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POLYPROPYLENE: AN INTRODUCTION

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POLYPROPYLENE: AN INTRODUCTION

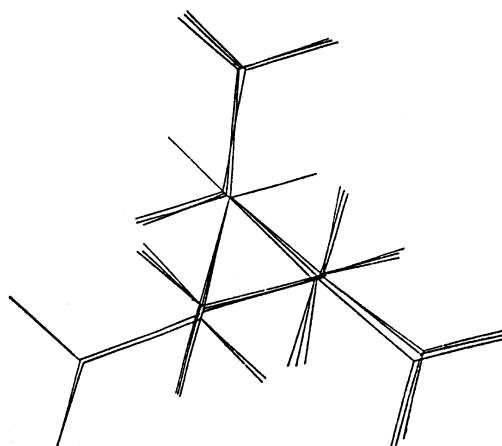
Otto Vogl

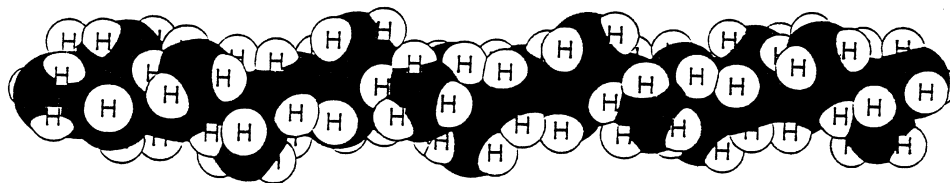
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Key Words: Polypropylene, Coordination Catalysts, Stereoregular Polymers, Isotactic Polypropylene, Polypropylene Production

ABSTRACT

Polypropylene now has a history of nearly 45 years since its discovery and 40 years since its commercialization. It has established itself as one of the most important polymers that has engineering plastic properties at commodity plastics prices. The end of the growth of polypropylene is not in sight.





INTRODUCTION AND HISTORY

Since the discovery and invention in 1954 and the beginning of commercial production by Montecatini in Ferrara in 1957 [1-3], polypropylene has become an exceptional commercial success. By the year 2000, about 30 million tons of polypropylene will be produced which amounts to over 15% of the entire plastics production which means, it the fastest growing commodity plastic.

For over 40 years, I have been peripherally involved with polypropylene, although in my own scientific interests only a small amount of research was concerned with propylene (co)polymerization. I began my industrial career in 1956, when I joined the Polychemicals Department of the DuPont Company. Warren Baxter at DuPont had, a short time before, discovered the polymerization of propylene [4], William Truett had polymerized norbornene [5] and the work on more efficient catalysts for propylene polymerization was in full swing. My own work was not in the polyolefin area. Shortly after joining the Polychemicals Department, I had been assigned to aldehyde polymerization, especially the then unknown polymerization of acetaldehyde, a close cousin of propylene. It was successfully polymerized in 1957 to an elastomeric polymer and in 1958 to a crystalline stereoregular isotactic polymer [6, 7].

By the early 60's, I became acquainted with Italian scientists who were associated with Professor Natta at Politecnico in Milan and had been involved in the development of polypropylene. With the late Professor Pino, the "right hand man" of Professor Natta, I developed a life-long friendship. I still remember his story how propylene polymerization was conceived at the Politecnico [8]. Propylene polymerization had been attempted before elsewhere with radical initiators but led only to n-hexadiene, the recombination product of the allyl radicals that were produced by radical abstraction from propylene. In 1952, there was a meeting of the ACHEMA in Frankfurt and Professor Ziegler gave the main address describing the "Aufbaureaktion" – an oligomerization of ethylene with

triethylaluminum that resulted in pentamers. At the time, rumors existed that ethylene could be polymerized to a high molecular weight polymer when transition metal compounds were added to the aluminum alkyl system. Natta and Pino attended Ziegler's lecture and when they left the lecture hall, Natta said: We should try similar polymerization conditions for propylene [8]. I told Pino that I also had been at Ziegler's lecture and had found it fascinating. At that time I did not understand the problems of oligomerization or polymerization because I was a young Assistant at the University of Vienna who was interested in natural products, steroids, and alkaloids.

While the Natta group forged ahead in the 1950's, and polymerized every olefin in sight with every kind of coordination compounds as catalysts, I continued my research work in aldehyde polymerization. I was interested in the development of stereospecificity and conformational specificity of polymerization based on the bulk and size of the side group using chloral polymerization as the example [9]. This led to the concept of the helicity of macromolecular asymmetry, and with chiral initiators gave optically active polymers. Pino had come to similar conclusions by studying stereospecific polymerization of substituted olefins with a chiral side group which gave isotactic helical polymers of preferred helical sense.

But back to the invention of polypropylene. Many years after my acquaintance with the Natta school, in fact, a few years ago I visited again the Politecnico in Milan, Professor Lido Porri, the successor of Natta at the chair at the Politecnico. Among current scientific topics we reminisced about the discovery of the polymerization of propylene. Figure 1 shows a picture of Giulio Natta, Figure 2 shows his Natta's desk and, Figure 3 the laboratory bench at the Politecnico where, on March 14, 1954, P. Chini synthesized the first sample of polypropylene [8].

Many years later, in 1975, when I had been a Professor at the Polymer Science and Engineering Department of the University of Massachusetts in Amherst for several years, I was invited by Montedison to function as a management consultant. I was subsequently appointed special Advisor to Italo Trapasso, the President of the Division of Plastics Materials of Montedison in Milan with specific responsibilities of developing options for the reorganization of the research organization of the Division (which at that time had sales of about \$1.5 billion per year). As a consequence of this reorganization, Paolo Galli was appointed Director of Research of the Center in Ferrara. Under his leadership, the objectives of research were redirected which led to spectacular developments in new products and new processes. Several new types of propylene



Figure 1. Picture of Professor Giulio Natta.

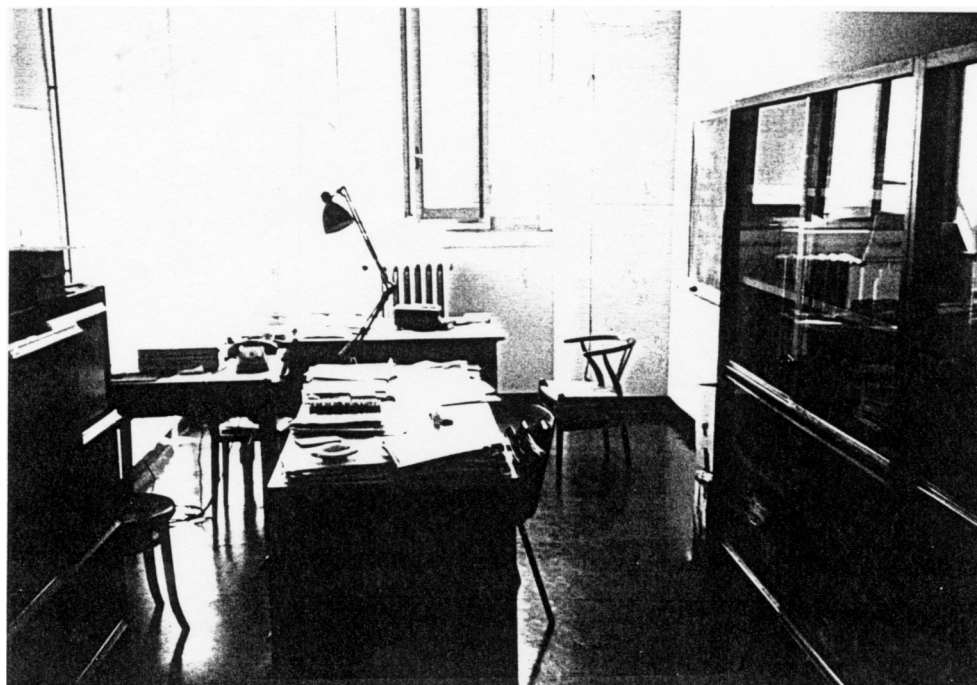


Figure 2. Natta's desk at the Politecnico.

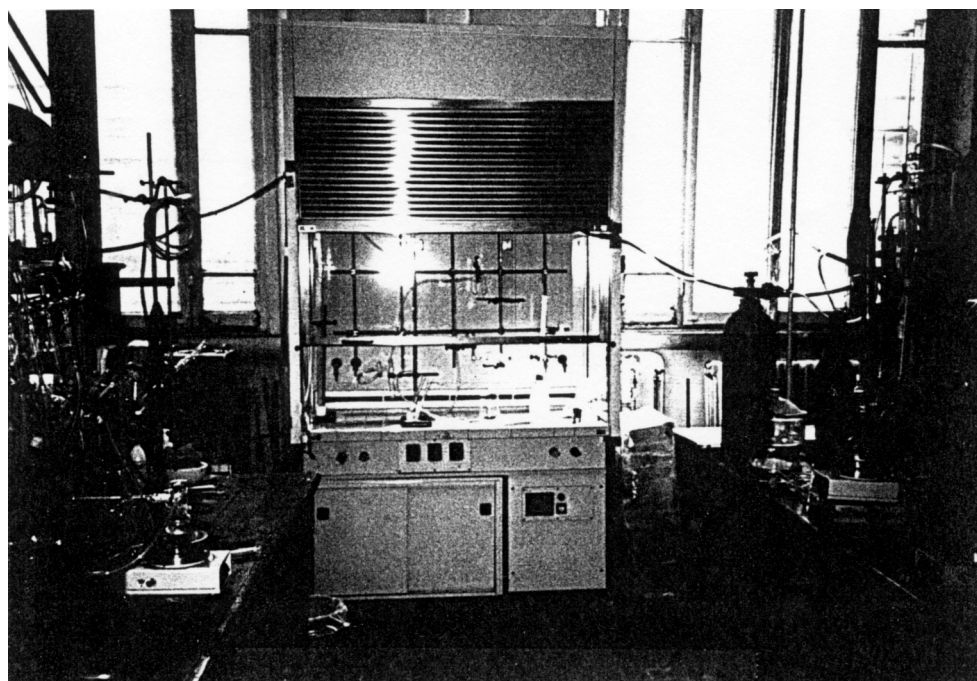


Figure 3. Laboratory where Polypropylene was discovered.

polymers were created and new polymerization processes which were more cost effective were brought into production. To commemorate over 20 years of success in polypropylene, Gallihad a statue commissioned, showing the helical structure of isotactic polypropylene (Figure 4). The Research Center in Ferrara was named in honor of Natta in 1980.

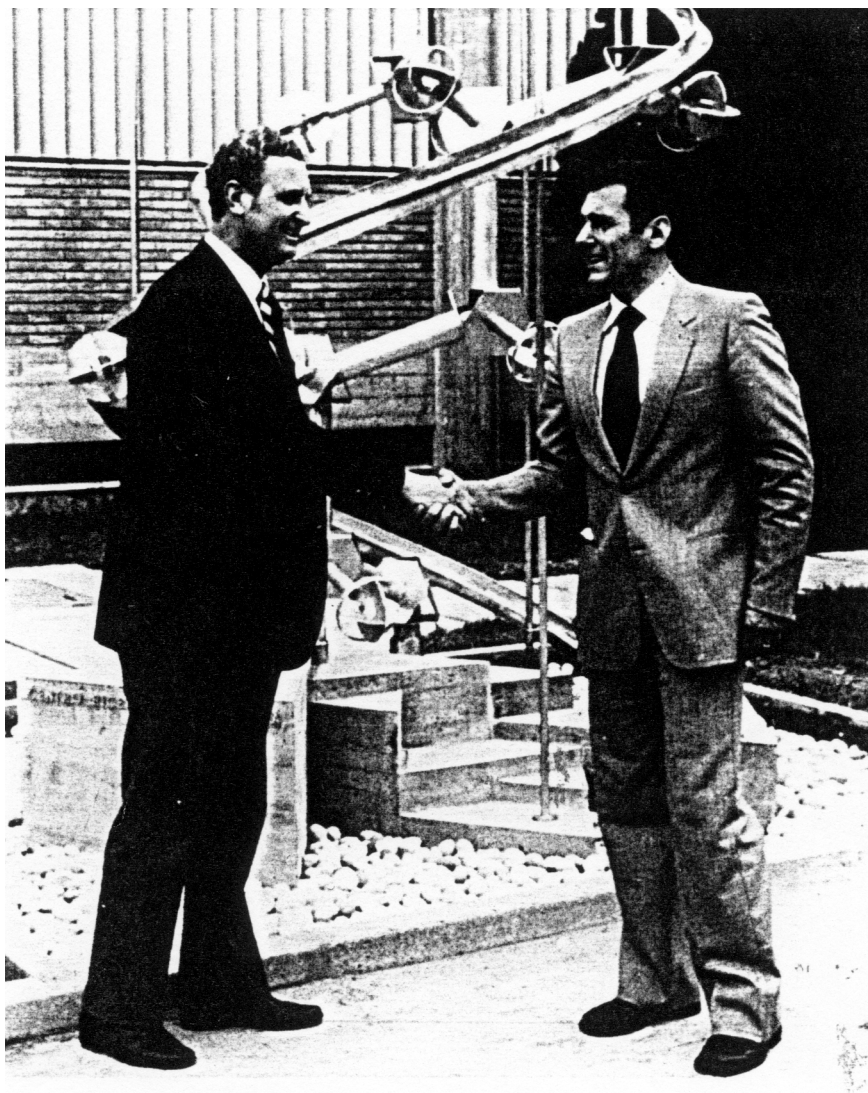


Figure 4. Statues of Polypropylene in Ferrara (with Paolo Galli and Otto Vogl in 1980).

My further relationship with polypropylene continued in 1989, when I became a Member of the Board of Chemie Linz in Linz Austria, and a consultant to PCD. PCD, the polyolefin company of Austrian Industries, (which has recently been sold to Borealis) was the successor of Danubia, Austria, which, in turn, was the first licensee of Montecatini's polypropylene process in the late 1950's. In 1991, Professor Manfred Rätzsch was appointed the research director at PCD, and he very rapidly transformed PCD research to a world class research organization.

Today, we honor Paolo Galli and Manfred Rätzsch for their outstanding contributions to the chemistry, technology, and business successes of polypropylene with the Herman F. Mark Medal of the Austrian Research Institute of Chemistry and Technic and the Austrian Plastics Institute.

Polypropylene: Structure and Business

Polypropylene, as we know, is a stereoregular polymer of high isotactic stereochemistry. In its crystalline state it has the structure of a 3_1 helix with a repeat distance of about 6.65 Å. It has three distinctly identifiable crystalline phases, the α -, β -, and γ - phase [10, 11]. The phases are distinguished by their fundamental structure as helical polymers. Polymers that crystallize in helical conformations, crystallize as 50:50 mixtures of left and right handed helices and the equal handedness of the polymer helices are formed by statistical nucleation. In polypropylene, the individual phases all have right and left handed 3_1 helical structures. The only difference between the phases is the exact relationship of the left and right handed helices in the unit cell of the polymer crystals. There are at least three energy minima of crystallization that can develop during polypropylene crystallization which are represented by the three phases. The ultimate structure, the single helix of polypropylene, the structure that would be obtained by crystallization with a chiral nucleating agent has not been found [12, 13].

In 1972, after 15 years of commercialization, the polypropylene production was only a few million tons, but the discovery of high yield catalysts that allowed the catalyst to be left in the final product without any noticeable side effects started the spectacular growth that averaged about 10% per year over the last 25 years and is still continuing strongly. The growth of the last few years, is estimated to have been over 10% and seems to continue (Figure 4), In 1997, polypropylene was produced in 157 plants locations by 115 companies (legal units) in 44 countries. One of the reasons for polypropylene's success is that

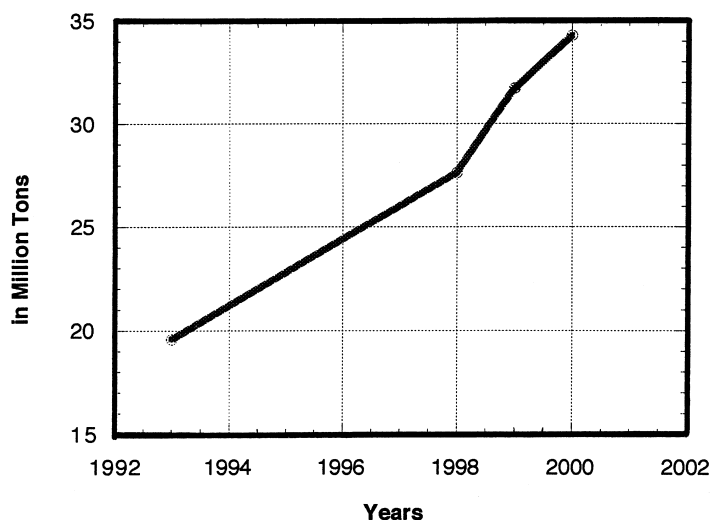


Figure 5. Growth of Polypropylene production.

major parts of the polypropylene market require properties of nearly “Engineering Plastics” character, at polyolefin prices.

The properties of polypropylenes and competitive polymers are shown in Table 1. Without discussing in detail the basic properties we are comparing polypropylene with high density polyethylene and polyoxymethylene with respect to melting point, tensile strength, modulus, elongation at break and, most importantly, the price of the base polymer.

In Table 2, we compare the world-wide production of polypropylene together with the companies that produce these products. About 70% of polypropylenes are homopolymers and the rest are copolymers with ethylene and other α -olefins, a small amount are atactic polyolefins.

In this introduction, we are concentrating on propylene homopolymers, stereoregular polypropylene with high isotactic content. Syndiotactic polypropylene has been synthesized and studied, found interesting but is not commercially produced at this time.

In Table 3, a short summary is presented describing the polypropylene capacities of 1998. The traditional slurry process is still being used in a number of companies, the liquid process by 12 and the gas-phase process by quite a few. Judging from the development in the 1990's, polypropylene using the liquid propylene process and the gas phase process is increasing and the slurry process

TABLE 1. Properties of Polypropylene and Competitive Polymers

	Polypropylene (Homopolymer)	Polyethylene HDPE)	Polyoxymethylene Copolymer, 165
T _m , in°C	165	136	178 Copolymer, 165
Tensile Strength (MPa)	25-40	20-30	60-75
Modulus (MPa)	1,300-2,300	600-1,400	2,800-3,200
Elongation at Break (%)	> 50	>50	20-50
Price Range of the Base Polymer per kg, in DM (Western Europe, May 1998 Injection Molding Grade)	1.1	1.4	4.5-5.5

is decreasing. To be more specific, in 1993, at 19.5 million tons, bulk processes had a share of 23%, gas phase of 19, slurry 38, and others 20%. In 1998 the percentage of the individual processes had shifted and at 27 million tons 36% were bulk processes, 25.5% gas phase processes, 28.5% slurry and only 10% others. For 1999, at a production of 32 tons of polypropylene per year the projection is: 38% bulk processes, 29% gas phase, 25% slurry and only 8% others.

TABLE 2. World-Wide Production of Polypropylene (in Million Tons)

A.) Polypropylene Homopolymers: 17
B.) Polypropylene Copolymers: 6
1.) With Ethylene: 5 - 5,5
2.) With Other α -Olefines
Catalloy Terpolymers: C ₃ -C ₄ Polymers: 0,5-1
C.) Atactic Polyolefins: 0.1
Eastman, Huntsman/Rexene, Ube, DSM/Hüls and APP as Byproduct

TABLE 3. Polypropylene Process Capacities, in Million Tons (Best Estimates for 1998)

Slurry Process*: 8 *(Companies: Many)

Liquid Propylene Process**: 12 **(Companies: Montell/Sheripol, Lipshac, Mitsui/Hypol, Sumitomo/Sumika.

Gasphase Process***: 8 *** (Companies: UCC/Unipol, BASF, Amoco/Chisso, Sumitomo/Sumika, Montell/Catalloy, in development: Borealis/Borstar (supercritical)

We can look at it in other ways by comparing the major polypropylene processes as shown in Figure 6. Both the bulk and the gas phase processes will continue to grow, and both at similar growth rates. The difference in those processes is in the dissipation of the heat of polymerization of propylene which is about 18 Kcal/mol. The bulk process is run in liquid propylene and the heat is dissipated in a refrigerator type technology, similar to the bulk polymerization of vinyl chloride (the Rhone-Poulenc process). The dissipation of the heat of polymerization in a vapor process is done in a fluidized bed reactor. The various processes require specially designed catalysts to produce the polymers in the right stereochemistry of the polymer structure and in the most efficient and economic way.

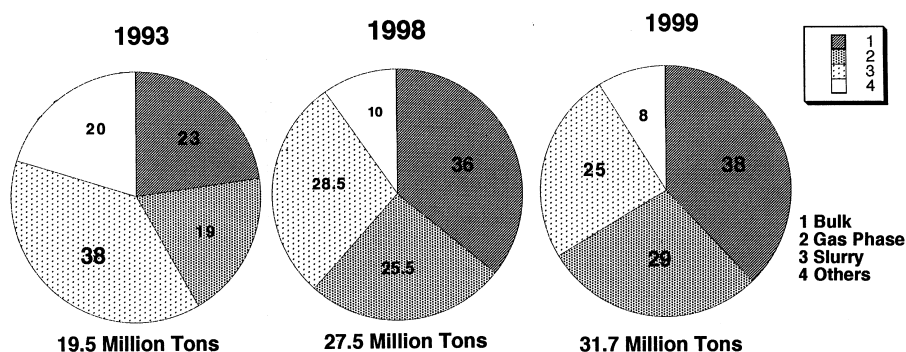


Figure 6. Percentage of individual Polypropylene processes (development of market shares in the last decade).

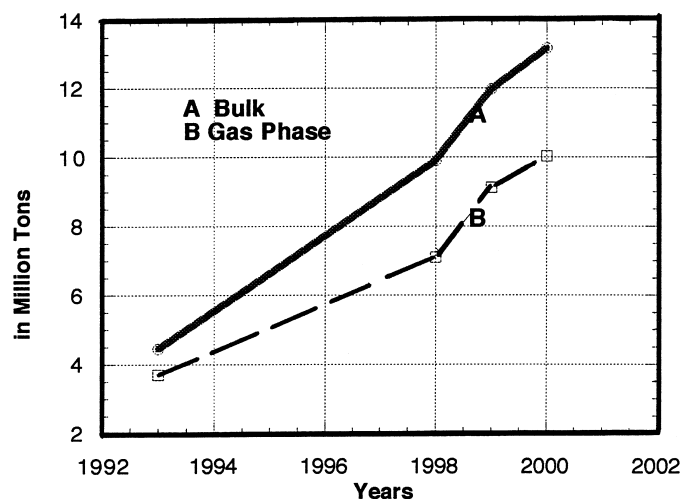


Figure 7. Major Polypropylene processes.

On the other hand, slurry and other traditional polypropylene processes (Figure 7) will decline and will be phased out as the economics dictate.

We have discussed in the few figures the principles of the individual processes for the production of polypropylene. Each process that we described has a principle basis, but the actual processes have some very significant verifications that might and do determine the productivity and the competitiveness for their market share. The most important processes in their production variables are shown in Figure 8. At this time, the dominant process for polypropylene production is the Spheripol process which commands about 51% of the market and can be used for liquid and gas phase use, followed by the Unipol process of 21%, the Novolen process of 14%, the Amoco-Chisso process of 7% similar to the Hypol process of also 7%.

The numbers and figures that we have accumulated in the study for this introductory paper are based in close consultation with the major producers of polypropylene, the numbers that are presented are common knowledge for the experts.

Polypropylene will continue to be a most exciting polymer with the possibility of far-reaching possibilities in properties and of reaching unusual property combinations [14].

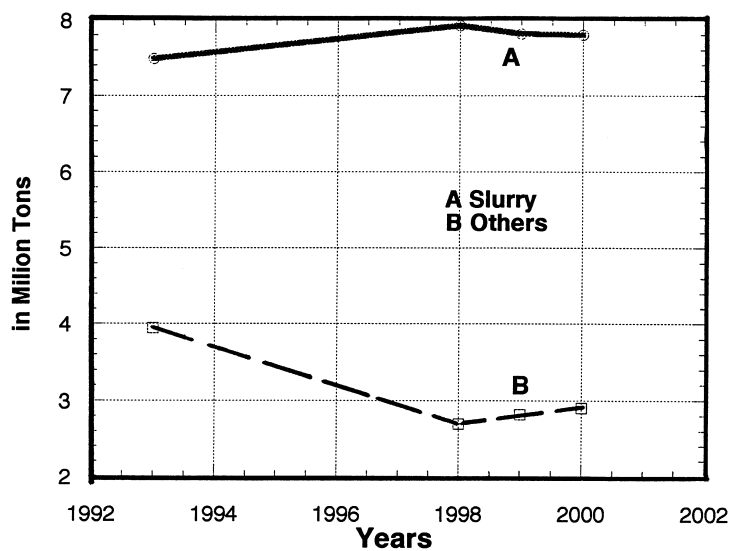


Figure 8. Other Polypropylene processes.

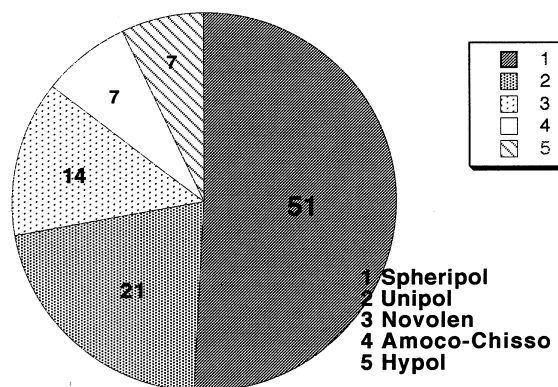


Figure 9. Percent of market share of Polypropylene processes at present.

ACKNOWLEDGEMENTS

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