Developing A Novel Hydrogen Sponge Polymer with Ideal Binding Energy and High Surface Area for Practical Hydrogen Storage

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Project ID
ST140

Overview

Timeline

- Project start date: 10/1/2016
- Project end date: 9/30/2019
- % complete: 25%

Budget

- Total project funding: $887,266

- DOE share: $682,715
- Penn State share: $204,551

- Funding for FY2016-17: $ 250,000
- Go/no-Go decision: Dec. 2017

Barriers

- System weight & volume
- System cost, efficiency, durability
- Charging/discharging rates
- Suitable H_2 binding energy
- High polymer surface area

Partners

- HyMARC consortium

- Sandia National Lab.
- Lawrence Livermore National Lab.
- Lawrence Berkeley National Lab.

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Relevance

Research Objectives

- **New H_2 sponge (microporous polymer) that can simultaneously exhibit an H_2 binding energy (ΔH) 15-25 kJ/mol, a specific surface area SSA>4000 m^2/g, and a material density >0.6 g/cm^3.**
- Design, synthesis, and evaluation of a new class of **B-containing polymers** with specific B-moieties and repeating microporous morphology.
- Molecular simulation and advanced structural characterization to support scientific understanding and polymer materials development.

Potential Benefits and the Impact on Technology

- Polymer morphology, free volume, and surface properties can be controlled **at molecular level**.
- Polymer can be produced in large-scale with low cost, good mechanical properties, and long term stability.
- If successful, this H_2 sponge can achieve gravimetric capacity of 5.5 wt% H_2 and volumetric capacity of 40g H_2/L @ ambient temperature under mild pressure (20-100 bar).

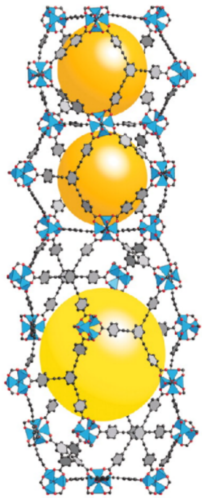
Relevance: 2020 DOE onboard H_2 storage targets

System	Temp. (°C)	Gravimetric capacity (wt%)	Volumetric capacity (g/L)
700 Bar Compressed H_2 system	Ambient Temp	~4.5	~25
DOE 2020 targets	Ambient (-40/60)	5.5 (1.8kWh/kg)	40 (1.3 kWh/L)

- Lower pressure operation = less cost at the station
- Fast hydrogen refill (5 kg in 3 to 5 minutes)
- Delivery pressure to fuel cell system (5-12 bar)
- Nominal thermal-management during refueling
- High efficiency (90%)
- Robotic and Durable (1500 cycles)
- Scalable and Low cost

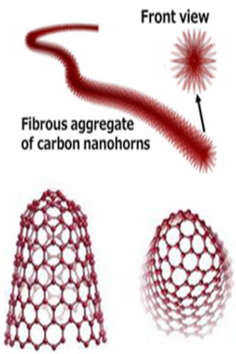
Relevance: Three H_2 storage materials

Physical approach | *Chemical approach*



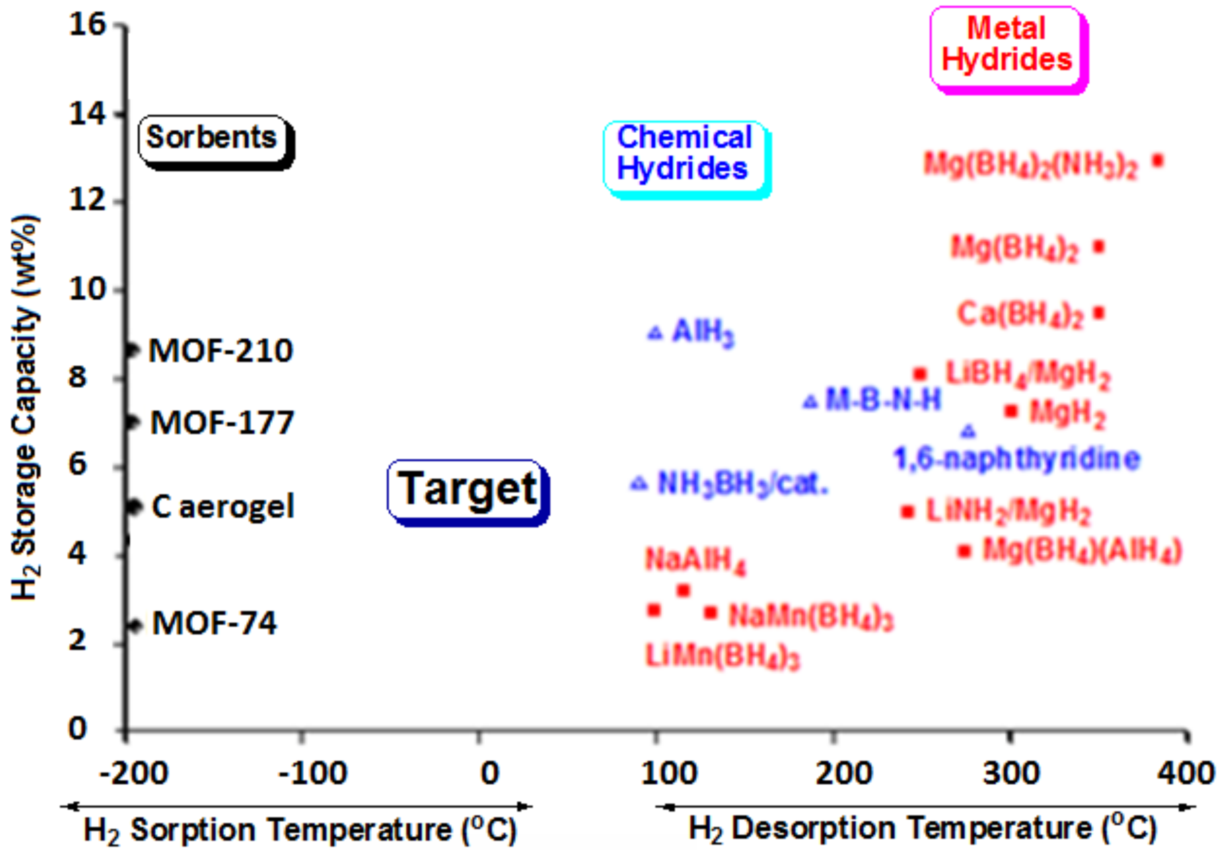
MOF-210

SSA: 6240 m^2/g
ΔH: <10 KJ/mol
Density: 0.25 g/cm^3
Pore size: 2-5 nm
Pore volume 3.6 cm^3/g



C Nanohorn

SSA: <2000 m^2/g
ΔH<10 KJ/mol
Density: 0.75 g/cm^3
Pore size: 1-3.6 nm

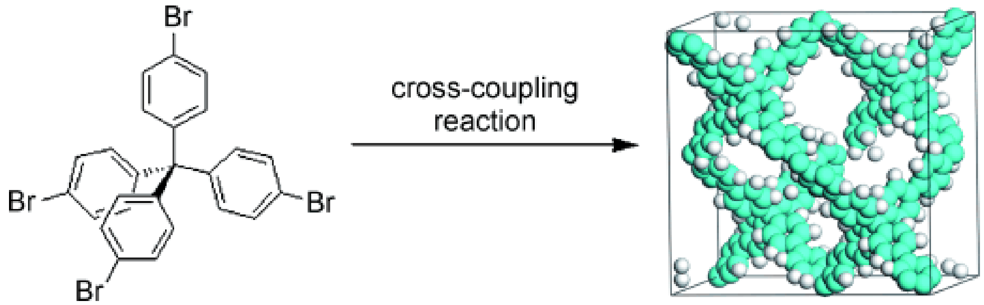


<10 KJ/mol | **>30 KJ/mol**

15-25 kJ/mol

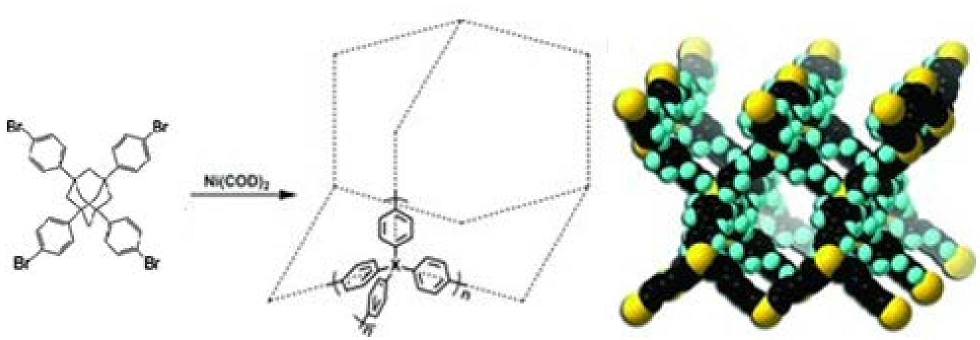
Relevance: Porous organic polymer networks

Qiu and Zhu at al. Angew Chem Int Ed **2009**, 48, 9457



PAF-1
BET: 6540 m^2/g
H_2 uptake: 7 wt% Total (48 bar/77K)
Density: 0.315 g/cm^3

Zhou at al. Adv. Mater. **2011**, 23, 3723



PPN-4
BET: 6461 m^2/g
H_2 uptake: 8.34 wt% Total (55 bar/77K)
ΔH ~4 kJ/mol

- **Porous Polymer Network (PPN) can offer high surface area (>4000 m^2/g)**
- **Polymers also offer good mechanical and thermal stability**
- **But low H_2 binding energy (<10 kJ/mol)**

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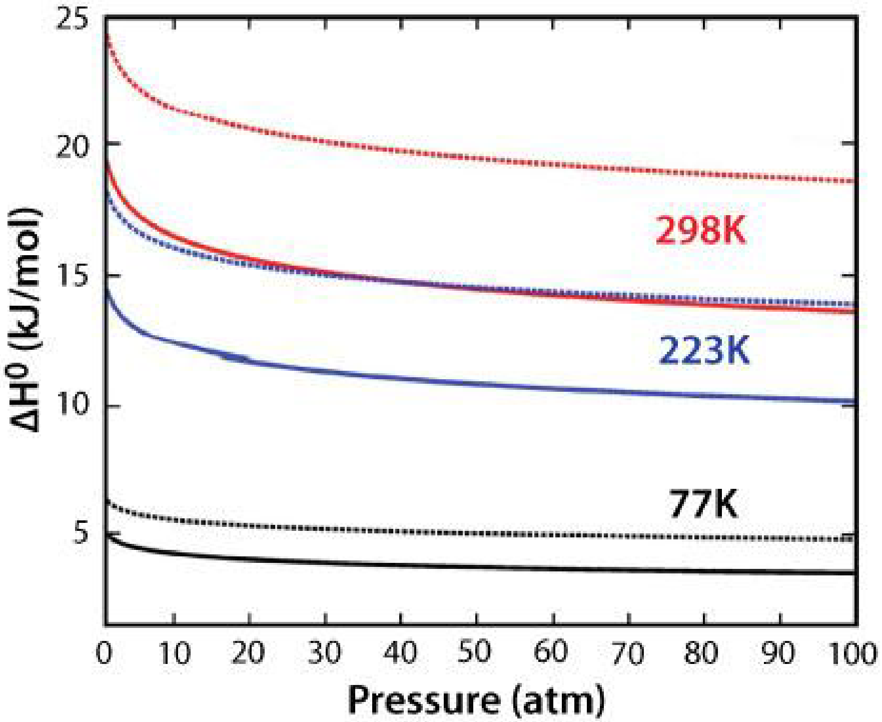
Relevance: Optimal sorbent material

Binding Energy

Bhatia and Myers 2006

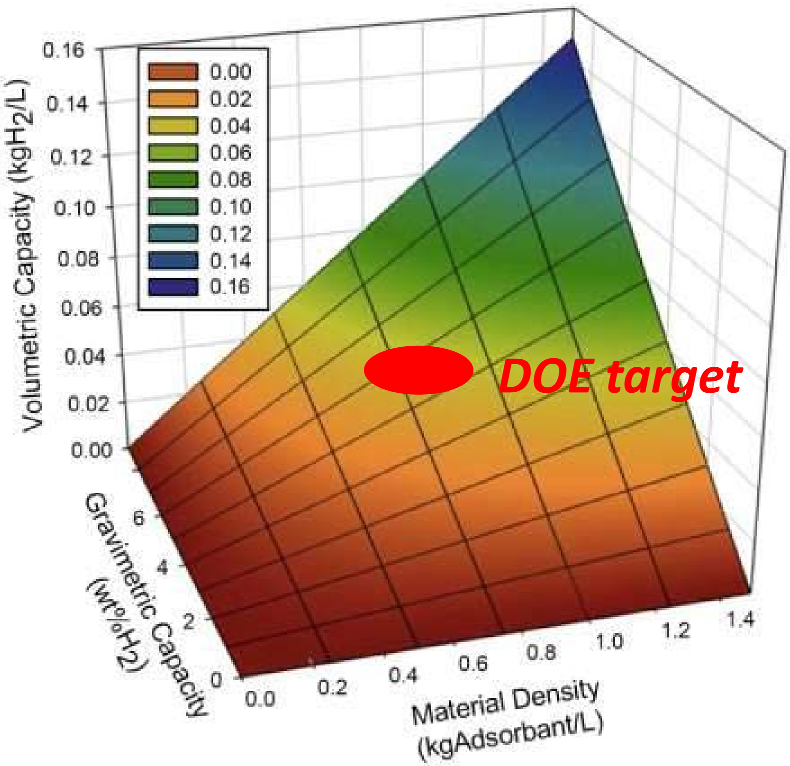
dotted lines ΔS=-10R
solid lines ΔS=-8R



ΔH: 15-25 kJ/mol

Bulk Density

Argonne National Laboratory



Bulk material density: >0.6 g/cm³

Practical H_2 storage at ambient temperature and pressure <100 bar

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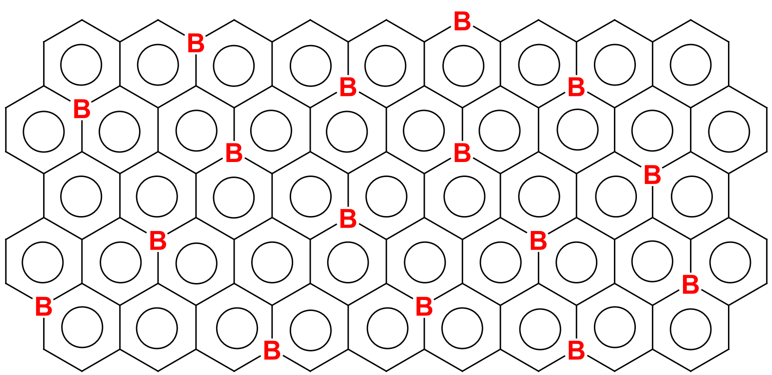
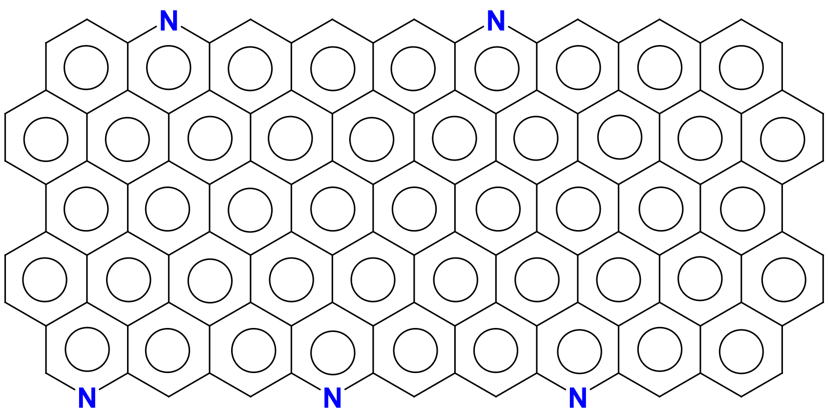
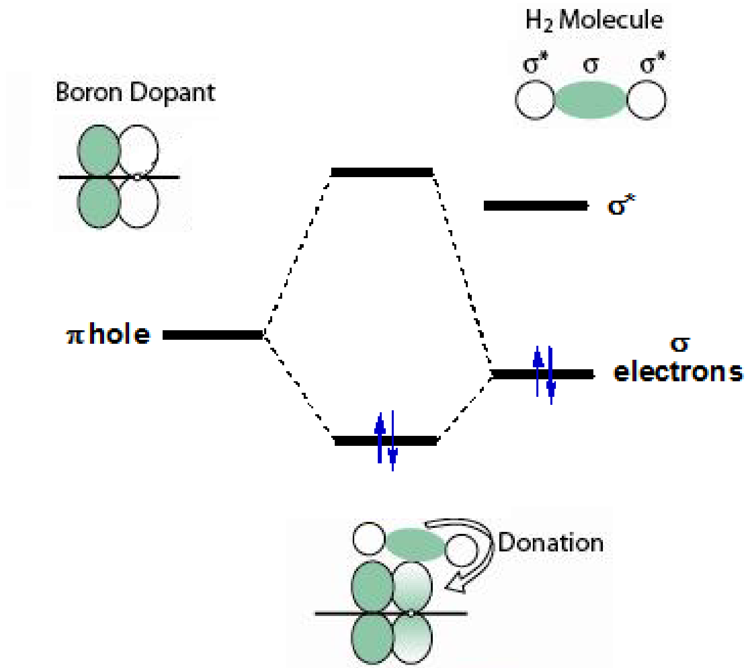
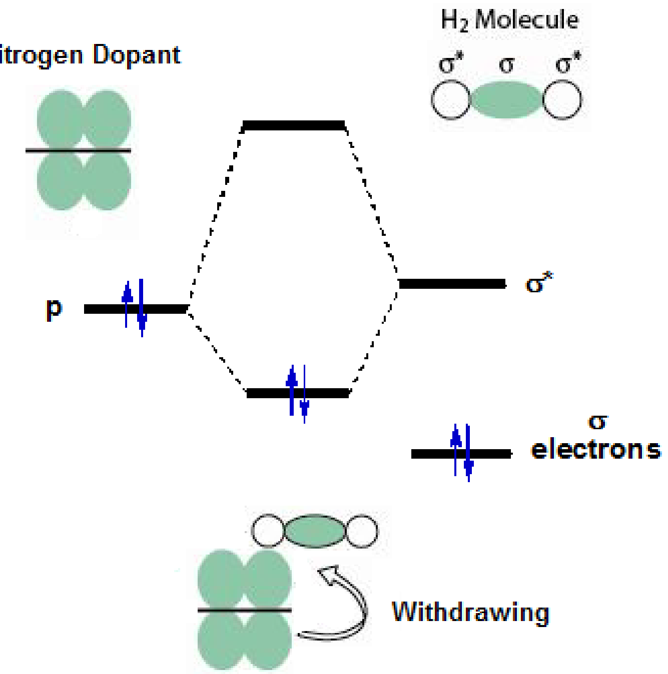
Relevance: Increase H_2 binding energy









NREL led H_2 Sorption Center of Excellence (HSCoE) 2005-10

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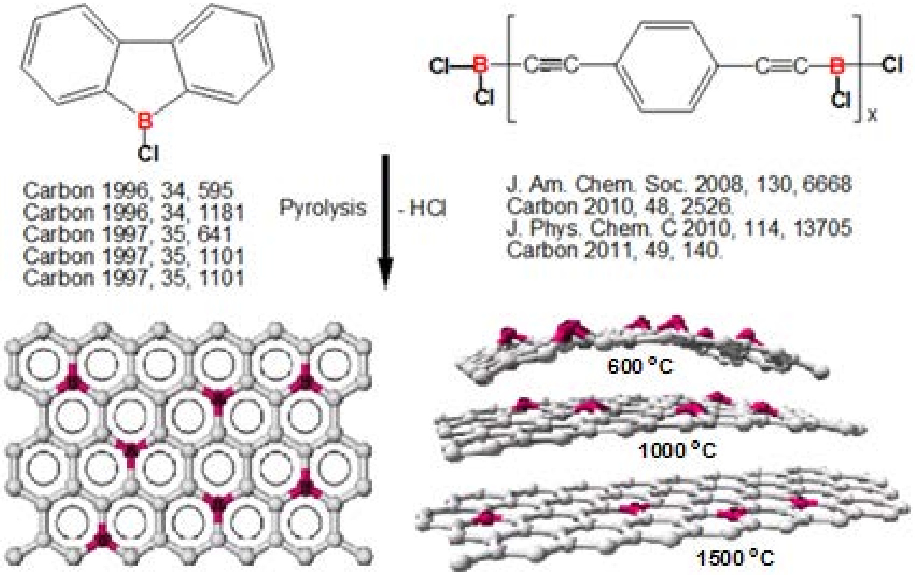
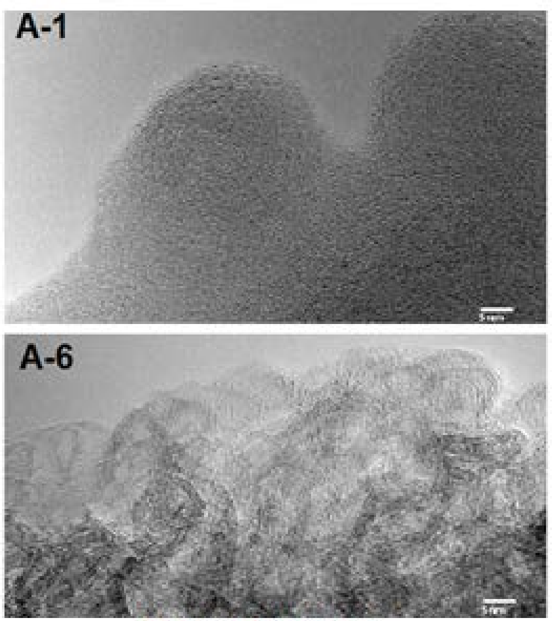
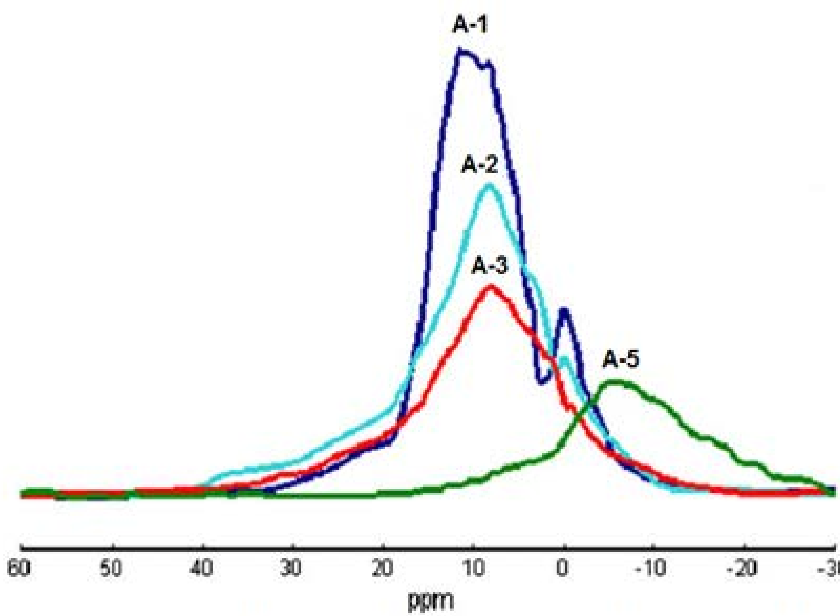
Relevance: Synthesis of BC_x by Precursors



Run no.	Pyrolysis temp. (°C)	BCx (B wt%)	d-Spacing (nm)	La (nm)	Lc (nm)
A-1	600	BC_{12} (7.7)	-	-	-
A-2	800	BC_{13} (6.4)	0.367	3.70	1.10
A-3	1100	BC_{21} (4.2)	0.356	3.73	1.23
A-4	1400	BC_{25} (3.5)	0.353	4.87	1.61
A-5	1500	BC_{28} (2.6)	0.347	5.04	1.64
A-6	1800	BC_{40} (2.2)	0.339	6.04	2.77



TEM micrographs



Solid state (MAS) 11B NMR spectra of BCx materials

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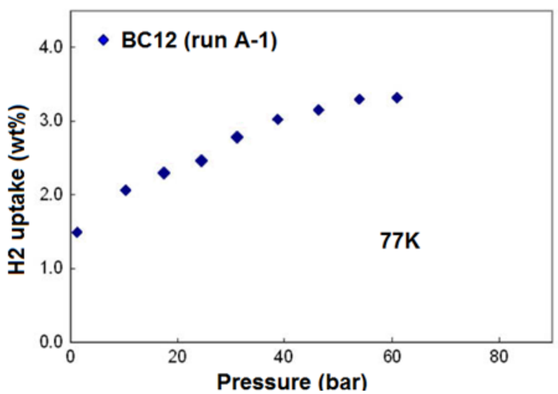
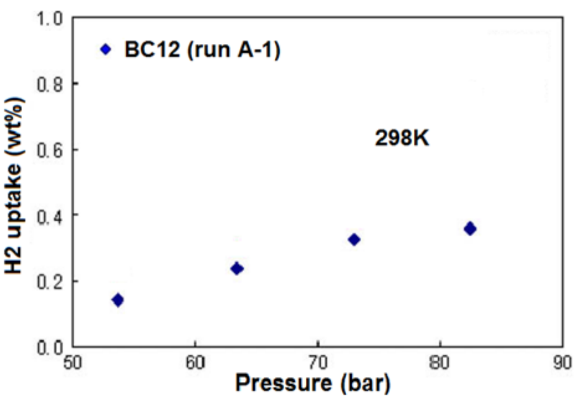
Relevance: H_2 adsorption isotherms in BC_{12}

Run no.	N_2 sorption at 77 K		CO_2 sorption at 273 K	
	Surface area (m^2/g)	Pore vol. (cm^3/g)	Surface area (m^2/g)	Micropore vol. (cm^3/g)
A-1	780	0.38 (0.43)*	873	0.33

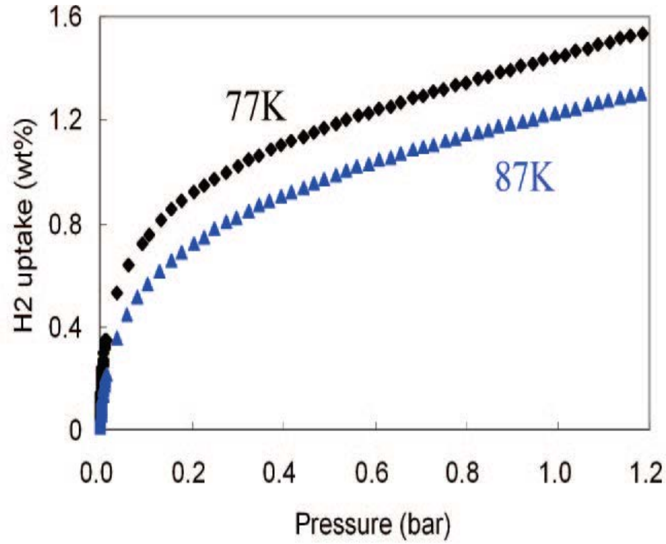
Volumetric measurement





Carbon **2010**, 48, 2526-2537

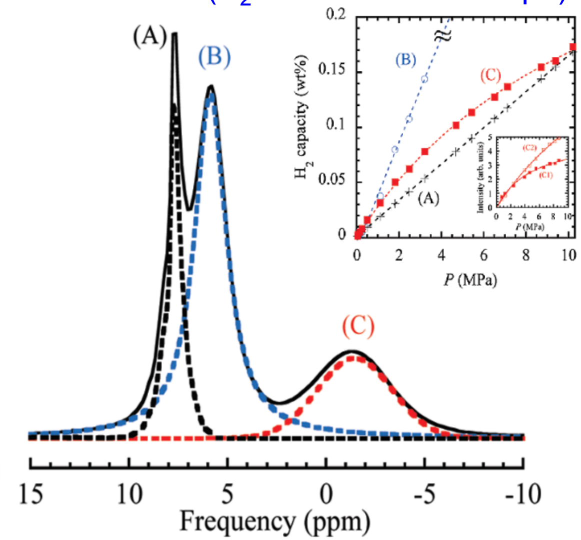
Gravimetric measurement



Clausius-Clapeyron equation estimates the initial isosteric heat of adsorption is 12.47 kJ/mol and maintains a high level (10.8 kJ/mol for 0.62 wt % H_2 uptake).

JACS **2008**, 130, 6668

^{1}H NMR (H_2 at 295 K and 10 Mpa)



Peaks B and C are associated with H_2 in two different types of confined regions. The Langmuir fit of peak C isotherm yields a H_2 binding energy of 11.4 kJ/mol.

J. Phys. Chem. C **2010**, 114, 13705

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Approach: New sorbent targets

System	Sorbent property				H_2 adsorption capacity		
	SSA (m^2/g)	Density (g/cm^3)	Pore volume (cm^3/g)	H_2 binding energy (kJ/mol)	Pres./Temp. (bar)/(K)	Gravimetric capacity (wt%)	Volumetric capacity (g/L)
MOF 210	6240	0.25	3.6	<10	60/77	8.6	24
Porous Polymer	>4000		<1.0	<10	90/77	>7.0	
Porous BC_{12}	**1500**	**0.98**	**0.43**	**10-12**	**60/77**	**3.3**	**34**
DOE and B-polymer targets	**>4000**	**>0.6**	**<0.7**	**15-25**	**<100 / 273**	**5.5**	**40**

New sorbent shall simultaneously exhibit H_2 binding energy 15-25 kJ/mol, SSA >4000 m^2/g, material density >0.7 g/cm^3.

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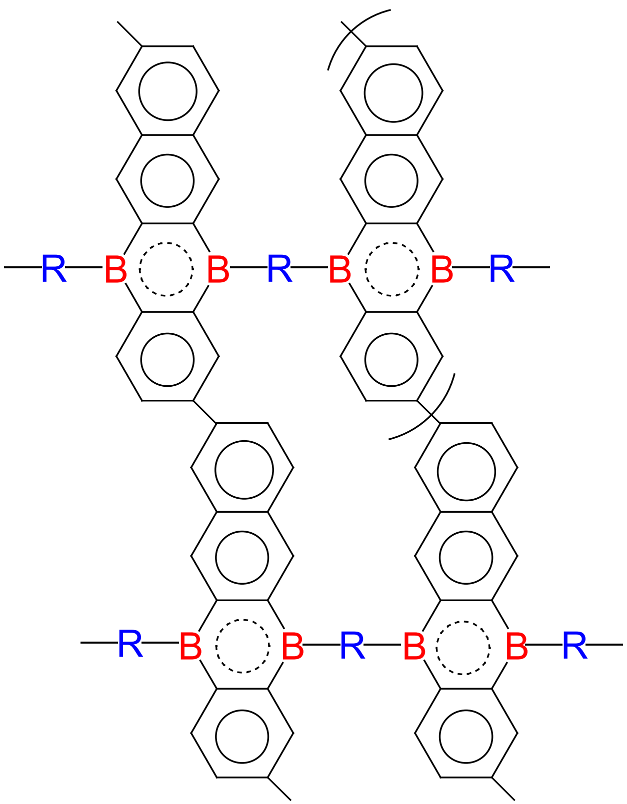
Approach: Two New B-containing Polymer Networks

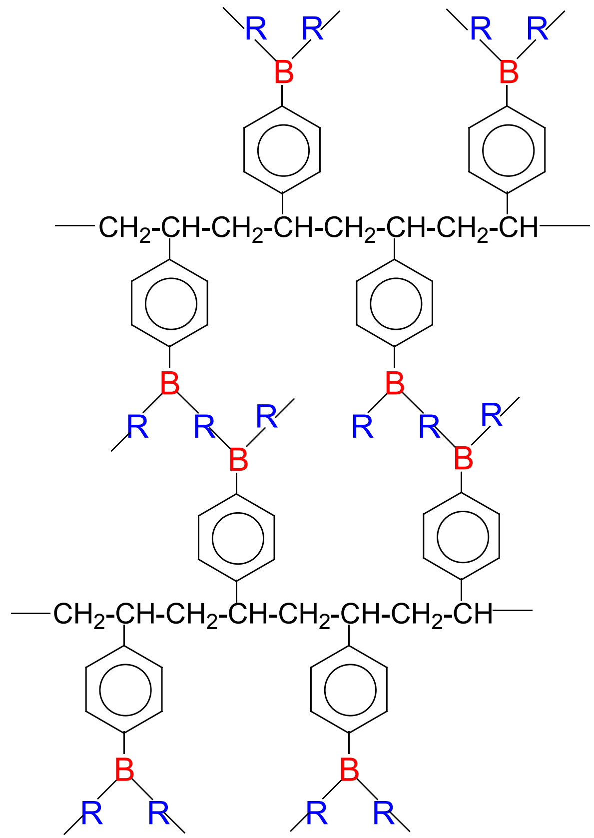
Condensation Mechanism

(A)

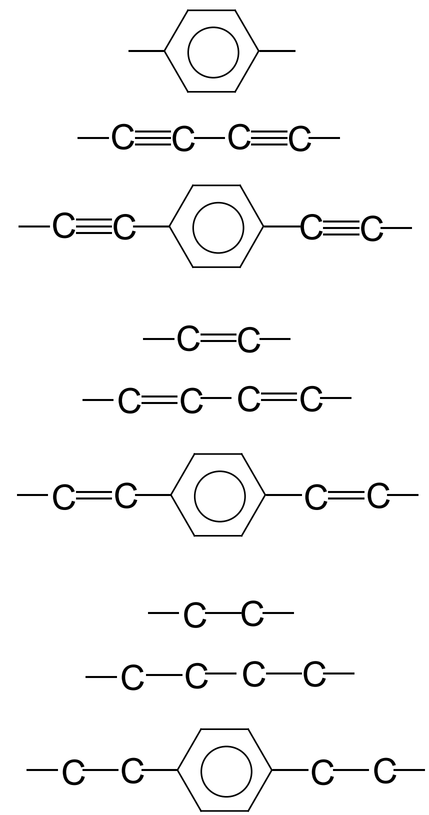


Addition Mechanism

(B)

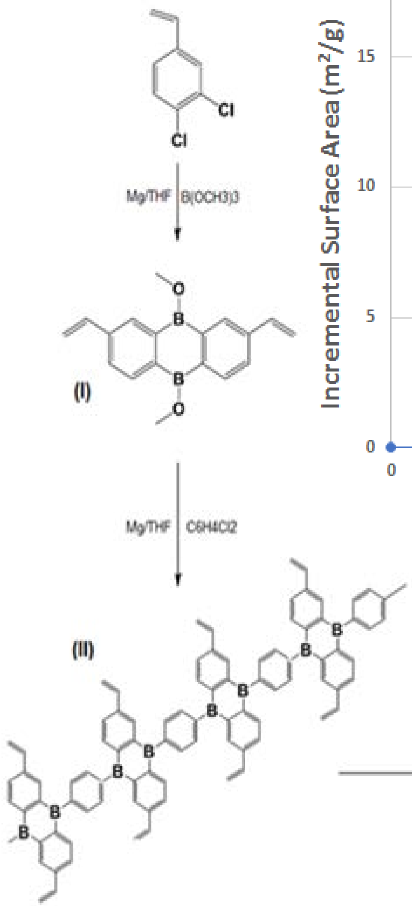


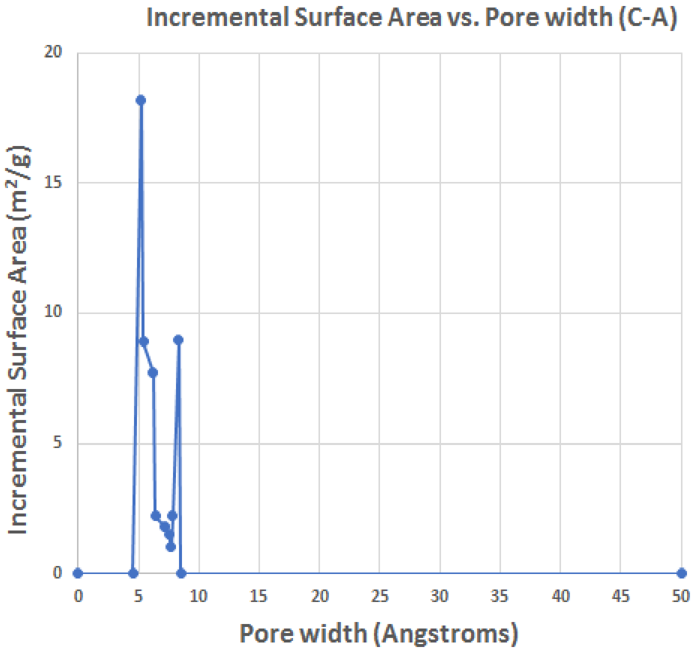
R Spacers:

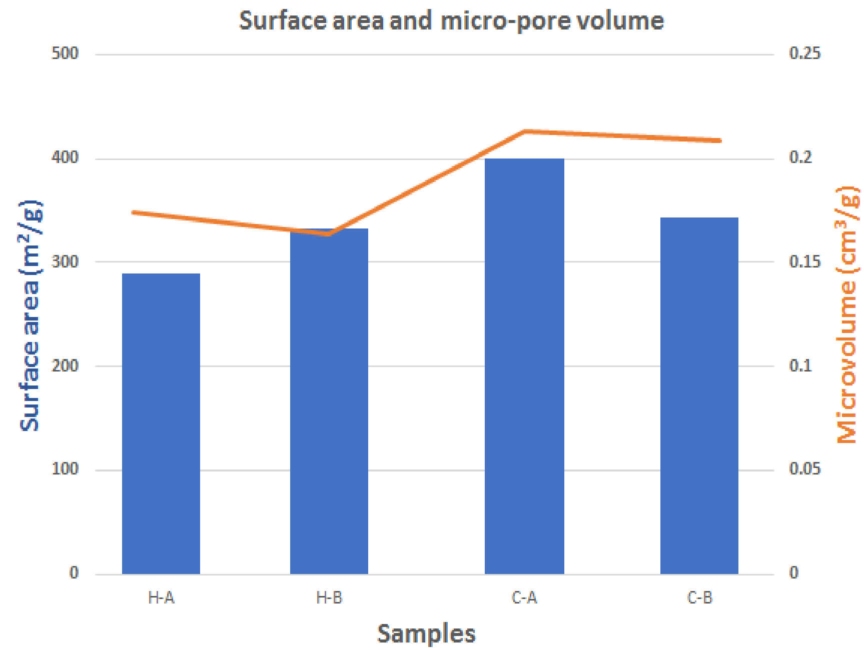


Organoborane moiety with suitable acidity (correlative ^{11}B chemical shift to H_2 binding energy)

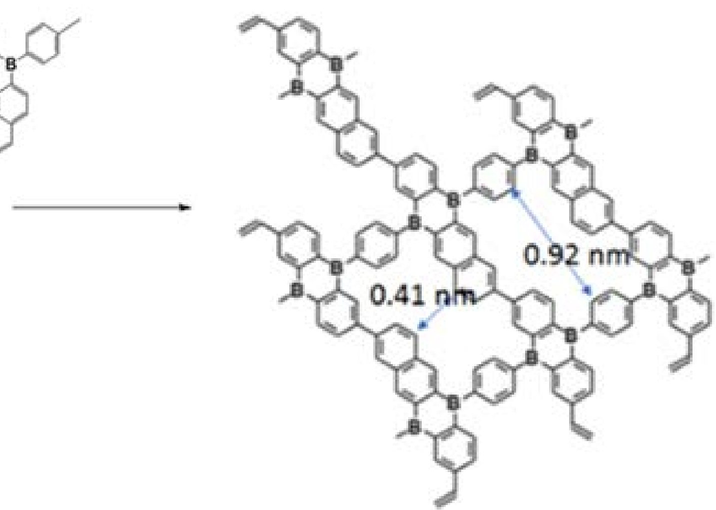
Accomplishments - Condensation mechanism; 2,6-divinyl-9,10-methoxyboraanthracene monomer

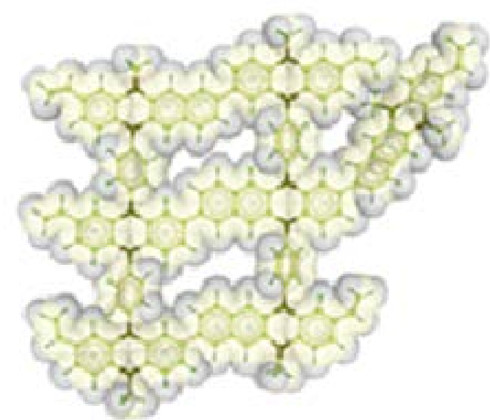






Bulk density= 0.95 g/cm³





(A)

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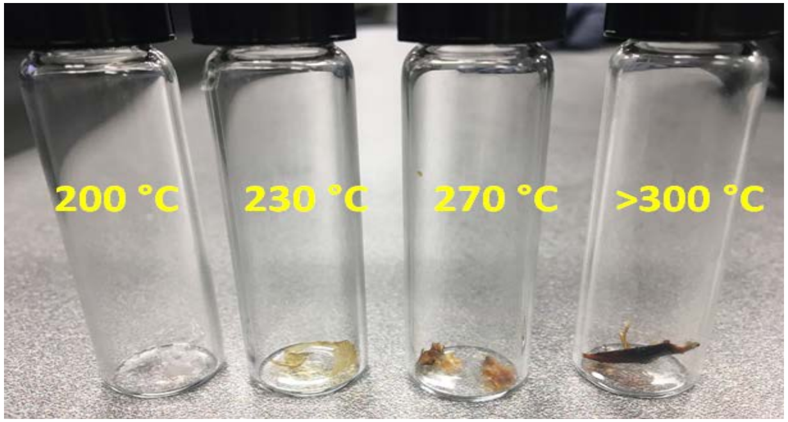
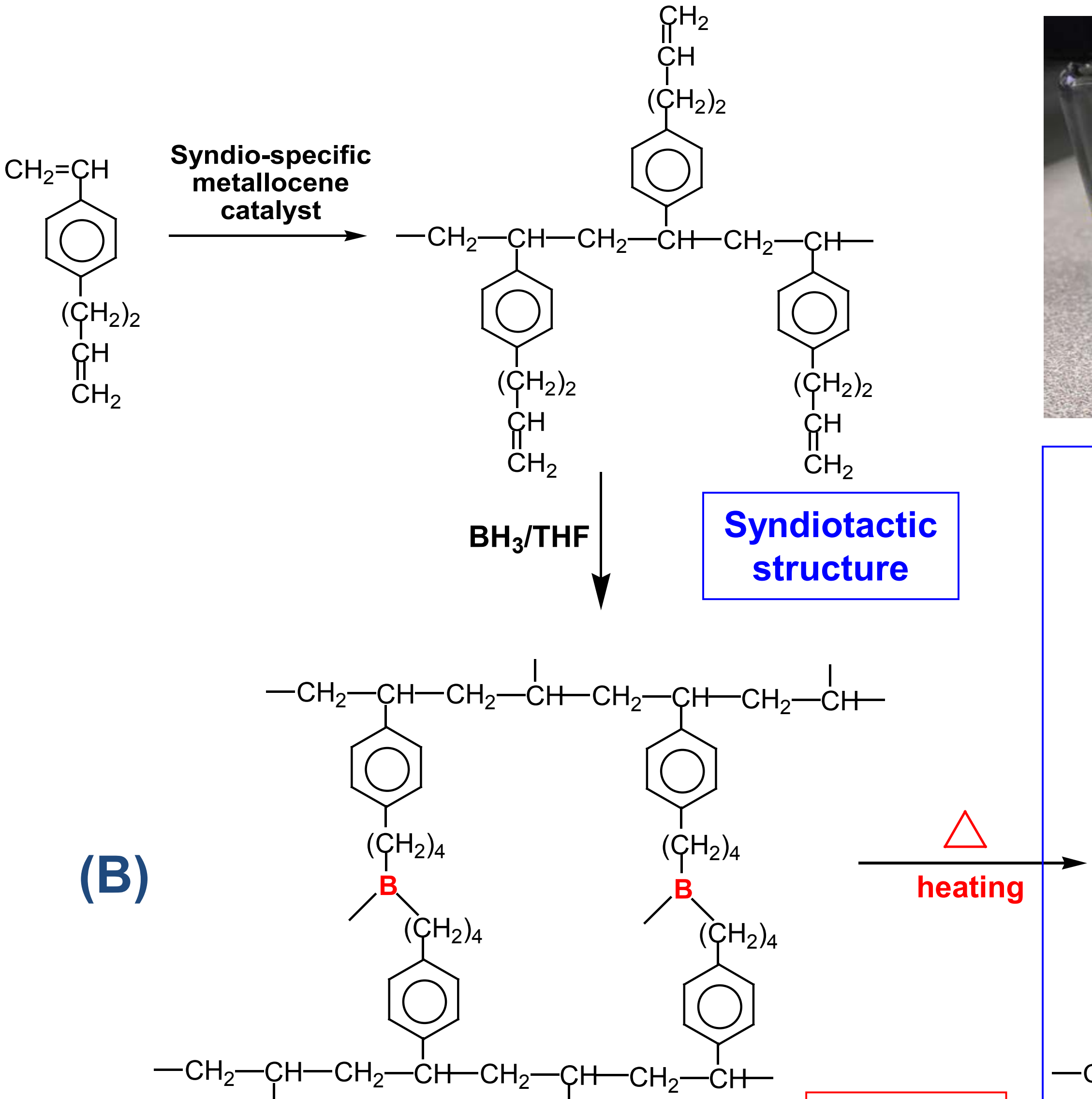
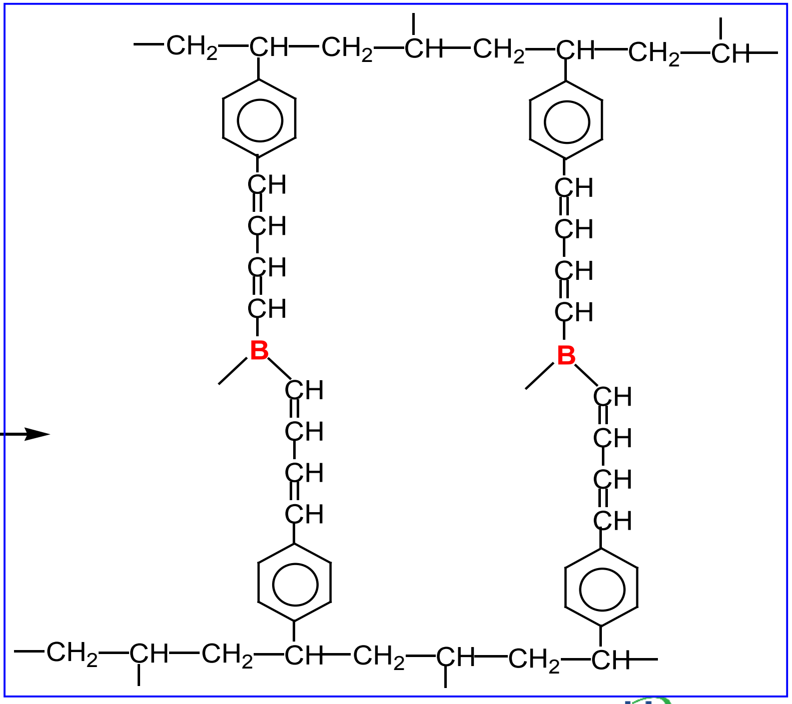
Accomplishments: Addition mechanism; B-containing poly(butylstyrene) (B-PBS)



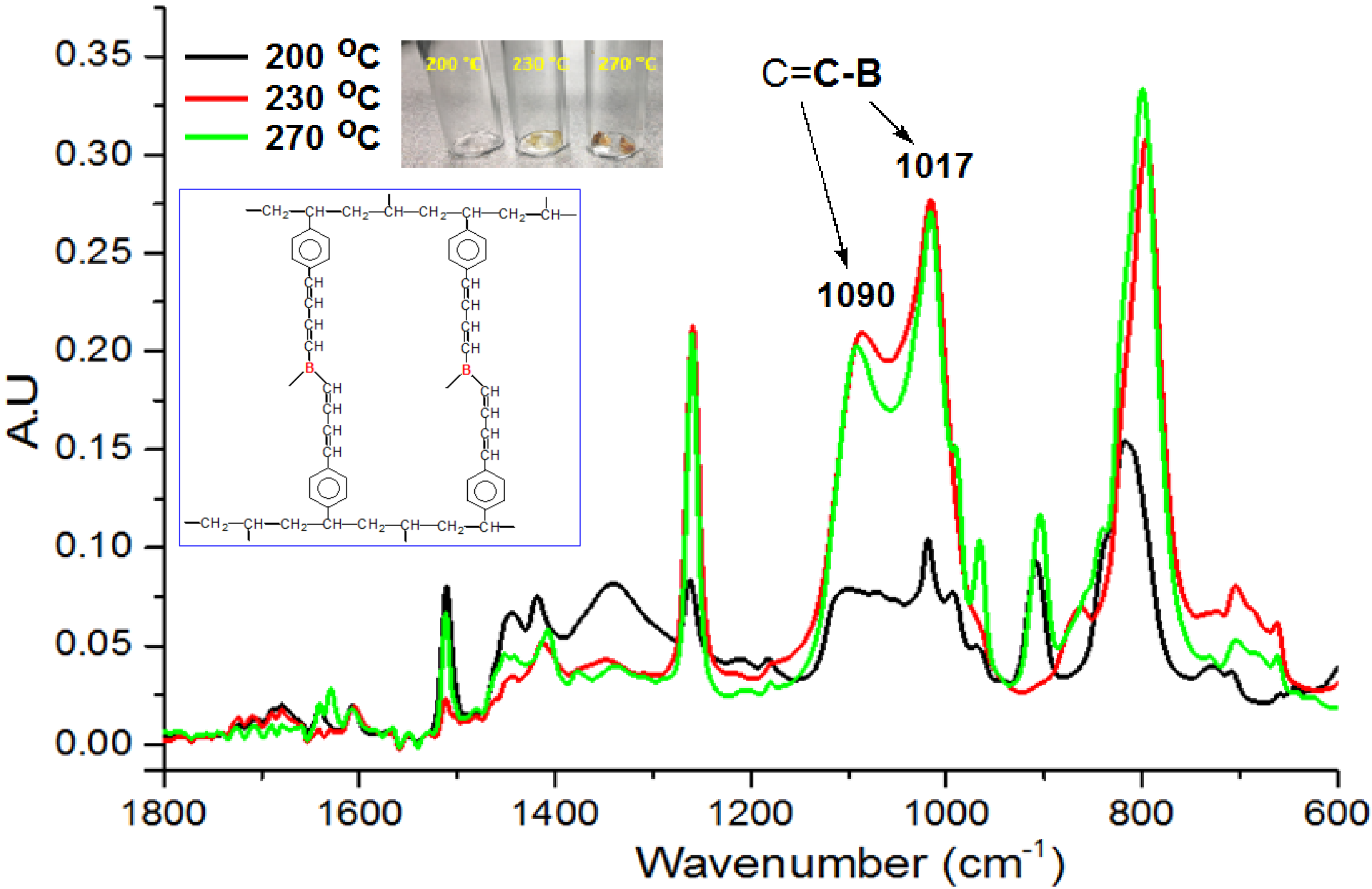
(B)



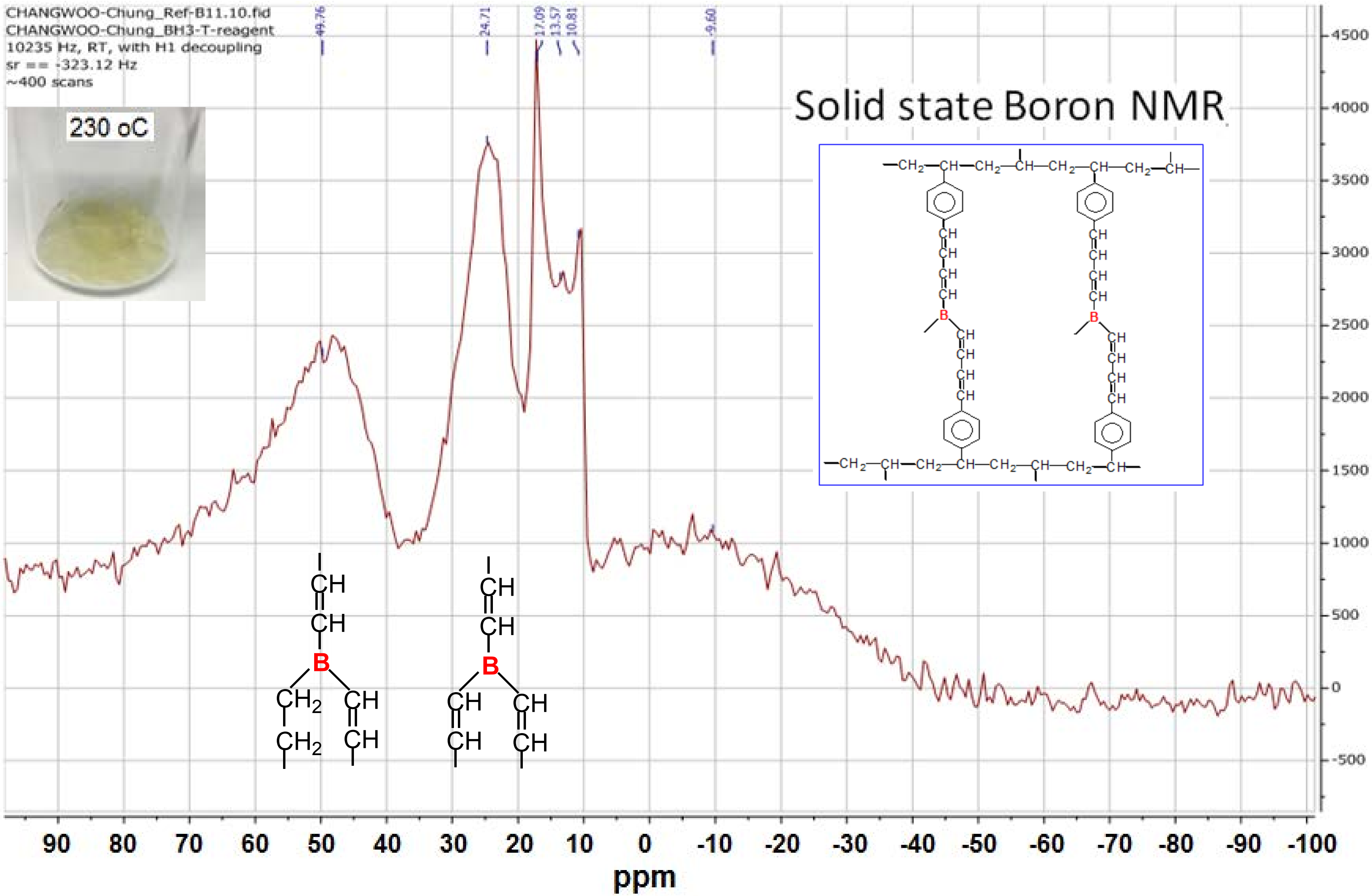


B-PBS

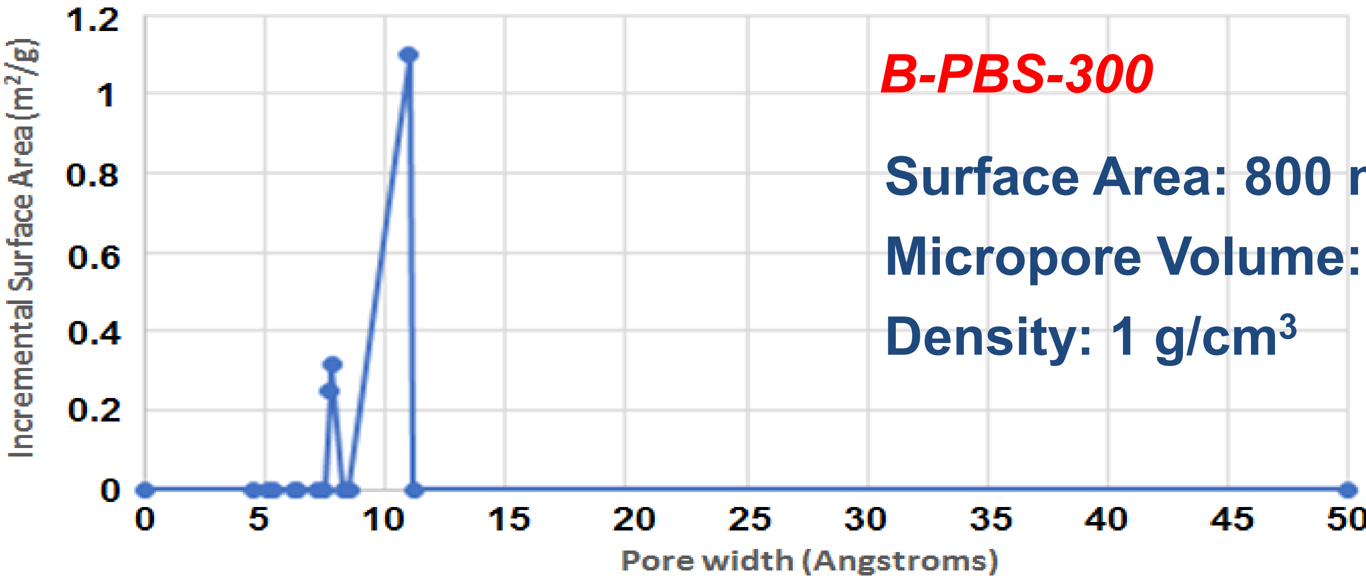
Accomplishments: FTIR spectrum of B-PBS polymer



Accomplishments: MAS ^{11}B NMR spectrum of B-PBS polymer



Accomplishments: Pore Structure of B-PBS polymers

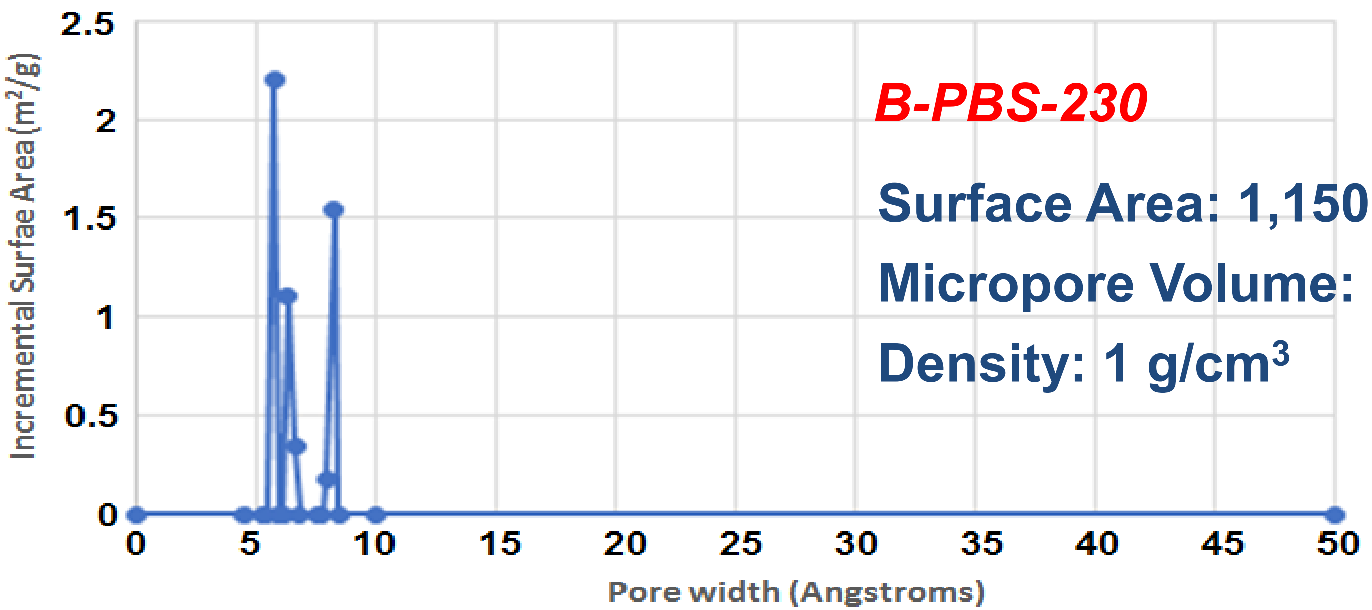


B-PBS-300

Surface Area: 800 m^2/g

Micropore Volume: 0.48 cm^3/g

Density: 1 g/cm^3



B-PBS-230

Surface Area: 1,150 m^2/g

Micropore Volume: 0.75 cm^3/g

Density: 1 g/cm^3

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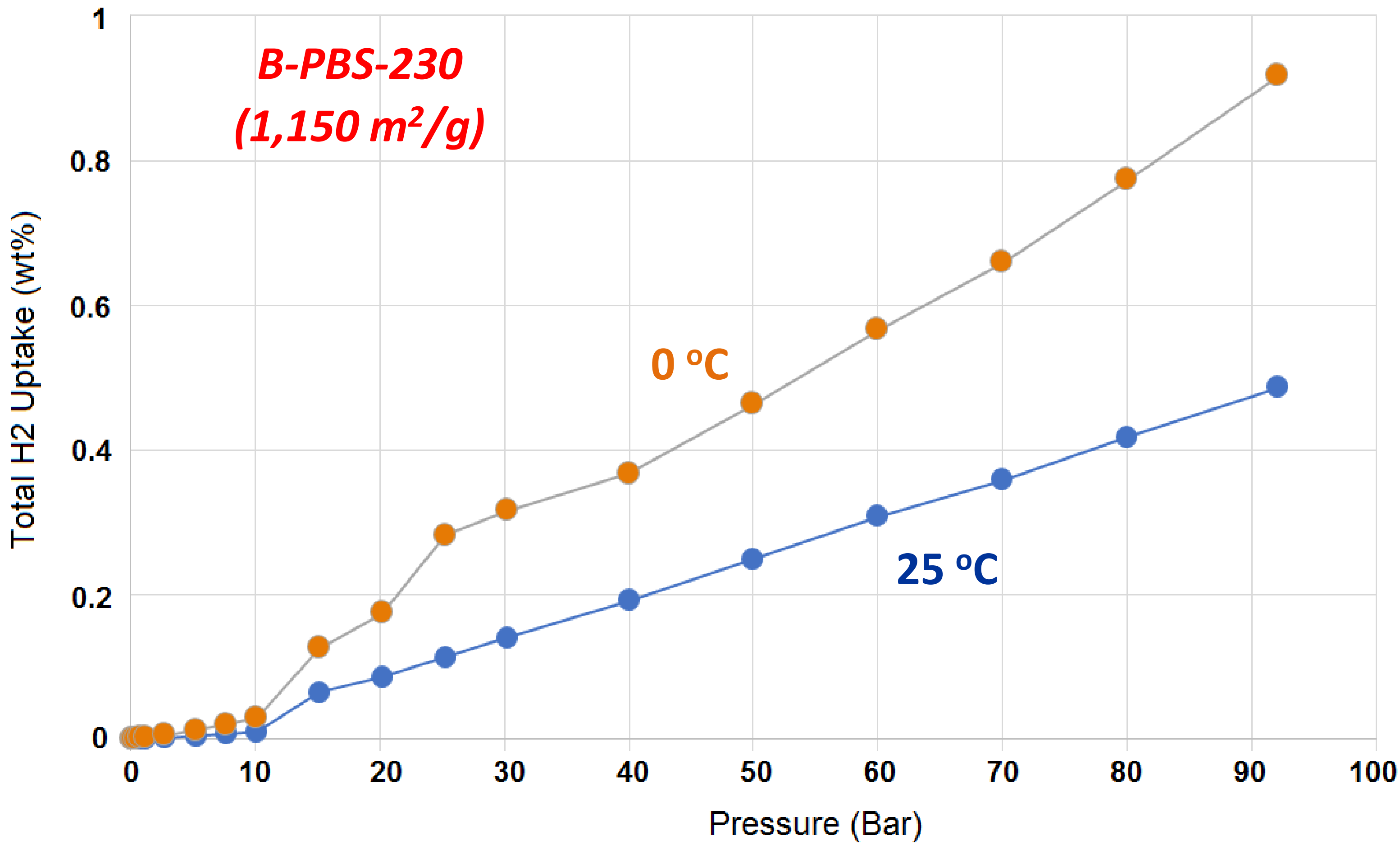
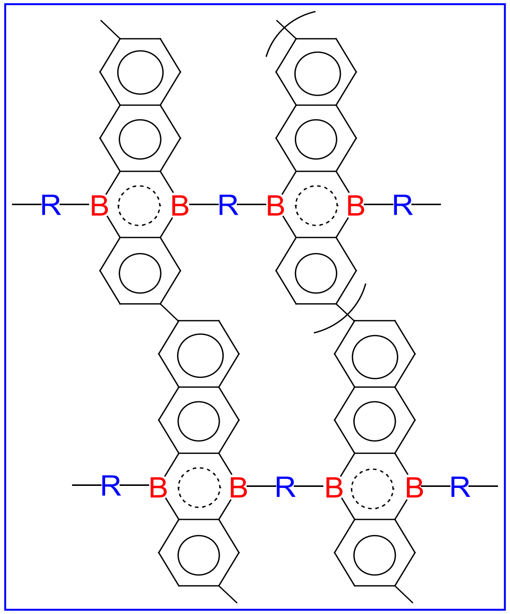
Accomplishments: H_2 Adsorption Isotherm

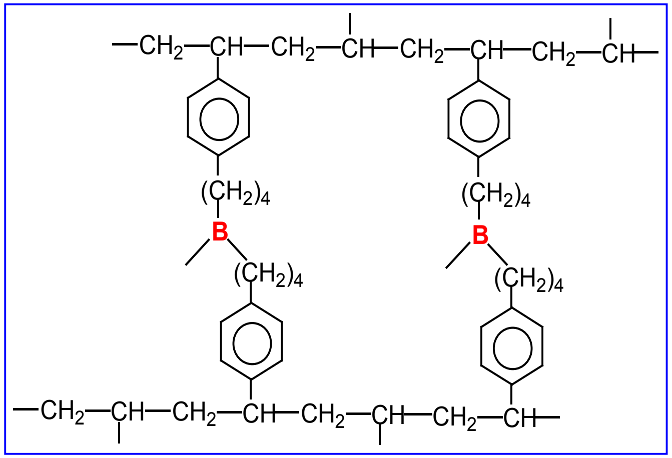


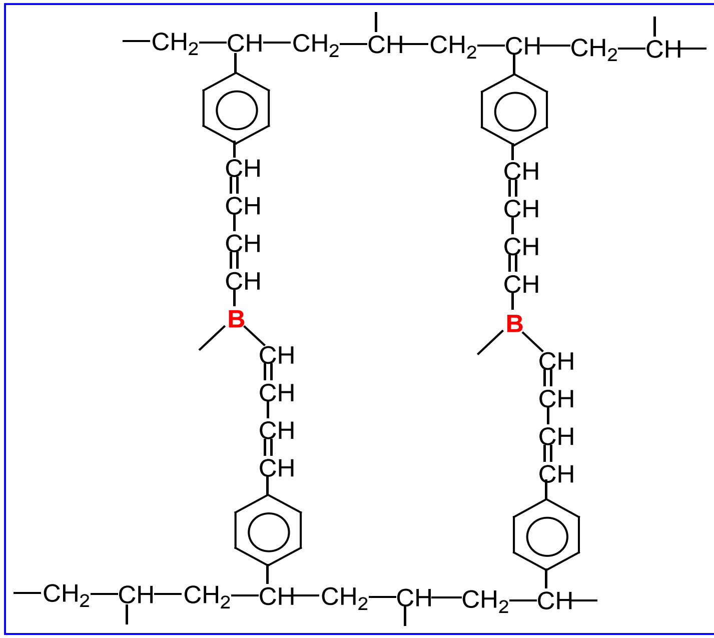
H_2 adsorption was measured at Sandia National Labs (Dr. Vitalie Stavila)

Summary

- Design and Synthesis of two new classes of microporous B-containing polymers.
- Structure characterization by FTIR, ^{1}H, ^{11}B, and ^{13}C NMR spectroscopies, SEM, micropores and surface area.
- Collaboration with HyMARC core team for H_2 adsorption isotherm measurements.

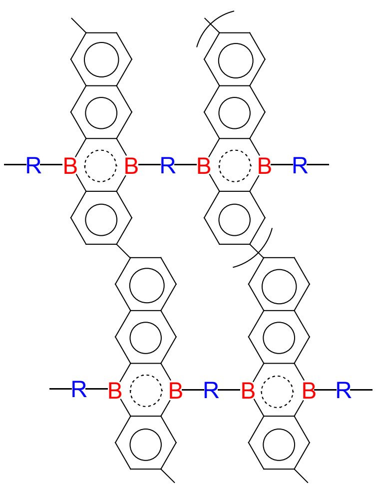
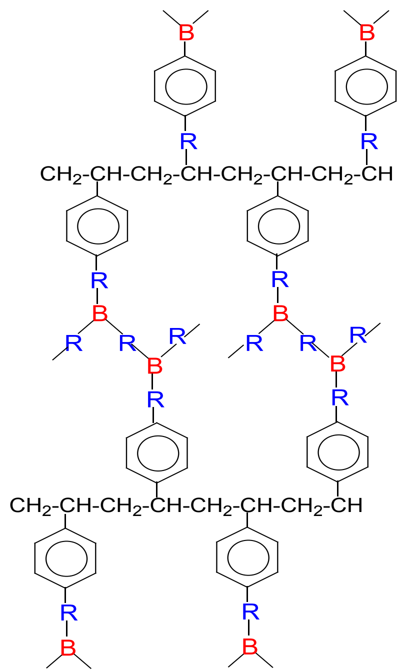


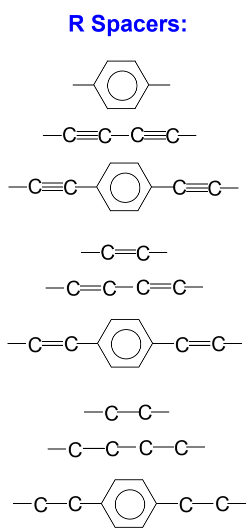


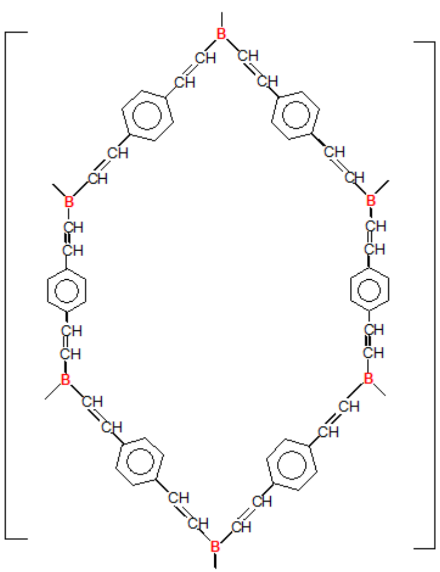
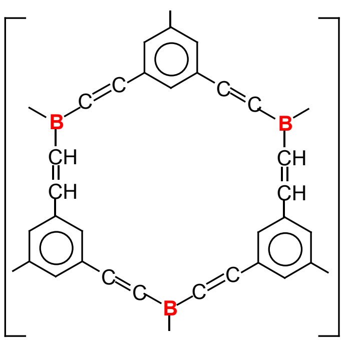


Proposed future work

- **Broadening B-polymer compositions**
- **Refining reaction conditions to control microporous morphology**
- **Titan TEM-EDS and FE-SEM electron microscopies to observe the microporous morphology with the elemental map.**
- **Correlating B chemical shifts (B-acidity) to H_2 binding energy (ΔH) and sorption-desorption cycles.**



Collaboration with HyMARC / HySCORE teams

Partner	Project Roles
Sandia National Lab.	H_2 adsorption isotherm measurements up to 200 bar H_2 pressure and various temperatures, also the stability tests up to 1000 bar H2 pressure and various temperatures.
Lawrence Livermore National Lab.	Computer simulation of B-polymer networks to understand morphology (pore size, pore volume, surface area, density, etc.) and surface energy for H_2 adsorption
National Renewable Energy Lab.	H_2 adsorption isotherm measurements / Verification of our experimental results

Future Work (cont.)

	Key Milestones & Deliverables
Phase 1 10/1/2016 ↓ 12/31/2017	• Synthesis routes to prepare B-monomers, B-polymers, and the corresponding B-networks. • Collaborating with HyMARC to examine B-network structures, SSA, H_2 binding energy and adsorption capacity. • A B-polymer network with SSA>3000 m^2/g, an average H_2 binding energy E_{ads}>15 kJ/mol, H_2 adsorption capacity 5 wt% excess (Go/No-Go criteria).
12/31/2017	**Go/No-Go decision**
Phase 2 1/1/2018 ↓ 9/30/2019	• Expanding B-polymer Networks by varying R spacer between B-moieties. • Collaborating with HyMARC to understand free volume and H_2 binding energy. • Understanding the structure-property relationship by a systematical study. • Achieving the DOE 2020 H_2 Storage Target.

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