

## PERP Program - Polystyrene

### New Report Alert

May 2006

Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, ***Polystyrene (04/05-4)***. To view the table of contents or order this report, please click on the link below:

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### Introduction

Polystyrene is a thermoplastic resin that is able to serve many end uses due to its low cost, ease of processability, and performance properties. 2003 marked the 65th anniversary of Dow Chemical's successful commercialization of the polymer in the United States. A number of polystyrene producers have made their technology available for licensing, including a continuous mass process from Innovene and ABB Lummus, as well as technology from Shaw/Stone and Webster and Nippon Steel's process from Toyo Styrene Company.

Polystyrene is categorized into four fundamental types:

- General Purpose Polystyrene (GPPS)
- High Impact Polystyrene (HIPS)
- Expandable Polystyrene (EPS)
- Syndiotactic Polystyrene (SPS)

Within these broad categories, there are numerous grades, including:

- High Temperature Resistant (HTR)
- Environmental Stress Cracking Resistant (ESCR)
- Flame Retardant (FR)
- Medium Impact Polystyrene (MIPS)
- Super-high Impact Polystyrene (SHIPS)
- Low Residual Monomer (LRM)
- High Gloss

The polystyrene homopolymer is amorphous; it is clear and colorless and exhibits excellent optical properties, along with high stiffness and good mechanical strength. Above the glass transition temperature ( $T_g$ , around 100°C), polystyrene is easily molded with less input energy than crystalline polymers because of its high melt strength and heat of crystallization. Polystyrene also has a low mold shrinkage rate (0.004 to 0.007 inch per inch) which is less than the shrinkage rate of crystalline

thermoplastics (polyethylene and polypropylene), giving it a molding advantage with respect to rates and scrap.

GPPS resins are generally available with melt flows of 1 to 20. Typical GPPS resin properties are shown in Table 1.

**Table 1**  
**Typical GPPS Resin Properties**

Specific gravity	1.04
Melt flow, g/10 min.	1-20
Tensile strength, psi	5,000-7,500 <sup>(1)</sup>
Flexural strengths, psi	17,000-15,000 <sup>1</sup>
Tensile elongation to break, %	2-3
Flexural modulus, psi	450,000-500,000 <sup>1</sup>
Vicat softening temperature, °F	195-228

<sup>(1)</sup> The higher ranges represent high heat (high molecular weight) resin grades.

High temperature resistant grades of polystyrene are also commercially available for use in applications that require resistance to high temperature distortion. These are higher molecular weight resins (lower flow) and they exhibit better mechanical properties than traditional GPPS.

Styrene polymers are nonpolar; they are chemically inert and resistant to water. This gives them favorable property advantages for use in electronics, food, automotive, and other applications. Polystyrene homopolymers have good UV stability and resistance to gamma-radiation, allowing them to be used in fabricated products subjected to sterilization.

Overall, polystyrene is a brittle material; however, it also exhibits high stiffness. A type of polystyrene referred to as oriented polystyrene (OPS) acquires a biaxial orientation during fabrication. This offers significantly enhanced mechanical properties and toughness (tensile strength can be doubled and elongation increased twenty fold).

Rubber-modified polystyrene grades were developed in the 1950s to enhance mechanical properties. They are manufactured by introducing rubber, typically polybutadiene, into the polymerization system, which creates a two phase polymer system consisting of a dispersed rubber phase and a continuous polystyrene phase. Impact-resistant grades are known for their rigidity, impact strength, and good dimensional stability, and typically these grades have less heat, chemical, and UV resistance than the homopolymer.

Product development in the polystyrene industry has primarily been focused on impact polystyrene with respect to rubber efficiency and enhanced or improved properties. Typical impact grades

include ESCR, FR, SHIPS and high gloss, chemical, and chlorofluorocarbon (CFC) resistant products. HIPS resins are typically white, but there are specialty clear resins that are commercially available. Many producers are targeting polystyrene to compete with engineering resin applications where the conventionally used materials are "over-engineered."

Typical properties of impact polystyrene are shown in Table 2. The impact grades - medium, high and super high - are generally categorized by Izod impact strength.

**Table 2**  
**Typical Properties of Impact Polystyrene <sup>(1)</sup>**

Medium impact, Izod, ft-lb/in	0.5-1.4
High impact	1.5-2.5
Super high impact	More than 2.5
Melt flow, g/10 min	2-15
Tensile strength, psi	3,000-7,000
Flexural strength, psi	2,000-8,000
Tensile elongation to break, %	15-65
Flexural modulus, psi	270,000-420,000
Vicat softening temperature, °F	185-225

<sup>(1)</sup> Properties are dependent on rubber and additive content.

Expandable polystyrene (EPS) is another commercial form of polystyrene, and it is used in insulating and crush resistant applications (cups, home insulation, packaging). Flame retardant EPS grades are also available and are used in building and construction. EPS is manufactured by introducing a blowing agent such as pentane or isopentane in-situ or into the post-process in order to form polystyrene beads with a typical diameter of 0.01 to 0.10 inches and a density of 1 to 3 pounds per cubic foot. Foamed sheet can also be produced by extruding solid polystyrene (GPPS) by using blowing agents in the extrusion step.

Syndiotactic polystyrene (SPS) is a relatively new form of the polymer first synthesized in 1985 according to Idemitsu. The material is particularly interesting because it offers the potential to overcome one of amorphous polystyrene's primary deficiencies - a low heat distortion temperature. It is crystalline in nature; its highly regular structure gives the polymer the important feature of a melting point of 270°C, which is in the range of commonly used engineering polymers such as nylon or polyacetal. (Normal or "atactic" polystyrene has no order with regard to the side of the chain on which the phenyl groups are attached). Typical properties of SPS are shown in Table 3.

**Table 3**  
**Typical Properties of Syndiotactic Polystyrene**

Specific gravity	1.02
Mold shrinkage, in/in	0.008-0.010
Tensile yield, psi	6,580
Tensile break, psi	6,580
Tensile elongation, %	30
Tensile modulus, psi	380,000
Flexural strength, psi	11,600
Flexural modulus, psi	465,000
Notched Izod impact , ft-lb/in	1.2

In addition to the polystyrene homopolymer and impact copolymers, other styrenic copolymers and terpolymers have been commercialized to enhance performance properties. Some of the key resins include styrene-acrylonitrile (SAN), styrene-butadiene-styrene (SBS), acrylonitrile-butadiene-styrene (ABS), and styrene maleic anhydride (SMA).

## Chemistry

There are three structural forms of polystyrene that can be prepared from styrene: atactic, syndiotactic, and isotactic.

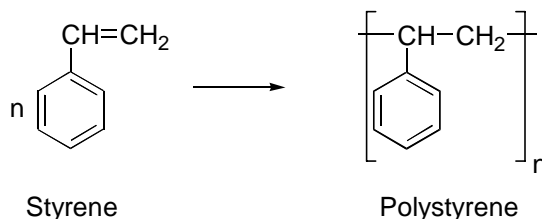
In atactic polystyrene, the phenyl groups are randomly placed on either side of the extended carbon chain. Atactic polystyrene is an amorphous material due to the high degree of random placement of the phenyl groups relative to the backbone. This type of polystyrene is the most common and well-known polymer, with widespread uses in packaging and durable goods. Consumption has steadily increased due to the excellent balance between cost and performance. In particular, the two most important property advantages afforded by polystyrene over similarly priced materials are stiffness (or rigidity) and processability. Primary weaknesses include brittleness (or low impact strength) and a low heat distortion temperature. Although brittleness can be improved with the addition of a rubbery phase, as is done in preparing high impact polystyrene grades, the deficiency related to heat distortion remains problematic.

In syndiotactic polystyrene (SPS), the phenyl groups alternate regularly from one side of the extended chain to the other. The highly regular structure of SPS gives it crystalline properties, similar to engineering polymers such as nylon or polyacetal.

In isotactic polystyrene, all the phenyl groups are on the same side of the stretched chain. Isotactic polystyrene has been synthesized using Ziegler-Natta catalyst systems. The material is highly

crystalline with a high melting point generally accepted to be about 240°C. This form of polystyrene is not commercially viable due to its slow crystallization rate.

The formation of polystyrene is represented by the following exothermic reaction (with a heat of polymerization of about 165 calories per gram, 300 Btu per pound):



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The molecule acts as both an electron donor and an electron withdrawing center. Styrene and its substituted derivatives can be polymerized via four different mechanisms; free radical, anionic, cationic, and Ziegler. However, the free radical mechanism has the most commercial relevance.

When heated to more than 100°C, styrene is capable of undergoing thermal or spontaneous polymerization, resulting in high conversion and a suitable molecular weight. In this system, the temperature typically increases from 100°C to 220°C across three stages of polymerization as the conversion of styrene increases.

Polymerization can be initiated either thermally or by using chemical initiators such as peroxides. Both types of initiation are commercially practiced in general purpose polystyrene (GPPS) and high impact polystyrene (HIPS) manufacturing. The method chosen largely depends on the producers' choice of operating conditions.

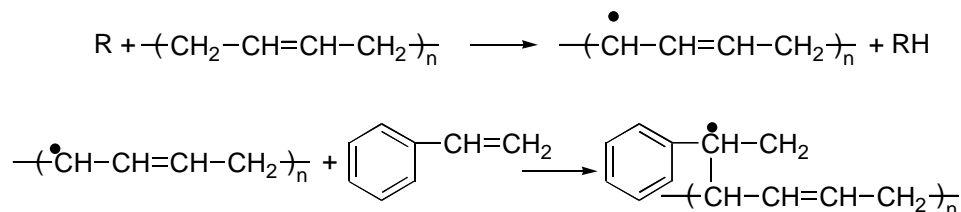
#### Copolymerization – High Impact Polystyrene (HIPS)

Rubber addition to polystyrene enhances resin impact strength. The system is made up of a dispersed rubber phase and a continuous polystyrene phase. The rubber initiates crazes in polystyrene without crack formation during elongation or impact, yielding a tough, impact resistant resin.

To improve compatibility, rubber is grafted to the polystyrene backbone. Typically, the rubber used is cis-polybutadiene, although copolymers with styrene and ethylene-propylene copolymers and terpolymers can also be used. The latter provides impact strength with improved outside aging resistance.

In bulk polymerization, grafting occurs when styrene free-radicals react with the rubber. Copolymer grafting is important because it occurs at the interface of the two phases and affects resin morphology and mechanical properties (impact strength).

The mechanism is believed to take place according to the following equations:



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## Process Description

Polystyrene has been commercialized for more than 50 years and is produced by several companies around the world. The bulk process, also known as the solution or mass process, is by far the most dominant commercial route, with the suspension process only being used for specialty grades.

While there are more than a dozen different technologies used in commercial operations throughout the world, they all employ the same fundamental steps. The various processes are distinguished by the specific hardware and configurations, as well as variations in operating conditions.

### Polymerization Reactor Design

A primary feature that characterizes commercial processes is reactor design and configuration. The key characteristics of the reactors are the method of heat removal, degree of axial mixing (end to end), degree of radial mixing (side to side), and the number of reactors in series, which includes any prepolymerizer.

Removal of polymerization heat for temperature control is accomplished by quench with added cold monomer and diluent, conductive heat removal by transfer surfaces, and reflux cooling. Commercially, both conductive and reflux cooling systems are employed, as the quench method alone is insufficient to remove polymerization heat. The cooling method does not affect the quality of the polymer, and the method chosen is generally up to the producer.

The degree of radial and axial mixing determines product characteristics and properties, regardless of the heat transfer method. Radial mixing is necessary to prevent temperature and concentration gradients across the reactor, which can lead to polymer layer formation on the vessel walls, resulting in poor process control (low heat transfer) and poor product quality (gel formation).

Boiling continuous stirred tank reactors (CSTR) are now commonly used commercially. The reactor operates at a capacity less than 70 percent or maximum to allow freeboard for foaming and boiling. These reactors allow for a high degree of radial and axial mixing to be achieved, and the type of

agitator used (e.g. turbine, anchor, or helical) depends on the viscosity of the reactor contents. An external recirculation loop is used to remove heat via condensing and refluxing.

Another reactor system used for polystyrene has a recirculating loop with static mixer reactors arranged in the loop. In this system, a high degree of heat removal is achieved due to high flow and multiple tube bundles, which results in good radial and axial mixing.

The second generation tower reactor is also commercially important. This reactor incorporates alternating rows of heat transfer tubes and agitator blades, allowing for a high degree of radial mixing and a moderate degree of axial mixing with good heat removal.

A further type of reactor used is horizontal and segmented with an agitation combination that provides a high degree of radial mixing and moderate axial mixing in each section, simulating plug flow, with a uniform temperature gradient along the reactor. The plug flow characteristic allows for faster, more distinct transitions between products and more uniform particle size distribution. Both latent and conductive heat-based removal systems are used commercially in this type of reactor.

#### Devolatilization

In the polystyrene industry, an important issue is the product's level of residual monomer, which becomes particularly critical in food packaging applications. Typically, 300-400 ppm are permitted in food applications and 500-600 ppm in non-food applications. Low residual monomer (LRM) grades containing only about 175 ppm are also commercially available.

Existing techniques for devolatilizing polymers are falling strand devolatilization (FSD), devolatilizing extrusion, and wiped film evaporation, with FSD being the more commonly used method. In the FSD method, melt from the reactors is preheated (to about 220°C to 250°C) and fed as strands to a jacketed flash vessel that is operated at a vacuum.

Although it gives producers flexibility of homogeneously incorporating additives into the product prior to pelletizing, devolatilizing extrusion is costly in terms of investment and operating costs, mainly power, and is therefore not widely used.

In a wiped film evaporator, a thin film of polymer is deposited on the heated wall of the vessel to effect devolatilization. A countercurrent stream of inert vapor can be used to enhance monomer stripping. This technique is rarely used commercially due to the high investment and operating costs.

Another general technique that is used to improve devolatilization is introduction of a chemical aid that has some solubility in the molten polymer but can be easily diffused. The aid acts as a stripping medium, as it lowers the partial pressure of monomers in the melt, and it is also reported to cause some foaming that enhances the amount of surface area for monomer removal. Typical aids include water and methanol.

## Copolymerization

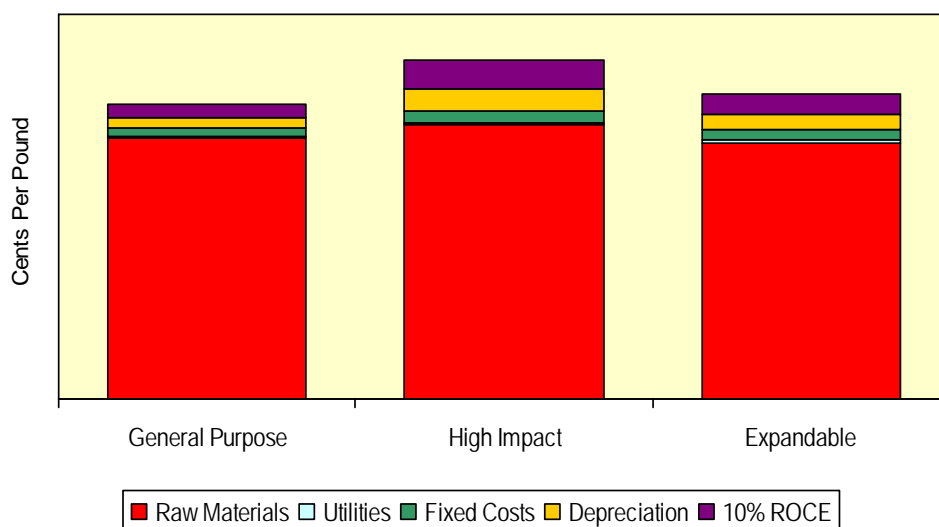
All processes in the production of high impact polystyrene start by grinding the baled rubber and dissolving it in styrene monomer. As the homogeneous styrene-polybutadiene polymerization proceeds, a two phase system forms when the conversion to polystyrene exceeds 1.0 percent. A dispersed phase of polystyrene in styrene droplets separates out of the continuous phase of polybutadiene in styrene. The droplets are stabilized by the graft copolymer, and larger droplets form. At this point, agitation is critical and high shear mixers are used to prevent coalescence of the droplets.

As polymerization proceeds, the polystyrene phase volume increases and the polybutadiene phase volume decreases. At a conversion of 8 to 12 percent, the phase volumes are approximately equal and, under intense agitation, phase inversion takes place and polystyrene in styrene becomes the continuous phase.

Particle size and distribution are controlled by the applied shear rate at phase inversion; factors such as viscosity and intersurface tension are also important. Once the phase inversion occurs, subsequent styrene polymerization takes place in both phases, and low speed nonshearing agitation is used to keep the polystyrene within the rubber particles. Once the required rubber phase is established, it is important not to have excessive crosslinking.

## Economics

**Figure 1**  
**Comparison of Polystyrene Production Costs**





## **Polystyrene Market**

### **United States**

Demand for GPPS and HIPS recovered in 2004 and 2005 after a decline in 2003. The packaging and electronic segments enjoyed the strongest growth, while the construction segment improved due to a healthy housing industry.

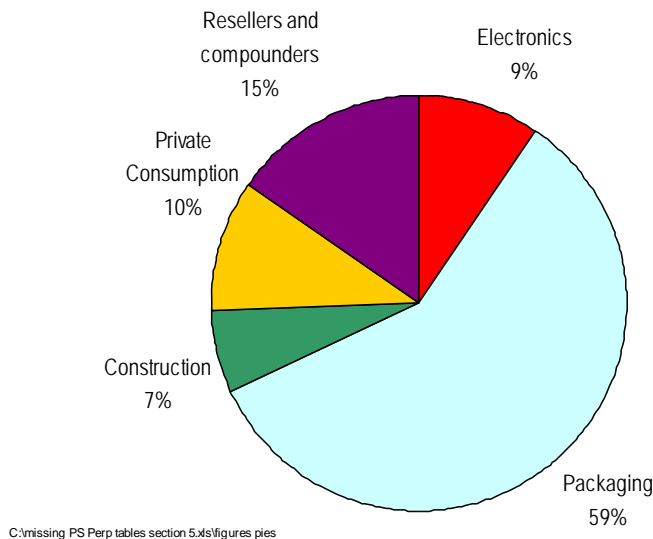
Overall polystyrene growth is mature when compared with other polymers. It is relatively a more expensive polymer, even more so considering the current high benzene costs for feedstock. As prices increase, inter-material competition, especially in packaging, will continue to be a threat and keep demand growth somewhat limited. Polystyrene mainly competes with polypropylene; however, it also experiences competition from other polyolefins. Over the last five years, the price of polystyrene has exceeded polypropylene by approximately \$200 per ton, and this gap has hindered the use of polystyrene in applications where the polymers are easily interchangeable. However, there are end-uses that are specific to each polymer. Crystal polystyrene has better stiffness and clarity than polypropylene, and is preferred for glass-replacement and cutlery end-uses. Impact polystyrene extruded sheets are as tough as polypropylene, but are more easily thermoformed, for applications like refrigerator liners.

Packaging comprises the largest end use application, representing about 58 percent of the GPPS/HIPS consumption in the United States in 2005. Most packaging grades are used in the food industry and include both foam and clear, oriented polystyrene single use containers for “take out” meals. Polystyrene remains an excellent packaging material because of its light weight, strength and insulation properties. Other packaging applications include DVD and CD-ROM cases. Packaging will continue to drive the demand for polystyrene.

The consumer electronics and office equipment markets continued to grow in 2005. Polystyrene is widely used in the components of personal computers, peripherals, printers, electronics products and small appliances. This market however, remains extremely competitive.

Figure 2 shows the breakdown of U.S. polystyrene consumption by end use for 2005.

**Figure 2**  
**United States Polystyrene Consumption by End Use, 2005**



## Western Europe

In 2005, the polystyrene market suffered from overcapacity and relatively poor margins. Activity in the packaging sector in Germany has been fairly modest. The strength of the Euro has affected exports of lower-value finished goods from countries across the region. France and Spain have seen a more robust growth with healthy increases in domestic consumption, while Italy experienced lackluster growth.

Historically, polystyrene prices have been higher than many thermoplastics, underpinned by the high cost of styrene. Despite the higher prices, its use in sectors such as food packaging has grown as a result of its easy processability relative to other thermoplastics. The recent large price premium over polypropylene has significantly impacted demand in disposable applications.

Packaging remains the largest end-use sector, accounting for 50 percent of consumption. Consumer products account for the other most significant end use sector, where polystyrene is utilized for applications such as refrigeration units, television, computer, housing and toys. In these areas, polystyrene has had some success in substituting for engineering plastics such as ABS.

Polystyrene consumption represents a relatively mature market in Western Europe, and projected growth rates are expected to be below global economic growth.

## Asia Pacific

Polystyrene demand is growing rapidly due to both local consumption and the manufacture of goods for export. Polystyrene has had some success in substituting for engineering plastics such as ABS. Further developments are expected to continue to target markets where ABS and polycarbonate are in common use. The appliance sector comprises some of the higher specification uses for polystyrene, and these can offer better margins than typical packaging applications.

The demand from the food packaging and consumer products sectors will continue to grow as a result of its easy processability and favorable properties relative to other thermoplastics, despite its frequently higher cost.

China accounts for a large proportion of the growth, and its consumption overtook the United States to become the largest market for GPPS in 2001. Consumer products such as refrigeration units, televisions, computers, and housing constitute one major application group, with the other being disposable housewares and food packaging.

In Japan, polystyrene consumption growth has resumed after a period of decline. Long-term growth is expected to be minimal.

South Korean polystyrene consumption growth has been relatively buoyant despite the maturity of some market sectors. South Korea and Japan have focused on supplying higher end polystyrene goods to China, rather than competing in lower specification applications. Demand growth in electronics manufacturing is forecast at a lower level in these countries due to their high costs relative to China.

Demand, supply, and trade estimates are provided for the United States, Western Europe, and Asia Pacific for the period 2003 to 2010, both for solid and expandable polystyrenes.

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