-phase polymerization (heterophasic impact and speciality copolymer), the gas-phase copolymer unit can be added at a later stage without affecting initial plant configuration or involving significant implementation costs; and finishing.

The catalytic system has three components: the solid catalyst, an aluminium alkyl used to activate the catalyst and a Lewis base used to control the crystallinity of the homopolymer grade.

Monomers fed to the reactors can be treated to remove poisons.

Bulk polymerization employs jacketed tubular loop reactors completely filled with liquid propylene to produce homopolymers, random copolymers and terpolymers. The catalyst, liquid propylene and hydrogen for molecular weight control are continuously fed into the loop reactor. Residence time in the reactor is lower than other technologies because of the high monomer density and increased catalyst activity. The polymerization reaction is exothermic; the heat of reaction is removed by means of cooling water circulating into the reactor jackets. The loop reactor is used because it offers low cost, high heat transfer and maintains uniform temperature, pressure and catalyst distribution. The low residence time also results in short transitions during grade changes, while the complete filling of the reactors eliminates any risk of contamination between different grades due to the presence of an interface between the actual reaction volume and disengagement.

A homogeneous mixture of porous polypropylene spheres (which contains active catalyst) suspended in liquid propylene is circulated inside the reactor loop by means of a dedicated pump. If the production of random copolymer or terpolymer is desired, ethylene and/or butene-1 are fed into the loop reactor. This process achieves very high solid concentration (at least 50% by weight), excellent heat removal (by water circulation in the reactor jacket), and temperature control (no hot spots). The resulting polymer is continuously discharged from the reactor through a flash heater into a first-stage de-gassing vessel. Unreacted propylene from the flash vessel is recovered, condensed, and pumped back into the loop reactor.

For the production of impact and speciality impact copolymers, polymer from the first flash vessel is fed to a gas-phase fluidized bed reactor that operates in series with the loop reactors. This gas-phase reactor can be bypassed when homopolymer or random copolymer is produced. In this reactor, an elastomer (ethylene/propylene rubber) polymerizes within the homopolymer matrix that resulted from the first reaction stage. The carefully developed pores inside the homopolymer particle allow the rubber phase to grow inside so without showing the sticky nature of the rubber to upset operation by forming agglomerates.

Fluidization is maintained by adequate recirculation of reacting gas: reaction heat is removed from the recycle gas by a cooler, then the cooled gas is recycled back to the bottom of the gas-phase reactor for fluidization. This type of gas-phase reactor is efficient because it maintains a high degree of turbulence in order to enhance monomer diffusion and reaction rates, and offers an efficient heat removal system.

In impact copolymer production, at least 60% of the final product is produced in the first-stage loop reactor. In addition, since ethylene is more reactive than propylene, the gas-phase reactors are smaller than would be required if this design were to be used for homopolymer production. Spherical morphology ensures high reliability and elimination of fouling phenomena, which frequently disrupt other gas-phase systems.

Polymer, discharged from the reactors, flows to a low-pressure separator and subsequently to a steam treatment vessel where catalyst residues are neutralized and the dissolved monomer is removed, recovered and recycled back to the reactor system. From the steamer, polymer is discharged into a dryer where water is completely removed. The final product is conveyed to an extrusion unit, where it is mixed with additives and extruded to pellets.

Process Capability. A range of single line capacities from 40–550 kT/y are available for homopolymers, random copolymers or heterophasic impact copolymers, either using polymer (99.5% typical assay) or chemical grade (94% typical assay) propylene.

This wide capacity range and the modular installation approach allows, within limits, easy debottlenecking. This minimizes initial capital costs and allows new capacity to be added later when required.

The product range can also be easily expanded. Often new entrants to the polypropylene business will build a plant to produce only homopolymer and random copolymer products as these are the least expensive, are easy to operate and their products account for 75% of all polypropylene sold in the world. A basic homopolymer plant can be easily expanded at a later date to produce heterophasic impact and speciality impact copolymers. Impact copolymers are more specialised products, which require additional capital investment and technical support.

In comparison with any wholly gas-phase technology, a Spheripol process plant offers on a single polymerization line the widest range of homopolymer, random copolymers and terpolymers, as well as heterophasic impact and specialty impact copolymers covering all PP application fields.

Key to this versatility is the application of high yield/high selectivity catalysts:

- High polymerization activity (mileage over 40,000 kg PP/kg catalyst), resulting in extremely high polymer purity
- Stereospecificity control of polymer
- Morphology control of particle size, shape and distribution
- Molecular weight distribution control
- Use of polymer or chemical grade monomer
- Homopolymer, random copolymers and terpolymers, heterophasic impact and speciality impact copolymer production

4.2. Spherizone Technology.

The development of the Spherizone technology started in 1995 and was subsequently scaled up from pilot plant to commercial plant in 2002, when the new multi-zone circulating reactor was installed at Basell's Brindisi, Italy plant. The plant has been running very well since start-up.

The Spherizone process, together with high yield / high selectivity catalysts, has the ability to produce spherical polymer particles directly in the reactor. Spherical polypropylene differs considerably from the small, irregularly shaped, granular particles obtained by some other technologies, and provides some significant advantages in terms of process reliability.

The Spherizone process is a modular technology and is typically composed of the following sections:

Catalyst feeding;
Polymerization;
Prepolymerization

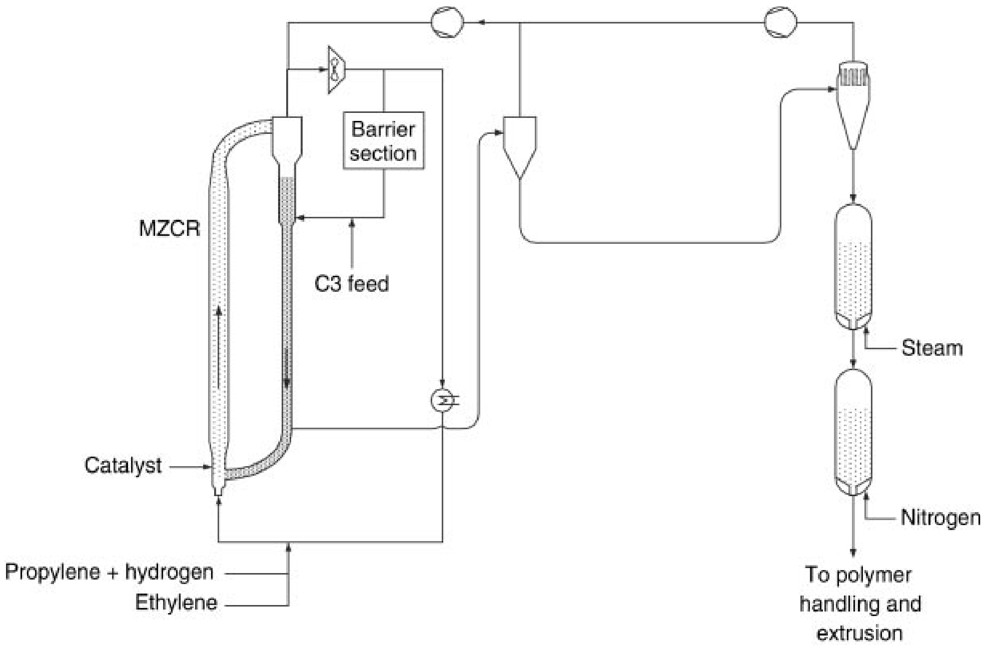


Fig. 4. Simplified process flow diagram (MZCR only, no GPR).

Polymerization in the MZCR (homopolymer grades, medium-wide-very wide MWD, random copolymers and terpolymers, two composition polymers, homopolymer/random copolymer-twin random copolymers- random/heterophasic copolymers)(Fig. 4).

Gas phase polymerisation in a fluidized bed reactor (heterophasic impact and speciality copolymer) as a further option. The gas phase copolymer unit can be added at a later stage without affecting initial plant configuration or involving significant implementation costs (Fig. 5).

- Finishing.

The catalyst, a spherical solid having a controlled particle size, is dispersed in a mixture of paraffinic oil and grease and fed continuously to the multi-zone circulating reactor, which is the core of this new technology. This loop reactor consists of two (or more) distinct reaction zones, each operating under its own peculiar fluid-dynamic regime.

In the so-called "riser" (see also Figs. 5 and 6) the polymer particles are entrained upwards by the monomer flow in a fast fluidization regime. Gas superficial velocities are maintained at much higher values than the average particles terminal velocities, so that a highly turbulent flow regime ensues. This generates an optimal heat exchange coefficient between the single particles and the surrounding gas, and ensures that the reaction temperature is kept constant along the reaction bed. Head losses in this area are comparable to those along a fluidized bed of the same solids hold-up, while maintaining a high bed voidage, as typical of fast-fluidized bed.

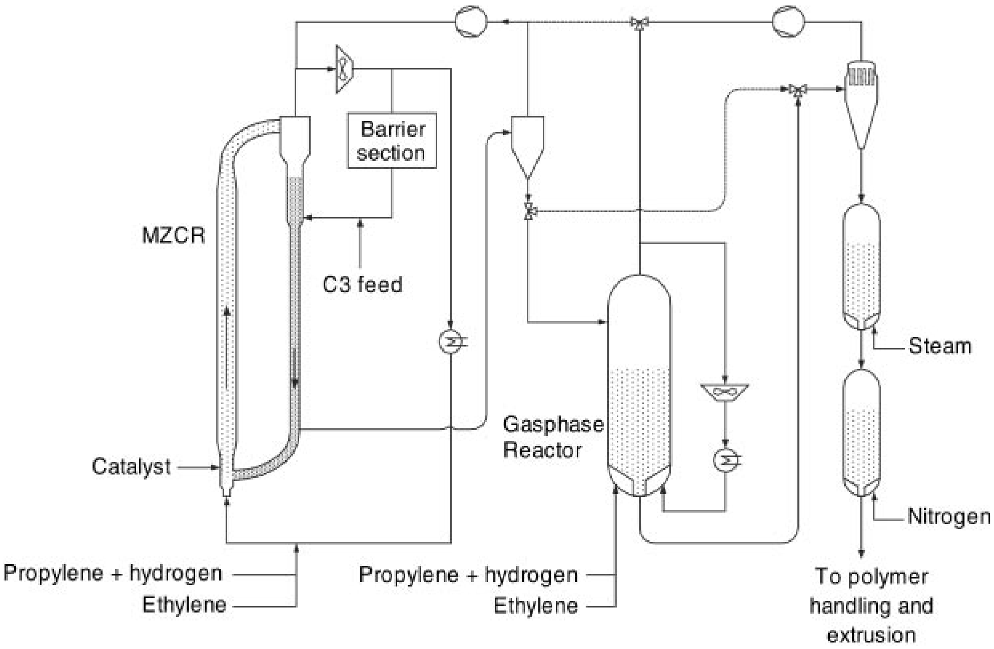


Fig. 5. Simplified process flow diagram (MZCR plus GPR).

In the top of the reactor, the riser gas is then separated from the solids, which enter the so-called "downcomer". This section operates as a moving packed bed, with the polymer flowing downward. As it operates adiabatically, the reaction heat will increase the temperature of the solid bed as the polymer descends. Therefore, care is taken to recirculate enough polymer to prevent the formation of hot spots and generally excessively high temperatures along the bed, which may jeopardise the flowability of the polymer and the recirculation itself.

The polymer's loop circulation is set up and defined by the pressure balance between the two polymerization zones. As it flows down under gravity, the downcomer polymer bed "pumps" the gas downwards and recovers the head losses developed in the riser, the gas/polymer separator and all other sections of the reactor. Actually, the moving packed bed develops a pressure profile increasing from top to bottom of the reactor as per Ergun's law, according to the pressure head necessary for recirculation. The overall pressure balance determines such required pressure head, which is at all times maintained lower than the maximum attainable in conditions of incipient fluidization.

The pressure head, in turn, will determine the differential (slip) velocity between the gas that shall flow down with the solids and the polymer itself. This is only a function of the reactor's fluodynamics, ie, of the solids flow and the pressure balance to be maintained in the reactor, and is in all cases independent of reaction conditions. The actual fluodynamic conditions of the reactor are such that the gas is in all cases flowing down with the polymer. As the pressure

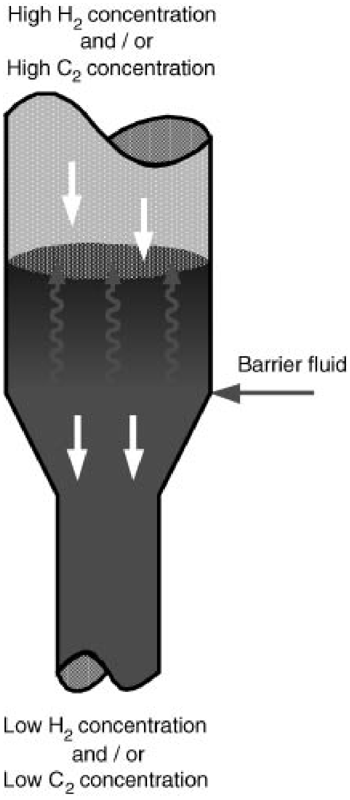


Fig. 6. Stripping zone principles.

head is determined by the differential in velocities between solids and gas, it is apparent that for the same overall head losses, and therefore the same slip velocity, higher polymer flows in the downcomer will in turn significantly increase the flow of gas entrained with the polymer. This plays an important part in the bimodal operation of the reactor.

At the bottom of the downcomer, the polymer particles are recirculated into the riser via a J-valve-like piece of equipment. Furthermore, any suitable valve may also be installed at the bottom of the downcomer as an additional device to further control the polymer flow.

The packed bed fluid-dynamics of the downcomer are essential to bimodal operation: the intergranular gas would normally have the same composition as the riser gas, resulting in a monomodal polymer. However, the two sections of the reactor can be operated at different compositions in hydrogen (used as chain-transfer agent) and co-monomer, allowing for the development of a bimodal polymer structure (in terms of MFR and/or comonomer concentration/ type) at a macromolecular level. This can be accomplished by the introduction of a liquid or gas propylene stream on the top of the downer just below the polymer level, so that the riser gas is replaced by one with a different composition (Figure 6). Typically, low molecular weights are produced in the riser, while the injection of a hydrogen-poor monomer stream in the liquid or vapor phase allows the production of higher molecular weights polymers in the downcomer.

The polymer recirculation rate has a direct influence on the amount of gas flowing down the downcomer, which results into the requirement to limit such polymer flow to the minimum allowable by the thermal balance of the downcomer.

Here, the use of a liquid barrier stream is particularly useful, as its latent heat helps remove the heat of reaction developed in the downcomer. The barrier stream is fed and easily distributed in the moving packed bed. The reaction heat and the solid heat vaporize the barrier liquid which is fed slightly in excess to the theoretical intergranular amount of gases moving downwards, so that a net gas flow upwards is created in the upper point of the downcomer. Thus, the polymer level above the injection point forms a "seal" which prevents contamination between the two reaction zones as long as the packed bed flow regime is maintained.

Obviously, the reactor can also yield monomodal homo- and random copolymer products by operating the sections under the very same conditions. In this case, the lack of the cooling effect of the evaporating barrier stream forces the use of higher solids recirculation rates to keep the polymer temperatures all along the downcomer well below the softening point.

The continuous, massive recirculation of the polymer particles between the two zones makes the residence time per pass in each zone one order of magnitude smaller that the overall residence time. In bimodal operation, this allows an intimate mixing of the different polymers being produced, giving a very good homogeneity of the final product. Moreover, the hold-ups and residence times in each leg can be adjusted to vary the split of production between the two areas to suit different requirements.

From the top of the reactor the unreacted monomer is recirculated to the bottom of the riser by a centrifugal compressor. A reactor cooler is positioned in that circuit to remove the heat of reaction and ensures that the desired operating temperature is maintained. The gas flow through the circuit can be varied according to the actual solids recirculation in order to maintain the desired conditions of fast fluidization and solids concentration in the riser. The pressure in the system is maintained by controlling the fresh monomer flow rates equal to those reacting inside the reactor.

From the delivery of the circulation compressor, a side stream is withdrawn and sent to a monomer distillation section where the desired barrier flow rate is recovered. The top, hydrogen-rich gas is recycled to the riser of the reactor.

The spherical product is continuously withdrawn from the reactor and separated from the unreacted monomer gas in a separator operating at intermediate pressure. The gas is then compressed and recycled back to the MZCR via a small, one-stage reciprocating compressor.

As an option, the polymer can then be fed to a fluidized bed gas-phase reactor, operated in series with the MZCR, where additional copolymerization can take place to yield high-impact copolymer PP. This gas-phase reactor may be bypassed when homopolymer or random copolymers are produced. In this reactor, an elastomer (ethylene/propylene rubber) formed by the introduction of ethylene is allowed to polymerize within the homopolymer matrix that resulted from the first reaction stage. The pores, developed inside the polymer particle in the MZCR upstream, allow the rubber phase to develop without the formation of agglomerates resulting from the sticky nature of the rubber.

The fluidization in the reactor's polymer bed is maintained by adequate recirculation of reacting gas. The reaction heat is removed from the recycle gas by a cooler, while the cooled gas is recycled back to the bottom of the gas-phase reactor for fluidisation. This gas-phase reactor maintains a high degree of turbulence and enhances monomer diffusion and reaction rates, and ensures an efficient particle heat removal.

Depending on the adopted configuration, from the intermediate pressure separator or the fluidized bed reactor the product is discharged to a low pressure filter, where the unreacted monomer gas is recovered. The polymer is then steam-stripped of any residual dissolved monomers in an additional vessel. The same unit also neutralises the residual active catalyst. The removed residual hydrocarbons are recovered and can be sent back to the reactor system, while the polymer is dried by a closed-loop nitrogen system in a small dryer.

The resulting polymer, free from volatiles, is pneumatically transported by nitrogen to the extrusion unit, where it is mixed with additives and extruded to pellets, typically by a single extrusion line. The product then enters a homogenisation silo, before it is stored, bagged or shipped.

The Spherizone technology can be operated using either polymer- or chemical-grade propylene.

Product Versatility. Product-wise, the versatility of the Spherizone process is demonstrated by the high- quality product range that includes all standard polypropylene grades, as well as many unique, special products.

One key to this versatility is, as mentioned above, the unique design and operation of the MZCR, allowing for many kinds of intimately mixed polymer compositions to be produced.

Another key is the application of the high yield / high selectivity catalysts, such as provided by Basell as *Avant* catalysts:

High polymerization activity (mileage over 40,000 kg PP/kg catalyst), resulting in extremely high polymer purity
Stereospecificity control of polymer
Morphology control of particle size, shape and distribution
Molecular weight distribution control
Use of polymer or chemical grade monomer

Homopolymer, random copolymers, high clarity random copolymers and terpolymers, two compositions (homopolymer/random copolymers, twin-random copolymers, random/heterophasic copolymers) in the MZCR only, and heterophasic impact and speciality impact copolymer production with an additional gas phase reactor.

5. Economic Aspects

5.1. Process Reliability and Operability. The Spheripol process has proven to be extremely reliable. In use since 1982, it has been continuously refined and optimized. Yearly world-wide surveys of operating Spheripol process lines reveal an average on-stream operability of around 98%. Of an average 2% downtime, less than 1% is due to process features.

The Spherizone process has been running consistently well at the first commercial; plant in Brindisi, Italy after a scale-up from pilot plant size to 160 kt/a. The new process builds on the extensive knowledge gained from the Spheripol technology offers further operability advantages. See Table 9.

5.2. Consumption of Raw Materials and Utilities. Spheripol process plant capital and operating costs are among the lowest in the industry as a result of:

- Smaller reactor volumes (completely full of reacting liquid, no dead space)
- Minimum transition time (due to very low residence time)
- Lowest monomer consumption (complete recovery of the unreacted monomer)
- Utilisation of low cost chemical grade or polymer grade monomer
- Low steam and electric power consumption see Table 8.

5.3. Product. The manufacture of polypropylene accounted for 60% of the world's propylene consumption in 2002. Other markets include acrylonitrile, oxo chemicals, propylene oxide, cumene, isopropyl alcohol and polygas chemicals.

Table 8. **Typical Specific Consumption of Raw Materials and Utilities, Spheripol Process (per 1000 kg of PP produced)**

	Homopolymer	Impact copolymer
monomers, kg[a]	1002	1002
hydrogen, Nm^3 [b]	0.01–0.5	0.01–0.5
catalysts and chemicals, $[c]	22–25	23–26
electric power, kWh[d]	250–270	280–300
steam, kg[e]	280	280
cooling water, m^3 [f]	110	120
nitrogen, Nm^3	15	15

[a] Net consumption of 100% monomers/co-monomers included.

[b] Depending of reactor composition, according to polymer MI.

[c] typical general purpose stabilization.

[d] Extrusion included, consumption depending on product MI.

[e] Low pressure steam, high pressure steam consumption for extruder die plate or barrels heating is excluded.

[f] At $\Delta T = 10°C$.

Table 9. **Typical Specific Consumption of Raw Materials and Utilities, Spherizone Process (per 1000 kg of PP produced)**

	Homopolymer	Impact copolymer
monomers, kg[a]	1002	1002
catalyst, kg	0.025	0.025
electric power, kWh[b]	110	135
steam, kg[c]	80	120
cooling water, m^3[d]	85	85

[a] Net consumption of 100% monomers / co-monomers included.
[b] Extrusion not included, consumption depending on product MI.
[c] Low pressure steam, high pressure steam consumption for extruder die plate or barrels heating is excluded.
[d] At $\Delta T = 10°C$.

Propylene is an established market and no significant new chemical uses are likely to emerge in the future.

The bulk of propylene production and consumption is concentrated in North America, Western Europe and Japan. In 2002, these areas represented about 61% of the world capacity and 62% of demand (a decrease from previous years). Demand in other regions has shown dramatic growth in the last decade and will continue to outpace growth in the established petrochemical centers during the next five years. Growth in propylene has been and will continue to be influenced primarily by the requirements of the polypropylene industry. World propylene consumption will increase at about 4.5–5% per year during the 2002–2007 period. The highest growth in consumption is expected in the Middle East (20% per year), Africa (10% per year), and Central and South America (8% per year). This is in contrast to the established consuming regions of North America, Western Europe and Japan, where the projected average demand growth will be 3.5%, 2.9%, and 1.8% per year, respectively (3).

6. Safety and Environmental Considerations

Features of the Spherizone process help to reduce both resource consumption and emissions. These include use of high yield, highly stereospecific catalysts, recovery and recycle of unreacted monomers, the absence of undesired by-products from the reaction and the low energy consumption. Due to the MZCR concept, in the polymerisation section of the process the overall energy consumption may be reduced by 0–30%, depending on the type of polymer produced.

6.1. Intrinsic Safety of the Process.

The design of each Spheripol process plant includes a number of safety features, such as:

- Proprietary Catalyst Deactivation System, which immediately stops all reaction
- Interlocks which help to prevent operator error
- Computer controlled emergency shutdown systems

- Uninterruptible Power Supply (UPS) for computer control and critical instrumentation control
- Instrument air emergency buffer
- Emergency Blowdown System to empty the plant quickly, in the event of an emergency
- Gas detectors which instantly determine and highlight (on a graphic easy-to-read board) the source of any hydrocarbons in the event of leakage into the atmosphere
- Automatic fire protection systems

Depending upon the severity of the situation, the plant can be shut down manually in a step-by-step, controlled fashion, more rapidly by both manual and computer control, or by instant automatic shutdown.

6.2. Reducing Resource Intensity. Features of the Spheripol process help to reduce both resource consumption and emissions. These include use of high yield, highly stereospecific catalysts, recovery and recycle of unreacted monomers, the absence of undesired by-products from the reaction and the low energy consumption.

7. Uses

Isotactic polypropylene is well suited for a variety of end uses, ranging from flexible and rigid packaging to fibers and large molded parts for automotive and consumer products. Polypropylene is recyclable, an important consideration in many packaging and automotive applications, and it can be incinerated without toxic emissions. It can be processed using most methods including extrusion, extrusion coating, blow molding and stretch blow molding, injection molding, and thermoforming. Its physical properties can be easily enhanced through the addition of fillers such as calcium carbonate or talc. Polypropylene has excellent chemical resistance and electrical insulating properties.

Typical applications for polypropylene products include fibers and filaments, oriented and cast film, injection-molding items, blow-molded bottles and parts, and thermoformed containers.

Random copolymers can be produced with excellent optical properties and sealing initiation temperatures in compliance with the U.S. Food and Drug Administration (FDA) regulations for food contact.

Heterophasic copolymers with outstanding low-temperature behavior, high-impact strength and enhanced stiffness can be obtained in the widest range of melt viscosities.

As a global average, homopolymer accounts for 65–70% of all polypropylene, random copolymer and terpolymer for 10–15% and heterophasic copolymer for 15–20%.

Film and fiber are the two largest segments in the global PP market, but injection/blow molding and extrusion account for significant quantities. Typical polypropylene fabrication processes and end uses include the major fields listed in Table 10.

Table 10. **Polypropylene Fabrication Processes**

Fabrication process	Markets/end uses
film extrusion	BOPP film / WQB film / cast film/ (flexible packaging for textiles, confectionery, bakery and cigarette wrap)
multifilaments	woven sacs (raffia)/fibrillated tape for carpet backing, geotextiles, rope and twine, upholstery and cigarette tow
nonwovens (meltblown and spunbonded)	geotextiles, medical application
injection molding	automotive, appliances, houseware, furniture, consumer products, packaging (crates, cases, caps and closures, thin walled and transparent containers)
blow molding	packaging
profiles extrusion	pipes, conduits, corrugated sheet, wire and cable extrusion coating, lamination.

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