

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 SO₃ or acetyl sulfate, yielding a solid core of unaltered PPS with a sulfonic acid-functionalized surface. The SO₃ method was the most efficient and achieved 0.9 mmol H⁺ 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 SO_3 , resulting in a gel [11,13,17,18], or by reacting a soluble methyl sulfonium PPS precursor polymer with 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 SO_3 sulfonation method referenced above [11] employing cooling, a shorter reaction time and less 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 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% 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 SO_3 (100% H_2SO_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% SO_3 . Because 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 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% H_2SO_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 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

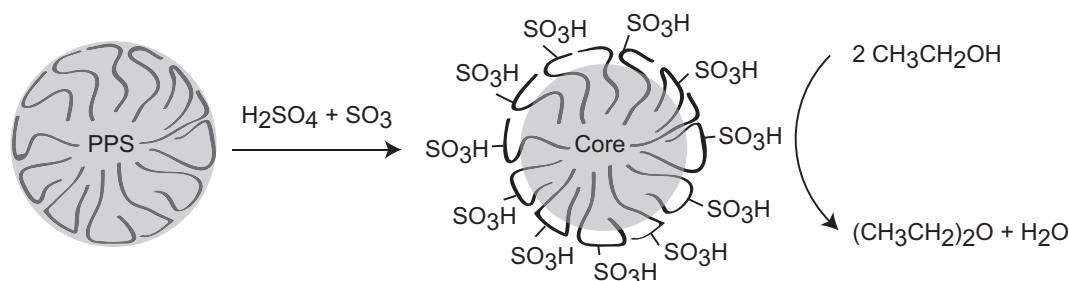


Fig. 1. Schematic drawing of catalyst synthesis and reaction. Our concept of a heterogeneous catalytic PPS substrate in which the surface regions of each polymer chain were sulfonated and became hydrophilic while the remaining parts of the polymer located in the inner particle core remain non-sulfonated 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.

of acetic anhydride was prepared in a dry round bottle and cooled to 0 °C using a stirred ice bath. We then slowly added 3.6 mL of 100% H₂SO₄ under constant stirring using a dropping funnel. A clear solution of acetyl sulfate was obtained. Due to the instability of the sulfonating agent, it was prepared immediately before use. For the sulfonation reaction, 10.00 g of PPS was placed into a three-neck bottle equipped with a gas inlet and a reflux cooler under a dry argon atmosphere. Subsequently, the acetyl sulfate solution was added to the polymer. The mixture was then heated to 90 °C and constantly stirred under reflux for 6 h or 18 h. The reaction was stopped by the addition of 50 mL of methanol. The resulting clear orange-brown solution containing the desired polymer as precipitate was then neutralized to pH 6 using a 1.0 M solution of NaOH in H₂O. Reactivation with HCl and washing were then performed, similar to the other sulfonation method. Finally, 9.7 g and 9.4 g of light brown pellets were obtained for the 6 and 18 h reaction times, respectively. Prolonged reaction times did not lead to further sulfonation, presumably due to the decomposition of the labile sulfonating agent.

We developed a method for the fabrication of porous PPS substrates based on the porogen leaching method originally developed for the production of porous tissue engineering scaffolds [22]. PPS powder (Ryton® V-1) was mixed with table salt (NaCl) at a mass ratio of 20%:80%. A cylindrical steel press form was filled and then pressed using a close fitting piston. The sample was then pressed for 2 min at room temperature with an external pressure of 40 kN. The complete press form containing the raw sample was then transferred to a preheated oven where it remained at 280 °C for 60 min. The hot sample was pressed again with a steady pressure of 40 kN and was then left in the press while it cooled to room temperature. The cooled sample was extracted from the form and washed with 2 × 200 mL of demineralized water for 15 min each to remove the majority of the salt. The remaining salt was then leached overnight by stirring in 250 mL of demineralized water at 90 °C. The samples were then dried and studied by computed tomography (CT). A portion of the samples was then treated with 100% H₂SO₄ for 1 h at room temperature or at 0 °C. The reactions were then stopped using cold ethanol, and the samples were washed and dried. A catalysis test was performed at 170 °C overnight using the batch catalysis method, as described below.

2.3. Characterization

Acid density was determined using a previously published protocol [23]. Briefly, 1 g of polymer was stirred with 100 mL of 1.0 M NaCl over 4 h to substitute Na⁺ for H⁺. Next, three 20 mL aliquots of the released acid were titrated with 0.1 M NaOH containing phenolphthalein as an indicator. The standard deviation is indicated.

Computed tomography (CT): High-resolution 3D X-ray images with a resolution of 5 μm per voxel were obtained using a SkyScan 1172 μCT scanner from Bruker, Belgium. All of the image analyses and segmentations were primarily performed using the open-source software ImageJ [24] with the algorithms developed under the BoneJ package [25]. The open-source 3D Slicer software was used for 3D visualization and analysis of the reconstructed data [26].

Scanning electron microscopy (SEM): SEM was performed using an Ultra55 microscope from Zeiss, Germany. Samples were placed on aluminum pin stubs and sputter coated with 10 nm gold particles before investigation. Images were collected using secondary electrons. The working distance, voltage and magnification are indicated in individual figures. Energy-dispersive X-ray spectroscopy (EDX) was performed using an X-Max 50 mm² detector from Oxford, UK. The standard deviation is given in parenthesis.

Infrared spectroscopy (IR): IR was performed in a diamond cell using a Nicolet iS50 FTIR from Thermo Fisher (USA). ATR-IR

measurements were performed on a Bruker Optics ALPHA FT-IR spectrometer.

2.4. Catalytic tests

Batch catalysis was performed by adding 5 mL of 99.9% EtOH and either 1.0 g of pellet catalyst or one porous substrate to stainless steel tubes (tube volume 38 mL), which were sealed at both ends and placed in a preheated oven at the indicated temperature for the indicated duration. Liquid was then extracted and stored, and the catalysts were washed with 99.9% EtOH and dried overnight before use in further catalysis experiments.

Continuous flow catalysis was performed by pumping 1 mL/min 99.9% EtOH through a heated steel tube (volume 38 mL) containing 7.0 g of pellet catalyst retained by glass wool. Before collecting the samples, the system was allowed to equilibrate at 35 bar and at the set temperature for 1 h with a continuous flow of 1.0 mL/min 99.9% EtOH to achieve stable conditions. The pump used was an Azura P2.1S from Knauer, Germany. Temperatures were measured using four thermocouples and logged using a TC-08 and PicoLog Ver. 5.20.3 data logging system from Pico Technology Ltd, UK. A graphical illustration of the setup is provided in [Supplementary Fig. 1](#).

For gas chromatography (GC), 200 μL of liquid was evaporated at room temperature in a clean gas sample bag filled with 1 L of N₂. When the liquid was completely evaporated, the contents of the bag were pumped through a GC for 2 min before closing the GC and analyzing the gas content. The GC used was a 7890B GC System from Agilent Technologies, and the gas content was separated on a DB-1 capillary column before detection using a flame ionization detector (FID). The integrated peak areas and effective carbon numbers were used to determine the concentration of each compound. Liquid from stock solutions/gases of diethyl ether, ethylene, ethanol, methanol, acetic anhydride and 1,2-dichloroethane was used to determine the peaks corresponding to the compounds.

3. Results

3.1. Sulfonation of PPS

PPS pellets were sulfonated using two different methods, one method based on SO₃ and one method based on acetyl sulfate. Unless stated otherwise, we used samples that were sulfonated for 1 h and 6 h, respectively. CT, SEM and EDX were then used to analyze the resulting pellets along with non-treated PPS and an Amberlyst®-15 control sample. Amberlyst®-15 is a commercial ion exchange resin composed of a sulfonated cross-linked styrene-divinylbenzene resin with known solid acid catalytic properties; it is included in this study as a positive control.

Using titration with sodium hydroxide, the acid density was determined to be 0.42 mmol/g (±0.01) for SO₃-sulfonated PPS after 1 h. After 2, 3 and 4 h of reaction time, the acid density was determined to be constant within the error margins (2 h: 0.93 mmol/g (±0.03); 3 h: 0.94 mmol/g (±0.03); and 4 h: 0.93 mmol/g (±0.03)). This result could indicate a surface-saturation of the sulfonic acid groups at prolonged reaction times. After 18 h of reaction time, acetyl sulfate PPS exhibited an acid density of 0.11 mmol/g (±0.03). We found the acid density of Amberlyst®-15 to be 4.41 mmol/g (±0.03), which is in good agreement with previously published values [23]. Non-sulfonated PPS did not possess a detectable acid functionality.

The CT images ([Supplementary Fig. 2](#)) showed that the pellets were variable in size, but the average diameter was approximately a few millimeters. Internally, the pellets were composed of compressed powder grains, as indicated by the manufacturer, and the

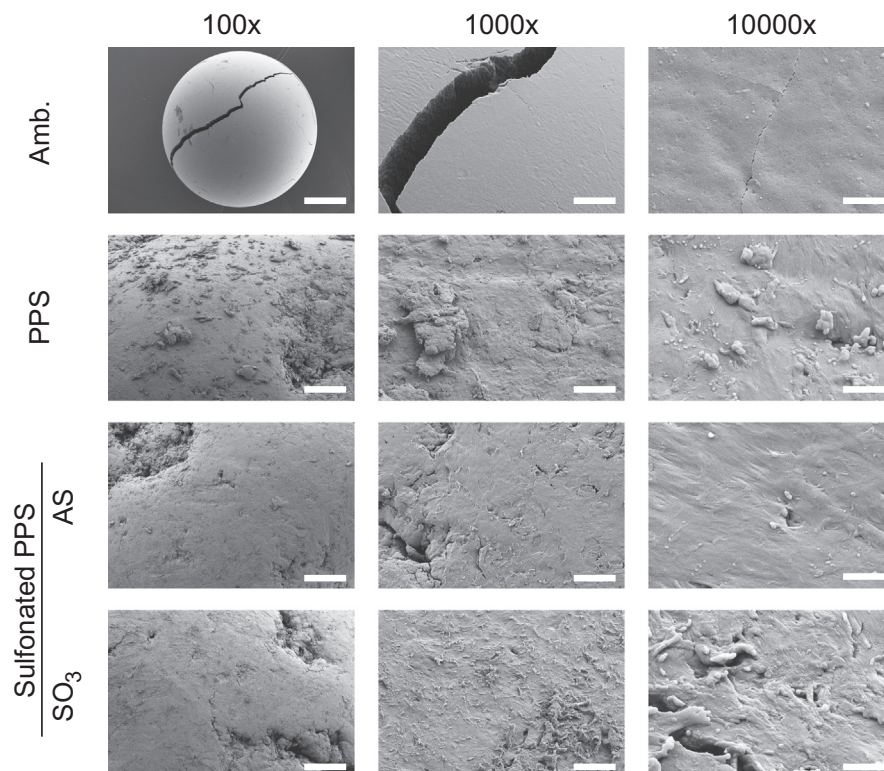


Fig. 2. SEM images prior to catalysis. SEM images of Amberlyst®15 (Amb.), non-treated PPS (PPS), acetyl sulfate (AS)-treated PPS and SO₃-treated PPS. Representative pictures are shown, and the scale bars are 200 μm, 20 μm and 2 μm at 100×, 1000× and 10,000× magnification, respectively.

porosity varied from 12% to 15% (void volume/total volume) with no differences between the samples. CT images showed the generally smooth rounded surface of the pellets. The 1 h SO₃-treated PPS pellets appeared to have a smooth superficial skin layer, with a rougher and likely slightly eroded surface under this layer. SEM images (Fig. 2) revealed surfaces containing large cracks (likely leading to the internal pores shown on the CT images) and a partially covered surface roughness on a scale below 10 μm.

The EDX results (Table 1) showed that the oxygen content increased in the 1 h SO₃- and the 6 h acetyl sulfate-treated samples compared with the non-treated sample, possibly because of successful sulfonation or oxidation. However, the increase in oxygen and sulfur was substantially less than the oxygen and sulfur content of Amberlyst®-15, which contains neither atom in its backbone. Therefore, the sulfonation density is likely substantially higher in Amberlyst®-15 than in our SPPS samples, as confirmed by the acid density titration. Non-treated PPS contained 1.3% oxygen, which it theoretically should not contain; this is likely background oxidation of, for example, the thioether link to sulfoxide.

The IR spectra of pristine and SO₃-doped PPS have been previously characterized [27]. Sulfonation of our 1 h SO₃- and acetyl sulfate-sulfonated samples was confirmed by analysis with IR spectroscopy (Supplementary Fig. 3) and by comparing the results with the cited article and with those of pristine PPS and Amberlyst®-15. We confirmed the appearance of broad bands corresponding to strongly associated OH groups from the sulfonic acids, and in our case, they stretched from 2500 cm⁻¹ to 3700 cm⁻¹. We also confirmed the appearance of a band at ~1169 cm⁻¹ due to asymmetric stretching vibrations of the SO₂-OH group in arene sulfonic acids. In contrast to the cited report, we did not observe an intensity decrease at 819 cm⁻¹ corresponding to out-of-plane vibrations of the two paired hydrogen atoms in the phenyl ring. This decrease would only be observed in the case of a high degree of sulfonation; thus, our samples likely have a

relatively low degree of sulfonation, which is confirmed by the relatively low oxygen and sulfur content increases as measured by EDX.

To determine the conservation of a non-sulfonated pellet core, larger pellets (diameters of 5–10 mm) were cut open after sulfonation with SO₃ for 2 h. Subsequently, the surface layer and the core were ground into a powder and separately analyzed via ATR-IR. The transmittance IR spectrum of the core exhibited 76% correlation with the spectrum of pristine PPS, whereas the IR spectrum of the surface layer showed only 52% correlation (Supplementary Fig. 4). Furthermore, the peaks characteristic of sulfonated PPS (the broad band from 2500 cm⁻¹ to 3700 cm⁻¹ and the band at 1169 cm⁻¹) were not visible in the spectrum of the pellet core. In this case, the decrease at 819 cm⁻¹ was observed in the surface

Table 1

EDX analysis before and after batch catalysis. Samples were analyzed by SEM, and EDX spectra of representative regions were collected. Average atomic w/w% values are shown with standard deviation in brackets. ND: Not Detected, AS: Acetyl Sulfate, Amb-15: Amberlyst®-15.

EDX sample	C (%)	O (%)	S (%)	Cr (%)	Fe (%)	Ni (%)
Pristine PPS	82.3 (±1.8)	1.3 (±0.3)	16.4 (±2.0)	ND	ND	ND
SO ₃ PPS – before	77.5 (±3.7)	5.2 (±2.9)	17.3 (±1.1)	ND	ND	ND
AS PPS – before	80.0 (±2.4)	2.4 (±0.1)	17.5 (±2.4)	ND	ND	ND
Amb-15 – before	74.8 (±0.5)	14.5 (±0.7)	10.7 (±0.2)	ND	ND	ND
SO ₃ PPS – after	76.1 (±3.5)	5.1 (±0.8)	18.8 (±2.8)	ND	ND	ND
AS PPS – after	81.9 (±1.3)	1.8 (±0.4)	16.4 (±1.7)	ND	ND	ND
Amb-15 – after	69.4 (±0.5)	15.9 (±0.8)	10.5 (±0.5)	1.1 (±0.5)	2.5 (±0.7)	0.6 (±0.7)

layer, likely due to the denser sulfonation of the 2 h samples, as confirmed by the titration.

3.2. Catalysis

To obtain a rapid evaluation of the catalytic properties, batch experiments were performed by placing ethanol and the catalyst in hermetically sealed steel tubes; these tubes were then placed in a preheated oven for 24 h. We used the two types of SPPS, obtained via each of the sulfonation methods, as well as Amberlyst®-15 as catalysts. After the reaction, the liquid was collected and stored, whereas the catalyst was washed and reused at a different temperature. Four runs were performed at 120 °C, 150 °C and 180 °C. The catalytic conversion of ethanol to DEE was measured with a GC (Fig. 3). Ethylene is a side product of ethanol dehydration, especially at high temperatures. No ethylene was observed in the spectra, but if ethylene was produced, it may have escaped before GC was performed. All of the samples contained a trace amount of methanol. The acetyl sulfate-treated samples also contained traces of acetic anhydride, acetic acid and 1,2-dichloroethane. At 120 °C and 150 °C, Amberlyst®-15 showed the best performance, producing 12% V/V and 37% V/V DEE, respectively. At 180 °C, the SO₃-treated PPS catalyst showed the best performance, resulting in a product that contained 54% V/V DEE versus 42% V/V for the Amberlyst®-15 and 35% V/V for the acetyl sulfate-treated PPS.

After the reaction at 180 °C, clear degradation of the steel tube containing Amberlyst®-15 was observed, and all of the catalysts turned darker in color (Supplementary Fig. 5). The catalysts were inspected using SEM–EDX and FTIR to search for degradation. SEM revealed that most of the samples remained visually unchanged from before catalysis (Fig. 4), except for the SO₃-treated SPPS, which became more porous, likely due to a partial loss of the skin layer. EDX showed steel degradation products (Fe, Cr and Ni) in the Amberlyst®-15 sample but not in any of the PPS samples; no other changes in elemental composition were observed (Table 1). IR spectroscopy revealed no significant chemical changes in the SPPS (Supplementary Fig. 6) or Amberlyst®-15 (Supplementary Fig. 7). Importantly, no aliphatic bands appeared in the SPPS samples, indicating that the polymer chains were intact. EDX and IR indicated that despite an obvious loss of sulfonic acid groups from Amberlyst®-15, which initiated the degradation of the steel tube, Amberlyst®-15 retained more sulfonic acid functionality than the SPPS samples after four rounds of catalysis at temperatures up to 180 °C.

To investigate the catalytic performance of SPPS in a more realistic scenario, a continuous catalysis setup was created using a heated, packed bed containing 7.0 g of SO₃-sulfonated PPS catalyst. Ethanol was then pumped through the catalyst at a rate of

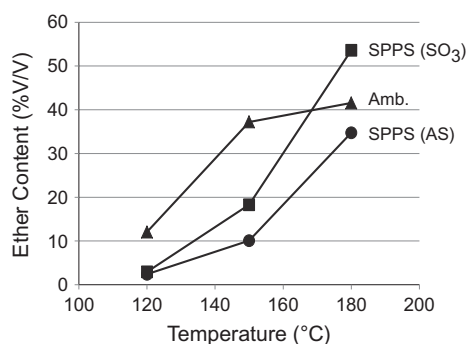


Fig. 3. Batch synthesis of ether. Batch production of DEE from ethanol using acetyl sulfate (AS)-sulfonated PPS, SO₃-sulfonated PPS or Amberlyst®-15 (Amb.).

1.0 mL/min. The resulting liquid was analyzed for DEE content using GC (Fig. 5). DEE production was exponentially dependent on the temperature up to 180 °C, after which the dependency was linear to 220 °C (Fig. 5a). At 180 °C, the processed liquid contained 4.5% V/V DEE, and at 220 °C, the processed liquid contained 14.5% V/V DEE. An Arrhenius plot of the logarithmic reaction rate versus the inverse temperature (Fig. 5b) reveals a straight line for the exponential range (120–180 °C, $y = -13008x + 20$, $r^2 = 0.9964$) and a poor fit over the entire temperature range (120–220 °C, $y = -4294x$, $r^2 = 0.5921$) due to the linear range above 180 °C. From the 120–180 °C slope ($-Ea/R$), we calculate the activation energy for the reaction as $108 \text{ kJ mol}^{-1} \text{ K}^{-1}$ using the formula $\ln(k) = \ln(A) - Ea/R * 1/T$.

Having established that PPS could be converted into a catalytic substrate using sulfuric acid, we sought to develop a porous structure with a large surface area that could be used as an improved catalytic substrate. PPS powder was mixed with NaCl, compressed, melted, compressed again and cooled. The NaCl was then washed off, leaving a porous substrate (Fig. 6a, left picture). This substrate was confirmed to be porous using a CT scan (Fig. 6b and c). The scan showed clear interconnected voids shaped similar to NaCl crystals, and the substrate was determined to be 71% porous. Porous PPS cylinders were then treated with 100% H₂SO₄ at either room temperature or at 0 °C. The resulting substrates were dried and photographed (Fig. 6a). The sample sulfonated at room temperature had a charred surface and a white center, whereas the sample treated at 0 °C had a white surface and center. The sample sulfonated at 0 °C was then placed in a closed container with 5 mL of ethanol, and catalytic activity was evaluated in a single sample batch experiment over 19 h at 170 °C and 12 bar. The resulting liquid contained 2.1% V/V DEE.

4. Discussion

The goal of this study was to explore a simple method for functional chemical modification of bulk PPS to create a new class of catalysts based on this polymer. We showed that PPS sulfonation yields a solid and stable structure capable of functioning as a catalyst.

It is unlikely that the core of the bulk structure is chemically altered because PPS has low permeability to most liquids and gases and sulfuric acid is a highly viscous liquid [28]. Permeability would be further reduced by running the reaction at 0 °C. Furthermore, if the bulk was sulfonated throughout, it would behave differently because SPPS is soluble [8,11] and has a behavior similar to a gel [11]; our product was hard (similar to the original pellets) and insoluble in water, ethanol and DEE. In addition, the mass of the PPS polymer before and after sulfonation was unchanged, whereas if all of the phenylene groups were sulfonated, a 74% weight gain would be expected after the synthesis. The unchanged mass could be explained by a relatively low amount of introduced sulfonic acid functionalities (only on the surface) as well as a partial dissolution of fully sulfonated PPS chains in water during the reaction and during the subsequent work-up procedure. IR spectroscopy also confirmed that the surface is sulfonated, whereas the core remained unaltered. These results demonstrate that a new chemical functionality was selectively introduced onto the surface of the polymer and that this functionality was anchored into an unchanged polymer core, as suggested in Fig. 1. The concept of anchoring hydrophilic molecules to a hydrophobic core using hydrophobic anchors has been previously explored for biomedical polymer particles because it provides a simple and stable method for surface functionalization [29].

The unchanged PPS core is of critical importance because it retains the qualities of the original PPS, including resistance to

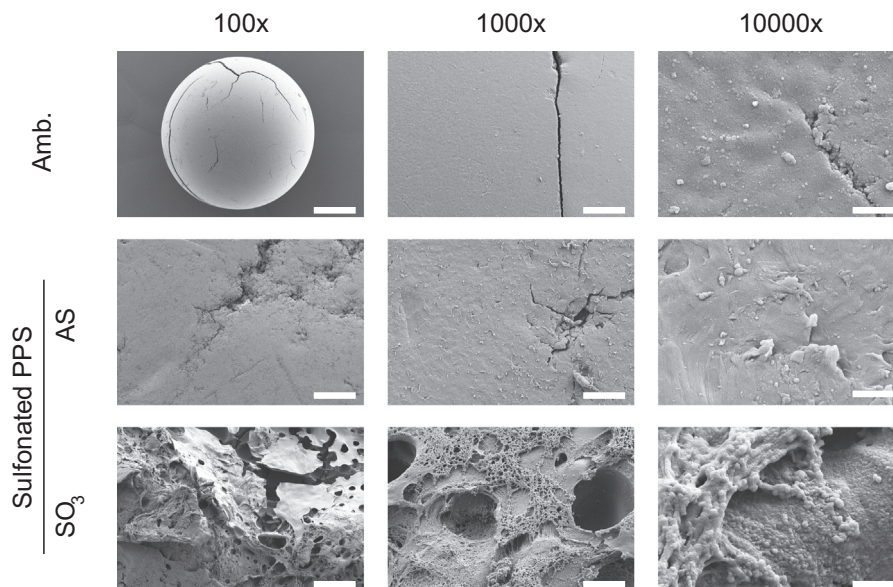


Fig. 4. SEM images after catalysis. SEM images of acetyl sulfate (AS)-sulfonated PPS, SO₃-sulfonated PPS and Amberlyst®-15 (Amb.) after four cycles of 24 h catalysis at 120 °C, 120 °C, 150 °C and 180 °C. Representative pictures are shown, and the scale bars are 200 μm, 20 μm and 2 μm at 100×, 1000× and 10,000× magnification, respectively.

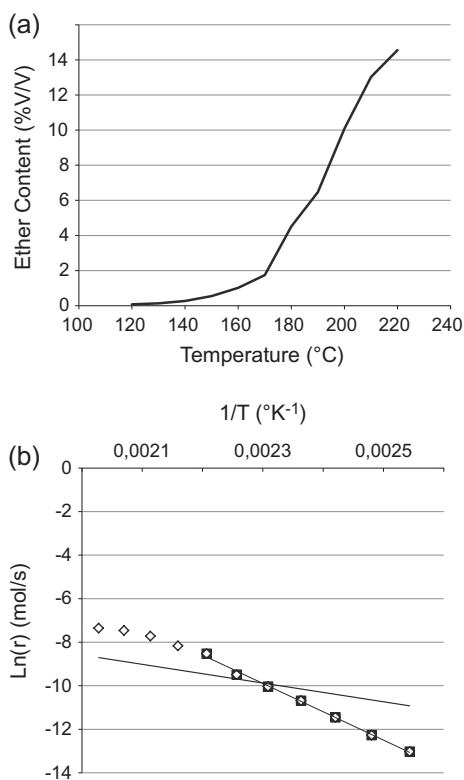


Fig. 5. Continuous synthesis of ether. (a) Ether content of the product as a function of catalyst temperature. (b) Arrhenius plot of the logarithmic reaction rate as a function of the inverse absolute temperature; two trend lines are shown, one for all of the points (data points = open diamond) and one for the exponential range used to estimate the activation energy (120–180 °C, data points = black squares).

heat, chemicals and solvents. Without a noticeable change in pellet size, the substrates were capable of surviving four rounds (~96 h) of batch catalysis at temperatures ranging from 120 °C to 180 °C as well as over 10 h of continuous flow catalysis at 35 bar and temperatures ranging from 120 °C to 220 °C in the presence of water, ethanol and DEE. The only change observed was a slightly darker

coloration of the pellets. The EDX and IR spectra obtained after four rounds of batch catalysis indicate that only a slight chemical change occurred.

The focus of this study was to chemically modify the surface of bulk PPS while retaining an unmodified core; however, we also conducted a study to show that the chemically modified surface could function as a catalyst. We selected sulfonic acid-catalyzed dehydration of ethanol to DEE as an exemplary reaction because it did not require further modification of the introduced surface functionality. Acid-catalyzed DEE synthesis is a well-known catalytic reaction first described by Valerius Cordus in the sixteenth century [30]. Resins bearing catalytic sulfonic acid have been used since 1958 [31] and have been known historically to catalyze DEE formation [32]. Recently, a renewed interest in sulfonic acid-bearing catalysts has been sparked partially because of their potential in the production of fatty acid methyl ester (FAME) biodiesel. A variety of new substrates have been sulfonated to create novel sulfonic acid catalysts [33–38]. The ethanol to DEE reaction has also gained relevance because it is currently being explored commercially for decentralized on-vehicle production of DEE for use as a stand-alone compression ignition biofuel using existing ethanol fuel logistics [39–43].

We show that the surface-functionalized PPS is capable of synthesizing ether with an activity comparable to that of the commercially available Amberlyst®-15 polymer catalyst. This result was surprising because our catalyst was not optimized for this reaction. The acid density titration and EDX performed on the samples before catalysis revealed that the SPPS samples likely have a ten-fold lower degree of sulfonation than Amberlyst®-15. Even after catalysis at 180 °C, during which Amberlyst®-15 released sulfuric acid, EDX revealed that Amberlyst®-15 retained a higher degree of sulfonation. In our continuous catalysis experiment, we find that ether formation increased exponentially with the temperature up to 180 °C and then linearly thereafter; we speculate that after 180 °C, the SPPS may begin to desulfonate and/or the competing dehydration product ethylene may begin to form. From the exponential part of the curve, we find that the SPPS-catalyzed reaction had an activation energy of 108 kJ mol⁻¹ K⁻¹, which agrees with the results of six previous studies on sulfonic acid-catalyzed DEE formation referenced in the literature [44], which found its activation energy to be over the range of 100–120 kJ mol⁻¹ K⁻¹.

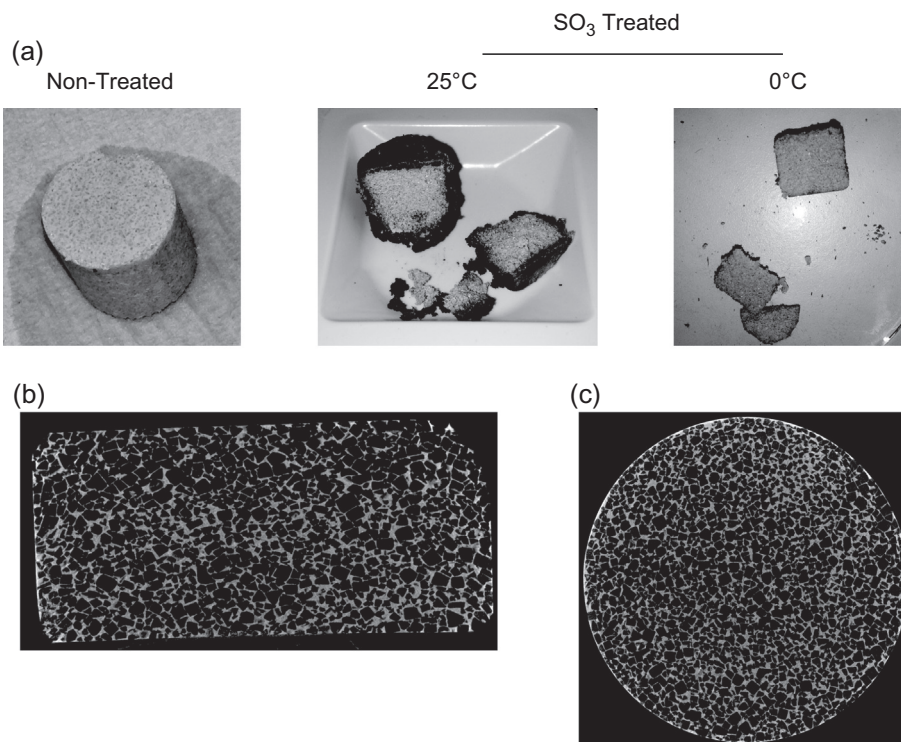


Fig. 6. Porous PPS. Porous cylinders composed of PPS (a), non-treated or treated with 100% H₂SO₄ at either room temperature or at 0 °C for 1 h. In a different experiment, non-treated cylinders were scanned by CT, 3D rendered and sliced in the x-axis (b) and z-axis (c).

This result indicates that the mechanism of catalysis on our substrate is the same as that on other sulfonated substrates. The reason for the relatively high activity remains unknown, but we speculate that the improved stability provided by the PPS core may play a role. For example, Amberlyst[®]-15 is known to desulfonate at temperatures above 150 °C [45]. However, we believe a substantially better catalyst could be fabricated by increasing the sulfonation density and the active surface area. Thus, we demonstrate a simple solvent-free method for the production of a porous PPS substrate. Other methods of producing porous PPS structures have also been explored using, e.g., thermally induced phase separation (TIPS), and these methods may provide a greater catalytic surface area, yielding a more powerful sulfonated PPS catalyst [46,47]. When sulfonated, our porous catalyst yielded a low conversion rate. We speculate that only the outer surface of the porous structure was sulfonated. To improve this result, a modified sulfonation strategy can be developed, possibly utilizing an SO₃ gas flow or a low viscosity sulfonation agent.

Note that the sulfonic acid-catalyzed reaction was only explored as a proof-of-concept reaction to prove that the surface was successfully and stably modified. While the developed SPPS catalyst worked well for the synthesis of DEE, there are other applications for which it may be even better suited. Steric hindrance, for example, plays an inhibitory role in the selective formation of large molecules when using penetrable sulfonic acid catalysts, such as Amberlyst catalysts, and these favor the production of small molecules [48]. Because SPPS is only surface sulfonated, we would expect it to favor the formation of larger molecules, such as long chain ethers or FAME, the synthesis of which primarily occurs where there is space around the acid group. Furthermore, the technique developed in this study has wider applications, as arene sulfonic acid groups, such as those on SPPS, can be exchanged with other functional groups [17] or can be reduced to sulfides using different strategies [49,50]. Sulfide-functionalized polymers are especially attractive because they can be used to bind enzyme

biocatalysts via natural disulfide linkages [51]. Therefore, surface sulfonation of bulk PPS may be the first step toward a novel class of surface-functionalized thermoplastic PPS structures that are useful over a wide range of catalytic reactions and in other areas, such as ion-exchange columns, water purification, anti-static materials and filtration applications.

5. Conclusion

We showed that bulk structures of durable thermoplastic poly (p-phenylene sulfide) (PPS) can be selectively surface modified to yield a sulfonic acid-functionalized substrate. This substrate is capable of catalyzing the dehydration of ethanol to diethyl ether and appears resistant to combinations of solvents, high temperatures, pressure and flow. We also developed a method for the production of a porous PPS substrate using compression molding and porogen leaching. While further analysis of the developed material is required, for example, to determine the turnover number (TON), we believe that surface-functionalized PPS may become a new important class of catalysts.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.reactfunctpolym.2015.02.006>.

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