

A Comparison Study of Two Synthesis Methods for Polymer of Intrinsic Microporosity 1 (PIM-1)

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Abstract

Polymers of Intrinsic Microporosity (PIMs) are an emerging polymeric material class for molecular sieving applications. This study focuses on PIM-1, an alternating copolymer of 5,5',6,6'-tetrahydroxy-3,3',3,3'-tetramethyl-1,1'-spirobisindane and tetrafluoroterephthalonitrile synthesized via nucleophilic aromatic substitution. PIM-1 has been widely studied as a gas separating material and filtering membrane, but in this case, it is studied as a battery separator material. PIM-1's microporous (pore diameters less than 2 nm) structure allows smaller favorable ions to transport while preventing larger ions and compounds from transporting. Two synthesis methods, round bottom flask synthesis and ball mill synthesis, of PIM-1 are compared to see any improved characteristics. The primary goal of this study is to observe an increase in molecular weight, but other properties are evaluated as well. The calculated yield was higher for ball milled PIM-1 (51.5% round bottom flask vs. 62.8% ball mill). Size-exclusion chromatography (SEC), nuclear magnetic resonance (NMR) spectroscopy, and Brunauer-Emmett-Teller (BET) analysis were used to characterize each synthesized batch. Both PIM-1s had the same overall molecular weight (98,468 round bottom flask vs. 97,331 ball mill), but the ball milled PIM-1 had a lower polydispersity (2.372 round bottom flask vs. 1.728 ball mill). The ball-milled PIM-1 also revealed broader peaks and fewer impurities than RBF PIM-1 with NMR analysis. BET analysis revealed that both PIM-1s had similar expected porosities (658 m²/g vs. 642 m²/g). More research is needed to affirm that ball milling is a superior method.

Introduction

Current battery technology has allowed devices to retain plenty of energy while being able to last for hundreds of charge cycles. This is because lithium-based electrochemistry is employed in portable electronics. Lithium is the third element in the periodic table, meaning that its small size allows for high energy densities. However, current Li-ion technology only has a specific energy (energy capacity per unit mass) of up to 200 W-h/kg. Lithium-sulfur (Li-S), an emerging battery technology, can reach specific energies up to 500 W-h/kg in practice¹. Therefore, Li-S may become the next battery technology to come into the commercial realm.

The four main components of a Li-S cell (anode, cathode, electrolyte, and separator) all interact with lithium ions in different ways to comprise a functioning Li-based energy storage device. In a typical Li-S cell, the cathode is made of sulfur, the anode is pure lithium, the electrolyte is an organic solution containing a lithium salt, and the separator is a polymeric material with mesopores. During discharging, lithium ions dissociate from the anode and forms polysulfide salts on the cathode, while upon charging, the lithium transports back to the anode and plates it. In theory, there would be no side reactions that could compromise the battery's operation.

The separator plays an important role because it insulates the cathode from the anode, while allowing ions to transport across the electrolyte. However, most separators in use today have large pores that allow unwanted compounds to traverse the electrolyte and degrade the battery, thereby limiting the cycling life. In Li-S cells, polysulfide compounds that form on the sulfur cathode can transport through the electrolyte and separator to parasitically attack the lithium anode². This reaction decreases the lifetime of

the Li-S battery and a size-sieving separator must be employed to prevent this.

Fortunately, microporous separators, with pores less than 2 nm in diameter, have been developed to prevent polysulfide compounds from transporting while allowing the lithium cation and the bis(trifluoromethylsulfonyl)imide anion to transport through the electrolyte.

Fortunately, such materials are being investigated. PIM-1 (Polymer of Intrinsic Microporosity 1), a copolymer of 5,5',6,6'-tetrahydroxy-3,3',3,3'-tetramethyl-1,1'-spirobisindane and tetrafluoroterephthalonitrile synthesized via nucleophilic aromatic substitution, as shown in Figure 1, is a microporous (pores of less than 2 nanometers in diameter) material that sieves out unwanted compounds, such as polysulfides and manganese ions³. This is because the polymer has a rigid structure that cannot rotate via sp³-hybridized bonds, thereby sustaining microporosity due to frustrated packing during post-solution casting. PIM-1 has been established as a material for gas separation⁴ and solvent nanofiltration⁵, but new research has been exploring it as a battery separator material^{6,7}.

The challenge right now is increasing the molecular weight of the PIM-1 using various synthesis methods. A greater molecular weight will improve the mechanical strength of the separator because more entanglement between the polymer chains increases strength and elastic modulus. This experiment compares two synthesis methods for differences in polymer characteristics: standard round bottom flask heating and ball milling. Round bottom flask synthesis is widely used to synthesize polymers, whereas ball milling is an unconventional method that mechanically promotes a chemical reaction. During ball milling, the surface area of starting materials via impact and friction from

balls and heating due to friction improves the kinetics. Ball milling is part of a wider field of study called mechanochemistry^{8,9}. The goal of this study is to evaluate whether ball milling is a viable synthesis process for PIM-1.

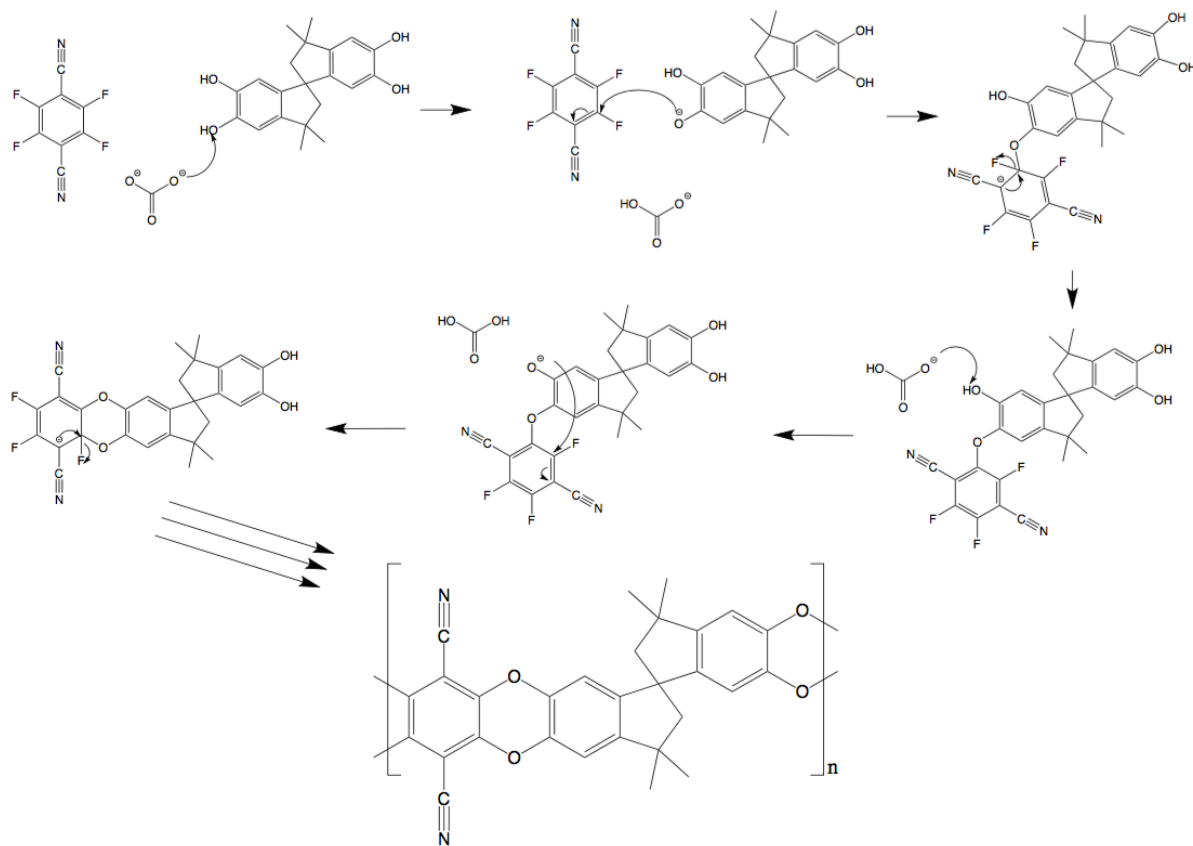


Figure 1. Step-growth mechanism for PIM-1 synthesis. The reaction is an iterative process that results in long polymeric chains.

Materials and Methods

Materials used to produce PIM-1 include 97% 5,5,6,6-tetrahydroxy-3,3,3,3-tetramethyl-1,1'-spirobisindane (TTSBI) supplied by Alfa Aesar, tetrafluoroterephthalo-nitrile (TFTPN) supplied by Oakwood Chemical, cesium carbonate (Cs_2CO_3) supplied by Oakwood Chemical, N,N-dimethylacetamide (DMAc) supplied by Sigma-Aldrich, and dimethylformamide (DMF) supplied by Fischer Scientific.

Round Bottom Flask Synthesis

1.7732 g of TTSBI, 1.007 g of TFTPN, 3.26 g of Cs_2CO_3 , and 39 mL of DMF in 150 mL round bottom flask was used as the reaction vessel. A stir bar was added to the round bottom flask to ensure proper dispersion. As the materials were added to the round bottom flask, nitrogen gas was pumped into the vessel to ensure an inert environment. The reaction was initiated by being placed into an oil bath heated to 65 °C while stirring and ran for 19 hours (Figure 2). Once completed, the solution was quenched with 20 mL of water.



Figure 2. Synthesis occurring in round bottom flask dipped into an oil bath maintained at 65 °C.

Ball Mill Synthesis

For ball milling, the first step in this process is to place all the materials into the 185 mL ball mill vessel (Figure 3). For each method, 1.7729 g (5 mmol) of TTSTBI was weighed out and placed into the vessel, using DMA used to wash it in. 1.006 g (5 mmol) of TFTP, 6.5166 (20 mmol) of cesium carbonate, and the remaining DMA (10 mL total) were placed into the vessel. Then, 285.50 g of tungsten carbide balls were placed into the vessel. The ball-milling vessel was taken to a ball miller and allowed to spin for 3 hours. The milling action heated the vessel, initiating the reaction. After milling, the vessel was cooled for 30 minutes, and then taken back to the lab for working up. No quenching was required for this batch.



Figure 3. Vessel containing synthesis reactants and balls for ball milling procedure.

Workup Procedure

Both the round bottom flask and ball milled synthesized PIM-1 underwent a similar post-synthesis workup procedure. The workup consists of a series of steps using solvents to remove unwanted materials, such as salts, oligomers, and cyclic polymers, from the desired product. First, the reactant is placed into a 5:1 (500 ml:100 ml) water:ethanol mixture, and heated it to boiling for one hour while stirred. Then, the mixture was filtered out and the remaining PIM was dried over the filter. Next, the polymer was dissolved into 200 mL of chloroform and heated the solution until boiling for 2 hours. New chloroform was added to the boiling solution during this process, and 400 mL of chloroform remained. The solution was then filtered into 400 mL of methanol to catch any insoluble compounds. Given the diluteness of the new mixture, the solution was rotary evaporated to drive off excess methanol and chloroform.

Once the polymer came out of solution, the rotary evaporator was turned off and the constituents were filtered. The PIM-1 batches were dried under vacuum at 65 °C for one hour. A second step of boiling the PIM in a 5:1 (250 ml:50 ml) water:ethanol mixture was employed to remove any remaining water-soluble compounds. This was done for 30 minutes while stirring. Once complete, the mixture was filtered off and the samples were dried overnight in a heated vacuum chamber. Dried samples are shown in Figures 4 and 5.

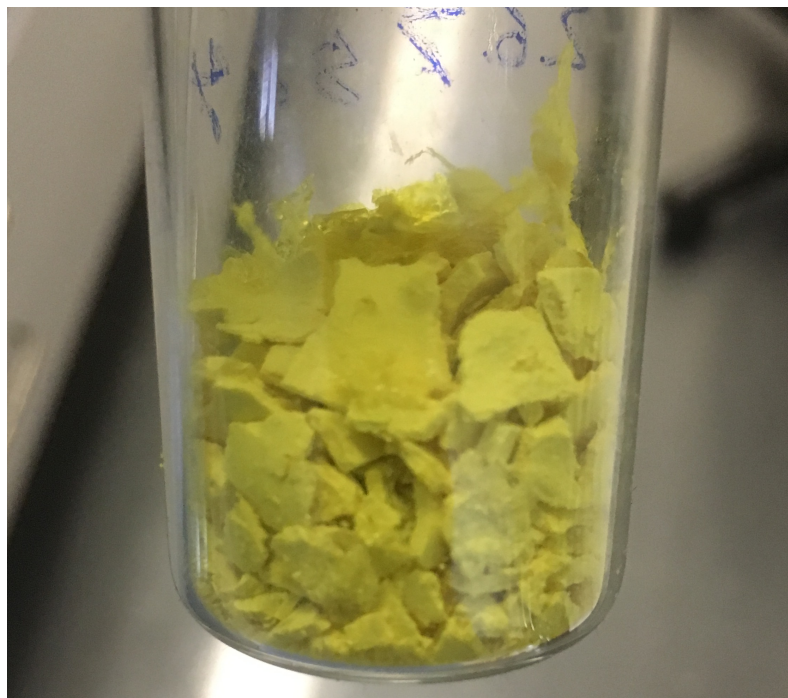


Figure 4. PIM-1 product from round bottom flask synthesis.

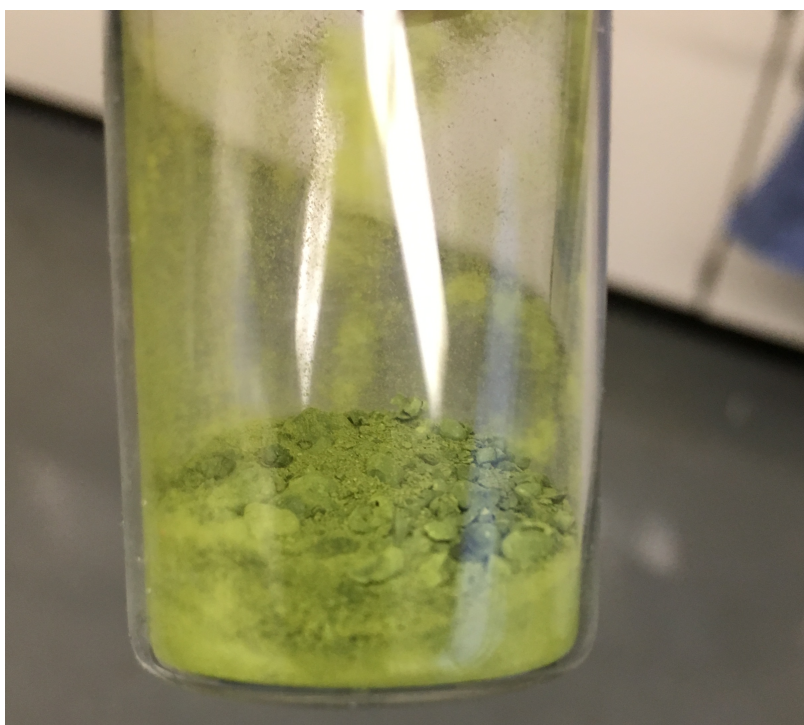


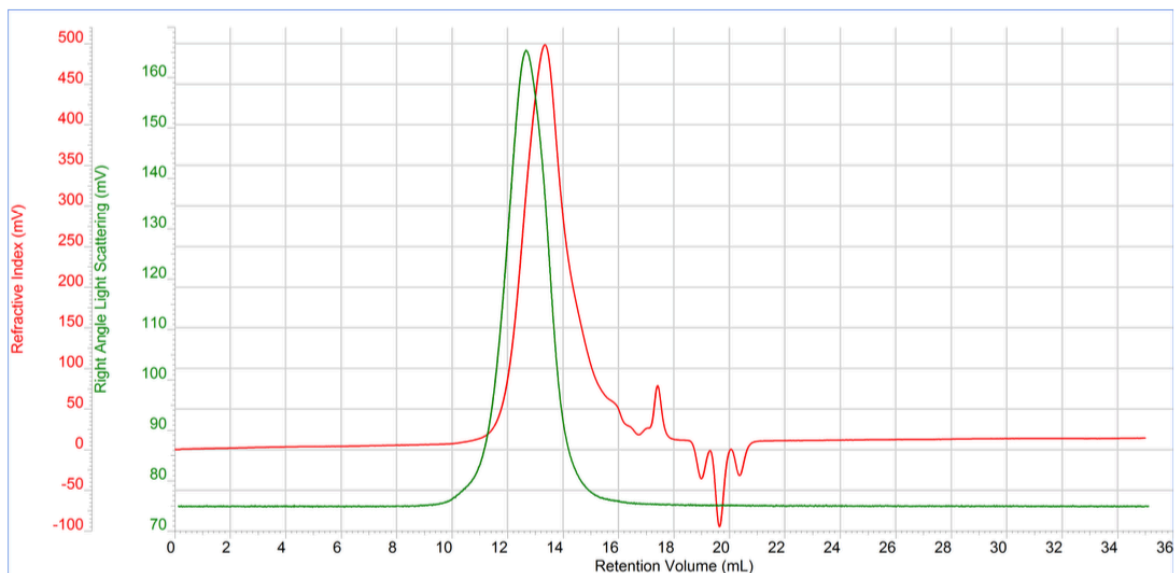
Figure 5. PIM-1 product from ball milling procedure.

Results and Discussion

After synthesis, yields were calculated for each product. The round bottom flask synthesis produced a yield of 51.5%, whereas the ball mill synthesis produced a yield of 62.8%. The difference in yield may be due to lower oligomer and cyclic polymer production in the ball mill, which are mostly filter off during workup.

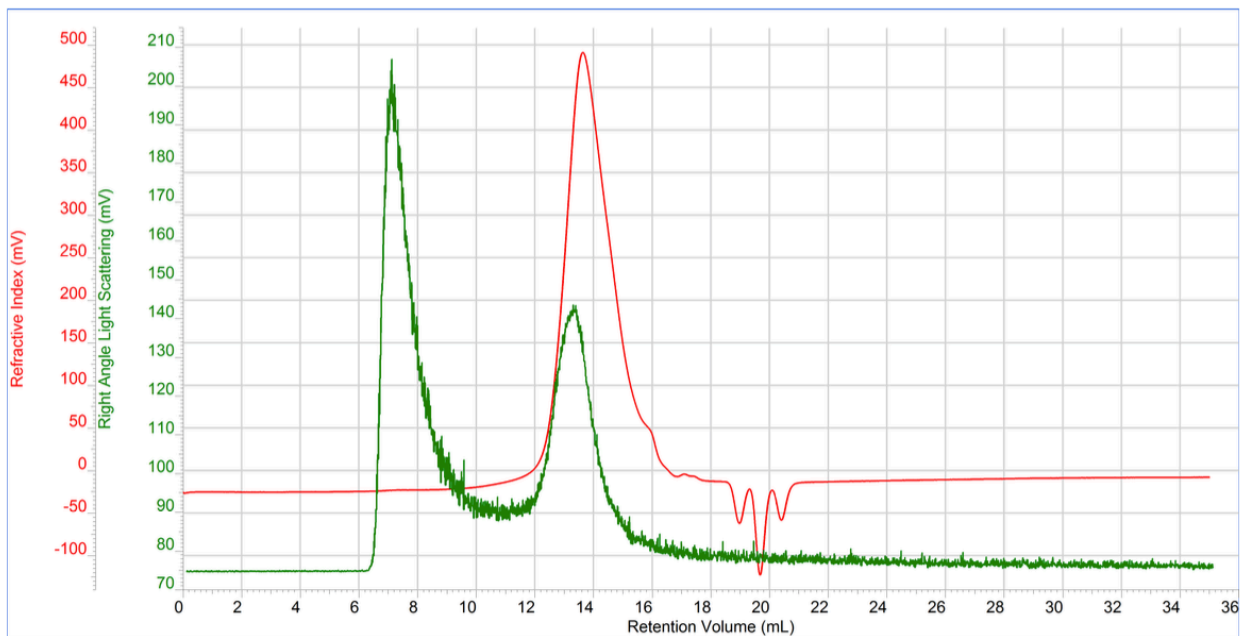
Size-exclusion chromatography (SEC) was used to measure the molecular weight and polydispersity of PIM molecules. As shown in Figures 6 and 7, both PIM-1 batches had similar molecular weights (98,468 g/mol round bottom flask vs. 97,331 ball mill, displayed as Mw), but a lower polydispersity was observed in ball milled PIM-1 (2.372 round bottom flask vs. 1.728 ball mill, displayed as Mw/Mn). The possible explanation for similar molecular weights is that an excess starting material, either TTSBI or TFTPn, limited the step-growth mechanism during synthesis. For polydispersity, the different environments promoted different kinetics, and ball milled PIM-1 may have been less disperse because the ball mill vigorously mixes the starting materials and the temperature during ball milling becomes much hotter than 65 °C, thereby promoting faster kinetics and equalizing the molecular weights of the polymer chains.

The bimodal distribution observed in the right-angle light scattering plot for ball mill batch is a peculiar observation because most PIM-1 distributions are unimodal. The first peak was excluded from calculations because it wasn't recorded by the refractive index curve, which could indicate an error from the machine. This observation can serve as a basis for further investigation.



Sample	Mn	Mw	Mz	Mp	Mw/Mn	IV	Rh(w)
2016-09-16_11:51:40_CP16-00:	41,518	98,468	214,878	69,948	2.372	0.2067	6.35

Figure 6. Fume hood synthesized PIM-1, displaying a molecular weight of 98,468 and a polydispersity of 2.372.



Sample	Mn	Mw	Mz	Mp	Mw/Mn	IV	Rh(w)
2016-10-12_11:34:12_CP16-00:	56,335	97,331	962,996	64,438	1.728	0.1770	5.94

Figure 7. Ball Milled PIM-1 with a molecular weight of 97,331 and polydispersity of 1.728.

Proton NMR spectroscopy was used to qualitatively evaluate the molecular structures of each synthesized PIM-1. As seen in figures 8 and 9, the leftmost peaks indicate protons associated with aliphatic carbons, and the rightmost peaks indicate protons associated with aromatic carbons. The spread in polymeric peaks is due to interactions between neighboring repeat units. In Figure 8, there are several linear peaks, indicating that some starting material, specifically TTSBI, ended up in the final batch. In Figure 9, all peaks shown are broad, indicating undetected starting material and high purity.

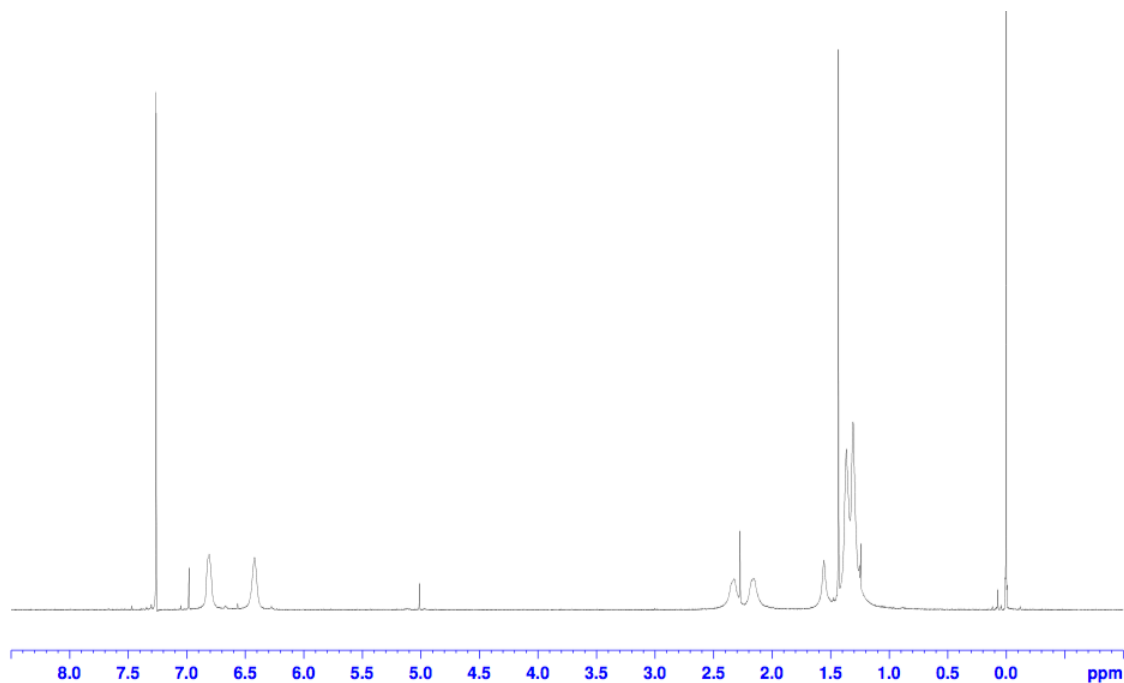


Figure 8. Proton NMR Spectra of Round Bottom Synthesized PIM-1. Broad peaks indicate hydrogen on polymer, and straight peaks indicate hydrogen on small molecular impurities, specifically the TTSBI precursor.

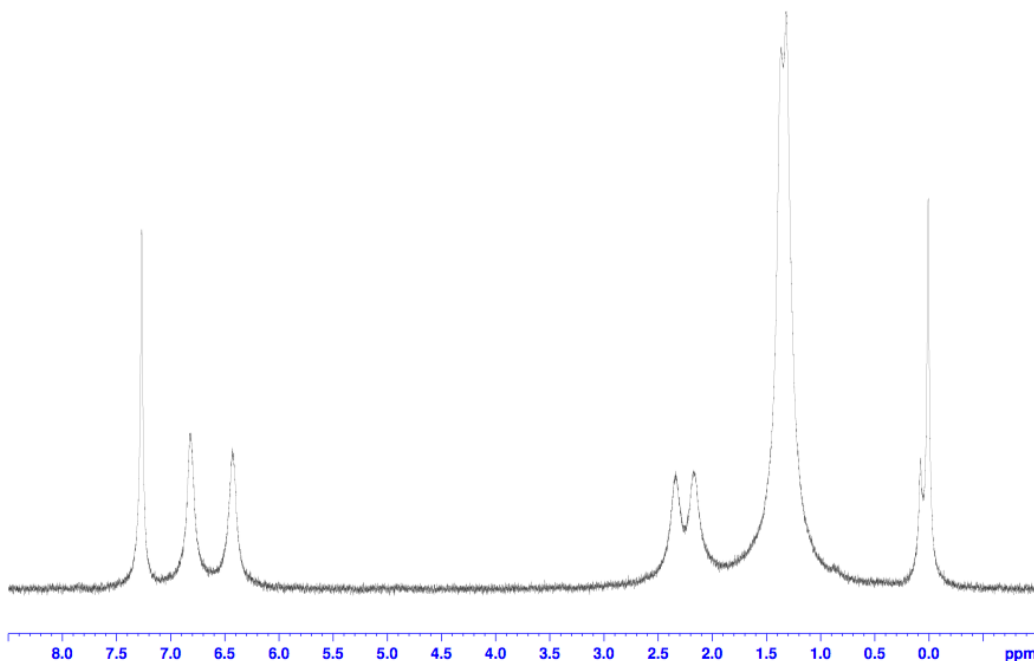


Figure 9. Proton NMR of Ball Mill synthesized PIM-1. Absence of straight peaks indicates high purity.

Brunauer-Emmett-Teller (BET) analysis was also employed to evaluate the porosity of each PIM-1 batch. For this characterization method, porosity is measured in terms of surface area per unit mass (m^2/g). Isothermal plots show sample absorption/desorption of nitrogen gas at 77 K (sample tube immersed in liquid nitrogen) over the course of several hours, as seen in Figure 10. BET analysis data derived from isothermal data are shown in Figure 11. The BET surface areas came out to $642 \text{ m}^2/\text{g}$ for the round bottom flask synthesis and $658 \text{ m}^2/\text{g}$ for ball mill synthesis. These values are consistent with the literature range of $600\text{-}750 \text{ m}^2/\text{g}$ for PIM-1³. Also, these measurements are similar enough to warrant that both batches have porous structures expected of PIM-1. The most important observation is that ball milled PIM-1 still retains high porosity, important for Sepion Technologies' prescribed application.

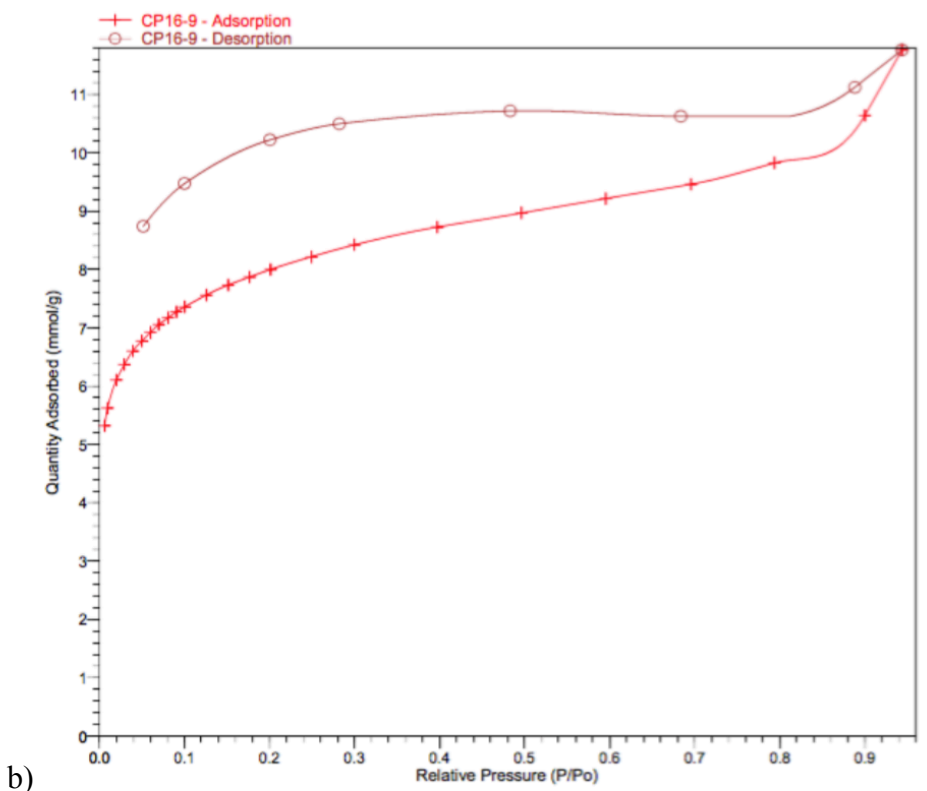
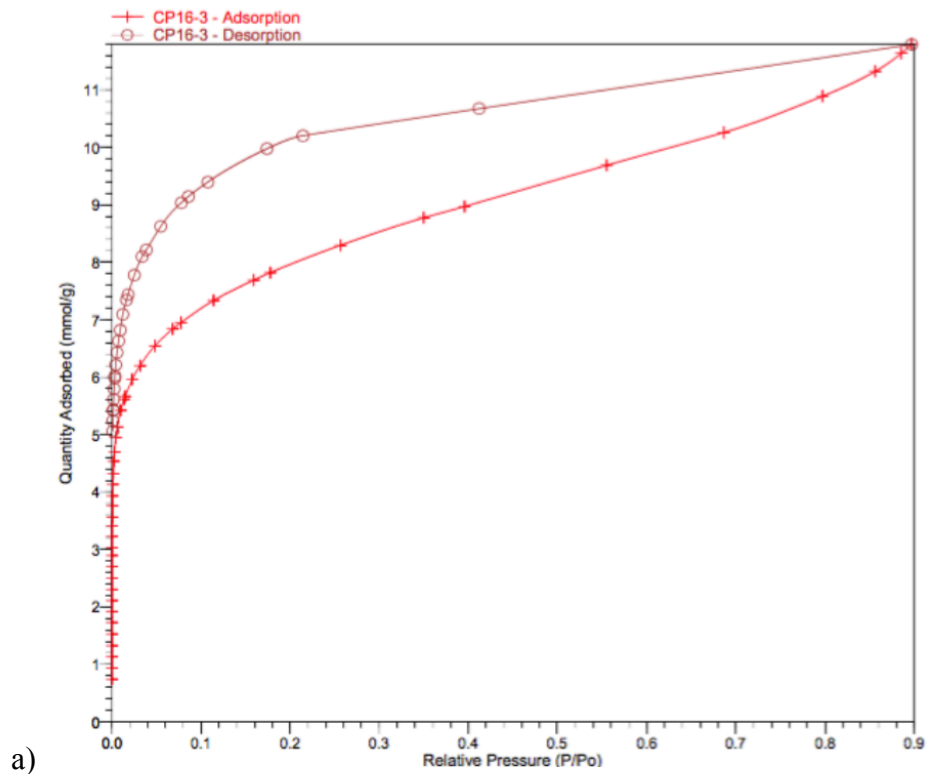
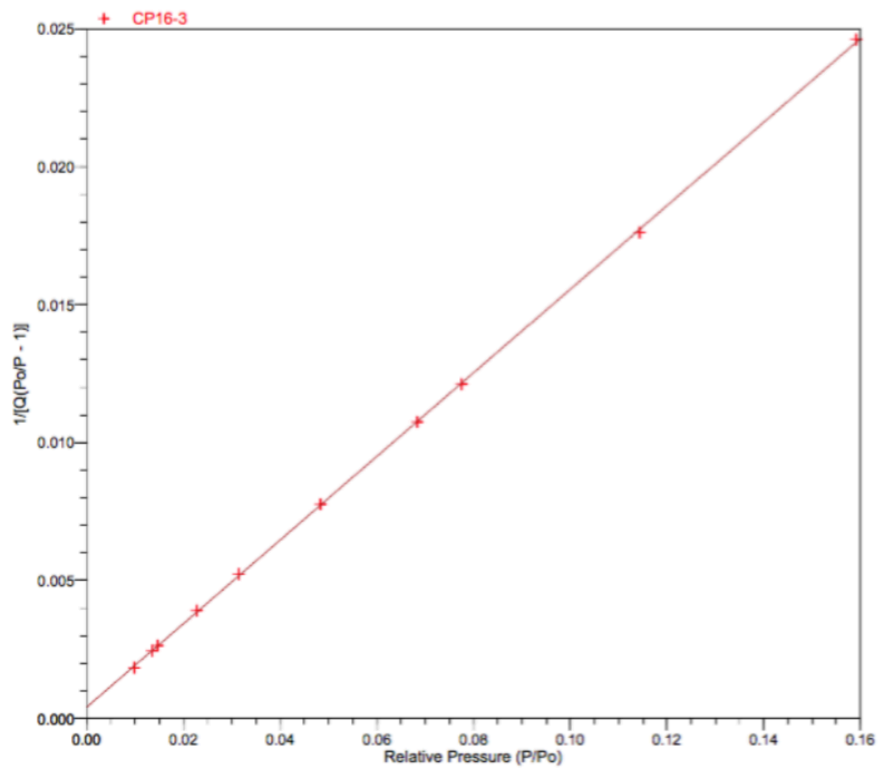
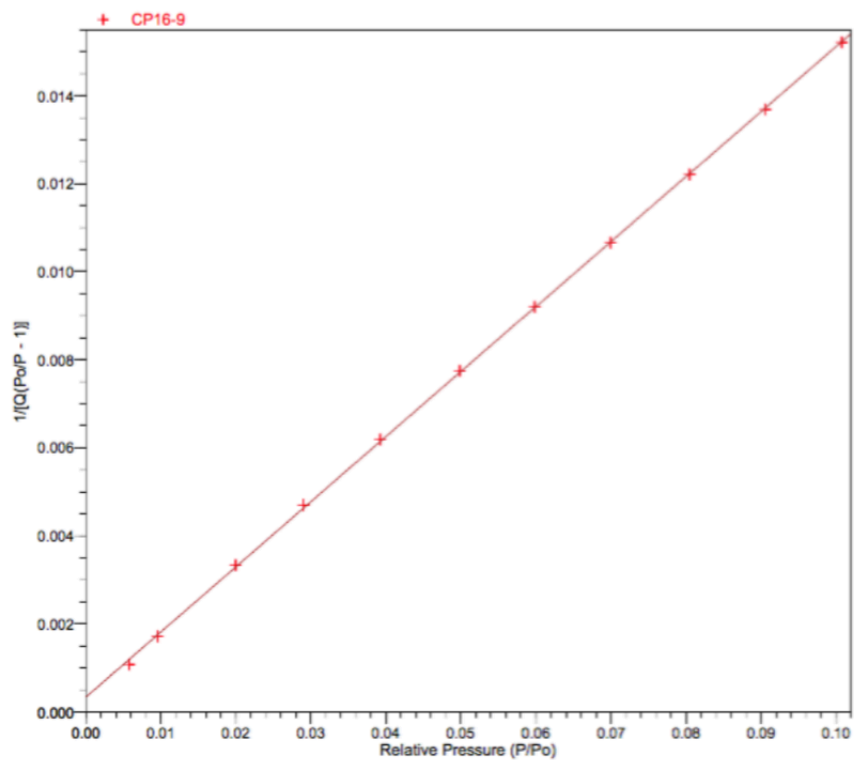


Figure 10. Isothermal plots of round bottom flask (a) and ball mill (b) PIM-1 batches. The y-axis is quantity of nitrogen gas absorbed per unit mass of sample (mmol/g) and the x-axis is relative pressure (P/Po).



a)



b)

Figure 11. BET surface area plots of round bottom flask (a) and ball mill (b) PIM-1 used to derive surface area. Round bottom flask synthesis yielded 642 m²/g while ball mill synthesis yielded 658 m²/g.

Conclusion

PIM-1 is a polymer used as a microporous separator in battery applications. The polymer can sieve out larger particles in order to increase cycle life by preventing electrode degradation. Two synthesis methods, solution mixing in a heated round bottom flask and ball milling, were compared to observe any differing properties. Both syntheses involved mixing, but the ball mill synthesis used friction and impact to promote the reaction instead of only heat. After workup and characterization, Ball milling had a higher yield (51.5% round bottom flask vs. 62.8% ball mill). The molecular weights appeared the same (98,468 g/mol round bottom flask vs. 97,331 g/mol ball mill), but ball mill synthesis PIM-1 had a lower polydispersity (2.372 round bottom flask vs. 1.728 ball mill). NMR revealed that some starting material might have remained in the round bottom flask PIM-1. BET analysis indicated that both batches had similar porosities (642 m²/g round bottom flask vs. 658 m²/g ball mill). So far, ball milling is indicated as a promising synthesis method, but more research is needed to affirm this.

Future Work

Besides studying synthesis methods, Sepion Technologies is evaluating structural derivatives of PIM-1. TFTPn can be replaced with another organic molecule with four halide groups, and this structurally similar alternative may provide properties more appropriate for battery applications. Copolymers of TFTPn and another structurally similar organic molecule are considered as well to tune the separator properties. Given that PIM-1 was first mentioned as a battery separator material in literature in 2015⁶, more research is needed to establish this application for PIM-1. The ultimate goal for Sepion is to bring a viable molecular-sieving battery separator material to market, and adjusting the chemistry of PIM-1 can warrant a favorable outcome.

Acknowledgements

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