

# Chemical surface functionalization of bulk poly (p-phenylene sulfide) yields a stable sulfonic acid catalyst



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## ABSTRACT

Catalytic materials are important in industrial chemistry; these materials must be inexpensive and easy to process as well as resistant to chemicals, heat and structural loads. Poly (p-phenylene sulfide) (PPS) is a widely used and exceptionally resistant thermoplastic. We demonstrate that the superficial regions of polymerized bulk PPS can be sulfonated using either SO<sub>3</sub> or acetyl sulfate, yielding a solid core of unaltered PPS with a sulfonic acid-functionalized surface. The SO<sub>3</sub> method was the most efficient and achieved 0.9 mmol H<sup>+</sup> per gram of polymer. We show that the sulfonated surfaces function as durable solid acid catalysts for the dehydration of ethanol to diethyl ether. We also develop a simple method for the formation of porous PPS structures based on compression molding and porogen leaching. Based on these results, we suggest that surface functionalization of bulk PPS can be used to develop a novel class of moldable, easily produced and durable heterogeneous catalysts.

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## 1. Introduction

There is a global demand for new clean technologies, such as those that can reduce our dependence on fossil fuels as well as reduce global warming and urban pollution. New catalysts may be such a technology because their efficiency reduces energy consumption in industrial chemistry and enables the sustainable production of important chemicals, such as biofuels [1]. Heterogeneous catalysts are used in a wide variety of organic reactions [2], including the production of biofuels [3], because they enable continuous processes and facilitate the separation of catalyst and product. The bulk materials used in heterogeneous catalysts must be thermally and mechanically stable to resist heat, temperature fluctuations and pressures during the reaction. These properties are often as important as catalytic activity, selectivity and chemical deactivation for practical applications [4,5]. A catalytic base material should also be easy to chemically modify for the introduction of catalytic groups, and it should be easily

processed into a physical form that can function as a catalytic substrate. These requirements are often contradictory.

Poly (p-phenylene sulfide) (PPS) is a commercial polymer commonly used for high performance coatings and structural parts in high-demand sectors, such as the automotive and chemical industries [6]. PPS is used because it possesses a unique combination of attractive properties, including high temperature performance, mechanical strength, low thermal expansion and extreme chemical resistance (it has no known solvent below 200 °C). PPS is a low-weight polymeric material that is relatively inexpensive and can be thermally processed using common methods, such as extrusion, injection, blow and compression molding. For a thermoplastic, PPS also has the rare property of converting into an electrical conductor when appropriately doped, and conductivities of up to 1 S/cm have been achieved with PPS [7].

Despite these beneficial attributes, few studies exist on the use of PPS as a catalytic substrate. The use of sulfonated PPS to catalyze ester formation was suggested in one patent but was not demonstrated [8]. To date, the only study that has investigated the use of PPS as a catalytic substrate employed a PPS dendrimer with a carboxylic acid end group as a catalytic substrate onto which a lipase enzyme was conjugated using carbodiimide chemistry [9]. This homogenous catalyst was then able to hydrolyze olive oil with high activity, even after 20 cycles, demonstrating the potential use

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of PPS as a catalytic substrate material. However, in this study, the carboxylic acid group was introduced before polymerizing the polymer into a dendrimer [10]. To process bulk PPS into a shape suitable for a heterogeneous catalyst, it would be desirable to use thermoplastic molding methods. These methods require the use of unmodified PPS during processing and require the introduction of functional groups onto bulk PPS material post-polymerization and post-processing.

PPS is highly chemically resistant, and although few chemicals can attack it, fuming sulfuric acid is known to react with PPS [11]. Sulfonated PPS (SPPS) has been utilized in a number of applications, including ion exchange resins [11,12] and proton-conducting fuel cell membranes [13–16]. Importantly, sulfonic acid groups that have been introduced into the PPS chain may be substituted with other groups [17]. Thus, PPS sulfonation may be considered the first step in introducing a wider variety of chemistry into PPS substrates. However, in all of these studies, sulfonation was achieved either by completely reacting PPS powder with  $\text{SO}_3$ , resulting in a gel [11,13,17,18], or by reacting a soluble methyl sulfonium PPS precursor polymer with  $\text{SO}_3$  before reducing its backbone to obtain PPS [12,14–16]. Bulk PPS in the form of pellets has also been sulfonated using chlorosulfonic acid. However, in this case, the objective was to form an ion-exchange membrane; therefore, sulfonated pellets were ground to a powder before characterization [19].

We hypothesize that if limited sulfonation is applied to a bulk structure fabricated with a long chain PPS, we could selectively sulfonate only the surface-exposed parts of the polymer chains, rendering these parts hydrophilic while leaving the remainder of the chain unmodified, insoluble and embedded within the non-sulfonated PPS core (Fig. 1). This part of the chain may then function as an anchor, retaining the hydrophilic layer on the substrate. Because the core of the PPS bulk material remains unmodified and insoluble, the structure should maintain its integrity when exposed to solvents, allowing for continuous heterogeneous synthesis of even strong solvents, such as diethyl ether (DEE).

In this study, we test this hypothesis by sulfonating bulk PPS in the form of millimeter-sized pellets using a modified version of the  $\text{SO}_3$  sulfonation method referenced above [11] employing cooling, a shorter reaction time and less  $\text{SO}_3$ . We also investigate a different method based on acetyl sulfate. To date, the latter method has only been used in the sulfonation of other polymers [20,21]. We demonstrate that both of the methods lead to sulfonated substrates that retain their original bulk structure. As a proof-of-concept, we then show that the sulfonic acid functionality introduced onto the PPS can be used to catalyze the dehydration of ethanol to DEE, and the PPS catalyst is sufficiently stable to be used in 10 h of continuous flow synthesis at 35 bar and at temperatures increasing from 120 °C to 220 °C. Finally, we show that a porous PPS structure can be fabricated using a novel compression molding/porogen

leaching method, and this bulk structure can be post-modified using  $\text{SO}_3$ .

## 2. Experimental

### 2.1. Materials

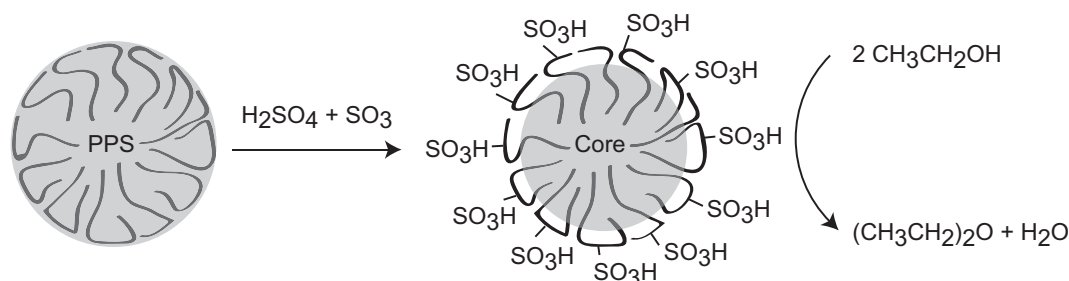
The chemicals and solvents used in this study were commercially available, and no further purification was performed. The PPS was commercial-grade Ryton® QA200 N (unfilled pellets composed of compacted powder) and Ryton® V1 (fine unfilled powder) from Chevron Phillips Chemical Company LLC, USA. These PPS variants were selected because of their high melt flow index (therefore, presumably longer chain lengths) relative to other commercial PPS variants. Potassium hydroxide and sulfuric acid (95–97%) were obtained from Sigma Aldrich (USA), whereas 35% hydrochloric acid, acetic anhydride, 1,2-dichloroethane, and fuming sulfuric acid containing 65%  $\text{SO}_3$  (oleum) were obtained from Merck KGaA (Germany). Ethanol (99.9%) was purchased from Kemetyl (Denmark). Sulfuric acid with a slight excess of dissolved  $\text{SO}_3$  (100%  $\text{H}_2\text{SO}_4$ ) was prepared by dehydrating the remaining water in 54.35 g of 95–97% sulfuric acid with 17.19 g of fuming sulfuric acid containing 65%  $\text{SO}_3$ . Because  $\text{SO}_3$  reacts violently, the addition was performed slowly under cooling and in a fume hood.

### 2.2. Synthesis

PPS pellets (Ryton® QA200 N) were dried in an oven overnight at 100 °C and were then sulfonated using one of two different methods.

Our  $\text{SO}_3$  method was based on previous publications [12,15,19]. We placed 30.0 g of PPS in a 250 mL Erlenmeyer flask that was cooled in a stirred ice bath; subsequently, 100 mL of 100%  $\text{H}_2\text{SO}_4$  was added slowly. The resulting bluish suspension was then stirred for 1 h at 0 °C. After 1 h, 200 mL of 99.9% ethanol was added. The acid was then neutralized with KOH under continuous cooling. The solution was filtered, and the residual pellets were washed with demineralized water until attaining a neutral pH. The acid groups were subsequently re-protonated using 1.0 M HCl, which was washed off with ethanol before a final drying at 100 °C for 24 h. Finally, we obtained 30.0 g of beige pellets. We also performed the same reaction on a smaller scale (3.0 g of polymer) with 2, 3 and 4 h reaction times to test the influence of time on sulfonation. We attempted running the reaction at room temperature and/or using higher concentrations of  $\text{SO}_3$ , but these conditions led to a violent reaction that destroyed the sample.

Our acetyl sulfate sulfonation method was developed based on a procedure successfully used for the sulfonation of PS brushes [20,21]. A mixture of 50.0 mL of 1,2-dichloroethane and 10.2 mL



**Fig. 1.** Schematic drawing of catalyst synthesis and reaction. Our concept of a heterogeneous catalytic PPS substrate in which the surface regions of each polymer chain were sulfonated and became hydrophilic while the remaining parts of the polymer located in the inner particle core remain non-sulfonated and hydrophobic, binding the polymer chains and maintaining the stable structure. The surface-bound sulfonic acid groups may then catalyze reactions, such as the dehydration of ethanol to diethyl ether.

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