Nexant
Chem Systems

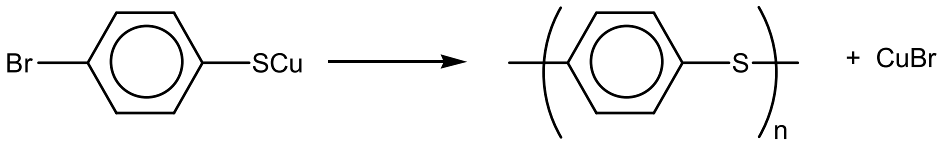
PERP Program – New Report Alert

October 2003

Nexant's ChemSystems Process Evaluation/Research Planning program has published a report, ***Polyphenylene Sulfide (PPS) (02/03S4)***.

Polyphenylene sulfide (PPS), sometimes called polythiophenylene or polyarylene sulfide, has a long history in the chemical literature. The material was first observed by Friedel and Crafts in 1888. In the late 1940s, it was recognized that PPS had significant commercial potential. Processes were developed to produce small quantities of PPS from elemental sulfur, *para*-dichlorobenzene, and sodium carbonate in sealed vessels at 275-300°C.

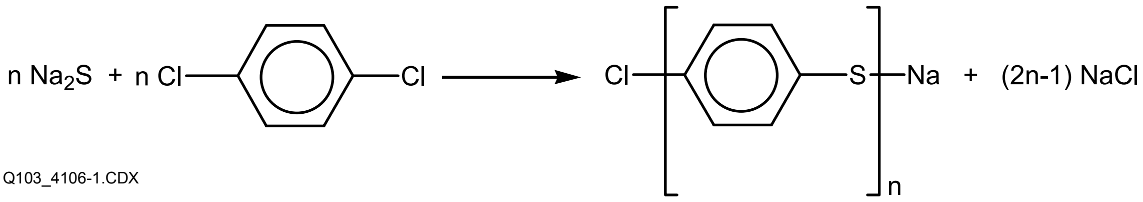
Dow initiated a detailed study into PPS in the 1950s and 1960s. Alternative routes to PPS were investigated, the most promising of which was nucleophilic self-condensation of cuprous *para*-bromothiophenoxide, carried out at 200-250°C in the solid state:



Q103_4106-1.CDX

While polymer architecture could be controlled, the monomers were expensive, and product purification difficult; ultimately scale-up difficulties led to the termination of the Dow work.

A commercial process to produce PPS was ultimately developed by researchers at Phillips Petroleum Company. The reaction involved the polymerization of *para*-dichlorobenzene and a sodium sulfide source in a polar organic compound at elevated temperature and pressure. The overall reaction may be written:



Q103_4106-1.CDX

Phillips' first patent for PPS was issued in 1967, and the company constructed a pilot plant between 1967 and 1973 to refine the process and establish market demand. Phillips started-up its first commercial PPS facility in Borger, Texas in 1973.

The expiration of Phillips' basic patent in 1984 encouraged a number of other firms to investigate PPS production, mainly in Europe and Japan. Presently, all commercial routes to PPS are quite similar, and rely on the nucleophilic substitution of an aromatic compound with elimination of alkali chloride, as initially described in the Phillips basic patent. While the reaction appears to be relatively simple, the actual pathways are through a complex series of partial reactions. Synthesis is difficult to control due to extreme differences in reactivity during the course of polycondensation. Strict control of the reaction parameters must be maintained in order to avoid the production of undesirable byproducts and cyclic oligomers.

The reaction product is a suspension that contains PPS and sodium chloride as the solid phase. The suspension is then flash evaporated to free volatile substances. The resulting powder consists of PPS and salt. The ionic salt content interferes with electrical/electronic applications, and must be removed by repeated washing at various temperatures, pressures, and with different solutions and alkalinity. The powder is then dried and stored for further finishing. Production is via a batch process, although continuous processes have been investigated. While other reaction solvents have been investigated, N-methyl-2-pyrrolidone (NMP) is preferred.

The initial PPS "flash" process produced a linear polymer with modest molecular weight and strength. While suitable as a coating resin, for injection molding applications the material had to be "cured" to extend the polymer chain and provide moderate cross-linking. Although some cross-linking is indeed present in the cured polymer, the polymer remains a true thermoplastic, and can be repeatedly melt processed if desired. This material is commonly referred to as branched PPS.

While curing can be effected in both the melt and solid state, it was found that curing could best be effected in the solid state by heating the polymer for an extended period of time at temperatures between 175 and 280°C in the presence of a small quantity of air. Note that 280°C is just below PPS's melting point of 285°C. Good mixing is required so as to avoid the development of "hot spots" which might produce gels or cross-linked material. The degree of curing can be easily monitored by measuring the melt viscosity. By varying the cure times, one base resin can yield a family of cured PPS powder. The cured polymer is then compounded with glass fibers and fillers, and pelletized for injection molding applications.

Phillips has also developed a technique for obtaining a high molecular weight linear PPS polymer directly from the polymerization process, without the need for curing. The modified technique uses an alkali metal carboxylate as a polymer or process modifier. The role of the metal carboxylate is not well documented, but is believed to act as a buffer to create a reaction medium which minimizes side reactions that lead to premature chain termination and low molecular weight polymer. Sodium acetate is a commonly used metal carboxylate, although other compounds, such as lithium carboxylate, are also used. Trichlorobenzene is also sometimes added as a means of introducing branching into the polymer. Long chain branching increases molecular weight, and also influences rheological properties.

Kureha practices a variant on the initial Philips process to produce a completely linear PPS material. This process, referred to as the quench process, employs a two-step reaction whereby a low molecular weight prepolymer is first produced. Then, additional water is added, the temperature raised, and the reaction continued. Following flash evaporation, the PPS powder is washed, dried, and stored for finishing; no curing is required.

It is claimed that the addition of excess water in the quench process results in a phase inversion of the reaction medium. The use of *meta*-dichlorobenzene, either as a comonomer or a block copolymer, is noted as a means of controlling crystallinity.

Polyphenylene sulfide is presently enjoying strong growth as a result of a continuing trend towards higher continuous use temperatures, particularly in the transportation and electrical/electronics sectors. In automotive, higher end-use temperatures are a result of the need for longer warranty periods and operating lifetimes, lower coefficients of drag which result in less air flow under-the-hood, encapsulation of the engine for acoustic and/or aesthetic reasons, introduction of turbo chargers and catalytic converter systems which generate considerable amounts of heat, and the size reduction of the engine compartment due to more compact designs. In electrical/electronics, the trend towards miniaturization of printed circuit boards leads to even smaller surface-mount devices with thinner wall thicknesses. These electronic components must be resistant to the high peak temperatures involved in modern infrared reflow-soldering techniques.

PPS is well suited to compete in transportation and electrical/electronics applications, as the polymer also offers chemical resistance, excellent electrical properties, outstanding dimensional stability, and good mechanical properties. The materials' inherent non-flammability is particularly attractive for electrical/electronic applications. The material typically competes against other heat-resistant engineering thermoplastic materials such as High Temperature Nylons (HTNs), and liquid crystal polymers (LCPs).

PPS has a continuous temperature rating of 240°C, and the ability to withstand temperature spikes up to 270°C. It is very dimensionally stable, displays low water absorption, and is essentially insoluble below 200°C. Above 200°C, strong mineral acid and oxidizing agents and a few organic solvents will attack the polymer.

PPS has a high affinity for glass and mineral fillers. By compounding PPS with reinforcing materials, the heat deflection temperature can be increased up to the region of the crystalline melting point. Mineral fillers can also be used to reduce cost, and to improve selected electrical properties such as arc resistance.

Electrical/electronics is the largest application for PPS, where the materials' superior electrical properties, inherent non-flammability and outstanding dimensional stability are key attributes.

The second largest end-use market for PPS is transportation. This sector is predominantly automotive. PPS is specified in under-hood applications because of its temperature resistance, mechanical properties, and because it is impervious to the corrosive effects of engine exhaust gases, as well as to ethylene glycol, gasoline, and other automotive fluids.

PPS is also used in industrial applications. Many of these applications utilize the mechanical properties, temperature resistance, dimensional stability (including long-term performance under high pressure) and chemical resistance of PPS. In fact, PPS often performs better than metal in applications where all of these attributes are required. Drawbacks of PPS in industrial applications include low impact and somewhat marginal UV resistance.

Over 90 percent of PPS resin is sold as a reinforced or filled compound for use in injection molding applications. PPS powder is used in the production of extruded film, extruded fiber, and powder coatings.

PPS films are used in flexible circuitry, motor insulation, information storage devices, and capacitors where high temperatures are required. Competition is primarily with polyimide films.

In fibers, PPS is typically used in applications requiring outstanding chemical and temperature resistance. PPS staple fibers are used in wet and dry filtration apparatus and fire-resistant clothing. PPS monofilaments are used in drying belts within the chemical and paper industry.

This report describes production of branched PPS via the flash process with curing, linear PPS via the flash process with metal carboxylate, and linear PPS via the quench process, and it presents cost of production estimates for these same processes.

Electrical/electronic, transportation, industrial, and other end use applications for PPS are enumerated. Demand estimates are provided through 2007 for the United States, Western Europe, Japan and rest of world, along with a global list of PPS suppliers and their plant capacities.

= =

Nexant, Inc. (www.nexant.com) is a leading management consultancy to the global energy, chemical, and related industries. For over 38 years, Nexant/ChemSystems has helped clients increase business value through assistance in all aspects of business strategy, including business intelligence, project feasibility and implementation, operational improvement, portfolio planning, and growth through M&A activities. Nexant's chemicals and petroleum group has its main offices in White Plains (New York) and London (UK), and satellite offices worldwide.

These reports are for the exclusive use of the purchasing company or its subsidiaries, from Nexant, Inc., 44 South Broadway, 5th Floor, White Plains, New York 10601-4425 U.S.A. For further information about these reports contact Dr. Jeffrey S. Plotkin, Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: hcoleman@nexant.com, Website: http://www.nexant.com.