Final Technical Report

Project Title: Developing a Novel Hydrogen Sponge with Ideal Binding Energy and High Surface Area for Practical Hydrogen Storage

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(There is no patentable material or protected data in this report.)

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Executive Summary

This Phase I (5 quarters) research project was to examine the validity of a new class of boron-containing polymer (B-polymer) frameworks, serving as the adsorbents for the practical onboard H_2 storage applications. As illustrated in Figure 1, three B-polymer frameworks were investigated, they are 2-D polymers with the repeating cyclic units that spontaneously form open morphology and the B-doped (p-type) π-electrons delocalized surfaces. The ideal B-polymer framework shall exhibit open micropores (pore size in the range of 1-1.5nm) with high surface area (>3000 m^2/g), and the B-dopants in the conjugated framework shall provide high surface energy for interacting with H_2 molecules (an ideal H_2 binding energy in the range of 15-25 kJ/mol). The final research objective is to develop new H_2 adsorbents with an ideal combination of high surface area and suitable H_2 binding energy to meet the DOE storage targets with material a gravimetric capacity of 1.8 kWh/kg (5.5 wt.% H_2) and volumetric capacity of 1.3 kWh/L (40g H_2/L) under mild (temperature and pressure) storage conditions.

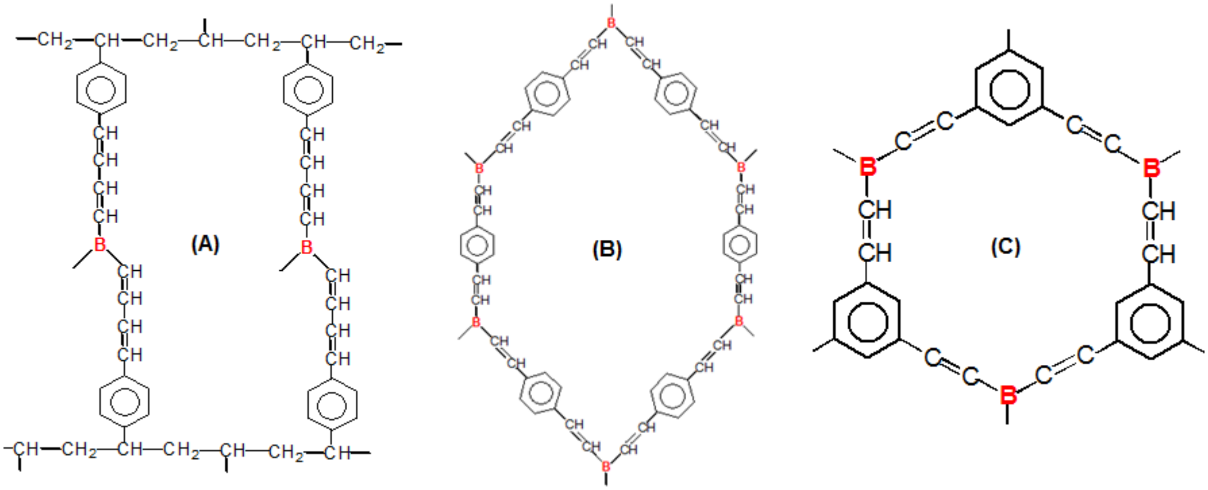


Figure 1. Three B-polymer frameworks containing π-electrons conjugated B-moieties, including B-PBS framework (A), B-PPDA framework (B), and B-PPTA framework (C).

Three B-polymer frameworks include B-poly(butyenylstyrene) (B-PBS) framework (A), B-poly(phenyldiacetyene) (B-PPDA) framework (B), and B-poly(phenyltriacetylene) (B-PPTA) framework (C). They were synthesized using various chemical methods. The pore size distribution and H_2 binding energy were investigated at both Penn State and NREL laboratories. So far, the experimental results show the successful synthesis of B-polymer frameworks with the relatively well-defined planar (2-D) structures. The intrinsically formed porous morphology exhibits a broad pore size distribution (in the range of 0.5-10 nm) with specific surface area (~1000 m^2/g). The miss-alignment between 2-D layers may block some micropore channels and limit gas diffusion throughout the entire matrix. In addition, the 2-D planar conjugated structure may also allow free π-electrons delocalization throughout the framework, which significantly reduces the acidity of B-moieties (electron-deficiency). Unfortunately, the surfaces of the resulting 2-D structure only exhibit a small increase of H_2 binding energy in the range of 8-9 KJ/mole (quite constant over the whole sorption range).

Project Objective

This research project includes two phases and a Go-No-Go decision between two phases. In Phase I (5 quarters), we focused on the reaction schemes to prepare B-polymer frameworks that could spontaneously form open micropore morphology and π-electrons conjugated molecular structure. The goal is to develop a new B-polymer framework with SSA>3000 m^2/g and a H_2 binding energy E_{ads}= 15 kJ/mol. After the Go decision, we will choose the suitable reaction scheme and framework structure for a systematical study to understand the structure-property relationship and identify the H_2 adsorbent that can achieve a combination of SSA>4000 m^2/g, E_{ads}=15-20 kJ/mol, and density>0.65 g/cm^3. The overall project goal is to meet the DOE storage targets with material a gravimetric capacity of 1.8 kWh/kg (5.5 wt.% H_2) and volumetric capacity of 1.3 kWh/L (40g H_2/L) under mild (temperature and pressure) storage conditions.

Background

A practical onboard H_2 storage technology is a major challenge in realizing the H_2 economy. Current 700 bar compressed gas method is expensive and provides insufficient H_2 storage capacity. On the other hand, three current H_2 storage materials, including metal hydrides, chemical hydrides, and sorbents, all show significant deficiencies and limitations. Among these options, adsorbents based on the physisorption mechanism would be an ideal and economic method for practical applications if the sorbent materials could show a sufficient adsorption capacity (>5 wt%) at moderate storage and operational temperatures (-20-40 ^oC) and pressures (20-100 bar). In physisorption, the adsorption capacity is proportional to the SSA accessible to H_2, ~1 wt% per 500 m^2/g as predicted by the Chahine rule. Some new materials, such as MOF-210 and PPN-4 polymer, show high surface areas with >6000 m^2/g and high H_2 uptake >7 wt% (exceeding DOE objective on volumetric capacity). However, due to low H_2 binding energy (<10 kJ/mol), the physisorption of H_2 requires a very low temperature (77K). So far, there is no sorbent material that can simultaneously offer both high surface area (>4000 m^2/g) and high H_2 binding energy (15-25 kJ/mol).

Comparison of Accomplishments and Project Goals

As discussed, Phase I focusses on the development of chemical routes to prepare the proposed B-polymer frameworks (Figure 1) with well-defined molecular structures. The major goal is to show a new B-polymer framework that can exhibit a combination of SSA=3000 m^2/g and H_2 binding energy E_{ads}=15 kJ/mol.

In Phase I study, the major accomplishments are listed below:

- Developing the chemical routes to prepare three new B-polymer (2-D) frameworks, including B-PBS (A), B-PPDA (B), and B-PPTA (C), with the spontaneously formed microporous morphology and B-doped π-electrons delocalized moieties.
- Improving chemical procedures to obtain a well-defined B-PPTA (C) framework. Solid State MAS ^{11}B NMR spectrum shows a single B chemical shift at 10 ppm, implying a single species of B-moieties in the well-defined planar (2-D) framework. A strong π-electrons delocalization presents throughout the entire planar structure.

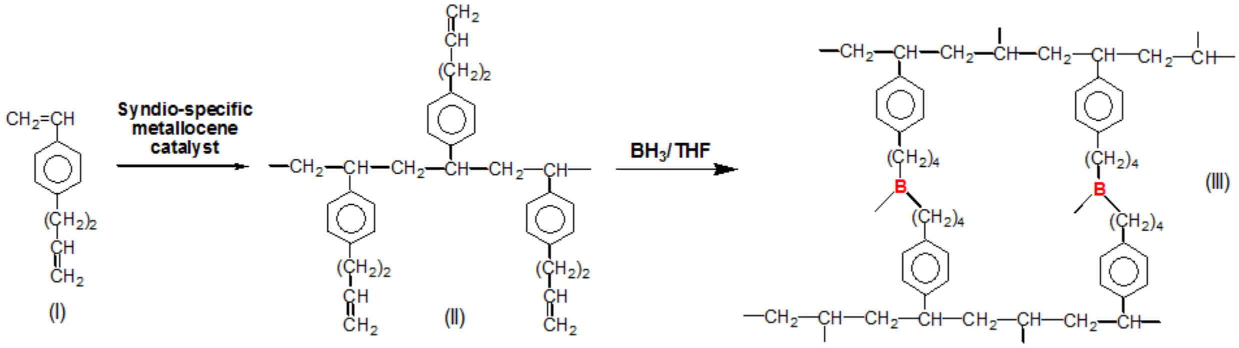
- Collaboration with NREL and HyMARC teams to evaluating H_2 adsorption isotherm measurements on the resulting B-polymer frameworks.
- Pore morphology was examined by Micromeritics ASAP 2020 sorptometer using N_2 and CO_2 gases at 77 and 273K, respectively. The experimental results show multiple B-moieties in B-PBS (A) framework with micropores (pore size <1 nm), surface area up to 1,150 m^2/g, and mass density about 1 g/cm^3. On the other hand, the relatively well-defined B-PPTA (C) framework shows the pore morphology containing both micropores (size: 0.4-0.85 nm) and mesopores (size: 1-11 nm), with ~1000 m^2/g in each pore size range.
- H_2 adsorption isotherms on well-defined B-PPTA (C) framework show H_2 binding energy in the range of 8-9 KJ/mole (quite constant over the whole sorption range).
- NREL team evaluates H_2 uptake on the same of B-PPTA (C) framework with H_2 pressure up to 110 bar and various temperatures. Excess gravimetric capacity of B-PPTA framework shows about 0.25 wt% under 100 bar at 303K and 273K. Except the 1st cycle, the subsequent H_2 adsorption-desorption cycles are reversible with almost linear relationship with H_2 pressure. At 77K, the excess gravimetric capacity reaches 2 wt% level saturated at about 40 bar H_2 pressure.

Overall, the experimental results fall short of our Phase I goals. Despite the chemical success, the resulting 2-D B-polymer frameworks (Figure 1) didn't show the desirable surface area and H_2 binding energy. In the hindsight, the well-defined 2-D B-polymer framework may not be an ideal structure for achieving high surface area and high H_2 binding energy. The lack of controlling the stacking sequence between 2-D layers, compounding with small micropores (size~1nm), may miss-align the pore structure and form some discontinuous channels (close pores) that limit gas diffusion throughout the entire matrix. Thus, the specific surface area was dramatically reduced, as well as broadening the pore size distribution. In addition, the 2-D planer structure allows somewhat unlimited π-electrons delocalization that neutralizes the acidity of B-moieties. In fact, ^{11}B chemical shift at 10 ppm in B-PPTA (Figure 5, Sample C) is almost the same as that of BC_x graphitic (2-D) material shown in our previous paper (Carbon **2010**, 48, 2526-2537). Therefore, it's not surprised to observe the same level of H_2 binding energy. Apparently, further structure modification is needed to control the exact stacking alignment of the layers, which may include some tetra-valence moieties. The corresponding 3-D B-polymer framework may overcome (at least minimize) both problems, i.e. channel blockage and too much π-electron delocalization.

Project Activities and Experimental Results

<u>Synthesis and Structure Characterization:</u> As shown in Figure 1, we have prepared three new B-polymer framework materials, including B-poly(butyenylstyrene) (B-PBS) framework (A), B-poly(phenyldiacetyene) (B-PPDA) framework (B), and B-poly(phenyltriacetylene) (B-PPTA) framework (C). They are all based on 2-D molecular structure design. The chemistry to prepare B-PBS framework (A) involves two reaction steps (Equation 1). First step is the metallocene-mediated polymerization of butyenyl styrene (I) containing two asymmetric olefinic units (styrene and α-olefin). We select a suitable homogeneous syndio-specific metallocene catalyst that can selectively initiate

styrene polymerization to form syndiotactic poly(butyenyl styrene) (II) with high polymer molecular weight and high crystallinity. The resulting polymer is a tough plastic. In second reaction step, the alternating arrangement of butyenyl side groups engage hydroboration reaction with tri-valence BH_3 to form highly cross-linked boron-containing poly(butyenyl styrene) polymer framework (III) with the spontaneously formed micropores between alternating side chains.



Equation 1. Synthesis of boron-containing poly(butyenyl styrene) polymer network.

The resulting polymer framework (III) with an open morphology was further heated at 200-300 ^oC, which transforms the boron-moieties to more stable π-electrons conjugated B-PBS framework (A) with rigid framework structure. The acidic B-moieties, connecting the conjugated side chains, also serve as *in situ* p-type dopants to increase the surface energy around the micropore surfaces. It is interesting to note that this low temperature (<300 ^oC) thermal-induced dehydrogenation reaction was also observed in our previous study in the preparation of boron-substituted carbon (BCx) materials by using boron-containing precursors. As shown in Figure 2 (right), the transparent and colorless polymer film gradually increases its color with heating. At 300 ^oC for 1 hour, the polymer becomes very dark, indicating long conjugated sequences that absorb all visible light.

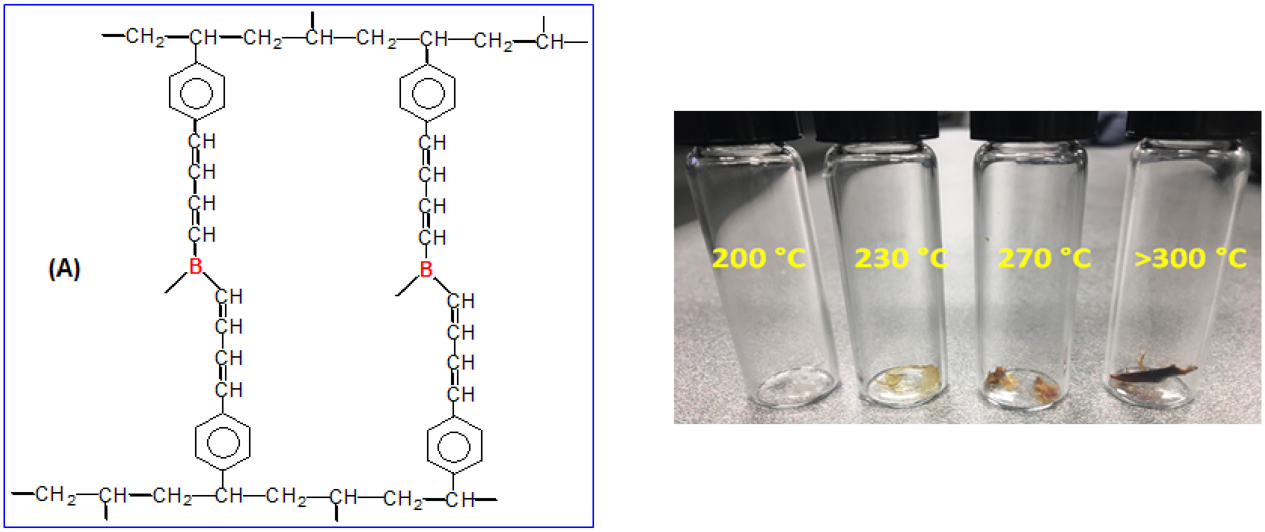


Figure 2. The conjugated B-PBS polymer framework (left) and the samples after heat-treating for one hour at various temperatures (right).

Figure 3 shows FTIR spectra of three thermal-treated B-PBS samples at 200, 230, and 270 °C for 1 hour, respectively. Upon heating, a new broad band with two absorption peaks at 1017 and 1090 cm^{-1}, corresponding to C=C-B vibrational modes, appears at 200 °C and sharply increases its intensity at 230 °C. These peak intensities then level off at 270 °C. Overall, the FTIR results clearly indicate the thermal-induced dehydrogenation happened in this organoborane moieties at relatively low temperatures and boron-enhancing the formation of π-conjugation sequence that is centered at the acidic (electron-deficient) boron species. Based on the peak intensity, it only requires a low temperature (230 °C) to achieve a highly π-conjugated B-PBS framework (A).

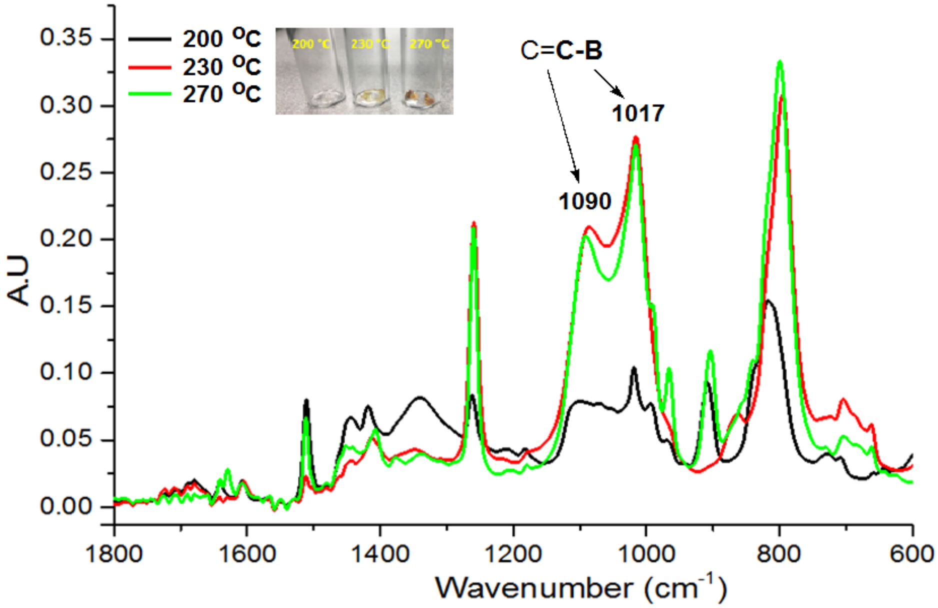


Figure 3. FTIR spectra of three B-PBS polymer frameworks after heat treatment at 200, 230, and 270 °C, respectively.

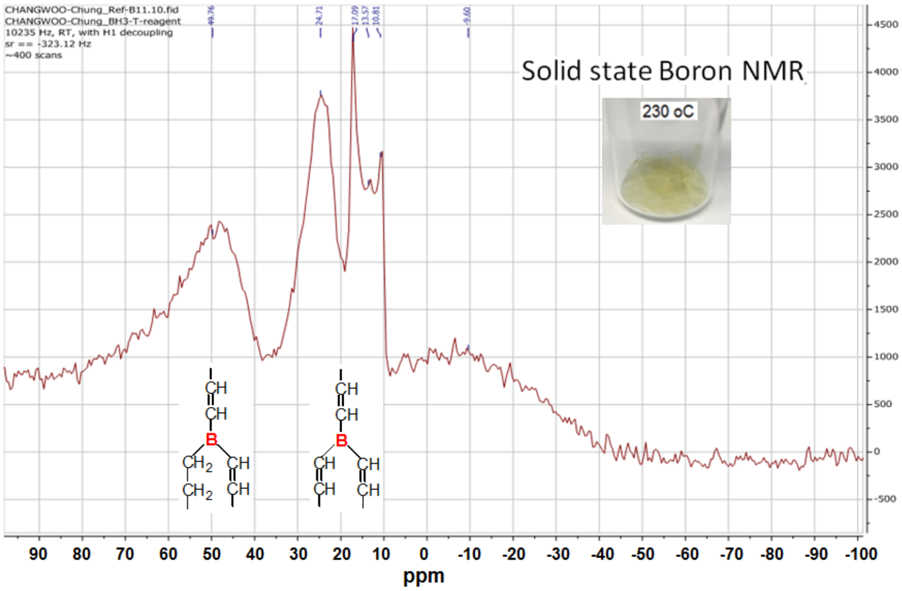
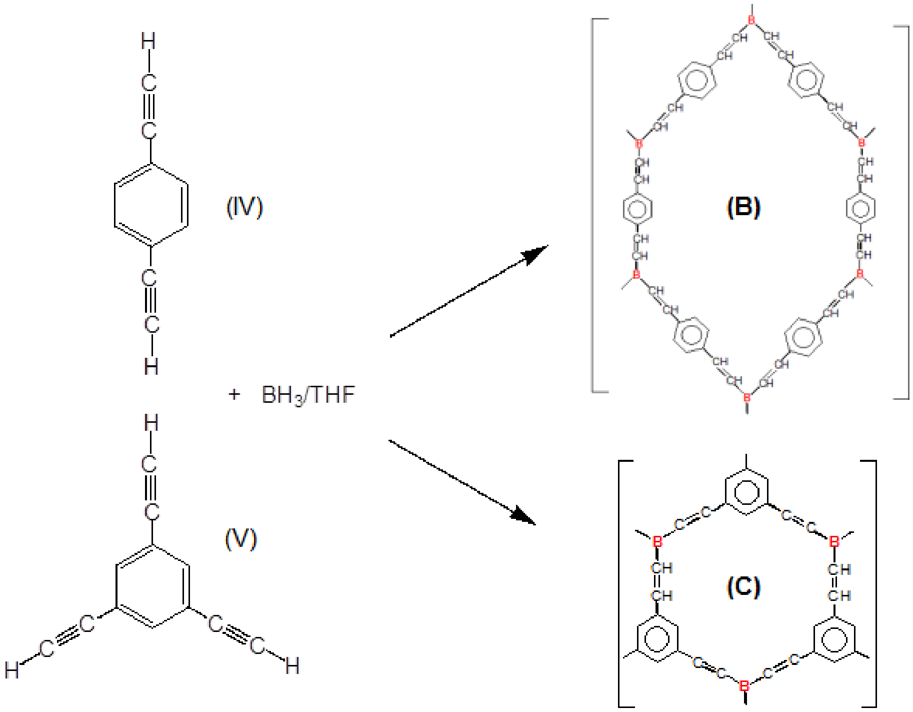


Figure 4. MAS ^{11}B solid state NMR spectrum of B-PBS-230 polymer framework.

Figure 4 shows a MAS ^{11}B solid state NMR spectrum of B-PBS framework (A), formed after heating the corresponding polymer (III) at 230 ^{o}C for 1 hr. Three chemical shift bands, peaked at 50, 25, and 17-10 ppm, imply multiple acidic boron moieties. Since the sample only contains B, C, and H elements, without exposure to air, the chemical shifts imply the boron moieties with various π-conjugated structures. The most acidic B species peaked at 50 ppm may only have two π-conjugated ligands as indicated by the structure in Figure 4. The other high field chemical shifts (between 30 and 10 ppm) shall be associated with tri-valence π-conjugated ligands having different conjugation lengths.

The difficulty to prepare a well-defined B-PBS framework (A) prompted us to investigate other chemical routes. The one illustrated in Equation 2 is a direct (one-step and one-pot) reaction route. The chemistry involves polycondensation (step-growth) mechanism based on hydroboration reaction between BH_3/THF and phenyldiacetyene (PDA) (IV) or phenyltriacetylene (PTA) (V). The combination of tri-valence BH_3 bonding pattern and multiple acetylene moieties in both PDA (IV) and PTA(V) reagents result in the corresponding rigid 2-D B-polymer frameworks (B) and (C), respectively.



Equation 2. Synthesis of B-PPDA framework (B) and B-PPTA framework (C) by hydroboration.

After mixing phenyldiacetyene/BH_3/THF (or phenyltriacetyene/BH_3/THF), the solution immediately turned into dark with a lot of solid precipitation from the solution. It was a pleasant surprise to see the facile hydroboration reaction between alkyne and BH_3/THF at ambient temperature to form the expected solid product with high yield and without by-product. The product was isolated by simple filtration, washing, and drying. However, this 2-D polycondensation (step-growth) reaction scheme is difficult to form a large and continuous 2-D framework structure due to the early product precipitation that results in the diffusion difficulties for continuing the step-growth mechanism under heterogeneous condition (discussed later). Ideally, the resulting 2-D B-polymer framework shall exhibit only one type of B-moieties with a single chemical shift in ^{11}B NMR spectroscopy. Figure 5 shows MAS ^{11}B solid state NMR spectra of three B-PPTA framework (C) samples prepared under various reaction conditions.

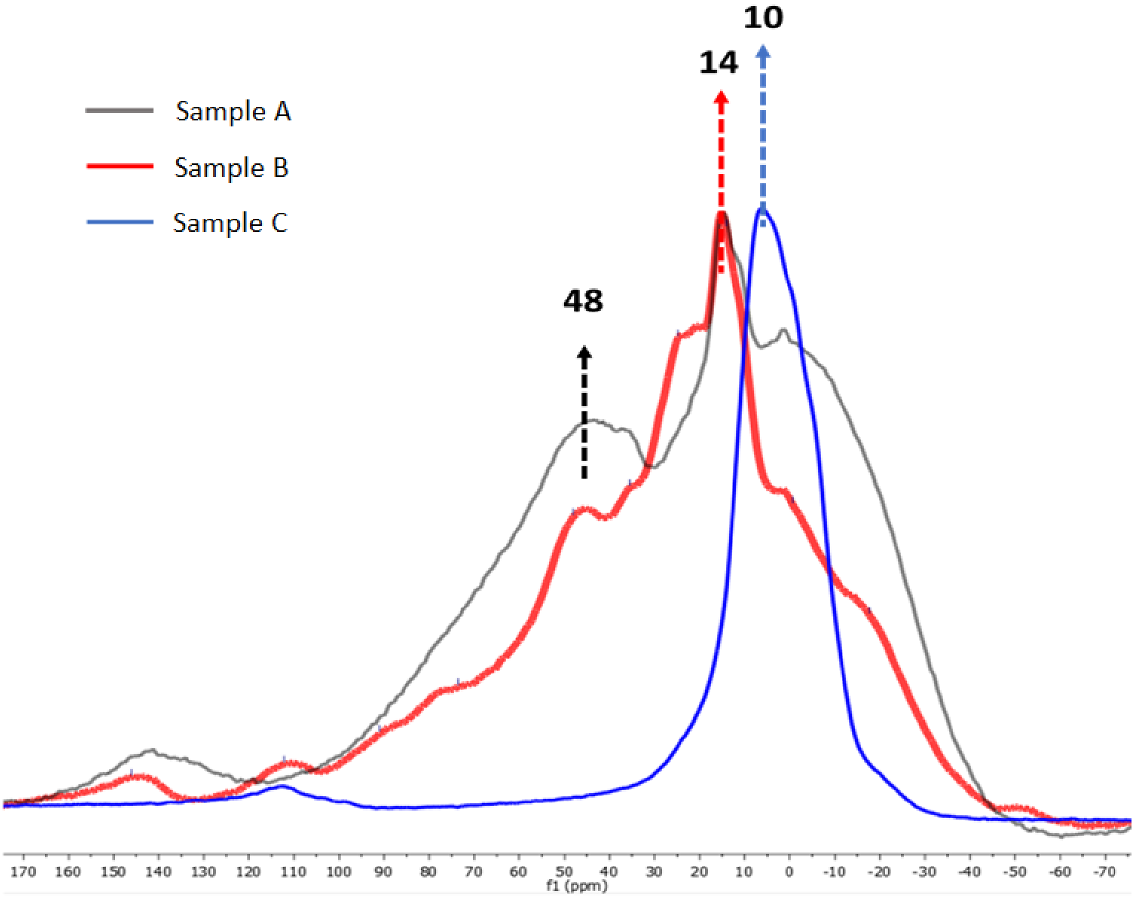
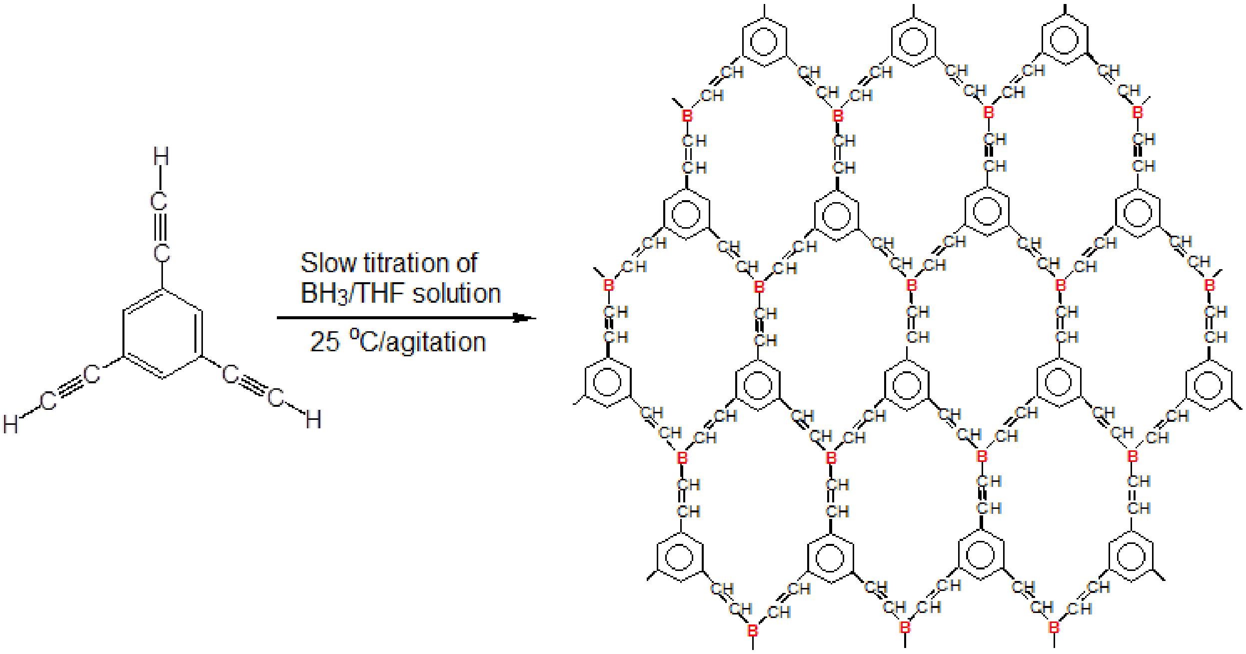


Figure 5. MAS ^{11}B solid state NMR spectra of three B-PPTA (C) polymer frameworks.

Sample A was prepared following the regular polycondensation procedures used to prepare linear (1-D) polymers, with a stoichiometric (1/1) mole ratio of phenyltriacetyene and BH_3 reagent. They were mixed in the beginning of the polymerization reaction. Sample A shows several broad ^{11}B chemical shifts, centered at 48, 14 and 10 ppm, indicating multiple boron moieties in a complicated molecular structure. As expected, the initial homogeneous chemical reaction quickly turned into a heterogeneous situation, due to the formation of 2-D (hyper-crosslinked) structure. With limited mixing, most of polycondensation reactions inevitably proceeded under slow solid-state reaction condition that results in incomplete hydroboration reactions to form an inhomogeneous (broken) framework with multiple B-moieties.

Thus, we decided to adopt a step-by-step framework-building process, with the same overall stoichiometric phenyltriacetyene/BH_3 (1/1 mole ratio), But, we slowly introduced (titrated) BH_3/THF reagent into phenyltriacetyene solution at ambient temperature with vigorous agitation. During this reaction process, a non-stoichiometric reaction condition was maintained with excess acetylene moieties until reaching to the final titration point.

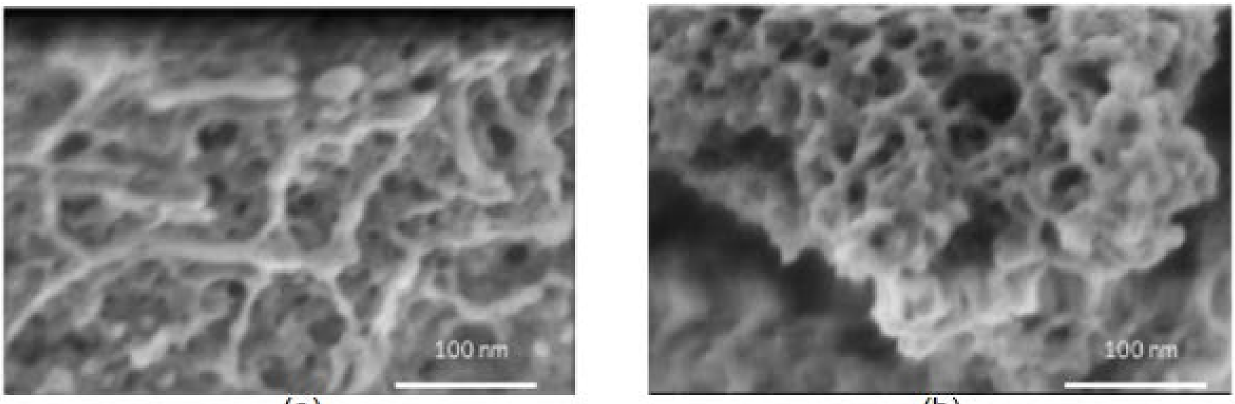
This none-stoichiometric reaction condition not only allowed the required time to complete each hydroboration reaction but also maintained a homogeneous reaction solution (because low molecular weight adducts formed under non-stoichiometric condition). After reaching to the final stoichiometric ratio, a large framework structure (insoluble product) was formed. Following this reaction scheme (Equation 3), Samples B and C were prepared over 10 and 120 minutes of the BH_3/THF titration period, respectively. The ^{11}B chemical shift of Sample B (Figure 5) was clearly sharpened with only a major peak at 14 ppm and some shoulders. With further slowing the titration step, we obtained Sample C with only a single ^{11}B chemical shift peaked at 10 ppm, indicating a relatively well-defined 2-D molecular structure with only one type of B-moieties. The NMR results are also consistent with pore morphology that exhibits higher pore volume and higher surface area for Sample C (discussed later).



Equation 3. Titration of BH_3/THF reagent into phenyltriacetylene solution for forming a large and continuous B-PPTA polymer framework (C).

Considering the ^{11}B chemical shift for $B(CH=CH_2)_3$ compound at 50 ppm (reference), the ^{11}B chemical shift peaked at 10 ppm for Sample C is quite surprising. The large up-field shift implies an extensive π-electrons delocalization from three surrounding ligands (-CH=CH-φ) into B-moieties in Sample C. Evidently, the planar structure of B-PPTA framework (C) offers the favorable π-electrons delocalization throughout the entire framework system. Unfortunately, this low ^{11}B chemical shift for BR_3 trivalence species also indicate almost neutralized B-moieties that may have limited electron-withdrawing power to enhance H_2 binding energy. In other words, all the B-moieties in the well-defined B-PPTA framework may loss their acidity by free π-electrons donation from the highly conjugated 2-D (planar) framework.

Pore Morphology of B-PPTA Framework: The porous morphology of B-PPTA framework samples were further examined by various techniques, including SEM and sorptometer. Figure 6 shows two SEM micrographs of Samples A and C, which confirm the porous morphology with many open pores penetrating from surfaces into the matrix. There are many mesopores, with pore size more than 4 nm in both samples. Sample C seems to contain smaller mesopores in the range of few nanometers. However, the resolution was not high enough to observe micropores with the size <2 nm, which is the expected pore size in an ideal B-PPTA polymer framework (C).



(a) (b)

Figure 6. SEM micrographs of (a) Sample A and (b) Sample C of two B-PPTA frameworks.

The pore size distribution was further quantified by Micromeritics ASAP 2020 sorptometer, using N_2 at 77K (for meso and macro pores) and CO_2 at 273K (for micropores), respectively. The mesopore surface area was calculated using the Brunauer–Emmett–Teller (BET) method based on N_2 adsorption data in the relative pressure (P/Po) range 0.02 to 0.22. The total micropore volume was calculated from the amount of the CO_2 adsorbed at P/Po = 0.99. On the other hand, the micropore surface area was calculated using Langmuir method based on a monolayer coverage in the relative pressure (P/P_o) range from 0.02 to 0.22. DFT (Density Functional Theory) uses the entire experimental isotherm to determine microporosity as a continuous distribution of pore volume with respect to pore size.

Figures 7 and 8 show pore size distributions for Samples A and C using N_2 gas at 77K and CO_2 gas at 273K, respectively. Table 1 summarizes surface area and pore volume of all three B-PPTA framework samples. Despite the large difference in B-moieties between Samples A and C (Figure 5) with a relatively well-defined Sample C structure, their pore size distribution patterns (micropores and mesopores shown in Figures 7 and 8) are somewhat similar with a broad pore size distribution. In addition to mesopores (size>4nm), both samples also contain a lot of micropores with very small pore size in the range of 0.4–0.85 nm, which are smaller than the expected pore size (1-1.5 nm) in the ideal B-PPTA framework (C). In details, Sample A is more favorable to larger mesopores (size >5 nm), and the Sample C contains smaller mesopores (in the range of 2-3 nm). The results are in consistence with SEM observation. Table I also shows significantly higher surface area and higher pore volume in Sample C for both micropore and mesopore ranges, with the total surface area reaching to ~2,000 m^2/g.

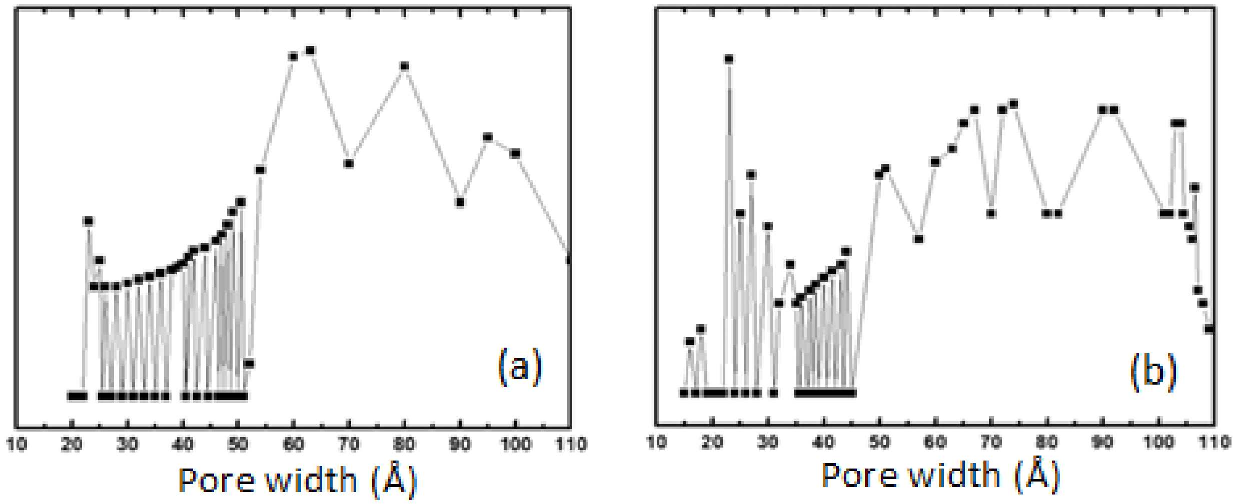


Figure 7. Meso and macro pore size distribution comparison between two B-PPTA frameworks (a) Sample A and (b) Sample C, measured by N_2 gas at 77K.

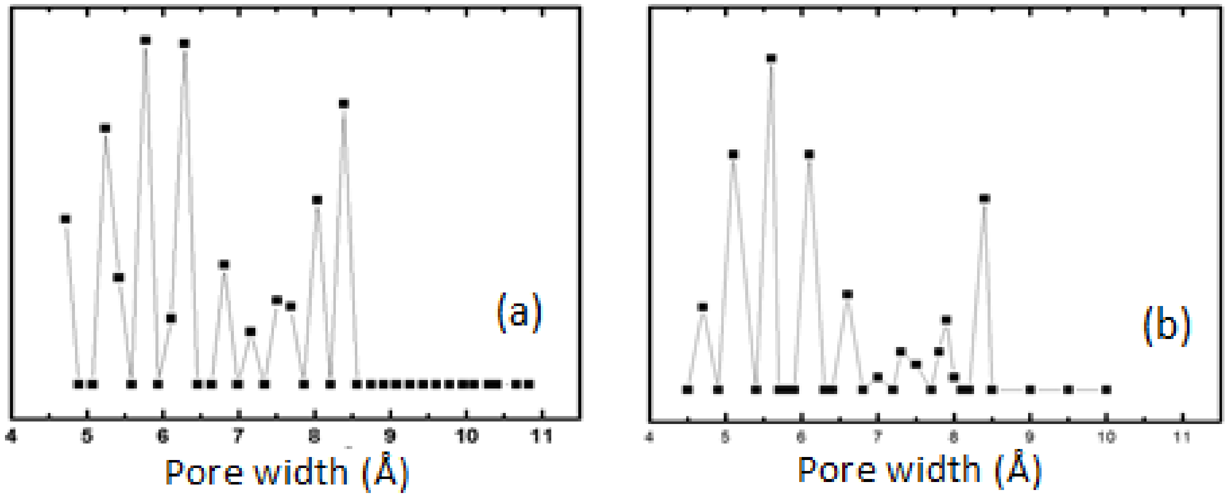


Figure 8. Micropore size distribution comparison between two B-PPTA frameworks (a) Sample A and (b) Sample C, measured by CO_2 gas at 273K.

Table 1. Summary of surface area and pore volume for three B-PPTA framework samples

Sample	N_2 sorption at 77K		CO_2 sorption at 273K	
	surface area (m^2/g)	pore Volume (cm^3/g)	surface area (m^2/g)	pore Volume (cm^3/g)
Sample A	372	0.215	450	0.222
Sample B	413	0.306	662	0.452
Sample C	1,049	0.871	999	0.671

Overall, the experimental results from pore morphology study indicate that the step-by-step framework-building process allows the preparation of a relatively well-defined 2-D B-PPTA framework (C). However, there is no control in stacking 2-D framework layers into the 3-D material structure. Many layer misalignment happens to block the pores, resulting in broad pore size distribution, close pores, and reduced surface area.

Heat of H_2 Adsorption on B-PPTA Framework (C): The isosteric heat of adsorption for H_2 on B-PPTA framework (sample C) was calculated as a function of H_2 coverage from comparison of the adsorption isotherms at 77K and 87K (Figure 9), based on the Clasuis-Clapeyron equation. Overall, the heat of H_2 adsorption is in the range between 8-9 kJ/mol. These values are little bit higher than those shown in other hyperlinked polymer systems but significantly lower than our project objective at the level of 15-20 kJ/mol. Based on the experimental results, I believe that B-moieties in π-electrons conjugated hydrocarbon polymer system can increase H_2 adsorption energy and lead to the additional H_2 uptake. However, current 2-D frameworks, with extensive π-electrons delocalization to neutralize the acidity of B-moieties, may not be the suitable structure for achieving the objective. The modification of 2-D to 3-D framework (incorporating some tetra-valence reagents) may cut down π-electrons delocalization and create local charge transfer phenomenon (polarized surfaces) to increase H_2 binding energy.

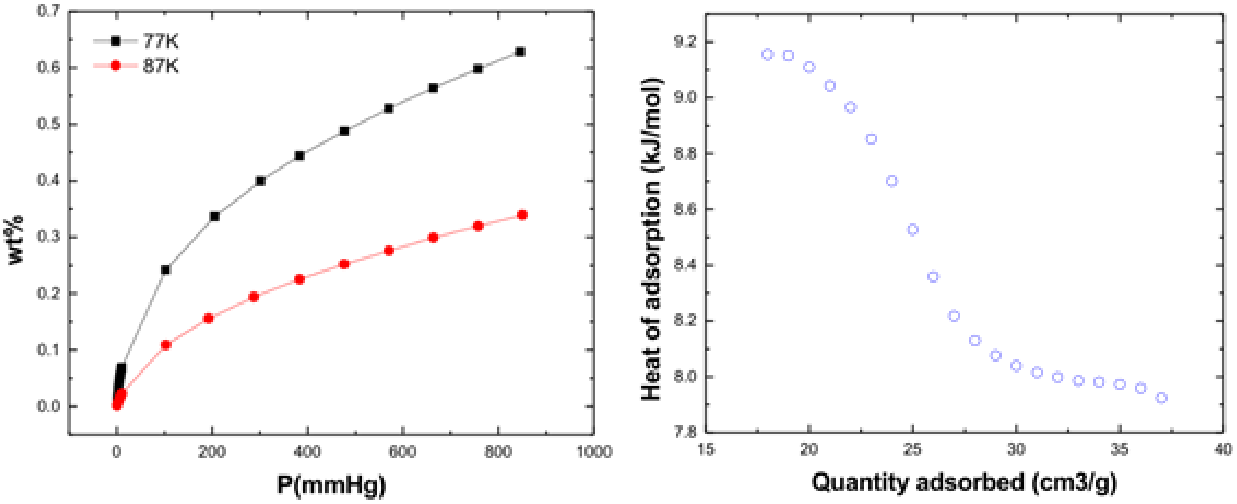


Figure 9. (left) H_2 adsorption isotherms up to >800 mmHg at 77K and 87K and (right) Isosteric heat of sorption for H_2 on B-PPTA (Sample C).

Evaluation of H_2 Adsorption-Desorption Cycle on B-PPTA Framework: The same B-PPTA sample C was also evaluated at NREL to understand its adsorption-desorption profiles and H_2 uptake level up to 110 bar H_2 pressure and under various temperature conditions. Figure 10 shows several H_2 adsorption-desorption profiles at 303K, 273K, and 77K, respectively. In the left Figure, there is a small hysteresis existed in the 1st adsorption-desorption cycle and the cycle does not go back to the origin. Both abnormal phenomena disappear after 1st cycle. Evidently, there is a small amount of reactive B-moieties that are inevitably existed at the planar edges of B-PPTA framework 2-D structure (Figure 1). These B-moieties are not fully reacted, therefore, containing some unreacted B-H groups that are very reactive. The trivalence BR_3 containing B-H group can form four-center borane complex (discussed in Q4 report) and also form strong complex with THF (observed by NREL). However, they can be easily de-activated by treating with methanol converting B-H bond to stable B-OCH_3 group.

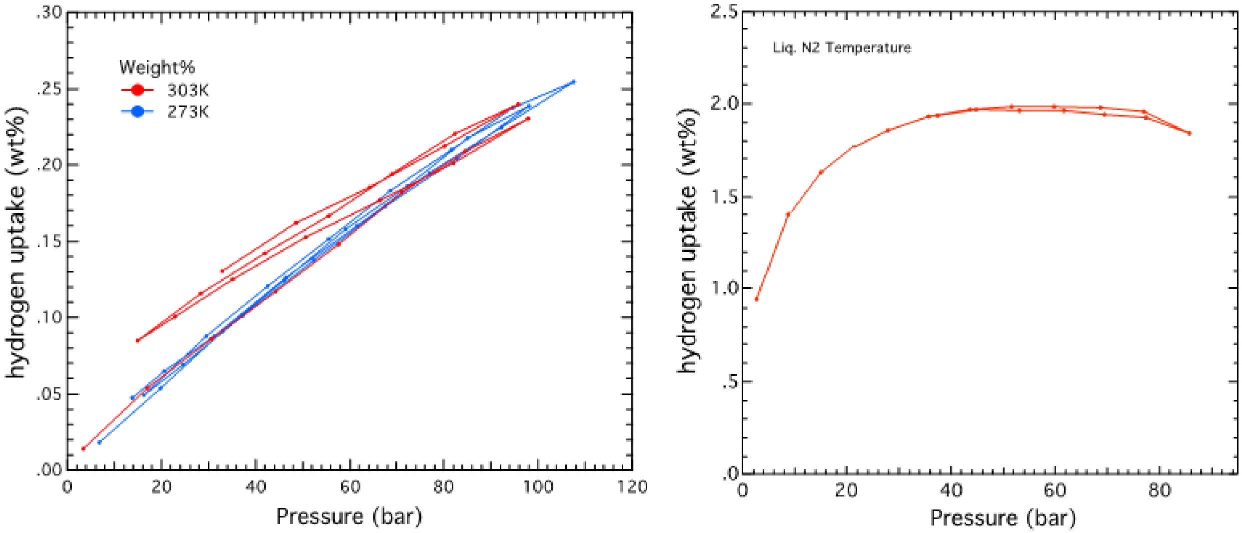


Figure 10. Excess gravimetric capacity of B-PPTA framework at (left) 303K and 273K and (right) 77K temperatures (NREL results).

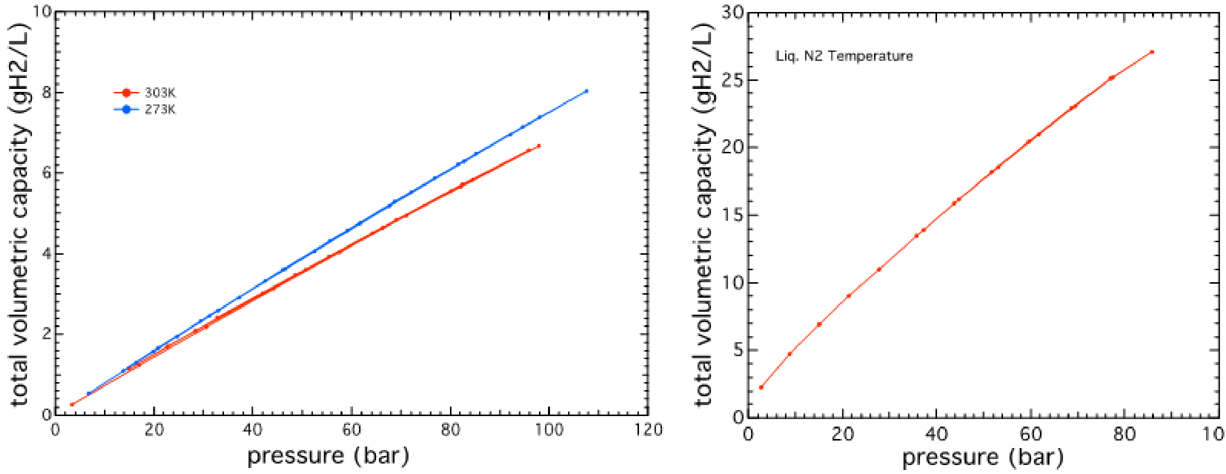


Figure 11. Total volumetric capacity of B-PPTA framework at (left) 303K and 273K and (right) 77K temperatures (NREL results).

Figure 11 shows total volumetric capacity of B-PPTA framework (C) at 303K, 273K and 77K. The overall H_2 storage level falls short of our project objective discussed in the beginning of this report.

Conclusion and Suggestions

We have investigated several approaches to prepare new B-polymer 2-D frameworks. The objective was to obtain a well-defined molecular structure and study its surface properties, especially H_2 binding energy and adsorption capacity. Following a step-by-step framework-building process, we have prepared the B-PPTA polymer framework (C) with a relatively well-defined structure, which exhibits a surface area about 2000 m^2/g (1000 m^2/g in each microporous and mesoporous ranges) and a single ^{11}B chemical shift peaked at 10 ppm. The chemical shift was surprisingly low for BR_3 trivalence species, indicating the near neutral B moieties in this 2-D (planar) framework structure. The loss of acidity in B-moieties may associate with the extensive π-electrons delocalization in the entire framework. Furthermore, despite the intrinsic microporous morphology of this 2-D framework structure, the lack of stacking control between 2-D layers may result in a miss-matched arrangement in forming 3-D structure with a significant portion of micropores blocked, which prevents the formation of open channels. Therefore, the specific surface area of the resulting (3-D) material was significantly reduced, and showing a broad pore size distribution.

In the hindsight, the 2-D B-PPTA polymer framework may not be an ideal molecular structure for achieving high H_2 binding energy and high surface area. The further molecular design, using some tetra-valence species to control the formation of 3-D structure, may provide the answer to overcome (at least minimize) both problems, i.e. too much π-electron delocalization and micropore channel blockage.