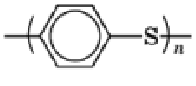
Kirk-Othmer Encyclopedia of Chemical Technology.

POLYMERS CONTAINING SULFUR, POLY(PHENYLENE SULFIDE)

Poly(*p*-phenylene sulfide) (PPS), **(1)** (poly(thiophenylene) [9016-75-5] or poly(thio-1,4-phenylene) [25212-74-2]) has a remarkably long history in the chemical literature, which has been reviewed in detail (1–4). The structure of PPS consists of alternating para-disubstituted aromatic rings (*p*-phenylene moieties) and divalent sulfur atoms (sulfide linkages). PPS is a semicrystalline polymer possessing a desirable combination of properties that include good mechanical properties, excellent electrical and thermal properties, as well as inherent flame resistance. Combined with the ease of molding (5), PPS plays an important role in the class of materials known as engineering thermoplastics. Designers have been exploiting the properties of PPS in end uses such as coatings, injection molding, film, fiber, pipe, and advanced composite materials (qv).



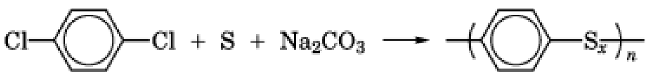
(1)

The earliest reported reference describing the synthesis of phenylene sulfide structures is that of Friedel and Crafts in 1888 (6). The electrophilic reactions studied were based on reactions of benzene and various sulfur sources. These electrophilic substitution reactions were characterized by low yields (50–80%) of rather poorly characterized products by the standards of 1990s. Products contained many by-products, such as thianthrene. Results of self-condensation of thiophenol, catalyzed by aluminum chloride and sulfuric acid (7), were analogous to those of Friedel and Crafts.

The first reported assignment of the PPS structure to reaction products prepared from benzene and sulfur in the presence of aluminum chloride was made by Genvresse in 1897 (8). These products were oligomeric and contained too much sulfur to be pure PPS. Genvresse isolated thianthrene and an amorphous, insoluble material that melted at 295°C. These early synthetic efforts have been reviewed (9–11).

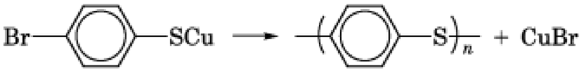
The electrophilic substitution reactions of benzene and sulfur, catalyzed by aluminum chloride, were reinvestigated in 1984 in the laboratories of Phillips Petroleum Company (11) and the findings of Genvresse and others were confirmed. Using improved spectroscopic and chromatographic analytical techniques, products containing a variety of structures, including phenanthrylene linkages, phenylene sulfide linkages, and polysulfides, were identified. Further, it was demonstrated that the desired phenylene sulfide structures were unstable toward the electrophilic substitution reaction conditions. The lack of reaction selectivity and the instability of the desired product contributed to the low molecular weight of the products. The molecular weight of polymers from electrophilic reactions of benzene and sulfur is typically only ca 3500, which is too low to have useful mechanical properties.

The recognition that PPS had significant commercial potential as an advanced material came in the late 1940s (12). Macallum's PPS process is based on the reaction of elemental sulfur, *p*-dichlorobenzene, and sodium carbonate in sealed vessels at 275–300°C (12). Typical products produced by the Macallum process contain more than one sulfur per repeating unit ($x = 1.2 - 2.3$):



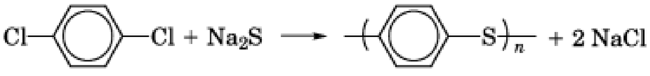
The reaction is highly exothermic, difficult to control, and incapable of being scaled up, but developmental products showed outstanding thermal stability. Also, Macallum's high molecular weight polymers could be molded into parts having good tensile strength and toughness (13). This recognition, among others, led to a growing interest in PPS in the industrial sector.

Dow Chemical Company purchased the rights to Macallum's patents (14), initiated a detailed study of the process and other improved syntheses of PPS in the 1950s and early 1960s, and published the results of their investigation (9, 15, 16). Clearly, alternative routes to PPS were desirable and the most promising of these involved the nucleophilic self-condensation of cuprous *p*-bromothiophenoxide, carried out at 200–250°C in the solid state or in the presence of pyridine (16):



The main benefit of the Dow process was control of the polymer architecture. The polymer from the self-condensation process possessed a linear structure, but there were other difficulties. The monomer was costly and removal of the cuprous bromide by-product was difficult (17); ultimately, scale-up difficulties terminated the Dow PPS development. However, there was a growing recognition that PPS was an attractive polymer with an excellent combination of properties.

Researchers at Phillips Petroleum Company developed a commercially viable process for the synthesis of PPS involving the polymerization of *p*-dichlorobenzene and a sodium sulfide source in a polar organic compound at elevated temperature and pressure. This Phillips process was patented in 1967 (18). Between 1967 and 1973, Phillips built and operated a pilot plant, established market demand, and constructed a full-scale commercial plant. In 1973, the world's first PPS plant came on-stream in Phillips' facility in Borger, Texas.



The expiration of Phillips' basic PPS patent in 1984 ushered in a large interest from the industrial sector. Companies, based largely in Europe and Japan, began acquiring patents worldwide for both the synthesis of PPS and a wide variety of applications, including compounds, blends, alloys, fiber, film, advanced composite materials, as well as end use products.

The first and largest commercial supplier of PPS, with a capacity of approximately 8000 t of neat resin per year, is Phillips Petroleum Company. Their product slate ranges from low to high molecular weight linear PPS, as well as a variety of cured and long-chain branched polymers. Phillips commercial trademark is Ryton poly(phenylene sulfide). Kureha Chemical Industry Company in Japan developed an alternative synthesis of PPS and commercialized their PPS process in Japan. Kureha markets PPS in combination with their compounding partner, Polyplastics, under the trade name Fortron PPS. Kureha has also formed a joint operation with Hoechst Celanese Corporation. Hoechst Celanese has constructed a new PPS commercial production facility at its Cape Industries plant in Wilmington, North Carolina. This is the second U.S. domestic PPS plant, increasing the U.S. neat resin capacity by approximately 2700 t/yr. This facility went on-stream in 1994.

Bayer AG in Germany has been active in PPS research since the mid-1980s, culminating in the construction of a commercial PPS plant in Belgium. Bayer marketed PPS compounds in the United States under the trade name Tedur, but the company has exited the PPS business. PPS is also marketed in the United States by GE Plastics, whose source of neat resin is Tosoh Corporation of Japan. GE Plastics markets PPS under the trade name Supec PPS. Patent activity by Tennessee Eastman describes an alternative process for the production of poly(phenylene sulfide/disulfide), although samples of such product have not appeared as of early 1996. Both Phillips and Hoechst Celanese have announced plans to debottleneck their existing U.S. facilities in order to meet anticipated market growth.

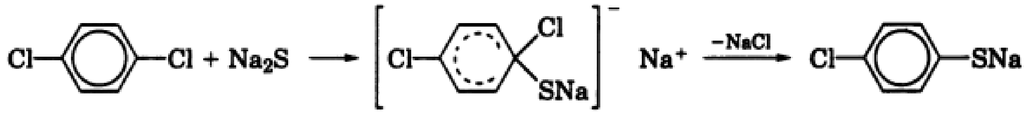
The roster of PPS suppliers in Japan is much larger than in the United States. Multiple market presences in Japan include TOPPS (Toray PPS, formerly TO–PP, which was a joint venture between Toray and Phillips); Dainippon Ink and Chemicals, Inc.; Tosoh; Tohpren; Kureha/Polyplastics; and Idemitsu. PPS marketed by Toray is sold under the Torelina trademark. Production capacity in Japan was estimated in 1995 at 11,400 t of neat resin per year. At the time that this capacity was created, the situation in Japan was characterized by overcapacity and underutilization. Additionally, further PPS capacity was brought on by Sunkyong in Korea, which is marketing a low cost PPS product. Although excess PPS capacity still exists in Japan, market growth has narrowed the gap between supply and demand.

1. Polymerization Processes

The neat resin preparation for PPS is quite complicated, despite the fact that the overall polymerization reaction appears to be simple. Several commercial PPS polymerization processes that feature some steps in common have been described (1, 2). At least three different mechanisms have been published in an attempt to describe the basic reaction of a sodium sulfide equivalent and *p*-dichlorobenzene; these are $\mathrm{S_NAr}$ (13, 16, 19), radical cation (20, 21), and Bunnett's (22) $\mathrm{S_{RN}1}$ radical anion (23–25) mechanisms. The benzyne mechanism was ruled out (16) based on the observation that the para-substitution pattern of the monomer, *p*-dichlorobenzene, is retained in the repeating unit of the polymer. Demonstration that the step-growth polymerization of sodium sulfide and *p*-dichlorobenzene proceeds via the $\mathrm{S_NAr}$ mechanism is fairly recent (1991) (26). Further complexity in the polymerization is the incorporation of comonomers that alter the polymer structure, thereby modifying the properties of the polymer. Additionally, post-polymerization treatments can be utilized, which modify the properties of the polymer. Preparation of the neat resin is an area of significant latitude and extreme importance for the end user.

There are two commercial PPS processes being practiced worldwide: the Phillips process and the Kureha process. Although these processes contain some common steps, there are distinguishing features, most notably in the reagents used to facilitate the synthesis of high molecular weight linear PPS.

The first commercial PPS process by Phillips synthesized a low molecular weight linear PPS that had modest mechanical properties. It was useful in coatings and as a feedstock for a variety of cured injection-molding resins. The Phillips process for preparing low molecular weight linear PPS consists of a series of nucleophilic displacement reactions that have differing reactivities (26).



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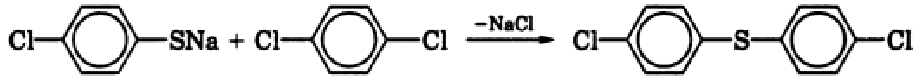


(2)

equation **1** is an oversimplification of the actual process. The polymerizable sulfur source for the PPS polymerization consists of a dehydrated product of *N*-methyl-2-pyrrolidinone [872-50-4] (NMP) and aqueous sodium sulfide feedstocks. During the course of this dehydration, one equivalent of NMP is hydrolyzed to form sodium *N*-methyl-4-aminobutanoate (SMAB) (eq. **3**).

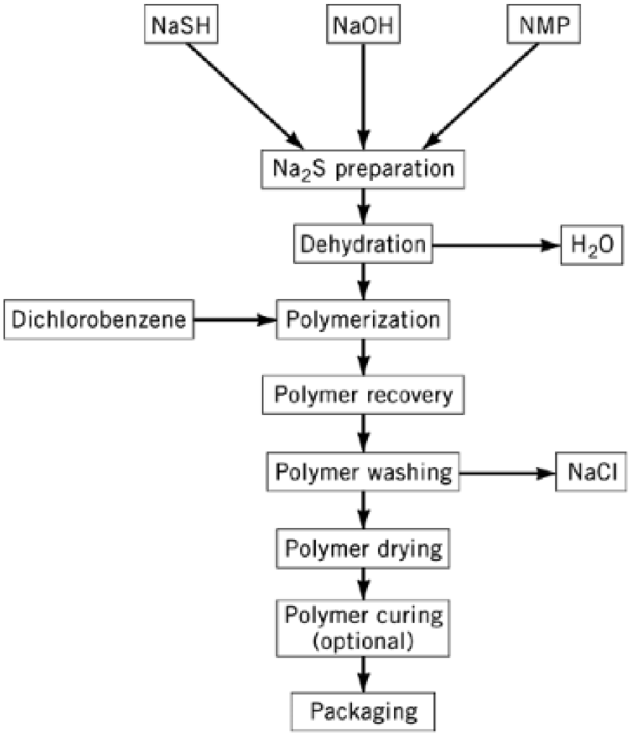
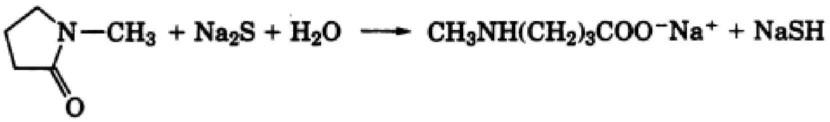


Fig. 1. The key steps for the Phillips PPS process are (*1*) production of aqueous sodium sulfide from aqueous sodium hydrogen sulfide (or hydrogen sulfide) and aqueous sodium hydroxide; (*2*) dehydration of the aqueous sodium sulfide and NMP feedstocks; (*3*) polymerization of the dehydrated sulfur source with *p*-dichlorobenzene to yield a slurry of PPS and by-product sodium chloride in the solvent; (*4*) polymer recovery; (*5*) polymer washing for the removal of by-product salt and residual solvent; (*6*) polymer drying; (*7*) optional curing, depending on the application; and (*8*) packaging.



(3)

The process implications of equation **3** go beyond the well-known properties (27–29) of NMP to facilitate S_NAr processes. The function of the aminocarboxylate is also to help solubilize the sulfur source; anhydrous sodium sulfide and anhydrous sodium hydrogen sulfide are virtually insoluble in NMP (26). It also provides a necessary proton acceptor to convert thiophenol intermediates into more nucleophilic thiophenoxides. A block diagram for the Phillips low molecular weight linear PPS process is shown in Figure 1.

The polymer produced by the Phillips low molecular weight linear PPS process is an off-white powder, having approximately 150–200 repeating units. There are no known solvents for PPS below 200°C, which complicates traditional molecular weight characterization methods. However, dilute solution light-scattering experiments and gel-permeation chromatography in 1-chloronaphthalene at 220°C show that the weight-average molecular weight is approximately 18,000 (30, 31). The inherent viscosity, as measured at 206°C in 1-chloronaphthalene solution, of PPS having this molecular weight is approximately 0.16 dL/g.

Low molecular weight linear PPS possesses only modest mechanical properties; however, it can be converted to a much tougher material by an oxidative heat treatment. It was recognized early in the development of PPS that the polymer had the property of undergoing change during thermal treatments and could favorably alter the usable properties of PPS (32). This ability to undergo change by appropriate thermal treatment is not to be confused with traditionally thermosetting polymers. PPS behaves as a true thermoplastic material during normal processing conditions. It can be repeatedly melted and reprocessed with only minor changes in its rheology. However, under more extensive oxidative heat treatments, PPS properties can be favorably altered and this behavior has been termed curing. Curing is a deliberate process step in which the polymer is heated in an oxidizing environment (often air) or after an oxidizing treatment for an extended period of time. Several changes in the polymer take place during curing: toughness increases, melt viscosity increases, rate and extent of crystallization decrease, and color changes from white to tan/brown/black. The extent to which these changes occur depends on the extent of cure, which is a function of both the time and temperature of curing. The reactions, which take place when PPS cures, are not well characterized, in part, because of the difficulties in analyzing a polymer that only dissolves at elevated temperatures.

The complex curing reactions have been studied (33–39) and the findings have been reviewed (1, 3). Evidence for thermally induced homolysis of carbon–sulfur bonds and the resultant reactions of thiyl and aryl radicals to produce cross-linking via biphenyl-type structures have been reported (17). Chain scission, cross-linking, and oxidation products are found during PPS curing (33). Curing of PPS also involves the loss of hydrogen from the aromatic moiety, resulting in cross-linking and the formation of new carbon–sulfur bonds and there is evolution of low molecular weight fragments, such as phenyl sulfide (33). Evidence for the evolution of low molecular weight species, such as the dimer and trimer of PPS and other sulfur compounds, has been found (34). Studies of the effects of variables such as temperature and atmosphere showed that the curing reactions are complex and result in polymers having increased viscosity and decreased crystallizability (35). The latter finding was the same as that found in a previous study (36), which showed that PPS cured below its crystalline melting point has no reduction in the percentage of crystallinity, but upon melting and annealing shows dramatically reduced crystallinity. The extent to which the crystallinity is decreased is a direct function of the extent of cure. Curing is dramatically faster in air than it is in nitrogen; oxygen is important in hydrogen atom abstraction during free-radical reactions forming biphenyl structures (35). Quinones can also function to abstract hydrogen atoms during PPS curing (37). Curing of PPS oligomers ($n = 6 - 8$) comprised a complex mixture of chain extension reactions, oxidative cross-linking reactions, thermally induced cross-linking reactions, oxygen uptake, reactions involving the extrusion of sulfur dioxide (presumably from sulfone moieties created by oxidation of PPS sulfide bonds), and arylthio metathesis (38). The rheological properties of PPS cured in the solid state, ie, below the crystalline melting point of the polymer, differ from those of PPS cured in the melt, ie, at temperatures above the crystalline melting point (39). Melt-cured PPS shows less shear rate sensitivity, ie, more Newtonian behavior, than does solid-state cured PPS.

PPS can be cured either in the solid state or in the melt. Melt curing (40) requires the polymer to be heated above the crystalline melting point of the polymer in the presence of air. As the melt cure progresses, the melt viscosity of the polymer increases. Extended curing results in continued increases in melt viscosity, gelation, and eventual vitrification, yielding a dark infusible solid. Solid-state curing of PPS (41) is a convenient process for curing large batches of powder, generally carried out at 175–280°C. The extent of cure is easily followed by measuring changes in the flow rate of the polymer in a modified version (316°C, 5 kg driving weight) of ASTM D1238 (42). The rate of solid-state curing is a strong function of the cure temperature, as Figure 2 shows. More rapid decreases in flow rate are observed when PPS is cured at higher temperatures.

Solid-state curing can be carried out effectively in the laboratory in an air-circulating oven. It is advisable to have good air–polymer contact for the purpose of exposing the polymer to air and maintaining good thermal control of the process. Solid-state curing is exothermic; if care is not given to maintaining good temperature control, localized hot spots may develop, resulting in fused or aggregated polymer. Ultimately, the result of such hot spots is uneven curing throughout the batch of polymer. One solution to this potential problem is to use an agitated bed of polymer in which air passes through the polymer.

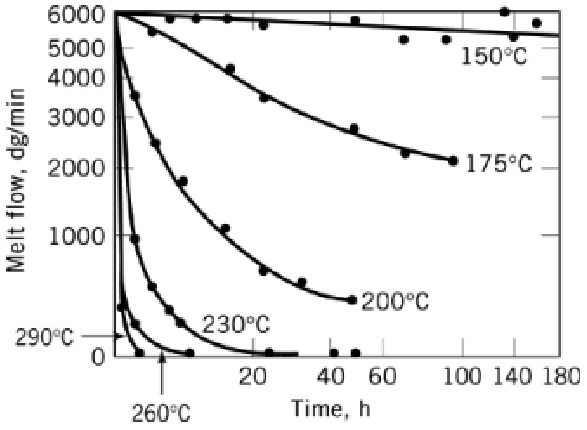


Fig. 2. Cure rate of PPS as a function of solid-state cure temperature.

Table 1. Typical Flow Rates for PPS Resins

PPS polymer	Flow rate, g/10 min
uncured PPS	3000–8000
powder coating PPS	1000
PPS for mineral- or glass-filled compounds	600
PPS for glass-filled compounds	60–150
compression-molding PPS	0

One of the conveniences afforded by curing PPS is that a single uncured feedstock can give rise to an entire family of cured polymers. The flow rates, ie, the extent of cure, of the cured polymers are optimized for specific applications. Table 1 shows typical melt flow values of cured PPS polymers for various types of applications.

Advances in the understanding of PPS polymerization chemistry in the Phillips Petroleum Company laboratories have made possible the synthesis of high molecular weight linear PPS directly in the polymerization vessel (30, 43). Although curable, high molecular weight linear PPS does not require curing prior to end use. The process for the Phillips high molecular weight linear PPS process is essentially the same as that shown in Figure 1 for lower molecular weight Ryton PPS. In the high molecular weight process, alkali metal carboxylate, a polymerization modifier, is added in the Na_2S preparation step; curing is optional. Such high molecular weight polymers are useful as extrusion resins for the production of film, fiber, and extruded profiles, such as pipe, and as feedstocks for injection-molding compounds and advanced composite materials.

The polymers produced by the alkali metal carboxylate-modified Phillips process are off-white polymers having a linear structure. The molecular weight of high molecular weight linear PPS has been reported to be approximately 35,000 (44). More recent measurements (45), however, indicate that weight-average molecular weight for linear, uncured PPS having a flow rate (42) of approximately 150 g/10 min is in the range of 50,000–55,000. High molecular weight linear PPS was commercialized in 1979 by Phillips.

Comonomers can be used to create a variety of polymer structures that can impart desirable properties. For example, even higher molecular weight PPS polymers can be produced by the copolymerization of a tri- or tetrafunctional comonomer (18). The resultant polymer molecules can have long-chain branching, which can be used to tailor the rheological response of the polymer to the application.

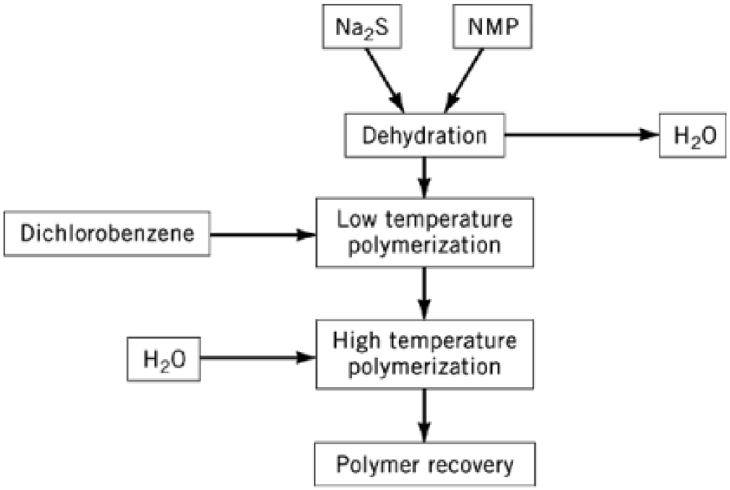


Fig. 3. The key steps of the Kureha process, as disclosed in the patent literature (48), are (*1*) dehydration of aqueous feedstocks (sodium sulfide or its functional equivalent) in the presence of *N*-methyl-2-pyrrolidinone; (*2*) polymerization of the dehydrated sodium sulfide with *p*-dichlorobenzene at a low temperature to form a prepolymer; (*3*) addition of water to the prepolymer; (*4*) a second, higher temperature polymerization step; and (*5*) polymer recovery.

The second PPS process practiced commercially was developed by Kureha Chemical Industry Company. Kureha has built a commercial PPS plant in Nishiki, Fukushima (46), and has formed a joint venture, Fortron Industries, with Hoechst Celanese (47). Fortron Industries has completed a commercial PPS plant at Hoechst Celanese's plant in Wilmington, North Carolina. Fortron Industries represents the only other PPS producer in North America. Figure 3 shows a flow diagram for the Kureha PPS process.

Although examples in the Kureha patent literature indicate latitude in selecting hold times for the low and high temperature polymerization periods, the highest molecular weight polymers seem to be obtained for long polymerization times. The addition of water to PPS polymerizations has been reported to effect polymer stabilization (49), to improve molecular weight (50, 51), to cause or enhance the formation of a second liquid phase in the reaction mixture (52), and to help reprecipitate PPS from NMP solution (51). It has also been reported that water can be added under pressure in the form of steam (53).

Other PPS processes have been described in the patent literature by Bayer (54–60). Distinguishing features of the Bayer PPS processes are the use of *N*-methylcaprolactam, which is a higher boiling analogue to the polar organic compound, NMP, reported by Phillips and Kureha. Many of Bayer's patent examples indicate the use of a branching comonomer, eg, 1,2,4-trichlorobenzene. Other polymerization modifiers reported by Bayer include carboxylic amides (54), carboxylic esters (56), carboxylic anhydrides (56), amino acids (57), and a variety of inorganic salts (58, 59). Bayer has also disclosed control over the end group chemistry via chain termination with monofunctional phenols (60) for the purposes of improved control of the polymer melt viscosity and also improved melt stability. Bayer built and operated a commercial PPS plant in Antwerp, Belgium (61), but chose to exit the PPS business in early 1992 (62).

Several polymerization processes for PPS or PPS-like structures have been reported but are not of commercial significance. However, they are of chemical interest. For example, Idemitsu has reported a process for the synthesis of PPS (63) in which an alkali metal sulfide and a dihaloaromatic compound react in a two-phase solvent system comprising high molecular weight ethylene glycol and water. A lower molecular weight poly(ethylene glycol) serves as a phase-transfer catalyst for the sodium sulfide monomer and the sodium chloride by-product. The polymer is reported to be isolated from the poly(ethylene glycol) phase.

A low temperature catalytic process has been reported (64). The process involves the divalent nickel- or zero-valent palladium-catalyzed self-condensation of halothiophenols in an alcohol solvent. The preferred halothiophenol is *p*-bromothiophenol. The relatively poor solubility of PPS under the mild reaction conditions results in the synthesis of only low molecular weight PPS. An advantage afforded by the mild reaction conditions is that of making telechelic PPS with functional groups that may not survive typical PPS polymerization conditions.

The Eastman Chemical Company has published extensively in the patent literature (65–74) and the scientific literature (75–77) on processes for making poly(phenylene sulfide)-*co*-(phenylene disulfide), and related copolymers. The Eastman process involves the reaction of elemental sulfur with *p*-diiodobenzene to yield a phenylene sulfide polymer that also contains phenylene disulfide repeating units in the polymer. The fraction of repeating groups containing disulfides, x in the equation shown, can be controlled by varying the monomer stoichiometry. Increasing the amount of sulfur reportedly increases the fraction of disulfides found in the polymer (65). Disulfide fractions of 0.001–0.5 are reported for the Eastman process and, surprisingly, have not been found to influence polymer properties such as chemical resistance and thermal stability (65–68, 76). Crystallization kinetics, however, are strongly influenced by the disulfide content. When the disulfide fraction is in the range of 0.2–0.5, the resultant polymers are reportedly amorphous or, at best, difficult to crystallize. Polymers having disulfide fractions lower than 0.2 show a clear trend toward faster kinetics of crystallization. Eastman has also reported that polymers made by this process can be further polymerized by a solid-state high temperature treatment in an inert atmosphere (72).

$$\mathrm{I{-}Ar{-}I+S \longrightarrow {-}\!(Ar{-}S)_{1-x}(Ar{-}S{-}S)_{x}\!{-} + I_2}$$

The synthesis of poly(arylene sulfide)s via the thermolysis of bis(4-iodophenyl) disulfide has been reported (78). The process leads to the formation of PPS and elemental iodine. This process presumably occurs analogously to that reported by Eastman Chemical Company.

$$\mathrm{I{-}Ar{-}S{-}S{-}Ar{-}I \xrightarrow{\Delta} {-}\!(Ar{-}S)_{n}\!{-} + I_2}$$

Alternative synthetic routes to poly(arylene sulfide)s have been published (79–82). The general theme explored is the oxidative polymerization of diphenyl disulfide and its substituted analogues by using molecular oxygen as the oxidant, often catalyzed by a variety of reagents:

$$\mathrm{Ar{-}S{-}S{-}Ar + O_2 \xrightarrow{catalyst(s)} {-}\!(Ar{-}S)_{n}\!{-} + O_2^{2-}}$$

Other PPS polymerizations involving the electrooxidative polymerization of thiophenols have also been reported (83). Polymerizations described in the early work by this research group were characterized by low molecular weight due to the limited solubility of the product. Although aromatic disulfide-containing monomers are costly, the mild and selective reaction conditions allowed the synthesis of many functionalized PPS analogues. Work by this group has resulted in many patents and patent applications (84–86). Idemitsu researchers have also published synthetic routes to PPS via oxidative polymerization of diphenyl disulfides or thiophenols in the presence of acids, catalysts, and oxygen (87). More recent (1993–1994) work describes the synthesis of other poly(arylene sulfide)s (88) as well as PPS (89, 90) via soluble polysulfonium cationic polymer precursors. The route for PPS is based on the self-condensation of methyl 4-phenylthiophenyl sulfide under oxidizing conditions in methane sulfonic acid. The oxidation is catalyzed by cerium(IV) salt. The resultant polysulfonium cation, a soluble precursor for PPS, is demethylated, yielding PPS qualitatively.

Mechanistic studies on the formation of PPS from polymerization of copper(I) 4-bromobenzenethiolate in quinoline under inert atmosphere at 200°C have been published (91). PPS synthesized by this synthetic procedure is characterized by high molar mass at low conversions and esr signals consistent with a single-electron-transfer mechanism, the $S_{RN}1$-type mechanism described earlier (22).

In another process for the synthesis of PPS, as well as other poly(arylene sulfide)s and poly(arylene oxide)s, a pentamethylcyclopentadienylruthenium(I) π-complex is used to activate *p*-dichlorobenzene toward displacement by a variety of nucleophilic comonomers (92). Important facets of this approach, which allow the polymerization to proceed under mild conditions, are the tremendous activation afforded by the π-coordinated transition-metal group and the improved solubility of the resultant organometallic derivative of PPS. Decomplexation of the organometallic derivative polymers may, however, be complicated by precipitation of the polymer after partial decomplexation.

2. Properties of PPS Neat Resins

Highly desirable properties of PPS include excellent chemical resistance, high temperature thermal stability, inherent flame resistance, good inherent electrical insulating properties, and good mechanical properties.

2.1. Thermal Properties

Thermodynamic stability of the chemical bonds comprising the PPS backbone is quite high. The bond dissociation energies (at 25°C) for the carbon–carbon, carbon–hydrogen, and carbon–sulfur bonds found in PPS are as follows: C–C, 477 kJ/mol (114 kcal/mol); C–H, 414 kJ/mol (99 kcal/mol); and C–S, 276 kJ/mol (66 kcal/mol). The large expenditure of energy required to dissociate these bonds (and therefore initiate thermal degradation) implies that PPS should have excellent thermal stability. Thermogravimetric analysis (tga) is used to measure the percentage weight loss of a sample versus temperature. The material is typically heated in a controlled atmosphere at a prescribed heating rate. Figure 4 shows tga results in a nitrogen atmosphere of PPS in comparison to several known polymers. PPS retained approximately 40% of its original weight even after reaching 1000°C.

Tga has been used to calculate apparent activation energies for the thermal degradation of commercially available PPS samples (94) and the activation energies used to predict 10-year maximum use temperatures for Ryton PPS (grade P4) and Fortron PPS (grade 0205B4). This temperature for Ryton PPS was calculated to be between 198 and 235°C, whereas that for Fortron PPS was between 180 and 222°C. Correlations of weight loss data to useful property retention should be supplemented with actual lifetime property measurements. Pyrolysis–gc/ms analysis of volatile compounds obtained from thermal decomposition of PPS showed predominantly random chain scission and cyclization reactions at lower pyrolysis temperatures (up to 550°C) (95). Temperatures higher than 550°C resulted in depolymerization and production of compounds such as benzene and thiophenol.

Other thermal measurements are more relevant to the melt processing of PPS into molded parts. PPS is a semicrystalline polymer comprising a crystalline fraction and an amorphous fraction. The crystalline fraction displays a crystalline melting point, T_m, which for PPS is a broad endothermic transition at approximately 285°C as measured by differential scanning calorimetry (dsc). The amorphous region displays a modest glass-transition temperature, T_g, at approximately 85°C. A typical dsc thermogram is shown in Figure 5. The crystallization behavior of PPS has been extensively investigated (13, 36, 96–110) and reviewed (2).

At temperatures between T_g and T_m, PPS crystallizes readily. However, because the rate of crystallization is slow, rapid cooling from the melt can result in a molded part that is not fully crystallized. If the cooling is sufficiently rapid, a nearly amorphous part is obtained. Amorphous PPS crystallizes readily when heated to temperatures above T_g, as indicated by the exothermic crystallization peak located at approximately

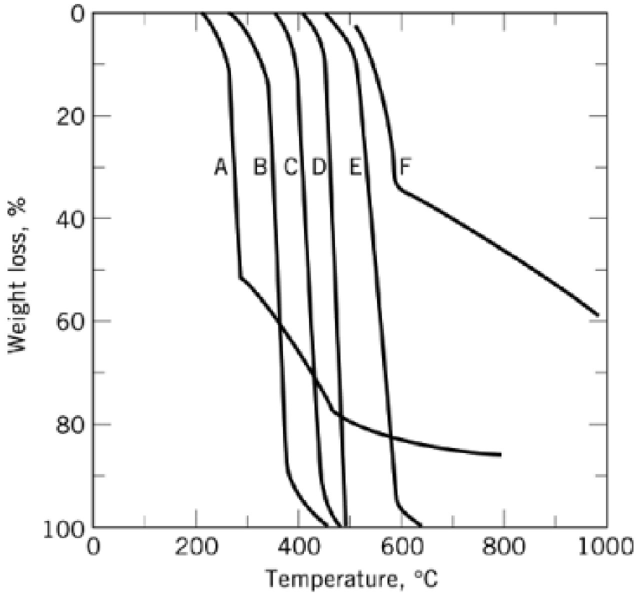


Fig. 4. Comparative thermogravimetric analyses of polymers in nitrogen: A, poly(vinyl chloride); B, poly(methyl methacrylate); C, polystyrene; D, polyethylene; E, polytetrafluoroethylene; and F, PPS (93).

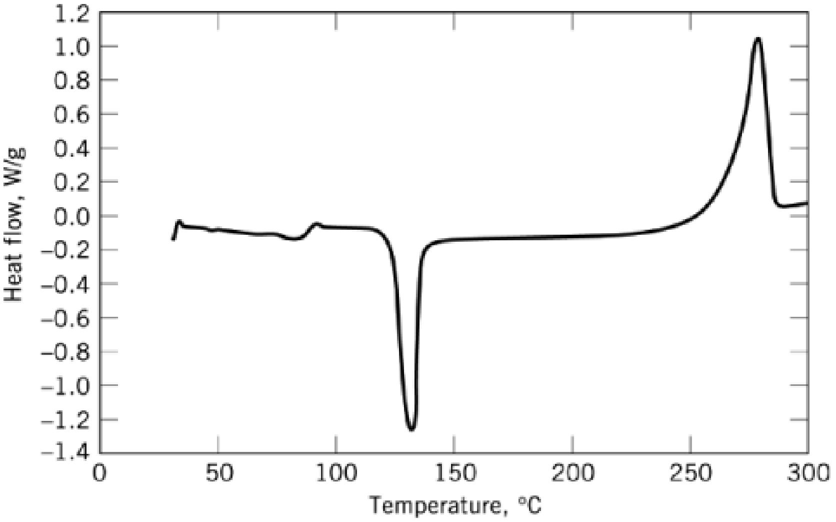


Fig. 5. Differential scanning calorimetry thermogram. Amorphous PPS is heated from room temperature to 325°C at 20°C/min.

120–130°C (Fig. 5). PPS also crystallizes readily when cooled from the melt. PPS displays a melt crystallization exotherm located between 160 and 250°C, depending on variables such as polymer structure (98–100), end-group chemistry (99), level of cure (36, 111), molecular weight (103, 105), the presence or absence of materials that function as nucleating agents (109), blends with other polymers (104), and plasticizing agents such as sorbed gases (110). The implication of these studies is that processing conditions can determine the level of crystallinity in molded PPS parts. Proper choice of molding and/or annealing conditions allows the molder to obtain crystalline parts having both dimensional stability and good mechanical properties.

The value for the heat of fusion of PPS, extrapolated to a hypothetical 100% crystalline state, is not agreed upon in the literature. Reported values range from approximately 80 J/g (19 cal/g) (36, 96, 101) to 146 J/g (35 cal/g) (102), with one intermediate value of 105 J/g (25 cal/g) (20). The lower value, 80 J/g, was originally measured by thermal analysis and then correlated with a measure of crystallinity determined by x-ray diffraction (36). The value of 146 J/g was determined independently on uniaxially oriented PPS film samples by thermal analysis, density measurement via density-gradient column, and the use of a calculated density for 100% crystalline PPS to arrive at a heat of fusion for 100% crystalline PPS (102). The value of 105 J/g was obtained by measuring the heats of fusion of well-characterized linear oligomers of PPS and extrapolation to infinite molecular weight.

2.2. Melt and Solution Properties

Melt rheology of PPS is complicated by the high temperatures needed and the requirement that air be excluded to avoid adventitious oxidative curing. One study (44) of the melt rheology of three commercially important classes of PPS, ie, linear and uncured, branched and uncured, and linear and cured, showed the unexpected result that the Newtonian viscosity of linear, uncured PPS increased with the 4.9 power of the weight-average molecular weight, rather than the expected 3.4 power. A homologous series of samples containing increasing amounts of long-chain branching showed increasingly non-Newtonian behavior. This was rationalized on the basis of the branched polymers having higher weight-average molecular weight and broader molecular weight distributions.

The melt rheology of products of the polymerization of *p*-diiodobenzene and sulfur have been described (112). The properties of PPS made by this synthetic route are complex and different from those made from sodium sulfide (or the chemical equivalent) and *p*-dichlorobenzene. During rheological testing, melt viscosities of PPS made from *p*-diiodobenzene and sulfur showed a significant increase, probably a result of continued polymerization reactions involving disulfide moieties. In contrast to these results (112), PPS synthesized from sodium sulfide and *p*-dichlorobenzene shows nearly constant or slightly decreasing dynamic viscosity as a function of time during measurements at temperatures from 316 to 360°C for up to two hours (113).

Other rheological studies have been directed toward understanding the effect of processing conditions on the properties of PPS neat resin and PPS reinforced with carbon fiber (114). The expected curing effects of processing PPS in air versus nitrogen were found. Similarly, the effects of melt curing on the rheological properties of PPS have been investigated; melt curing of PPS resulted in a polymer still possessing Newtonian behavior, indicating maintenance of a predominantly linear structure (39).

PPS is well-recognized for its exceptional chemical resistance. There are no known solvents for PPS below 200°C. A comprehensive survey of solvents for PPS has been published (115). Extreme conditions are required to dissolve PPS in both common and exotic solvents. Solution viscosity measurements are made difficult by this high temperature requirement. Inherent viscosity measurements are performed in 1-chloronaphthalene at 206°C at a concentration of 0.4 g of polymer per deciliter of solution. The inherent viscosity of PPS solutions shows a useful response to increasing molecular weight. Table 2 shows a correlation of inherent viscosity measurements with melt flow measurements.

Molecular weight distribution for a polymer affects polymer properties. Hence size-exclusion chromatography (sec) has become an essential analytical tool for the synthetic polymer chemist striving to enhance the performance characteristics of a polymer. The molecular weight distribution of PPS was first measured by using a custom-built, high temperature size-exclusion chromatograph (45) utilizing a viscometric detector. The methodology was based on combining the infinite dilution approximation with a universal calibration (116) that allows the use of well-characterized standard polymer samples having different chain structures. This method requires knowledge of the Mark-Houwink-Sakurada parameters, K and a, for the particular polymer–solvent

Table 2. Inherent Viscosities of PPS[a]

PPS polymerization process	Melt flow, g/10 min	Inherent viscosity, dL/g
unmodified	>6000	0.18
carboxylate-modified	1295	0.24
	665	0.28
	93	0.35

[a] Ref. 43.

system being studied. K was determined as 8.91×10^{-5} and a as 0.747 for PPS in 1-chloronaphthalene at 208°C (45). Although the concept of high temperature sec for PPS was clearly proven, viscometric detection of low molecular weight species was found to have low sensitivity. To improve the detection of low molecular weight species, a flame ionization detector (FID) was employed as a concentration detector (117). Concern about complete removal of the carrier solvent, 1-chloronaphthalene, from the moving quartz belt of the FID led to the speculation that this method, too, might suffer from detector nonuniformities for low molecular weight species (118), but this concern was later shown to be unfounded in a study using dual detector sec (119) in which virtually identical chromatograms were obtained using FID and uv–vis detectors. Use of a nonaromatic carrier solvent, 1-cyclohexyl-2-pyrrolidinone, has extended the window for uv–vis detection, allowing polystyrene standards to be used in an sec experiment with PPS (120). Suggestions of the utility of sec for PPS have also been found in the patent literature (121, 122); however, workable details of the analytical technique are not disclosed.

3. Properties of PPS Injection-Molding Compounds

PPS injection-molding compounds are distinguished among other thermoplastic compounds for their high performance properties, including excellent high temperature resistance, dimensional stability, and chemical resistance; inherent flame resistance; high electrical resistance properties; and a good balance of mechanical properties.

3.1. Thermal Properties

The inherent thermal stability of PPS translates into high temperature resistance for short- as well as long-term exposure and retention of properties at elevated temperature.

Highest thermal performance with PPS compounds requires that parts be molded under conditions leading to a high level of crystallinity. Glass-filled PPS compounds can be molded so that crystalline or amorphous parts are obtained. Mold temperature influences the crystallinity of PPS parts. Mold temperatures below approximately 93°C produce parts with low crystallinity and those above approximately 135°C produce highly crystalline parts. Mold temperatures between 93 and 135°C yield parts with an intermediate level of crystallinity. Part thickness may also influence the level of crystallinity. Thinner parts are more responsive to mold temperature. Thicker parts may have skin-core effects. When thick parts are molded in a cold mold the skin may not develop much crystallinity. The interior of the part, which remains hot for a longer period of time, may develop higher levels of crystallinity.

A useful measure of an engineering material's resistance to short-term exposure to heat is the heat deflection temperature (HDT). This test (ASTM D648) indicates the temperature at which a molded test specimen deflects 0.254 mm under a stress (1.82 MPa for engineering plastics) when heated at a rate of 2°C/min. This test does not predict long-term thermal performance of a plastic. The heat deflection temperatures for a variety of fiber glass-reinforced engineering plastics are shown in Table 3. Glass-filled PPS compounds have

Table 3. Heat Deflection Temperatures of Various Fiber Glass-Reinforced Engineering Materials[a]

Polymer	Heat deflection temperature, °C
liquid crystal polymer (LCP)	241
poly(phenylene sulfide) (PPS)	252–268
poly(etherimide) (PEI)	209–215
poly(cyclohexyldimethylene terephthalate) (PCT)	249
poly(ethylene terephthalate) (PET)	224
polyphthalamide (PPA)	275
phenolic resin	182–315
polycarbonate (PC)	142–152

[a] Ref. 123.

Table 4. UL Index of Various Glass-Filled Engineering Materials[a]

Polymer	UL temperature index, °C
liquid crystal polymer (LCP)	220–260
poly(phenylene sulfide) (PPS)	200–240
poly(etherimide) (PEI)	170–180
phenolic resin	150–180
poly(ethylene terephthalate) (PET)	120–150
poly(cyclohexyldimethylene terephthalate) (PCT)	120–140
polycarbonate (PC)	100–125

[a] Ref. 124.

high heat deflection temperatures, indicating excellent short-term retention of properties at high temperatures. This is important when a part is exposed to high temperatures for short periods of time, such as in soldering operations where temperatures are typically 224°C, but can reach 260°C, for short periods (usually <1 min).

Long-term exposure to high temperature is best described by the Underwriters' Laboratory (UL) temperature index. The UL temperature index is determined by oven-aging test specimens at several temperatures, usually considerably higher than the expected use temperature. Samples are removed at regular intervals and tested (usually tensile strength) at room temperature. A plot is made for each temperature to determine the time required for 50% property reduction. These times are used to make a plot of time to failure versus temperature. Extrapolation of the data to an arbitrary time (usually 100,000 h) results in the temperature index. Because this method measures long-term polymer degradation as a function of time, it is a good measure of a material's long-term performance at elevated temperature. UL temperature indexes are usually reported as ranges to account for different properties tested. The UL temperature indexes for a variety of engineering plastics are in Table 4. Glass-filled PPS compounds exhibit a high UL temperature index, which indicates excellent retention of properties for long-term exposure to high temperature. Other fillers, eg, mineral (talc), may also be used.

For semicrystalline polymers such as PPS, the relationship between a strength property and the temperature is not linear. As the test specimen goes through the glass-transition temperature (85–95°C for PPS), the strength of the material falls off fairly rapidly. However, with semicrystalline materials, a significant amount of mechanical strength is retained due to the crystalline portion of the polymer matrix. The effect of temperature on flexural strength of a 40% glass-filled PPS is shown in Figure 6. This figure demonstrates that glass-filled PPS compounds exhibit good strength up to 200°C.

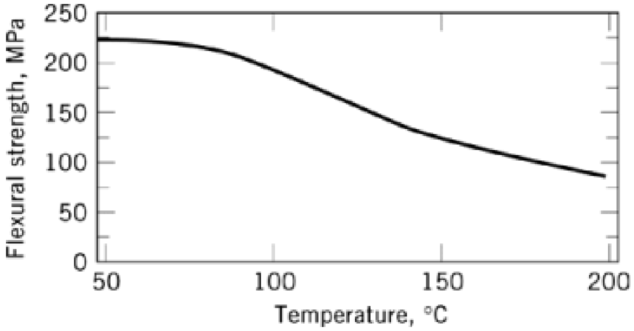


Fig. 6. Flexural strength vs temperature for Ryton PPS R-4 02XT. To convert MPa to psi, multiply by 145.

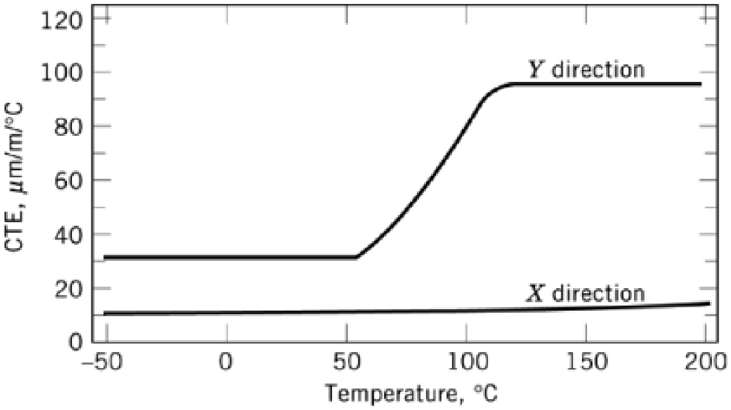


Fig. 7. CTE of a 40% glass-filled PPS as functions of both temperature and direction. CTE values are measured in micrometers of dimensional change per meter of sample per degree C.

3.2. Dimensional Stability

Plastics, in general, are subject to dimensional change at elevated temperature. One important change is the expansion of plastics with increasing temperature, a process that is also reversible. However, the coefficient of thermal expansion (CTE), measured according to ASTM E831, frequently is not linear with temperature and may vary depending on the direction in which the sample is tested, that is, samples may not be isotropic (Fig. 7).

Long-term irreversible dimensional change is described by creep modulus, which provides a numerical value to predict the load-bearing capability of a material as a function of temperature and time. Apparent creep modulus, measured according to ASTM D2990, is determined by applying a constant tensile load and measuring the percentage of linear strain as a function of time. At constant load, any change in measured strain can be considered tensile creep. A calculation of the tensile modulus at this point in time can be made by dividing the applied stress by the measured strain. Changing test conditions such as temperature and stress level provide data for specific applications. The tensile creep modulus of a 40% glass-filled PPS at various stress levels and temperatures is shown in Figure 8. Glass-filled PPS exhibits low creep even at high load and temperature.

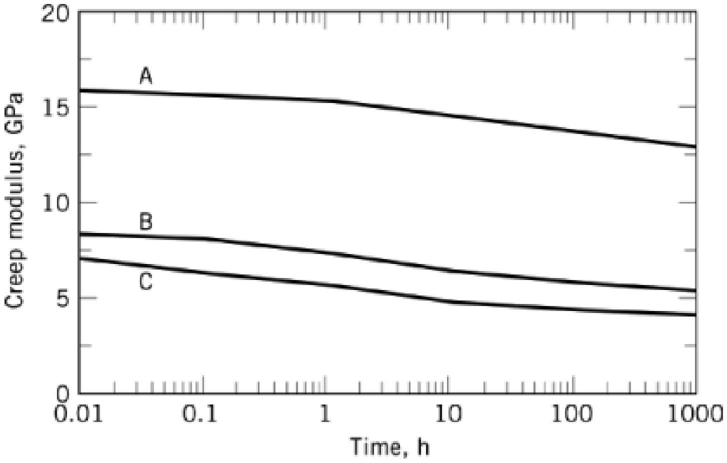


Fig. 8. Tensile creep of Ryton PPS R-4XT. Conditions: A, 65°C and 34.5 MPa (5000 psi) stress; B, 121°C, 34.5 MPa; and C, 121°C, 70 MPa (10,000 psi). To convert GPa to psi, multiply by 10,000.

3.3. Chemical Resistance

The chemical resistance of PPS compounds is outstanding, even at elevated temperatures, but as an organic polymer, PPS can be affected by some chemicals under certain conditions. Time and temperature are critical factors which must be considered when determining the level of chemical resistance required for a specific application. The effective chemical resistance should be evaluated on the basis of how well the material performs over time to chemical exposure relative to the required performance level. In a comparison of chemical resistance of various plastics (125), five materials were exposed to 127 different reagents for 24 h at 93°C. A passing grade was assigned if the material retained at least 75% of its initial tensile strength. PPS was the best performer, passing on 120 reagents. Phenolic resins were closest at ∼109, followed by nylon at 70, PPO at 65, and PC at 50. More detailed discussions of specific chemical exposure have been published (1, 3). To characterize the chemical resistance of PPS compounds, tensile specimens of 40% glass-filled PPS were immersed in various chemicals at 93°C and tested periodically for their retention of tensile strength. Based on these data, a rating was established as a general guide to illustrate the degrees of chemical resistance one might expect PPS compounds to exhibit within a chemical class (125).

3.4. Flame Resistance

Because of its aromatic structure and its tendency to char when exposed to an external flame, PPS is inherently flame-resistant. There are several tests that measure the flame resistance of plastics, including ignition temperature, flash point, UL flammability rating, oxygen index, and smoke obscuration time. The ignition temperature is a UL test which determines the minimum temperature that induces the material to burn. For 40% glass-filled PPS, the minimum reported combustion temperature is 540°C. The flash point for 40% glass-filled PPS was determined by ASTM D1929 and is above 499°C. In the standard UL 94 laboratory flammability tests, 40% glass-filled PPS is classified as either V-0 or 5VA, depending on the thickness of the test specimen. This rating indicates that the compound neither supports prolonged combustion nor drips flaming particles. The oxygen index is a relative indication of flammability under a specific set of conditions. The oxygen index is the minimum concentration of oxygen required to maintain continued burning of the material. The oxygen index of glass-filled PPS is greater than 46%, which demonstrates its excellent flame resistance. The NIST smoke test yields the time to reach a critical smoke density called the obscuration time. This test is designed to provide

Table 5. Electrical Properties of PPS[a]

Electrical property	Ryton PPS R-4XT, 40% glass-filled	Ryton PPS R-7, glass–mineral-filled
	High voltage	
dielectric strength, kV/mm	19.7	17.7
arc resistance, s	130	167
comparative tracking index, V	130	225
	Low voltage	
dielectric constant at 1 MHz	3.9	4.0
dissipation factor at 1 MHz	0.004	0.0088
volume resistivity, Ω·cm	1×10^{16}	1×10^{15}
insulation resistance, Ω at 90°C, 95% rh, 48 h	1×10^{11}	1×10^{12}

[a] Ref. 126.

an estimate of the time available before typical occupants in typical rooms find their vision obscured by smoke that hinders escape. The obscuration time for glass-filled PPS is 15.5 min smoldering and 3.2 min flaming.

3.5. Electrical Properties

PPS resins and compounds possess good overall electrical properties which indicate that they are good insulators. The importance of any particular electrical property depends on the application (either high or low voltage use). For high voltage applications, the key properties are dielectric strength, arc resistance, and comparative tracking index (CTI). The dielectric strength of a material, measured by ASTM D149, is the voltage required for electrical breakdown through the material. It is obtained by dividing the total breakdown voltage by the thickness of the specimen, and is reported in kilovolts per millimeter. The arc resistance of a material is a measure of the ability of a material to resist the formation of a permanent conductive path or track when exposed to arcing. Arc resistance measurements, tested by ASTM D495, determine the resistance of specimens to surface tracking by a high voltage arc. The value reported is the average number of seconds required to initiate surface tracking. CTI is also a measure of arc resistance; however, it is measured in a wet environment with an electrolyte present. Table 5 summarizes these high voltage properties for both 40% glass-filled PPS and a glass–mineral-filled PPS. PPS compounds that contain minerals in addition to glass fiber tend to exhibit better high voltage properties (see also Table 4).

For low voltage applications, the key properties are dielectric constant, dissipation factor, volume resistivity, and insulation resistance. The dielectric constant, measured by ASTM D150, determines the extent to which a material polarizes when placed in an electric field. It can be significant because it affects the amount of energy stored in dielectric components of an electrical circuit. Although a small added capacitance may not cause a problem, it is usually preferable to minimize the dielectric constant rather than to compensate for it via circuitry design. Thus, low dielectric constant is particularly desirable for communications and electronic circuits that rely on rapid switching and low loss transmission. Dissipation factor, measured by ASTM D150, is the ratio of energy dissipated as heat compared to the energy stored in the system. The energy dissipated as heat in many applications remains small in terms of temperature rise; however, the effect on the signals being transmitted can be substantial. Volume resistivity, measured by ASTM D257, is the inherent resistance of a material to current flow through its volume. It is generally an indication of a material's insulation characteristics. Insulation resistance is a measure of surface or volume resistance at use conditions, combining high temperature and high humidity. Table 5 summarizes the low voltage electrical properties for both 40% glass-filled PPS and glass–mineral-filled PPS. Glass-filled PPS compounds exhibit the lowest dielectric constant and dissipation factor, but they all possess a good combination of low voltage electrical properties.

Table 6. Mechanical Properties of PPS Compounds[a]

Property	Ryton PPS R-4XT, 40% glass-filled	Ryton PPS R-7, glass–mineral-filled
tensile strength, MPa[b]	193	128
elongation, %	1.6	0.8
flexural strength, MPa[b]	276	186
flexural modulus, GPa[c]	14.5	17.2
modulus of elasticity, GPa[c]	15.1	17.2
compressive strength, MPa[b]	235	172
Izod impact, J/m[d]		
notched	85	70
unnotched	560	240

[a] Ref. 126.

[b] To convert MPa to psi, multiply by 145.

[c] To convert GPa to psi, multiply by 145,000.

[d] To convert J/m to $\mathrm{lbf \cdot ft/in.}$, divide by 53.38.

3.6. Mechanical Properties

Articles molded from PPS compounds are generally characterized by high strength, high stiffness, and moderate impact. In addition to standard grades, PPS can be custom-tailored with fillers, additives, and fibers to suit specific applications. The mechanical properties of 40% glass-filled and glass–mineral-filled PPS is shown in Table 6. PPS compounds possess a good combination of mechanical properties.

4. Applications

PPS resin and compounds combine a unique and useful combination of properties, facile processing conditions, and an attractive price for the level of performance afforded by the polymer. Inherent properties of PPS that determine the utility of PPS resins and compounds include excellent electrical insulation, excellent long- and short-term thermal stability, inherent flame resistance, easy moldability, outstanding chemical resistance, good mechanical properties, and dimensional stability of molded parts. PPS finds acceptance in a wide variety of applications, including coatings, injection-molding compounds, fiber, film, composites, blends, and alloys. Market segments utilizing PPS resins and compounds comprise electrical, electronic, automotive, appliance, and industrial.

4.1. Coatings

PPS coatings can be applied to a variety of substrates, usually metal, by a variety of techniques and have been reviewed (127, 128). Corrosion-resistant, pinhole-free, thermally stable coatings of PPS having good release characteristics can be applied to steel, aluminum, and other metals from aqueous slurries of PPS, by electrostatic powder coating, fluidized-bed coating, and powder spraying and flocking. Cured coatings of PPS with proper additives may be used in cookware applications (129).

Low molecular weight linear PPS is conventionally used in coatings. A curing cycle is required to melt the polymer and cure the fused coating into a tough, insoluble coating. Cure time and temperature must be selected so that the polymer melts and forms a contiguous coating, and that appropriate curing takes place to yield a durable coating. Undercured coatings are brittle as a result of low molecular weight and polymer crystallization. Overcured coatings are likewise brittle because the cross-link density is too high. Optimum curing conditions have been described (127).

Table 7. Properties of PPS Fiber

Property	Value
tenacity, N/tex[a]	0.31
elongation, %	40
modulus, N/tex[a] at 10% extension	1.4
elastic recovery, %	
2% extension	100
5% extension	96
10% extension	86
dry shrinkage, % at 130°C	4
moisture regain, %	0.6
specific gravity	1.37

[a] To convert N/tex to gf/den, divide by 0.08826.

Substrate surface preparation such as grit blasting, heat treating, and primer application can enhance adhesion of PPS to steel. Adhesion to aluminum is good and does not require special pretreatments. Downhole oil well applications are challenging adhesion tests for any coating. Special low molecular weight grades of PPS have been developed (130) which provide good adhesion in these demanding environments.

4.2. Injection-Molding Compounds

PPS injection-molding compounds typically contain reinforcing fibers such as glass or carbon fiber, often with coupling agents, and/or mineral fillers to enhance specific properties. Filled compounds also have good processibility and can be used for molding of intricate parts. Typical barrel temperatures range between 300 and 360°C. High temperature increases flow and reduces equipment wear. Typical molding conditions utilize high injection pressure, slow injection rate, medium screw speed, and maximum clamping pressure.

Mold temperature can vary widely. Typical temperatures range from 40 to 150°C. Higher mold temperatures favor polymer crystallization and result in more dimensionally stable parts. Crystallinity can be developed in parts molded in cold molds by annealing at approximately 200°C.

Although PPS compounds do not absorb much water, drying is recommended to minimize any effects of hygroscopic fillers. Typical drying conditions are 150°C for 6 h.

4.3. Fiber

High molecular weight linear PPS is well-suited for fiber applications. The inherent properties of PPS (flame resistance, chemical resistance, and thermal stability) make PPS fiber highly desirable in textile applications (128). PPS fiber has been designated by the U.S. Federal Trade Commission as a new generic class of materials called sulfar. Typical fiber properties are listed in Table 7 (see High performance fibers).

PPS fiber has excellent chemical resistance. Only strong oxidizing agents cause degradation. As expected from inherent resin properties, PPS fiber is flame-resistant and has an autoignition temperature of 590°C as determined in tests at the Textile Research Institute. PPS fiber is an excellent electrical insulator; it finds application in hostile environments such as filter bags for filtration of flue gas from coal-fired furnaces, filter media for gas and liquid filtration, electrolysis membranes, protective clothing, and composites.

4.4. Composites

High molecular weight PPS can be combined with long (0.6 cm to continuous) fiber to produce advanced composite materials (131). Such materials having PPS as the polymer matrix have been developed by using

Table 8. Properties of PPS Composites

Property	Stampable sheet	Prepreg or laminate
fiber reinforcement	glass, carbon	glass, carbon, aramid
fiber form	random mat	unidirectional, fabric
fiber loading, wt %	20–40	40–70
strength, MPa[a]	90–207	207–1724
modulus, GPa[b]	6.2–13.8	13.8–138
impact, J/m[c]	534–1335	64–1600

[a] To convert MPa to psi, multiply by 145.

[b] To convert GPa to psi, multiply by 145,000.

[c] To convert J/m to $\mathrm{lbf \cdot ft/in.}$, divide by 53.38.

a variety of reinforcements, including glass, carbon, and Kevlar fibers as mat, fabric, and unidirectional reinforcements. Thermoplastic composites based on PPS have found application in the aircraft, aerospace, automotive, appliance, and recreation markets (see Composite materials, polymer-matrix).

The preparation of composite materials has been described extensively in the patent literature (132–142). Stampable sheet composites are prepared by combining PPS with chopped or continuous fiber mat. Long reinforcing fibers result in dramatic increases in toughness. Mat-reinforced composite materials can be rapidly compression-molded into parts. Unidirectional (132, 139) and woven fabric prepreg materials (137) are produced using proprietary processes. Comingling of PPS fiber and long reinforcing fibers produce yarns that, when heated above the melting point of PPS, produce long-fiber-reinforced PPS composite materials (138). PPS resins have been custom-synthesized for composite applications (133–135) that result in improved composite properties. PPS prepreg materials have unlimited shelf life, are tack-free, and, unlike many of the thermosetting prepreg materials, do not require refrigerated storage. PPS prepregs can be easily laid up and held into place by spot welding. They are converted into laminates by heating the prepregs above the crystalline melting point of the polymer and applying pressure of about 345–1380 kPa (50–200 psig). PPS laminates and prepregs can be further shaped in subsequent melt processing operations (139). PPS prepreg material can be formed into useful shapes using a heated filament winding technique (140). Subsequent operations can be carried out to form ribs and other reinforcing shapes on already formed laminates (141, 142). PPS composite materials are characterized by exceptional flexibility in manufacturing technology. Typical properties of PPS composites are shown in Table 8.

4.5. Film

High molecular weight PPS is suitable for film-making applications (143). PPS film is amenable to biaxial orientation (144). Biaxially oriented film is manufactured by extruding sheet that must be amorphous to accommodate the drawing operation. After biaxial stretching, the drawn film is heat-set to allow polymer crystallization. Biaxial orientation of amorphous PPS results in some strain-induced crystallinity as indicated by a modest increase in density. The level of strain-induced crystallinity is likely to be influenced by process variables such as the rate and temperature of drawing, as well as polymer variables such as the molecular weight, molecular weight distribution, and the distribution of structural features (eg, long-chain branching) within the molecular weight distribution. Amorphous PPS film has a density of 1.321–1.323 g/cm^3, which increases to approximately 1.323–1.325 g/cm^3 after biaxial orientation. Subsequent heat setting increases the density to approximately 1.36 g/cm^3.

Biaxially oriented PPS film is transparent and nearly colorless. It has low permeability to water vapor, carbon dioxide, and oxygen. PPS film has a low coefficient of hygroscopic expansion and a low dissipation factor, making it a candidate material for information storage devices and for thin-film capacitors. Chemical and thermal stability of PPS film derives from inherent resin properties. PPS films exposed to toluene or

Table 9. Properties of Biaxially Oriented PPS Film

tensile yield, MPa[a]	90–110
tensile strength, MPa[a]	117–158
elongation, %	40–60
tear strength, N/mm[b]	1.57–3.14
haze, %	2–10
shrinkage	2–5
thermal expansion coefficient, cm/cm/°C	2.2×10^{-5}
hygroscopic expansion coefficient, cm/cm/%rh	0.18×10^{-5}
dielectric constant at 1.0 kHz	3.0
dissipation factor at 1.1 kHz	0.0005
volume resistivity, Ω·cm	1.3×10^{-17}
permeability, nmol/(m·s·GPa)[c]	
H_2O	1.44
CO_2	84
O_2	20

[a] To convert MPa to psi, multiply by 145.

[b] To convert N/mm to ppi, divide by 0.175; to convert to Elmendorf tear (gf/mil), multiply by 2.549.

[c] To convert nmol/(m·s·GPa) to (cc·mil)/(100 in. 2·d·atm), divide by 2.

chloroform for 8 weeks retain 75% of their original strength. The UL temperature index rating of PPS film is 160°C for mechanical applications and 180°C for electrical applications. Table 9 summarizes the properties of PPS film.

4.6. Blends

Several research groups have investigated the properties of blends comprising PPS and thermotropic liquid crystalline copolyesters. These blends have been found to be incompatible, resulting in a dispersed LCP-phase in a continuous PPS matrix (145). The dispersed LCP-phase possesses a processing-dependent fibrilar morphology. Films of these blends were drawn, causing orientation of the LCP fibrils and thereby producing dramatic improvements in the torsional modulus. Injection-molded specimens of PPS–LCP blends were studied to determine mechanical properties and morphology (146). Tensile and impact properties of the blends were improved over those of pure PPS. PPS was found to be incompatible with the LCP. Blends of PPS and LCP were extruded into monofilaments and the mechanical properties of drawn fibers studied (147). The strength and modulus of fibers of PPS–LCP blends were higher than those of pure PPS. A study of the morphology and crystallization kinetics of blends of PPS with thermotropic liquid crystalline copolyesters showed that PPS–LCP blends are incompatible (148); however, the crystalline morphology of the PPS showed considerably smaller spherulite size. The linear growth rate of the PPS spherulites was shown by optical microscopy to be virtually unaffected by the presence of the LCP. The bulk kinetics of crystallization, however, were enhanced by the presence of the LCP, leading to the conclusion that the LCP functioned as a nucleating agent for PPS.

The effect of a second polymer blended with PPS which causes enhanced nucleation of PPS has been previously observed. It was found that low concentrations (1–2 wt %) of poly(phenylene sulfide ketone) and poly(ether ether ketone), when melt-blended with PPS, function effectively to increase the nucleation density of PPS (149).

The crystallization kinetics of blends of PPS and poly(ethylene terephthalate) have been studied (150–152). Isothermal crystallization kinetics of PET–PPS blends showed that the crystallization of the PPS was accelerated over that of pure PPS. The nucleation density for PPS was increased in the PPS–PET blend as determined by polarized light microscopy, resulting in smaller spherulite size. PPS blends with a variety of nylons have been reported (153, 154). Blends comprising aromatic amorphous appeared to impart greater

Table 10. Exposure Limits for PPS Decomposition Products

Decomposition product	OSHA PEL, ppm
carbon dioxide	10,000
carbon monoxide	35
sulfur dioxide	2
carbonyl sulfide	not established

toughness than corresponding blends made with aliphatic nylons. Blends of PPS and polyethylene (155) were prepared by melt-mixing and displayed immiscibility at all blend ratios. Blends of PPS and polyetherimide have been prepared by reactive extrusion (156). Compatibilization of PPS and PEI, presumably accomplished by block copolymers of PPS and PEI being synthesized during reactive extrusion, resulted in a dramatically reduced PEI domain size.

5. Health and Safety Considerations

Information on health and safety considerations cited herein for Ryton PPS powders and pellets can be found in Reference 157. Ryton PPS [26125-40-6] is listed in the Toxic Substance Control Act (TSCA) Inventory of Chemicals.

For personal protection when using PPS, employ adequate ventilation to control airborne powder concentration and off-gases from molding and extruding processes. Local exhaust may be needed to control off-gases. No respiratory protection is generally required unless needed to control respiratory irritation from dust or off-gases. To control off-gases during molding, use a NIOSH- or Mine Safety Health Administration (MSHA)-approved air purifying respirator equipped with an organic vapor cartridge and face mask. For eye protection, use safety glasses with side shields and provide eyewash stations in the work area. No special garments are required for skin protection; avoid unnecessary skin contamination with material. Use heat-resistant gloves when handling hot or molten material. When cleaning thermal decomposition off-gas condensate from equipment, use full-body, long-sleeved garments to prevent skin contact. Molten polymer may cause severe thermal burns. The interior of molten masses may remain hot for some time because of the low thermal conductivity of the polymer.

PPS dust should be treated as a nuisance particulate. The OSHA permissible exposure limit for respirable dust is 5 mg/m^3 for dust containing no asbestos and less than 1% silica. The principal decomposition products released during molding of PPS and their permissible exposure limits are given in Table 10. Sulfur dioxide and carbonyl sulfide are the most significant off-gases for production of mucous membrane irritation.

Acute effects of overexposure are as follows. Exposure to dust may cause mechanical irritation of the eye. PPS is essentially nonirritating to the skin, although freshly molded material may occasionally cause dermatitis. Inhalation of PPS dust may cause mechanical irritation to mucous membranes of nose, throat, and upper respiratory tract.

Subchronic effects of overexposure have been studied in feeding tests of PPS powder at dietary levels of up to 5%. No detrimental effects in laboratory animals were observed (157).

The flash point of PPS, as measured by ASTM D1929, is greater than 500°C. Combustion products of PPS include carbon, sulfur oxides, and carbonyl sulfide. Specific hazards are defined by the OSHA Hazard Communication Standard (158). Based on information in 1995, PPS does not meet any of the hazard definitions of this standard.

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