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Polypropene Product Innovation by Reactor Granule Technology

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SUMMARY: Continuous fine tuning of both chemistry and architecture of heterogeneous, isospecific $MgCl_2/TiCl_4$ catalyst systems for propene polymerization has led to a significant improvement in their performances in terms of activity, stereoselectivity, and capability to control both molecular parameters and morphology of the resulting polymers. As a result, a number of improved/innovative propene-based products has recently been developed that clearly outperform the previously available materials. In particular, a family of reactor-grade polymers has been synthesized including homopolymers and heterophasic copolymers offering, respectively, an unprecedented relationship between fluidity and stiffness and between stiffness and impact strenght, and supersoft polypropene alloys that could not have been achieved even via mechanical blending.

1. Introduction

It is well known that the catalyst system plays a fundamental role in polypropene manufacture in general and polypropene product innovation in particular. In this regard, the discovery and exploitation of isospecific heterogeneous catalysts based on magnesium chloride-supported titanium tetrachloride and electron donors, can be considered revolutionary in its significance due to the unprecedented control it offered over both propene polymerization processes and product performances.

Over the years, significant progresses have been made in understanding how catalyst activity, stereoselectivity, hydrogen response etc. can be finely tuned by operating at the active center level, mainly acting on the nature of electron donors. On the other hand, the catalyst system has an equally important characteristic that needs fine control, e.g. the morphology of the solid catalyst particle in terms of size, shape, surface area and porosity.

It is exactly this capability to control and fine tune both catalyst chemistry and physics or, perhaps better, architecture, that is the basis of what has been termed "Reactor Granule Technology" (RGT) and defined as[1]:

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"controlled, reproducible polymerization of olefinic monomers on an active magnesium chloride supported catalyst, to give a growing, spherical polymer granule that provides a porous reaction bed within which other monomers can be introduced and polymerized to form a polyolefin alloy".

RGT exploitation has led to the implementation of a number of innovative, advanced and versatile industrial polymerization processes for polypropene like *Spheripol* and *Catalloy* as well as to a tremendous expansion of polypropene product properties, or better, property balance. Today, RGT is able to provide a class of polypropene products ranging from superstiff, high fluidity homopolymers to stiff/impact or clear/impact heterophase copolymers and supersoft alloys so as to cover the most sophisticated application areas.

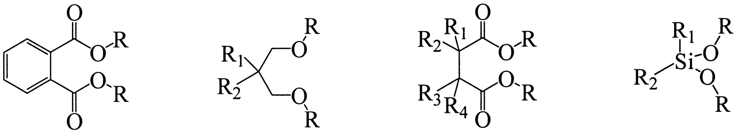
Aim of this paper is to show how each of these product families can be optimized taking advantage of one or more catalyst attributes resulting from its chemistry or physics and how the catalyst system can be designed accordingly.

2. The catalyst system

2.1 Chemistry

Heterogeneous, high-activity, high isospecificity Ziegler-Natta systems consist of solid particles or grains comprising "activated" magnesium chloride support, titanium tetrachloride and an "internal" electron donor. In polymerization, they are typically used in combination with an aluminium alkyl cocatalyst, e.g. $AlEt_3$, and an "external" donor.

Considerable progresses have been made over the years to understand the function of donors and their structure has been designed accordingly. As a result, catalyst performances have been largely improved, especially activity and stereoselectivity, by displacing the first generation of internal/external donors (ethylbenzoate/aromatic esters) with the couple diisobutyl phthalate/alkoxysilane and, more recently, with the introduction of diethers, typically a 2,2-disubstituted-1,3-dimethoxypropane, used without or in combination with an alkoxysilane. But in addition to activity and stereocontrol, other catalyst attributes exist that need fine tuning to drive product innovation. These are in particular: hydrogen response and control of polymer molecular weight distribution (MWD)[2). In this respect, whereas phthalate-based catalysts are characterized by high isospecificity, medium hydrogen sensitivity and provide medium MWD polypropene, diether-based catalysts are characterized by very high activity, medium-high isospecificity, high hydrogen sensitivity and are able to provide narrow MWD polymers. Quite recently, we patented[3)] and introduced a very new catalyst system based on a particular family of internal donors, namely succinates, which looks particularly interesting since it was found to provide both high polymer stereoregularity and broad polymer MWD.



Phthalate Diether Succinate Silane

Fig. 1: General formula of Internal and External Donors.

Thus, as a function of donor structure, it is possible to modulate both catalyst performances and polymer structure. In particular, three families of catalyst systems have been developed that are complementary to one another (Tab. 1, Fig. 1-2); we will show in the polymer section why and how product optimisation and innovation are strictly connected to the peculiarities of each of these systems.

Table 1. General performances of different electron-donor classes

Cat.	I.D.	E.D.	Yield (KgPP/gCat)	X.I. (%)	mmmm (%)	Mw/Mn	H_2 response
A	Phthalate	Silane	70-40	96-99	94-99	6.5-8	medium/low
B	Diether	Absent	130-100	96-98	95-97	5-5.5	excellent
B	Diether	Silane	100-70	98-99	97-99	4.5-5	excellent/high
C	Succinate	Silane	70-40	96-99	95-99	10-15	medium/low

I.D. = Internal Donor; E.D. = External Donor; X.I.= Xylene Insolubles; mmmm = isotactic pentads according to ^{13}C-NMR
The ranges are mainly function of the structure of I.D. and E.D. employed.
Bulk polymerisations at 70°C for 2 h, $[AlEt_3]$ = 2.5 mM, Al/E.D. = 20 molar, $[H_2]$ = as needed to obtain an intrinsic viscosity of 2 dl/g

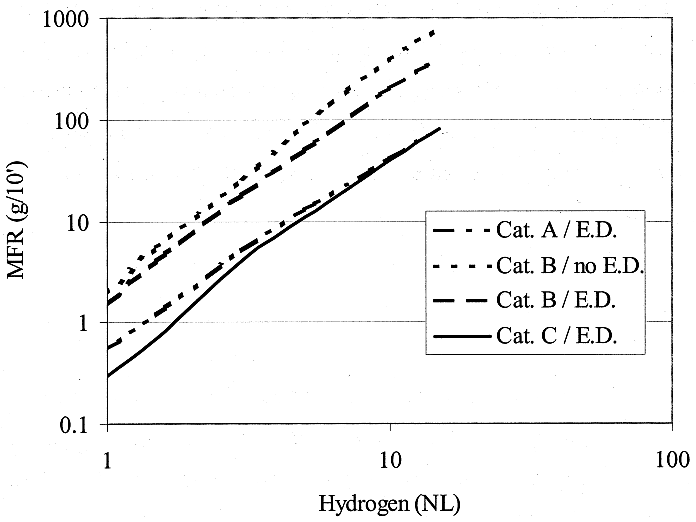


Fig. 2: Hydrogen response of different catalyst systems
Polymerisation conditions: see Tab. 1.

2.2 Architecture

In olefin polymerization over heterogeneous Ziegler-Natta catalysts, solution processes excepted, polymer grows and solidifies around the microcrystallites within each catalyst particle or grain. Any single polymer granule constitutes thus a completely segregated system that behaves like a microreactor characterized by its own kinetics and balances of mass and energy[4)].

The understanding and rationalization of polymer growth mechanism has been, and still is, one of the most stimulating and important investigation fields in Ziegler-Natta catalysis, both in the academia and in industry. Actually, whereas on the one hand the knowledge of this phenomenon is fundamental for the comprehension of the intimate mechanism of Ziegler-Natta polymerization, on the other hand its control can constitute the scientific and technological platform for the implementation of advanced and innovative processes and materials.

Based on SEM and TEM investigations into the micromorphology of spherical $MgCl_2$-supported catalysts and the grains of the resulting nascent polymers, including both propene prepolymers and homopolymers, and its multiphase copolymers, we recently proposed[5)] a mechanism of polymer growth characterized by the following (Fig.3):

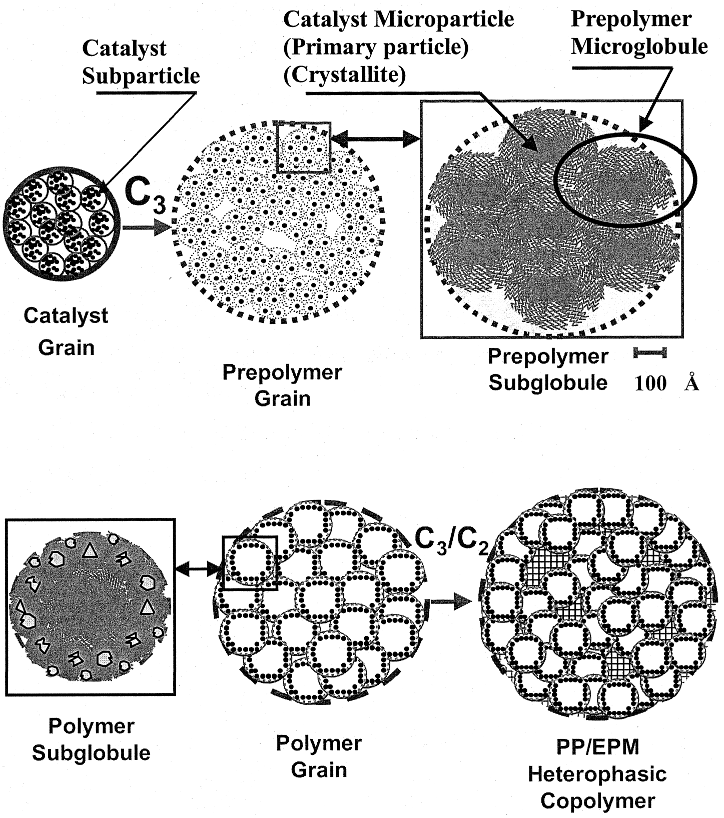


Fig. 3: Mechanism of polypropene growth over spherical $MgCl_2/TiCl_4$ catalysts: prepolymerisation step, main polymerisation step and sequential propene-ethene copolymerisation.

- the catalyst grain (macroparticle) consists of microparticles, likely constituted by $MgCl_2$ crystallites, and larger microparticle agglomerates (subparticles)
- the major contribution to catalyst porosity is due to macropores formed by the interstitial spaces between subparticles
- the active centers are located on the surface of the microparticles

- catalyst fragmentation starts since the very beginning of the polymerization: in other words, just a few grams of polymer per gram of catalyst are sufficient to break the catalyst macroparticle into its components: micro- and subparticles
- the polymer grain reproduces the dual morphological texture of the catalyst grain: the monomer diffuses readily even into the catalyst bulk and forms a polymer shell (microglobule) around each catalyst microparticle
- polymer microglobules tend to merge into each other to form larger, relatively dense agglomerates (subglobules)
- as polymerization proceeds, catalyst microparticles likely undergo further fragmentation and tend to be convected from the bulk to the surface of polymer subglobules, and it is just this surface that sustains the “main” polymerization reaction.

The proposed mechanism of polypropene growth might still be oversimplified but it explains the experimental results and also, perhaps more important, it teaches us what and how the optimal catalyst architecture should be according to the nature of the material we wish to synthesize. Based on this model, the polymer grain tends to reproduce both the shape, the dual structural hierarchy and porosity of the parent catalyst grain, enlarging of course its size as polymerization yield increases. Thus shape, size and porosity of the catalyst macroparticle can be predicted, designed and tailored to meet any specific product and/or process requirement.

3. The Reactor Granule Technology

RGT, originally devised in the late sixties with a view to solving what we now consider the trivial problem of “fines”, has evolved over the years in order to meet a number of stringent and ambitious targets that were considered visionary at that time, such as complete control over catalyst chemistry and architecture, as well as polymer growth, in order for the catalyst grain to generate polymer particles having spherical shape, narrow particle size distribution, controlled size, porosity and bulk density.

The control of all these features allows us to:

- maximize the operativity and productivity of polymerization plants (better slurry or gas flow; less tendency to plug; higher polymer concentration etc.)
- increase the output of extruders
- optimize the quality and consistency of the material

- extend the property envelope of polyolefin materials

This is not only the result of the understanding of the polymer growth mechanism but also, and especially, of the ability to fine control both the chemistry and architecture of the catalyst grain accordingly. In this regard, apart from the stereoregulating role of electron donors, the following scientific and technological breakthroughs are to be regarded as the most relevant ones:

- the chemical route to $MgCl_2$-supported catalyst via $TiCl_4$ treatment of $MgCl_2.nEtOH$ adducts$^{6)}$;
- the possibility to shape $MgCl_2$ adducts into particles having spherical morphology, controlled size and narrow particle size distribution$^{7)}$;
- the capability to alter both surface area and porosity of the spherical $MgCl_2.nEtOH$

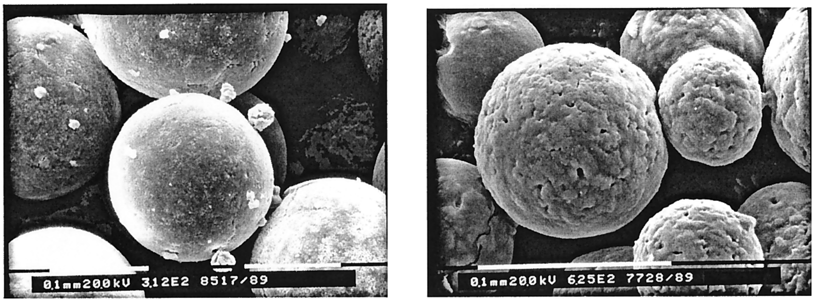


Fig. 4: SEM micrographes of catalyst supports having different porosities.

In particular, the exploitation of the "porosity" concept, can be considered as a revolutionary technical platform that has been, and still is, the basis for the generation of a family of previously unachievable "reactor grade" or "in-situ" polymer alloys.

4. Catalyst attributes and polypropene product innovation

By combining RGT and the above mentioned processes, a whole class of polypropene-based, reactor-grade polymers can be synthesized ranging from superstiff to supersoft materials all of which, needless to say, come out of the reactor as spherical granules having controlled morphology. Without pretending to deal with all the above mentioned product mix, the discussion that follows will be dedicated to some selected examples on how RGT has been and still is instrumental in driving polymer product innovation or optimization.

Among the most important product performances, particular attention will be devoted to the following balance of properties: stiffness and fluidity/processability (homopolymers); stiffness/impact-strength and softness (multiphase copolymers). As already mentioned, each of these performances exploits one or more catalyst attributes resulting from its chemistry or architecture.

4.1 Homopolymers

According to their specific application areas, polypropene homopolymers need to be tailored so as to optimise their mechanical properties, their rheological behaviour, or both.

For instance, whereas thin-wall injection molding requires both high fluidity of the melt, which means short cycle times and thus productivity, and stiffness, which means possibility of down-gauging of the final article, extrusion or fiber spinning mainly need a very fine tuning of polymer rheology in order to maximize processability and thus, once again productivity, compatibly with the quality of the final article. It is known that melt rheology of polymers is mainly affected by molecular parameters such as M_W (zero-shear viscosity) or MWD (shear sensitivity, processability). In particular, whereas extrusion of pipes and thick sheets requires both high zero-shear viscosity and melt strength, and thus both high M_W (fractional melt flow rate MFR) and broad MWD, fiber spinning requires from relatively high MFR's (about 25 g/10' for spun-bonded applications) to extremely high MFR's (up to 2000 g/10' for melt-blown applications) and very narrow MWD (incidentally, for this specific applications, morphology control of polymer particles is particularly important since the product is directly transformed as it is and even a very low amount of fines would be detrimental). Again, whereas rigidity is mandatory for pipes, this property is relatively less important for fibers, where spinning speed and continuity, minimum achievable filament denier (diameter) and strength are the key factors.

Injection molded articles often demand the maximum rigidity and thus crystallinity. Now, this property is not only related to the isotactic index (wt% insoluble in xylene at 25 °C) of the polymer and to its sterical purity (mmmm% of the isotactic fraction) as expected, but also shows a more subtle, but significant dependence on its MWD. Actually, it has been found that, sterical purity of the polymer being the same, a broad

MWD brings about a considerable increase in its stiffness. It has been demonstrated that this is the result of an acceleration of the nucleation rate, and thus of the overall crystallization rate of the material[9]. A broad MWD is thus able to translate potential crystallinity into actual crystallinity. The increase in nucleation rate has been attributed to the possibility for some very high M_W polymer tails to survive during the melting process and to act as crystallization nuclei during subsequent cooling and solidification (self nucleation).

Very high rigidity thus requires both high sterical purity and broad MWD. In this regard, and so far, MWD broadening had been promoted by running the polymerization process in at least two reactors in series differing in the concentration of chain transfer agent, namely hydrogen. This "staged" polymerization technique proved to be a very effective tool for controlling both rheology and mechanical properties of the resulting product but, at least in principle, it suffers from two limitations:

- polymer MWD cannot be broadened at will due to the difficulty of effectively mixing, in the melt, polymer fractions that are largely different in their MW: this means the possible occurrence of gels, fish eyes, or heterogeneities in general, in the finished article, with consequent deterioration of its aesthetical and/or mechanical properties
- it is difficult, if not impossible, to synthesize products having at the same time both fractional MFR and very broad MWD (the limit to MWD broadening is, in this case, set by the highest achievable M_W in the absence of chain transfer).

With the discovery of succinate based-catalysts, these constraints have been completely removed due to their peculiarity to provide intrinsically polydisperse polypropenes having controlled stereoregularity.

Based on the above discussion, and the catalyst properties reported in Tab. 1 and Fig. 2, it is now easy to sort out the best catalyst/product combination to meet each specific application:

- **Phthalate-based systems:** can be regarded as a family of general-purpose catalysts with which it is possible to cover the majority of product properties and applications.
- **Diether-based systems:** can be considered as "specialized" catalysts that are able to cover the high fluidity, controlled rheology areas of applications demanding very narrow MWD such as: thin-wall injection moulding, fiber-spinning (both spun-bonded and, especially, melt-blown).

In addition, due to their extremely high activity, their are particularly suited to generate high purity polypropene with very low ashes content (capacitor grade polymer).

Owing to their peculiarities, diether-based systems can rightly be regarded as the "heterogeneous" reply to metallocenes in that the resulting polymers tend to approach the performances (purity and narrow MWD) of those generated by single-center catalyst systems.

- **Succinate-based systems:** like diethers, can be regarded as a "specialized" catalyst family that, thanks to its peculiarities, can cover the broad-MWD end of the controlled rheology applications, down to very low fluidities, such as pipe and sheet extrusion and, of course, the area of superstiff injection molded articles. In this regard, their ability to provide intrinsically polydisperse and very stereoregular polymers can lead not only to a considerable improvement in the performances of rigid polymer grades (Tab. 2), but also to a simplification of polymerization process for obtaining them (broad MWD with a single reactor). It is to be pointed out that, even if the differences in the flexural moduli reported in Tab. 2 do not seem to be very impressive, they are to be considered significant, especially in a fiercely competitive application area like injection molding.

Table 2. Mechanical properties of polypropene homopolymers[a)]

Catalyst Type		A	A[b)]	B[b)]	C	C[b)]
MFR	(g/10')	20	20	16-24	22	16
P.I.		4.3	6	8-10	6	12
X.I.	(wt%)	98.5	98.4	98.3	98.2	98.4
mmmm[c)]	(%)	98.7	98.6	97.8	98.4	98.2
M.P.	(°C)	164.5	164.4	164.2	164.2	164.3
Flex. Mod.[d)]	(Mpa)	2000	2250	2250	2280	2380
Stress at yield[e)]	(MPa)	39	40	39	40	40.8
Stress at break[e)]	(MPa)	34	35	31	34	33.4
Elongation at break[e)]	(%)	10	11	10	10	10

[a)] Nucleated with talc; [b)] Bimodal polymerisation; [c)] Measured on xylene insoluble fraction; [d)] ASTM D790; [e)] ASTM D238

In addition, succinate-based catalysts can be modulated so as to provide polypropenes having a controlled degree of stereoirregularity while maintaining broad MWD: these polymers are particularly suited to enter the application field of bi-oriented polypropene films (BOPP).

All the above mentioned polymers, apart from the ubiquitous replication phenomenon, take advantage of the chemical attributes of the catalyst system that result from the capability of donors to modulate the molecular properties of the polymer chain. As for the porosity of the catalyst grain, it should be at the lowest level so as to guarantee the maximum bulk density of the resulting polymer granules and thus the maximum output of the polymerization plants.

4.2 Multiphase or Heterophase Copolymers

4.2.1 Stiffness/Impact Materials

It has long been recognized that the incorporation of an ethene-propene rubbery (EP) fraction into a polypropene matrix (PP), either via mechanical blending or sequential copolymerization, results in a dramatic improvement in impact properties of material, even at low temperatures, without excessive deterioration of its rigidity. This results from a multiphase morphology of the PP/EP system, consisting of spherical rubber domains embedded in a semicrystalline polypropene matrix, which is particularly effective in dissipating the impact energy, possibly via both crazing and shear yielding mechanisms. In this regard, it has long been established that the optimal balance of properties can be achieved when the compositions of the rubber fraction is in the range of 50-60 %wt ethene and the diameter of the rubber domains is around 1 micrometer.

Other conditions being the same, it has been shown9) that the crystallinity of the polypropene matrix plays an important role as well; in particular, it is possible to improve the stiffness/impact performances of heterophase copolymers by using the same tools we exploited to “stiffen” homopolymers. More in particular, Fig. 5 points out how stiffness/impact can be considerably improved as the polypropene matrix changes from monomodal (phthalate-based) to bimodal (diether-based) and to bimodal (phthalate based). Succinate-based copolymers are particularly interesting since they already match, as monomodal, the performances of bimodal phthalate-based copolymers, whereas, as bimodal, largely exceed their characteristics, showing an unprecedented property balance. We can speculate that this might be the result of a matrix that is particularly homogeneous while having a sufficiently broad MWD. On the other hand, the nature of the heterophase can play a role as well. Actually, although the nominal composition of the ethene-propene component is the same (50/50 wt/wt in our case), we cannot exclude that its composition distribution and/or sequence distribution could change as a function of the nature of the electron donor. This aspect is under investigation.

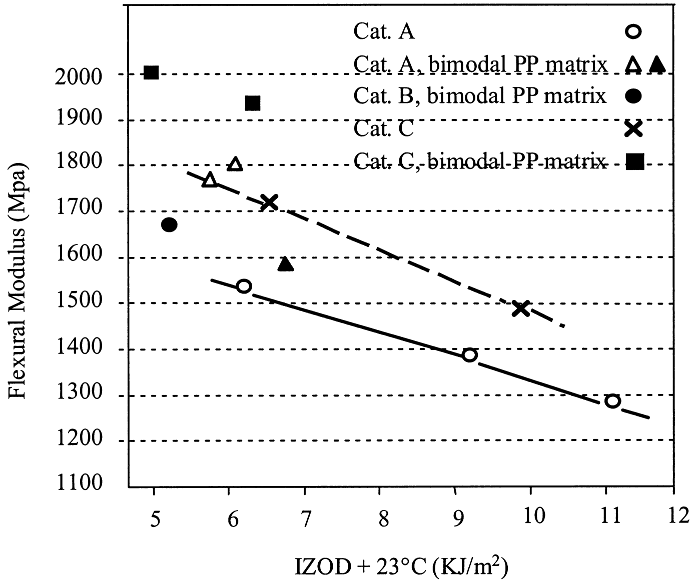


Fig. 5: Polypropene heterophase copolymers (MFR = 10-15 g/10')
Balance of flexural modulus/IZOD impact resistance.

In summary we can state that, whereas diether-base systems are the catalyst of choice for the synthesis of high fluidity heterophase copolymers and phthalate-based system are able to provide, especially under "bimodal" polymerization conditions, excellent materials, succinate-based systems are the most promising ones to bring innovation in this field, which includes a number of very important applications like rigid packaging, luggage, garden furniture, pails, corrugated pipes, battery cases, automotive interior and exterior trims, bumpers etc.

Finally, it has to be pointed out that these materials not only exploit catalyst chemistry, including comonomer incorporation and distribution, but also catalyst architecture. In particular, the porosity of the catalyst grain should be adequately tuned so as to permit the resulting homopolymer grain to accommodate the desired amount of rubberlike heterophase.

4.2.2 Supersoft polypropene alloys

Supersoft polypropene alloys constitute a class of materials having both very low flexural modulus (around 100 Mpa) and hardness (Shore D 30-35), high elongation (900-1000%) and melting point (145-155 °C), and reasonable tension set at room temperature (around 35-40% at 23 °C and 100% elongation). It was found that the targeted product properties required that about 70 %wt of a substantially amorphous, propene-rich, ethene-propene copolymer be incorporated "in situ" into a slightly modified polypropene matrix. As a result, the synthesis of these products, via sequential copolymerization of propene and ethene-propene mixtures, proved to be particularly challenging, due to the necessity to satisfy at least two contrasting needs: incorporation of large amounts of rubbery component (softness) and flowability of the resulting polymer granules (plant operability). In this case, as opposed to the previously mentioned ones, catalyst stereoselectivity is logically relatively unimportant, whereas its architecture, porosity in particular, proved to be the key factor to get the desired product properties.

Actually, and in agreement with the mechanism of polymer growth we have proposed, it has been demonstrated that the rubbery component grows around the preformed subglobules within the homopolymer matrix and tends to fill the pores that are in between5) (apart from the morphological evidence, this mechanism is also supported by the fact that the bulk density of the nascent polymer grain increases with its rubber content). When large amounts of rubber are involved, and the internal porosity of the host polypropene matrix is insufficient, the rubbery fraction first fills the available internal space and then, because of its mobility, tends to migrate to the surface of the polymer grain. This, of course, causes the polymer particles to stick to each other and to the reactor walls, leading to reactor fouling and eventually, blocking. Thus, the porosity of the catalyst grain should be the maximum possible, compatibly with its mechanical integrity, in order for the resulting homopolymer granule, which reflects the porosity of the parent catalyst grain, to accommodate large amounts of intimately dispersed rubbery components without sticking problems. In this regard, both absolute porosity and pore distribution within the catalyst macroparticle are of fundamental importance: the best compromise between these catalyst attributes and its morphological stability was found to correspond to porosity values around 50 %vol (mercury porosimeter), pore distribution ranging from 20 to 10000 angstroms and mean pore radius around 1000 angstroms.

It is exactly the discovery and implementation of the porosity concept8) that led for the first time to the "in situ" synthesis of this family of previously unavailable and unachievable supersoft products.9)

After transformation by injection molding, supersoft polypropene products show a particular morphology9) which results from both the high volume fraction and nature of the rubbery component: a cocontinuous texture consisting of semicrystalline fibrils aligned along the injection direction, containing in turn small rubber inclusions, intercalated with rubbery zones; the semicrystalline fibrils consist of lamellar polypropene stacks mainly oriented perpendicularly to the fibril axis. Apart from softness, this particular morphology accounts well for the other peculiarities of these products, like high elongation, considerable strain hardening and elastic recovery, high melting point and processability. In addition, the fine dispersion of the phases, due to the "controlled" compatibility of the polypropene matrix with the "unconventional", propene-rich (around 70%wt) propene-ethene copolymer, together with the absence of spherulitic superstructures, accounts well for the satisfactory transparency of some products (haze of about 20%).

Owing to their performances, supersoft copolymers are particularly suited to enter a number of important industrial applications such as roofing and geomembranes as well as, at least in perspective, the medical sector.

As previously mentioned, high catalyst isospecificity is not important for supersoft polypropene copolymers; they are currently synthesized by using phthalate-based catalysts, but other donors are being evaluated that could either improve the comonomer composition distribution of the rubbery fraction or/and introduce a controlled amount of stereo-errors along the homopolymer chain.

The importance of catalyst architecture to obtain this family of materials has been already stressed; actually, they could not have been achieved without the full exploitation of RGT including, in particular, porosity control. But, in this case, polymer design proved to play a fundamental role. In particular, both nature, composition, amount and viscosity of the phases need very fine tuning so as to achieve the desired polymer morphology and softness, especially if we take into account process constraints: actually high content of amorphous rubbers and plant operability are contrasting factors that need accurate control.

5. Conclusions

The exploitation of the Reactor Granule Technology, a scientific and technological concept that entails fine tuning and control of both the chemistry (role of electron donors) and architecture of $MgCl_2$-supported catalysts (size, shape and porosity of the catalyst grain) has led to the implementation of a number of advanced and versatile industrial processes for the production of polypropene-based polymers as well as to a tremendous expansion of polypropene product properties. Actually, not only the performances of the existing materials have been largely improved over the years thanks to a parallel and continuous improvement in the catalyst performances (new donors, new supports etc.) but also a number of very innovative products have been developed. Among these, it is worth mentioning homopolymers and heterophasic copolymers offering an unprecedented relationship between fluidity, stiffness and impact strength; heterophasic copolymer combining the optical properties of conventional random copolymers and the mechanical properties of impact copolymers10) and, finally, supersoft polypropene alloys.

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