

Polypropylene

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Introduction

Spain, 1954, polypropylene was first produced by Professor Giulio Natta. Natta was able to produce the resin by using catalysts from the polyethylene industry and applying them to propylene gas. The first commercial production began in 1957.

Polypropylene is a very versatile material. It offers a great combination of properties such as lightweight, strong, high heat resistance, as well as stiffness and flexural retention. Among these and many other great properties, polypropylene is easily fabricated. Polypropylene can be subjected to a wide range of fabrication methods and applications.

Chemical Names

The chemical name for polypropylene is poly(1-methylethylene).

Common Names

Some of the common names for polypropylene include the following:

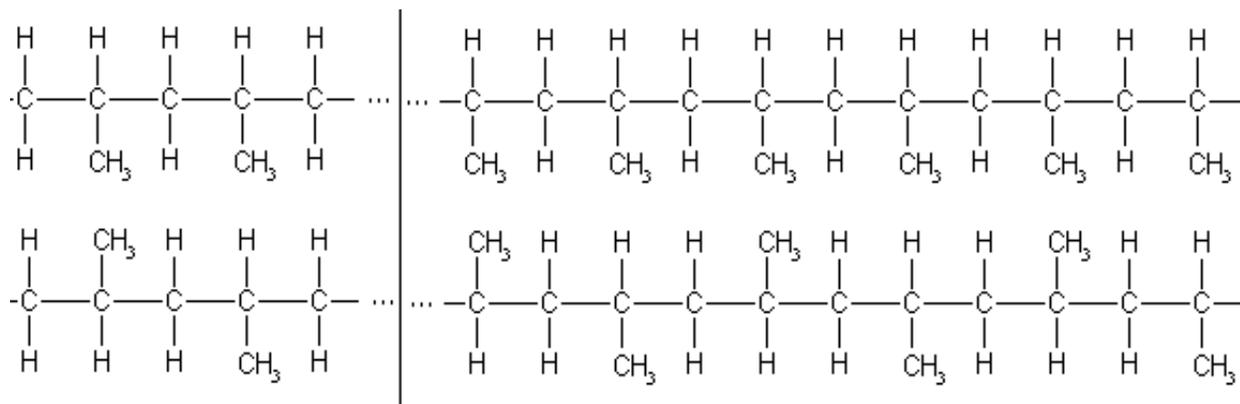
- Polypropylene
- Polypro
- Polypropene
- Polipropene 25
- Propene polymers
- Propylene polymers
- 1-Propene homopolymer

Brand Names

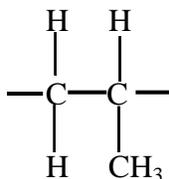
There are many different brand names for polypropylene used in industry. A small selection has been listed below:

- Carlona P
- Herkulon
- Moplen
- Napryl
- Profax
- Propathene

Drawing of Monomer



The top drawing represents a small portion of the structure of isotactic polypropylene and the syndiotactic structure. Polypropylene can also be produced in an atactic form using Kaminsky catalysts, but such a form proves not very useful. Atactic polypropylene blocks are generally joined with isotactic blocks to produce elastomeric polypropylene. Elastomeric polypropylene is not commercially produced. The polypropylene monomer is a single bond between two carbon atoms. The first carbon atom has two hydrogen atoms connected to it, while the second carbon atom has one hydrogen atom, and one methyl group (CH₃) attached to it. This can be seen below:



Polymerization

Polypropylene is generally made from propylene via Ziegler-Natta polymerization or metallocene catalysis polymerization, but can also be produced by Kaminsky polymerization. The typical production of polypropylene starts with crude oil which is distilled into naphtha. Naphtha then undergoes a cracking process, which occurs while being used as feedstock in petrochemical steam crackers. The cracking breaks naphtha down into various olefins, including propylene. Propylene then produces polypropylene via one of the previously mentioned methods.

The typical progression of production is as follows:

(Cracking via
Petrochemical Steam Crackers)

(Ziegler-Natta Polymerization /
Metallocene Catalyst)

Naphtha \longrightarrow **Olefins (including Propylene)** \longrightarrow **Polypropylene**

Yearly Production

The annual production of polypropylene is about 8.4 million metric tons. This production statistic is for the U.S. only. The rate of production is increasing, but more slowly than in previous years.

Domestic Market

Polypropylene prices have been climbing steadily. A \$.05/lb increase is expected this month. Large volumes of offgrades have been moving quickly, while generic prime has been available, but only on a limited basis. Domestic demand is a little stronger than average, but the buying activity does not indicate inventory building.

Export Market

The steadily increasing price of polypropylene has put strain on the export market. Also, rail and packaging delays in Houston have caused export deals to become thin, and too risky. March is seasonally a stronger month for polypropylene, so perhaps the domestic market will pick up where the export market is lacking.

Product Form

Polypropylene is often found in pellet form. It can also be found as a fiber, such as in tape, strapping, and continuous filament. Sheets, rods, and flakes are also available. The common uses of these different polypropylene forms, broke down into percentages, is 26.5% packaging, 15.6% fabrics, 13.9% carpets & rugs, 11.0% housewares, 9.3% motor vehicles, and 23.7% other.

Available Grades

Polypropylene is currently available in three different main grades.

- Homopolymers - General purpose grade, very versatile.
- Block Copolymers - 5-15% ethylene, improved impact strength to below 20° C.
- Random Copolymers - co-monomers arranged randomly on molecular chain, more flexible and better clarity.

Also available are many different sub-grades of polypropylene. These include UV resistant, flame retardant, aramid fiber, glass fiber, carbon fiber, mineral, lubricated, impact resistant, chemical resistant, and many others.

Melt Index

The melt index test measures the rate of extrusion of a thermoplastic material through an orifice of a specific length and diameter under prescribed conditions of temperature and load. This test, being the most common test for plastics, is used to measure and determine the flow rate of the material. The melt indexer is good for lot to lot comparison, which can be determined by the melt flow rate. The molecular weight will fluctuate with the MFR. As the MFR increases the molecular weight will increase, and vice versa.

	g/10min
Melt Index	.5 - 136

Density and Specific Gravity

Specific gravity, similar to relative density, is a ratio of the weight of a certain volume of material to an equal volume of water at 23° C. Determining the specific gravity of a material is done by weighing the sample in air then weighing it again, submerged in distilled water. These two weights will be entered into a formula where the specific gravity can be found.

Relative Density/ Specific Gravity	0.095
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Mold Shrinkage

ASTM D955 is the test used for mold shrinkage. Mold shrinkage is the amount of shrinkage the material undergoes after the molding process has taken place. These tests are used so molds can be precisely machined to ensure up to standard final product dimensions.

	in/in
Mold Shrinkage	0.01-.025

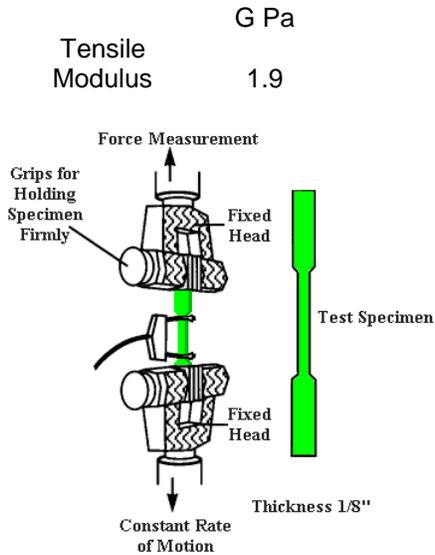
Tensile Strength @ yield

Tensile strength is determined through tensile testing, which is a measurement of how much force a plastic can withstand before fracturing or breaking. Throughout the tensile testing, information such as brittleness or ductility of a material is revealed. This information is used when designing parts to be absolutely positive that the part will withstand all environmental forces it will encounter. A stress vs. strain graph, created from the tensile test, is commonly used to find out the materials tensile strength at its yielding point and its tensile modulus.

	psi
Tensile @ Yield	5,000

Tensile Modulus

The tensile modulus is a ratio of stress to elastic strain in tension. The tensile modulus of different resins may be acquired through tensile test ASTM D638, as shown in the picture below.



Ultimate Tensile Elongation

Ultimate tensile elongation is the percentage of the material's length which has increased before failure. Ultimate elongation is read directly from the stress vs. strain graph resulting from the tensile test.

	%
Ultimate Tensile Elongation	10-20

Elastic Modulus in Flex

The elastic modulus measures the stiffness of a material, which is extremely important when it comes to designing of products. When in flex, measurements of how much force the material can withstand before deforming are taken.

	G Pa
Elastic Modulus in Flex	1.7 - 2.5

Hardness

When measuring the hardness of materials, the Rockwell Hardness Test is used. The hardness is determined by penetrating the material with an indicator on a hardness testing machine. The further the indicator penetrates the sample, the larger the number measured, and the harder the material.

	(R)
Hardness	80 - 110

Izod notched or un-notched

An apparatus known as an Izod impact tester is used to measure a material's resistance to impact from a swinging pendulum. A specified notch is cut into the samples which will prevent them from deforming when under impact. The ASTM D 256 test is useful to compare the toughness of materials. There are several different types of breaks including complete, hinged, partial, and incomplete. Samples are conditioned in different environments before being tested to determine how they react under different climates. Results of the impact test, which are read in ft-lb/in., are calculated by dividing the impact energy by the thickness of the sample.

	ft-lb/in
Izod notched	.5 - 2.2
Izod un-notched	121 - 31.1

Deflection Temperature

Deflection temperature is a material's resistance to distortion under a given load at elevated temperatures. ASTM D648, also known as Deflection Temperature Under Load (DTUL), is the test commonly used for deflection temperature. The two common loads used are 0.46 MPa (264 psi) and 1.8 MPa (66psi).

	°C
66 psi Deflection Temperature	200 - 250
	°C
264 psi Deflection Temperature	125 - 140

Dielectric Strength

Dielectric strength is the maximum voltage required to cause a dielectric breakdown through a material. It is used to measure a material's electrical strength as an insulator. The dielectric strength is reviewed when comparing two materials to see which better acts as an insulator. The better insulator will have the higher dielectric strength of the two.

	Kv/mm
Dielectric Strength	500 - 600

Flammability

Measuring a material's response to heat or flame is known as testing its flammability. When a product may be exposed to heat or flame, the testing of flammability is extremely important. It is absolutely vital for users to know if products are flammable and if they produce toxic gases while burning. Under the UL 94 testing, polypropylene is classified as HB (Horizontal Burning). For a material to receive a flammability rating of HB it has to undergo testing with a one inch flame for 30 seconds at a 45° angle. Once in position a continuous flame is applied to the material. A set distance is determined and the time it takes to burn the distance is recorded.

Thermal Conductivity

Thermal conductivity is the rate at which heat is transferred through a section of material. When it comes to materials which are exposed to the most extreme temperatures, the measure of heat flow through a material is a testing essential. The molecular make-up, thickness, and density of a material, all directly relate to its thermal conductivity.

	W/m K
Thermal Conductivity	2.8

Heat Capacity

Heat capacity is a ratio of the heat added to a material to its change in temperature. This is simply a measure of the amount of heat the material will store before becoming defective. If a material's temperature rises greatly when heat is added then its heat capacity is low, and vice versa.

$\text{Heat added} = \text{heat capacity} \times (\text{change in temperature})$
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	BTU/lb- °F
Heat Capacity	0.478

Crystallinity

The level of crystallinity of a material is a very important factor to deal with before the product is put to use. The amount of crystals formed in a semi-crystalline material, such as polypropylene, can not only affect the material's thermal properties, but its overall strength, and also quality control. The optimal crystallization temperature occurs between the T_m and T_g of the material. The degree of crystallinity of a sample can be found by using Differential Scanning Calorimetry (DSC). The overall crystallinity of polypropylene may reach upwards of 75 %.

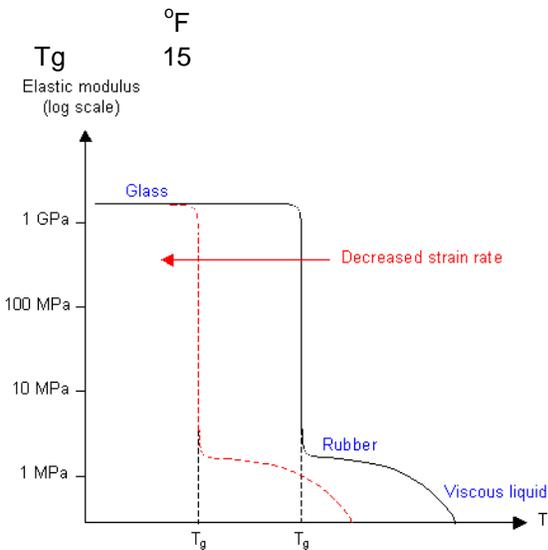
Crystalline Melting Temperature

The point at which material's melt and crystallize is known as the material's melt temperature (T_m).

T_m °F
 350

Glass Transition Temperature

Glass transition temperature (T_g) is the temperature where a material in a solid state changes to a rubbery state. The glass transition temperature is one of the main parameters used to select a polymer for a specific use. The graph below illustrates a material's transition from solid to liquid.



Major Suppliers and Producers

The major polypropylene suppliers and manufacturers are Exxon Mobil, Honam Petrochemicals, Hyundai Petrochemicals, Shell, Samsung, and Dow Chemicals. The United States leads the race in polypropylene production, followed by Germany and Japan in second and third respectively. In 2004, the U.S. produced approximately 8.4 million metric tons of polypropylene. Total Petrochemicals, Huntsman Polymers, and Exxon were contacted for comment on their companies' polypropylene production. Unfortunately, Exxon proved very difficult to contact anyone with any knowledge of their polypropylene production.

Trademark Names for Polypropylene

There is a vast selection to choose from when it comes to trademark names for polypropylene. Since so many companies produce and use polypropylene, there are many different company trademarks. A few examples include Bapolene used by Bamberger Polymers Inc., Marlex by Phillips Sumika, and ComAlloy, Comtuf, Hiloy, and Voloy all by Aqualoy.

Resin Availability

Polypropylene is most commonly available in bags, gaylords, trucks, and railcars. Total Petrochemicals utilizes 55 gallon drums, 25 kg bags, 1500 lb. super sacks, and tractor trailers. They mainly utilize 4 compartment railcars, capable of carrying 50,000 lbs. per compartment. Huntsman Polymers sells the majority of their products by the railcar, truck, and gaylord boxes.

Capacity of Plants

Total Petrochemicals' North American plant is located in LaPorte, Texas. It is their largest site, and also the largest single polypropylene production site in the world. They also have three production sites located in Western Europe, and own a share of the Samsung plant in Daesan, South Korea. The production levels are 200,000 lbs. per large reactor, and 20,000 lbs. per small reactor. 95% of this product is in the prime category. Total Petrochemicals specializes in many types of polypropylene including copolymers, impact copolymers, random copolymers, and homopolymers. They use these to make polypropylene suitable for blow molding, extrusion, thermoforming, and injection molding, among many others. They produce five grade levels of polypropylene; prime, generic prime, wide spec, wide spec with no contaminants, and scrap. Prime is their best product. Generic prime is slightly below the target level melt flow index, and wide spec materials range from additives out of spec to a missed melt flow index. Scrap could consist of anything from a plugged reactor, to a spill on the floor, or metal, rocks, and other contaminants mixed in. They target a 95% efficiency rate and typically hit or exceed these standards.

Huntsman Polymers, located in The Woodlands, Texas, sells a polypropylene homopolymer, random copolymer, impact copolymer, as well as some highly specialized grades for engineering purposes. They have three polypropylene plants which manufacture 500 different products and produce 600,000 metric tons per year of polypropylene.

Production Volume

The total production volume of polypropylene varies yearly, but in 2004 it was 8.4 million metric tons. The Total Petrochemicals plant located in LaPorte, Texas produces 1 million metric tons per year. Huntsman Polymers produces 600,000 metric tons of polypropylene per year. Many other companies, from large to small, contribute to the total yearly production volume.

Market Position

The market position is determined by the total amount the company produces out of the total U.S. production volume. Total Petrochemicals produces 1 million metric tons per year, putting their position in the market at 12% of the total production in the U.S. Huntsman Polymers produces 600,000 metric tons of polypropylene per year, putting their market position at about 7% of the total U.S. production.

Proprietary Positions

Proprietary positions are patented processes, or products, that companies develop and patent. One example is Borpact polypropylene made by Borealis. The company saw a need for a transparent, deep freeze resistant, polypropylene product. They designed and patented this material to make the display of frozen desserts more aesthetically pleasing. Mainly used for ice cream packaging, Borpact straddled the technical challenge of integrating transparent and extreme low temperature resistance in a thin walled injection moldable part.

Vertical and Horizontal Integration

If a company owns its own oil, and produces its own polymers, it is considered vertically integrated. Examples of vertically integrated companies are Exxon, Shell, and Total Petrochemicals. Horizontally integrated is when a company sends out for plastic to process. BASF is a good example of this.

Structure of the Company

The company structure of Total Petrochemicals has sales offices, headquarters, and research centers spread out all over the world. Total Petrochemicals has sales offices located throughout Europe and the Far East. Their headquarters are located in Texas, France, Belgium, United Kingdom, China, and Singapore. Research centers are located in France, Spain, Belgium, and Texas. Along with this cohesive unit of dedicated professionals they provide sales and service for polypropylene, polyethylene, and polystyrene.

Relationship between Marketing, Manufacturing, and Technical

The relationship between marketing, manufacturing, and technical, is extremely important, not only for plastics companies, but for any company that wishes to stay competitive in today's market. Each department must keep open lines of communication for the company to be truly successful. For example, when contacting Total Petrochemicals, the transferring between departments and information sharing was imperative to receive the information requested.

Local Sales Person

The local sales person to be contacted for information on polypropylene is listed below.

Port Erie Plastics Sales / Marketing Manager:

Jon Connole

814-899-7602 (Ext. 314)

jconnole@porterie.com

Local Technical Service

For local technical service contact A. Schulman Inc. Technical Service Department with the information listed below.

1-800-54-RESIN

info@aschulman.com

Company Tech Services

Total Petrochemicals offers a variety of services, including an e-customer service option which can be accessed from their website, www.totalpetrochemicals.com. They also offer technical product data sheets, and online troubleshooting guides. They can be contacted by phone for questions at 1-800-344-3462.

Costs

The current price of polypropylene monomer quoted from Total Petrochemicals is in the range of \$.45/lb. This price, just like gas, is always changing because it depends on the price of oil. Since polypropylene is made from propene which is made from oil products, the cost of oil has a significant affect on the price of polypropylene. Price is affected by multiple variables, including amount of filler, what type of polymer it is, and amount purchased. Market factors that influence price are economic growth of polypropylene countries, domestic industrial growth and development, and demand in the international market. The chart that follows shows some pricing information for the homopolymer and copolymer from August 2006.

DOMESTIC PRICES

HOMOPOLYMER:

Click for Price History

				Price Range		Four weeks ago	USD/MT
BULK (INJ)	US CTS/LB	n/c	63.00-66.00	n/c	65.00-68.00		1389-1455
BULK (RAFIA)	US CTS/LB	n/c	61.00-64.00	n/c	63.00-66.00		1345-1411
BULK FILM (BOPP)	US CTS/LB	n/c	66.00-69.00	n/c	68.00-71.00		1455-1521

COPOLYMER:

Click for Price History

			Price Range			USD/MT
BULK	US CTS/LB	n/c	67.00-70.00	n/c	69.00-72.00	1477-1543
GP FILM	US CTS/LB	n/c	69.00-72.00	n/c	71.00-74.00	1521-1587

5 Year Price History

Chart 1 below shows a 5 year price history for the polymer and chemical grade of polypropylene. Chart 2 shows the price progression using the data from chart 1. Chart 3 compares the price of polypropylene in relation to the cost of oil.

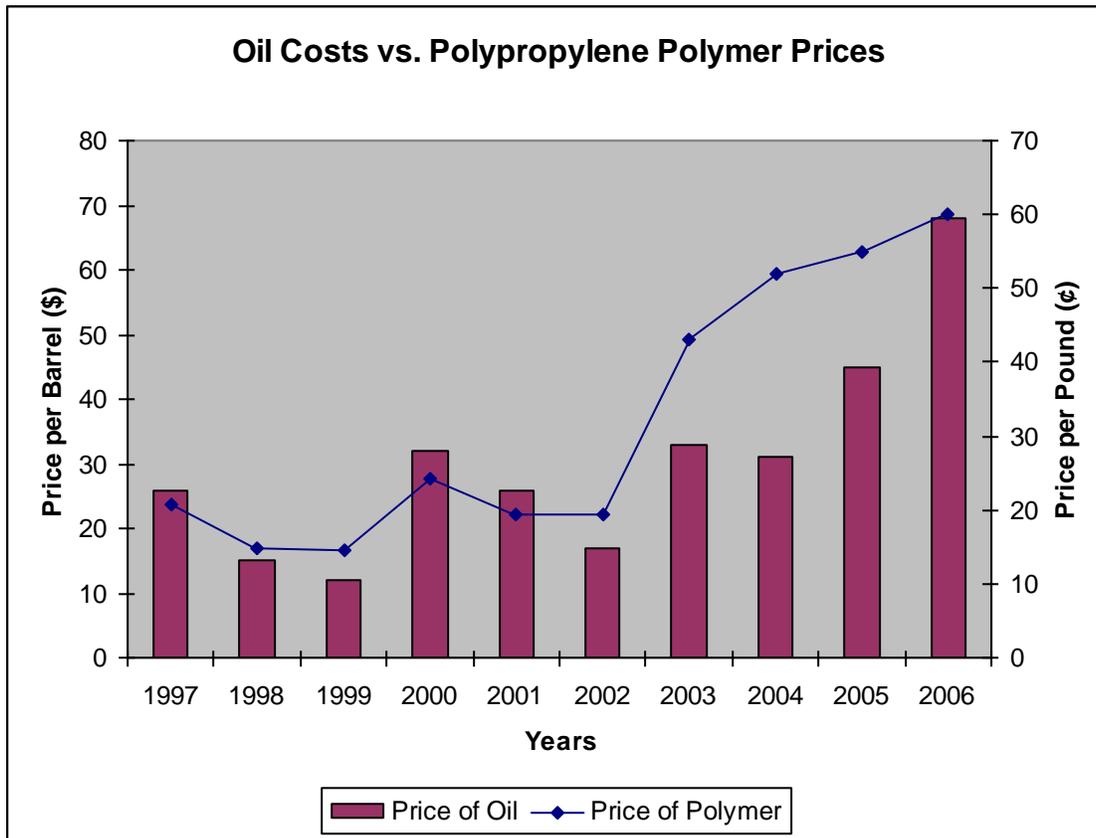
1.

Year	Demand Millions of pounds, propylene	Price*	Price*
		Polymer Grade ¢ Per pound, an. aver., Gulf, contact, dlvd.	Chemical Grade ¢ Per pound, an. aver., Gulf, contact, dlvd.
1997	30,359	20.70	19.25
1998	34,111	14.75	13.20
1999	38,426	14.50	12.95
2000	41,268	24.35	22.90
2001	36,718	19.30	18.20
2002	41,143	19.50	17.90

2.



3.



Published Values

In most cases the published values and real prices given by the companies will not match. Companies use the published values as a price guide, and determine their own prices based on a multitude of factors affecting the company.

KEY:

I-Annual volumes greater than 20 million pounds.

II-Annual volumes of about 2 million to 5 million pounds

PP Published Values		I		II
Homopolymer Injection GP	↑	75 - 77	↑	78 - 81
Extrusion Fiber	↑	74 - 76	↑	77 - 79
Extrusion Film	↑	76 - 79	↑	80 - 81
Extrusion Profiles	↑	78 - 81	↑	83 - 87
Extrusion Sheet	↑	77 - 80	↑	81 - 83
Random Copolymer Injection	↑	78 - 80	↑	81 - 83
Random Copolymer Film	↑	80 - 81	↑	82 - 84
Random Copolymer Blow molding	↑	80 - 81	↑	83 - 86
Impact Copolymer High Impact	↑	89 - 93	↑	94 - 97
Impact Copolymer TPO	↑	109 - 114	↑	116 - 120

Off Spec Material

Total Petrochemicals labels their off spec material as scrap. This material is usually sold to a broker company at a discounted price.

Huntsman Polymers also has off spec materials that usually consist of an additive mixture being too high or low, or an out of spec viscosity. When these situations occur, the customer is contacted to determine if the material is still within the quality requirements. If the material is out of spec for the customer, they also sell it to a broker company at a discounted price.

Spot Market Price

The spot market price for homopolymer injection grade polypropylene is \$.52-.635/lb. The price for the copolymer injection grade is \$.535-.645/lb. Listed below is a spot floor summary for polypropylene and other resins, for comparison.

Spot Floor Summary (21,646,452 lbs)			
Resin	Total lbs	Low	High
LLDPE - Film	4,501,968	0.505	0.655
LDPE - Film	4,076,000	0.513	0.575
PP Homopolymer - Inj	3,197,368	0.52	0.635
PP Copolymer - Inj	2,644,184	0.535	0.645
HDPE - Blow Mold	2,084,736	0.515	0.62
HIPS	1,172,276	0.695	0.735
HMWPE - Film	1,172,276	0.695	0.735
GPPS	938,552	0.65	0.75
LLDPE - Inj	840,000	0.55	0.585
LDPE - Inj	528,000	0.59	0.625
HDPE - Inj	491,092	0.545	<u>0.645</u>

Works Cited

"Borealis Borpact(TM) Polypropylene Delivers Transparency and Impact Resistance for Deep Freeze Packaging." NPI Center. 21 Feb. 2007
<<http://www.npicenter.com/anm/templates/newsATemp.aspx?articleid=14111&zoneid=6>>.

"Commodity Polypropylene." CRN India. 18 Feb. 2007
<<http://www.crnindia.com/commodity/pp.html>>.

"Commodity Thermoplastic Resin Pricing." Plastics News. 21 Feb. 2007
<<http://www.plasticsnews.com/subscriber/resin/price1.html>>.

"DoITPoMS Micrograph Library." University of Cambridge. 22 Feb. 2007
<<http://www.msm.cam.ac.uk/doitpoms/miclib/index.php>>.

"Materials Tests." Materials Innovation Service. 22 Feb. 2007 <<https://fp.uni.edu/rtrtc/mts/NM-Index.asp>>.

"MatWeb Material List." MatWeb Material Property Data. 8 Mar. 2007
<<http://www.matweb.com/search/GetAllMatls.asp?p=101>>.

"Polypropylene." Answers.Com. 2007. 19 Feb. 2007
<<http://www.answers.com/topic/polypropylene>>.

"Polypropylene." Huntsman Polymers. 18 Feb. 2007
<<http://www.huntsman.com/polymers/index.cfm?PageID=996>>.

"Polypropylene." MatWeb. 21 Feb. 2007 <<http://www.matweb.com/search/GetKeyword.asp>>.

"Polypropylene." Polymer Science Learning Center. 2005. University of Southern Mississippi. 19 Feb. 2007 <<http://www.pslc.ws/macrog/pp.htm>>.

"Polypropylene." San Diego Plastics, Inc. 19 Feb. 2007
<<http://www.sdplastics.com/polypro.html>>.

"Polypropylene." The Innovation Group. 21 Feb. 2007 <<http://www.the-innovation-group.com/ChemProfiles/Polypropylene.htm>>.

"Polypropylene." Wikipedia, the Free Encyclopedia. 18 Feb. 2007. 19 Feb. 2007
<<http://en.wikipedia.org/wiki/Polypropylene>>.

"Polypropylene Division." Total Petrochemicals. 18 Feb. 2007
<<http://www.totalpetrochemicals.biz/side0/hpbiz.asp?lg=en&biz=b2>>.

"Polypropylene PP." British Plastics Federation. 2003. 19 Feb. 2007
<http://www.bpf.co.uk/bpfindustry/plastics_materials_polypropylene_PP.cfm>.

"Polypropylene Price Report." ICIS Pricing. 21 Feb. 2007
<http://www.icispricing.com/il_shared/Samples/SubPage144.asp>

Polypro1 Report. Behrend Plastics. 2006.

"Type of Tests." Plastics Technology Laboratories Inc. 2007. 22 Feb. 2007
<<http://www.ptli.com/default.asp>>.

"UL 94 Flammability Testing." Underwriters Laboratories. 7 Mar. 2007
<<http://www.ul.com/plastics/flame.html>>.

"Week in Review." The Plastics Exchange. 2005. 21 Feb. 2007
<<http://www.theplasticsexchange.com/Research/WeeklyReview.aspx#Polypropylene>>.