

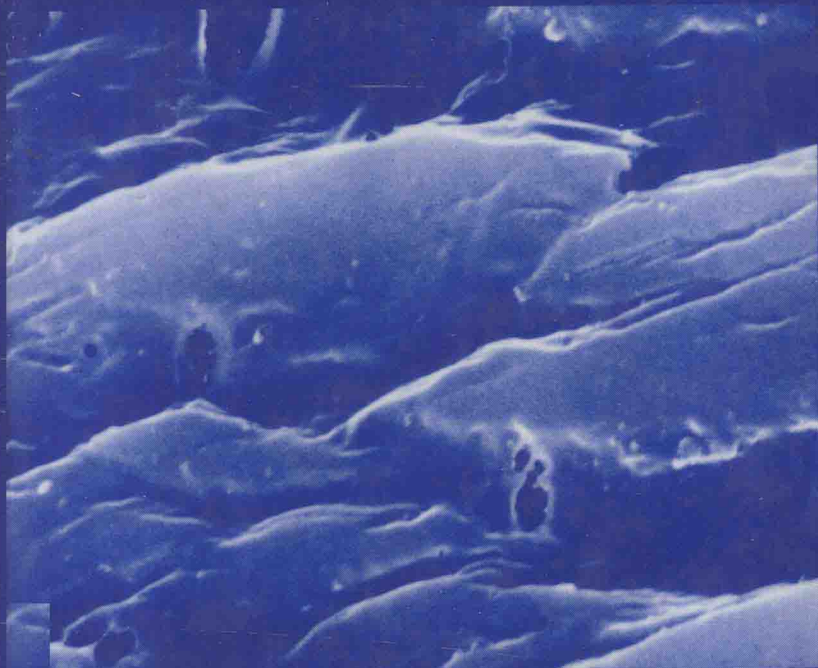
# POLYPROPYLENE

Structure, blends and composites

2

## Copolymers and Blends

EDITED BY **J. Karger-Kocsis**



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# Polypropylene

## Structure, blends and composites

### *Volume 2 Copolymers and Blends*

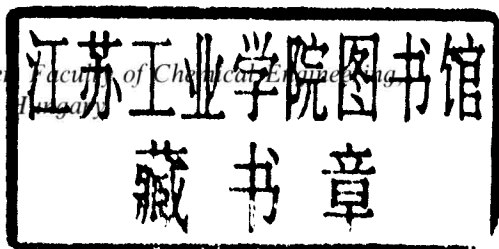
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# Preface

Crystalline polypropylene (PP) was invented in the early 1950s by independent groups in the United States and Europe. The commercial production of PP began in 1957 in the USA and in 1958 in Europe [1]. The reader will find different data, about this issue even in this book. On the other hand, there is no doubt that PP became the winner among the commodity of large-volume thermoplastics into the group of which polyethylene (PE), poly(vinyl-chloride) (PVC) and polystyrene (PS) belong, too. The mean consumption rate of PP was about 10% per year in the past, in given application fields this value was even higher. The forecast for the future trend of PP use is still quite optimistic.

Which are the contributing factors to this success? The key issue is related to the versatility of PP *per se*. This means that the structure and properties (including processability) of PP can be tailored to requirements. Modifications of PP can be performed in different ways: during the polymerization (e.g. production of syndiotactic homopolymers or copolymers with different comonomer content), in the reactor (reactor-blends), in compounding (e.g. manufacturing of filled and chopped fibre reinforced grades) or in further separate processing steps (e.g. wetting of glass mat by PP-melt, manufacturing of textile composite preforms).

PP, being a stereoregular polymer, exists in different tacticities and in various crystalline forms which affect its overall performance. PP exhibits many beneficial properties such as low density, relative high thermal stability, resistance to chemical attack, easy processing and recyclability. In addition, its mechanical property profile is very closely matched to that of the engineering thermoplastics. Some of the drawbacks of PP are its low temperature and impact resistance. This was the driving force of many R&D works which resulted in the commercialization of different PP copolymers and blends. This achievement was the next milestone in the history of PP and that is the reason why Volume 2 of this set is devoted to Copolymers and Blends. This volume contains comprehensive surveys about the nucleation and crystallization behaviour of the related systems. A concise chapter deals with the morphology development and its effects on the rheology and mechanical properties of PP-based alloys and blends. For readers interested in the latter issue with blends other than PP-based ones, Utracki's book [2] is recommended. It is intended further to demonstrate

how the morphology, and thus the resulting mechanical properties, are influenced by the processing (drawing). Volume 2 finishes with a review on PP-based thermoplastic elastomers. Their manufacture by blending and dynamic vulcanization can be regarded as an adequate way for upgrading large-volume thermoplastics. Recently issued books in this field clearly indicate the reality of this issue [3–5]. I would like to emphasize here that several aspects surveyed in this volume had a strong influence on the state-of-the-art of polymer science. This statement holds especially when morphology control in copolymers and blends and factors of impact-modification are considered. Readers interested in the latter topic should refer to the excellent book by Michler [6].

This book is designed to serve as guidelines for property improvement, upgrading and engineering use of PP. It is for this reason that such important fields of PP application as textile fibres, packaging films and foils etc., are not covered. Nevertheless, I am sure that both the concept and realization of this book will fulfill the expectations of the reader and older books about PP will remain on the bookshelves of the libraries. Extensive referencing, included with most of the contributions to this volume, helps to deepen one's knowledge of the desired field. During editing I did not try to 'harmonize' the conclusions and opinions of the authors and my comments were restricted to a few footnotes. This is due to my belief that subjects of dispute must be settled by time, since that is the task of science.

Thanks are due to the contributors, who kindly agreed to cooperate on this 'venture' for their efficient work. I have also to acknowledge here the engaged work of the publisher Chapman & Hall, whose staff cut the time delay in the publication of this book, caused by the transfer from Elsevier Applied Science to the present publisher.

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# Manufacturing and properties of polypropylene copolymers

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*P. Galli, J.C. Haylock and T. Simonazzi*

## 1.1 INTRODUCTION

The synthesis and production of polypropylene copolymers was a natural development in polyolefin technology after the initial discovery and industrial manufacture of the polypropylene homopolymer [1]. The production of random copolymers directly in the polymerization reactor significantly expanded the property envelope of this versatile polymer, giving lower melting resins with improved clarity, particularly in film form. Heterophasic copolymers with increased toughness and durability were developed by melt compounding blends of different preformed polyolefins. More recently, such polymer blends have been produced by polymerization of the monomers directly in the reactor. This is not only economically advantageous but has led to the tailoring of specific polymer structures with a unique balance of properties, enabling polyolefins to meet a wide range of industrial needs, from flexible packaging barrier films to stiff, impact resistant containers and engineered structural plastic applications.

## 1.2 ZIEGLER–NATTA CATALYSIS

At the heart of both random and heterophasic copolymer polypropylene production is the Ziegler–Natta catalyst system, developed from the initial discoveries of Professor G. Natta at Politecnico di Milano in 1954 [2–4]. The initial catalyst system used by Natta for the synthesis of polypropylene was based on Ziegler's catalyst system for the synthesis of polyethylene and consisted of  $\text{TiCl}_4$  and an  $\text{Al}(\text{C}_2\text{H}_5)_3$  activator. Unlike polyethylene,

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however, polypropylene can exist in a number of isomeric forms and Natta's initial studies gave a resin in which less than 40% of the polypropylene had the characteristics of a stereoregular polymer. The remaining polymer was atactic, with a low degree of structural uniformity and a rubbery consistency.

In order to develop a viable polymer with commercially acceptable properties, Natta's research was directed to a more stereospecific catalyst system. He soon realized that the polymer isotacticity was directly connected to the heterogeneity of the catalyst surface, and by employing solid, crystalline  $\text{TiCl}_3$  obtained by reduction of  $\text{TiCl}_4$ , in polymerizations with  $\text{Al}(\text{C}_2\text{H}_5)_3$  he obtained a higher percentage of isotactic product. The high isotacticity (about 90%) allowed a scaled-up industrial process to be developed by Montecatini, which contained a large section for the removal of catalyst residues that would affect product quality. In a remarkably short period of three years a scientific discovery in the laboratory had been transformed into a major new industrial plastic resin. The production process for this new polymer was, however, very complicated and expensive, requiring a large section for separation of the undesirable atactic fraction from the isotactic fraction in addition to the removal of catalyst residues. Because of its complexity, therefore, the process was not very versatile and was essentially restricted to homopolymer production.

Polypropylene research and development in the 40 years since Natta's initial discoveries and first generation industrial process has been concerned with improvements in both stereoregularity [5–9] and in the yields and efficiency of polymer production. This resulted, in 1975, in the discovery of highly efficient and stereospecific active  $\text{MgCl}_2$ -supported catalysts [10–12]. Such high yield, high isotacticity, superactive third generation catalysts are now widely used in today's commercial polypropylene production facilities. The polymer production process requires only three basic operations:

1. Polymerization.
2. Unreacted monomer flash and recycle.
3. Product finishing.

The need for atactic polymer and catalyst residue removal has been eliminated, resulting in a simple, vastly more reliable and versatile process.

### 1.3 THE MECHANISM OF ZIEGLER–NATTA CATALYSED POLYMERIZATION

The knowledge and understanding gained in the development of third generation, active  $\text{MgCl}_2$ -supported catalyst systems has made the polypropylene production process more versatile, allowing the synthesis and commercial production of novel polyolefins, random and heterophasic copolymers with properties never envisaged by the original discoverers of

Ziegler-Natta catalysed olefin polymerization. It is the understanding of supported catalyst architecture that is providing the major contribution to advances in Ziegler-Natta polymerization technology today.

The influence of the catalyst architecture is one of the most complex and difficult to control aspects of Ziegler-Natta catalysed polymerizations [13–15]. It is the physical and chemical structure of the active sites on the support that provide a three-dimensional shape that can be duplicated by the growing polymer particle. In a supported catalyst polymerization, when the monomers reach the catalyst particle, reaction occurs initially at the most accessible active sites. The polymer begins to grow, not only on the active sites on the surface, but also on those inside the crystal granule. The polymer chains grow outward from the surface, but also inward, causing the granule to expand progressively. It is this process that is particularly critical in the initial phases of polymerization. The mechanism of polymerization can vary from diffusion control to reaction control, and depends on the physical and mechanical properties built into the support and on the reaction medium [16–23]. Although kinetic studies of  $\text{TiCl}_4/\text{MgCl}_2$  catalysts for polypropylene polymerization are inconclusive [24–28], it is well known that all these systems are characterized by the lack of a constant polymerization rate, and demonstrate the following general features:

1. A very high initial polymerization rate, followed by a rapid decay and a stationary state.
2. Maximum productivity at a reaction temperature around 60 °C.
3. An increase in the polymerization isotactic index with an increase in temperature up to 70 °C.
4. An inverse correlation between stereospecificity and productivity.
5. The possibility of reversibly varying catalytic activity and stereospecificity of the system by acting on the instantaneous composition of the co-catalyst mixture, in particular, the ratio between aluminium alkyl and donor.
6. Absence of monomer diffusive phenomena in the reaction mixture and throughout the polymer layer covering the catalyst particle.

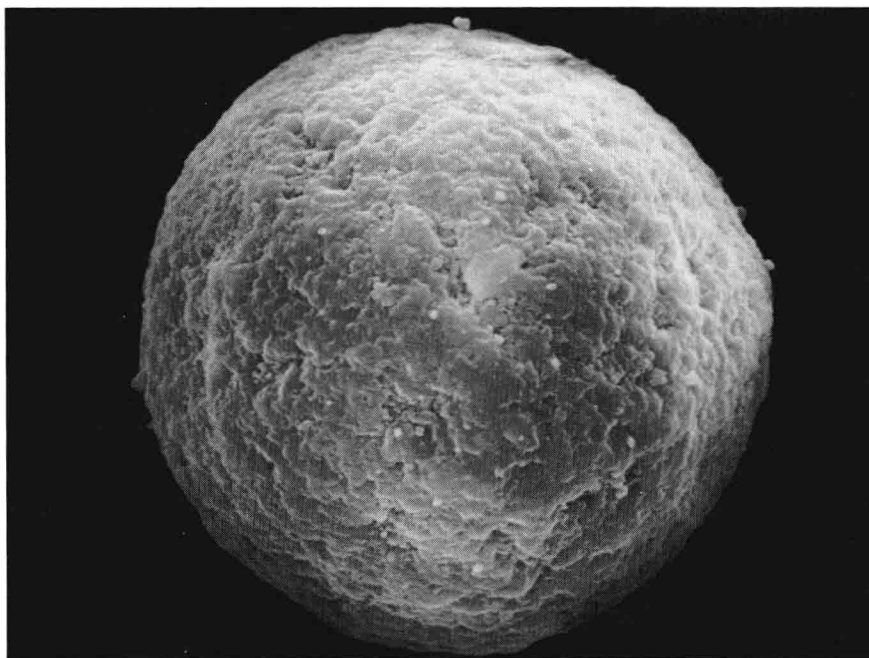
Experimental results have been rationalized by assuming a chemical deactivation of some of the active centres and the presence of at least two types of species on the catalyst surface. These are: (i) isospecific polymerization centres which are unstable with time, and (ii) less specific polymerization centres which, in turn, are stable with time. The latter appear to be preferentially and reversibly poisoned by the outside donor.

In order for the polymer particle to provide true replication of the catalyst particle, the mechanical strength of the granule must be in balance with the catalyst polymerization activity. If reactivity is too high, an uncontrolled 'explosion' occurs, and the mechanical forces generated by the growing polymer chain fracture the granule into a fine polymer powder. If the

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mechanical strength of the catalyst particle is too great, a low level of reactivity occurs because the internal active sites cannot generate polymer due to lack of space. Good replication and high activity only occur when the mechanical strength and polymerization reactivity of a supported, third generation catalyst are well balanced [29, 30].

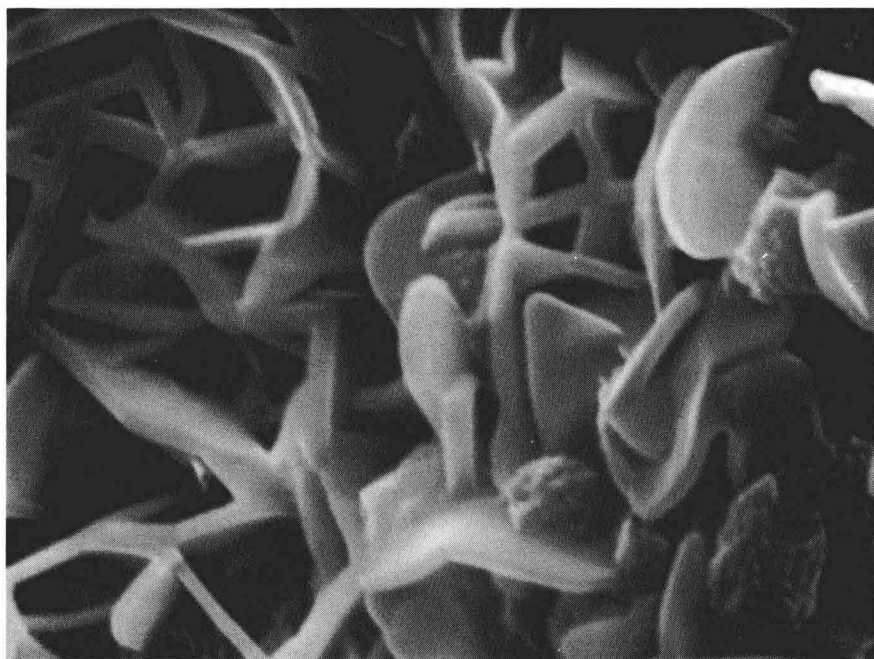
Figures 1.1–1.4 illustrate how a porous catalyst particle expands during prepolymerization, replicating its shape, the ‘structure’ held together by the intermingling of the polymer chains growing from the active polymerization sites spread throughout the catalyst particle [29]. Figure 1.1 shows a Ziegler–Natta polypropylene catalyst formed into the spherical shape characteristic of an activated  $\text{MgCl}_2$  support. Figure 1.2 illustrates a cross-section of the growing particle during the initial stages of polymerization at a polymer/catalyst ratio of 0.1. The break up of the catalyst particle and the intermingling of the polymer chains growing from the polymerization sites can be seen. It is important to note here the first appearance of a continuous skin that surrounds the porous interior of the particle where the polymer chains are continuing to grow. It is this skin that provides mechanical strength to the growing particle. Figure 1.3 illustrates the growing particle at a later stage of polymerization when the polymer/catalyst ratio is of the order of 1.



**Figure 1.1** Active  $\text{MgCl}_2$ -supported Ziegler–Natta catalyst ( $\times 1500$ ).



**Figure 1.2** Cross-section of polypropylene prepolymer. Polymer : catalyst ratio 1:1 (wt%) ( $\times 3100$ ).



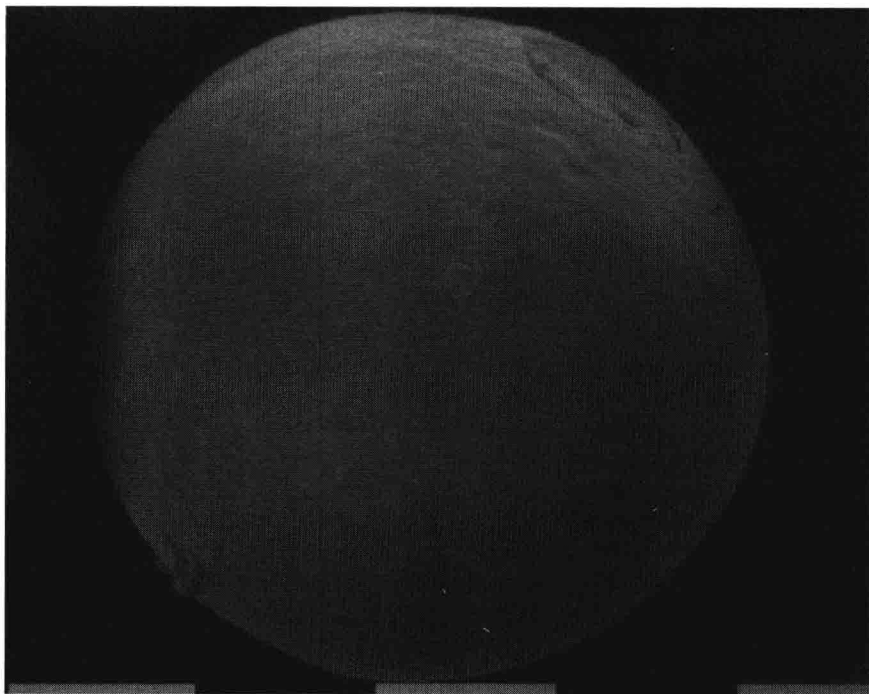
**Figure 1.3** Cross-section of polypropylene prepolymer. Polymer : catalyst ratio 1 : 1 ( $\times 5000$ ).

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Under appropriate conditions of catalyst preparation and polymerization, uniformly sized, compact polymer particles can be obtained, having the desired size and spherical form since they reproduce the original shape of the catalyst particle. Figure 1.4 illustrates a polypropylene particle at the end of the polymerization reaction. The duplication of the original spherical catalyst shape is obvious from this picture. Interestingly, it has been found in Himont's laboratories that only a few grams of polymer per gram of catalyst are needed to disintegrate the solid particle structure. Thus a large, active surface is exposed right from the very beginning of polymerization. In the case of the super-active third generation catalysts, the replication factor (the ratio between the size of the polymer granule and that of the catalyst particle) can reach values of up to 40–50 in comparison to 7–10 with conventional catalysts, without forming fine particles.

The five basic, indispensable requirements for a super-active catalyst are:

1. High surface area.
2. High porosity with a large number of cracks evenly distributed throughout the mass of the particle.
3. High enough mechanical strength to withstand mechanical processing, but low enough to allow the forces developed by the growing polymer

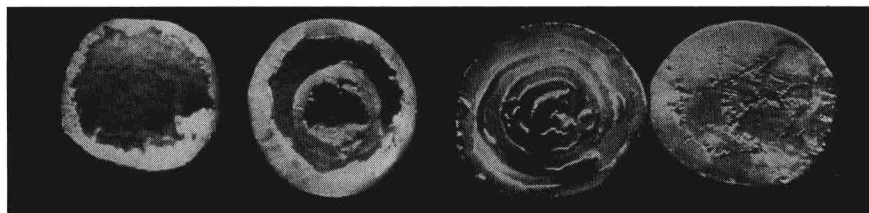


**Figure 1.4** Final shape of particles ( $\times 22$ ).

to break down the catalyst into the microscopic particles that remain entrapped and dispersed in the expanding polymer.

4. Homogeneous distribution of the active centres.
5. Free access of the monomers to the innermost regions of the catalyst.

Manipulation of the catalyst architecture and control of mass and heat transfer during the polymerization allow relative changes in the polymerization rate in the interior of the granule compared to that on the surface. Diffusion limitations can be induced by controlling porosity and preferential distribution of active centres on the catalyst surface. The net result is that during polymerization the polymer granule can be varied from a relatively uniform density to a layered, open structure and even a hollow particle with a thick polymer skin. Figure 1.5 shows polymer particles formed under different polymerization conditions that illustrate this effect.



**Figure 1.5** Cross-section of polypropylene particles formed under different reaction conditions.

It is the ability to controllably develop a growing solid, porous polymer particle that Himont/Montecatini has called 'reactor granule technology' [30–33]. The continually growing polymer particle can provide a solid reaction matrix, enclosed within which copolymer, terpolymer or multi-monomer random and heterophasic copolymer systems can be produced. The introduction of other monomers to the internal active sites during the polymerization process can produce a second or third different polymer within the original polymer granule, intimately dispersed among the pre-existing lattice structure of the initially generated polymeric matrix.

Control of the catalyst architecture and the reactor granule technology allows the freedom to conceive of and create new materials through the production of totally new polyolefin copolymers and alloys directly in the reactor [34]. Conventional third generation Ziegler–Natta catalysts, for example, limit the production of random polypropylene copolymers to relatively low levels of a second monomer. Low-melting random copolymers are difficult to produce in a conventional polypropylene industrial process because the 'sticky' nature of the resin causes fusion and blockage during the polymerization process. The porous, open structure of the reactor granule enables much higher levels of two or more monomers to be introduced, producing copolymers and terpolymers with unique properties.



Such low-melting copolymers can be encapsulated in a higher melting solid polymer matrix, effectively eliminating the problems of blockage in the polymerization reactor.

Since polymerization can take place within a solid polymer matrix, the mechanical containment aspects of the polymerization process became secondary. Bulk, gas phase and slurry processes are all equally adaptable for use with the catalyst system, and are chosen on the basis of economics, mechanical reliability and reaction control criteria in order to maximize reactivity and productivity.

This technique removes almost all of the previous process constraints on Ziegler–Natta polymerization, allowing reactor-made resins to be produced with properties no longer limited by mechanical considerations of the process.

#### 1.4 THE POLYPROPYLENE MANUFACTURING PROCESS

Polypropylene was the first stereoregular polymer developed and its production was considered to be complicated and difficult to control. The first commercial processes used low yield catalysts and made homopolymer by reacting propylene with a solvent or diluent and a catalyst in a stirred reactor, which produced a resin that contained about 10% atactic polymer. The atactic resin was reduced to less than 5% by extraction with hot hexane or heptane. The catalyst residues were removed by washing with short chain alcohols and with water. To make random copolymers in a diluent plant a slurry of propylene and ethylene, solvent and catalyst are fed into a stirred reactor at 60–70 °C, at around 1 MPa [35].

Heterophasic copolymers require the addition of one or more secondary reactors where the homopolymer or random copolymer exiting from the first reactor is allowed to react with an ethylene–propylene mixture to produce an ethylene–propylene rubber as a second phase within the polymer matrix. The processes that used these early generation catalysts required the purification and recovery of solvents and the disposal of contaminated waters. The reactors frequently fouled and extruders often failed, resulting in a very limited range of copolymers that could be made.

The development of the high yield, high activity supported catalysts significantly changed the process economics and environmental impact and greatly expanded the range of possible copolymer structures that could be produced. It became possible to eliminate the diluent altogether by conducting the reaction in liquid propylene, thus creating what have become known as the ‘liquid bulk’ processes.

Some producers, however, have retrofitted their old slurry plants with the new high yield, high activity catalysts that can produce a resin with less than 1% atactic polymer, eliminating the need for resin purification and catalyst removal. The economics of that approach compared to the construction of a new liquid bulk process are in doubt, however. Although the de-ashing and