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

Mike Chung, Changwoo Nam, Houxiang Li, Hannah Pohlmann

Department of Materials Science and Engineering
The Pennsylvania State University

DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting
Washington, D.C., June 5-9, 2017

Project ID ST140

This presentation does not contain any proprietary, confidential, or otherwise restricted information

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.

PENNSTATE

HyMARC

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

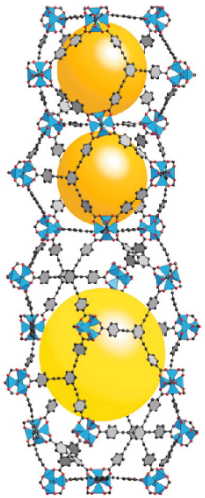
- Polymer morphology, free volume, and surface properties can be controlled **at molecular level**.
- Polymer can be produced in large-scale with low cost, good mechanical properties, and long term stability.
- If successful, this H_2 sponge can achieve gravimetric capacity of 5.5 wt% H_2 and volumetric 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)

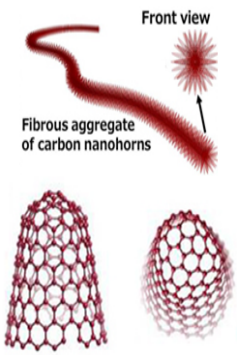
- Lower pressure operation = less cost at the station
- Fast hydrogen refill (5 kg in 3 to 5 minutes)
- Delivery pressure to fuel cell system (5-12 bar)
- Nominal thermal-management during refueling
- High efficiency (90%)
- Robotic and Durable (1500 cycles)
- Scalable and Low cost

Relevance: Three H_2 storage materials



MOF-210

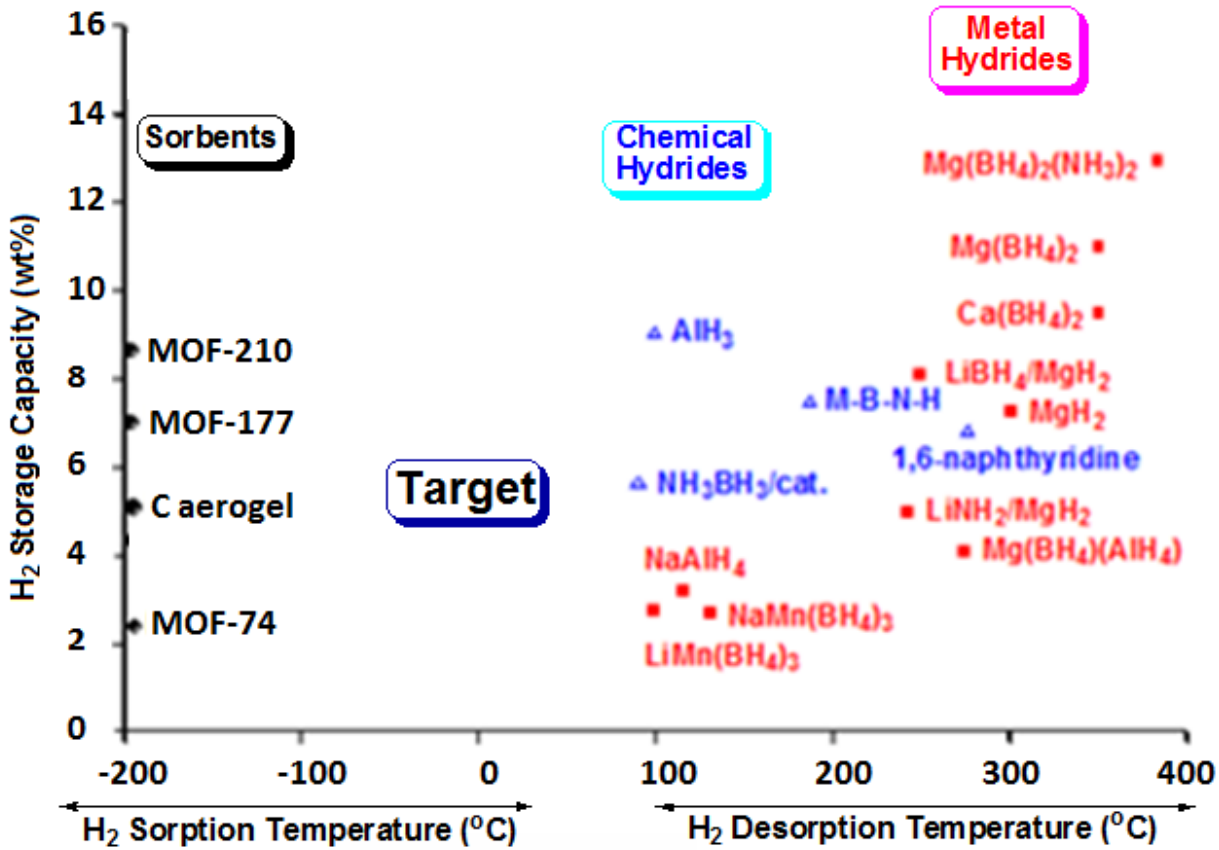
SSA: 6240 m^2/g
ΔH: <10 KJ/mol
Density: 0.25 g/cm^3
Pore size: 2-5 nm
Pore volume 3.6 cm^3/g



C Nanohorn

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

Physical approach *Chemical approach*



<10 KJ/mol

>30 KJ/mol

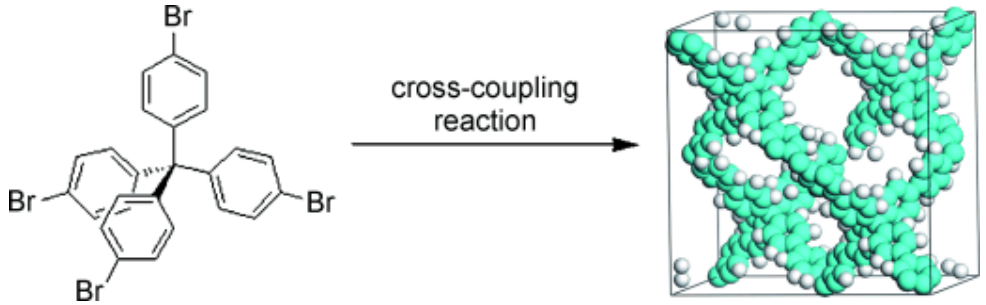
15-25 kJ/mol

PENNSTATE

HyMARC

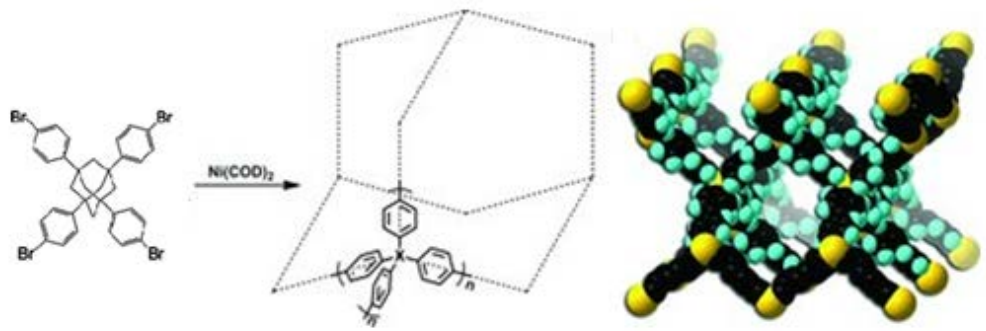
Relevance: Porous organic polymer networks

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

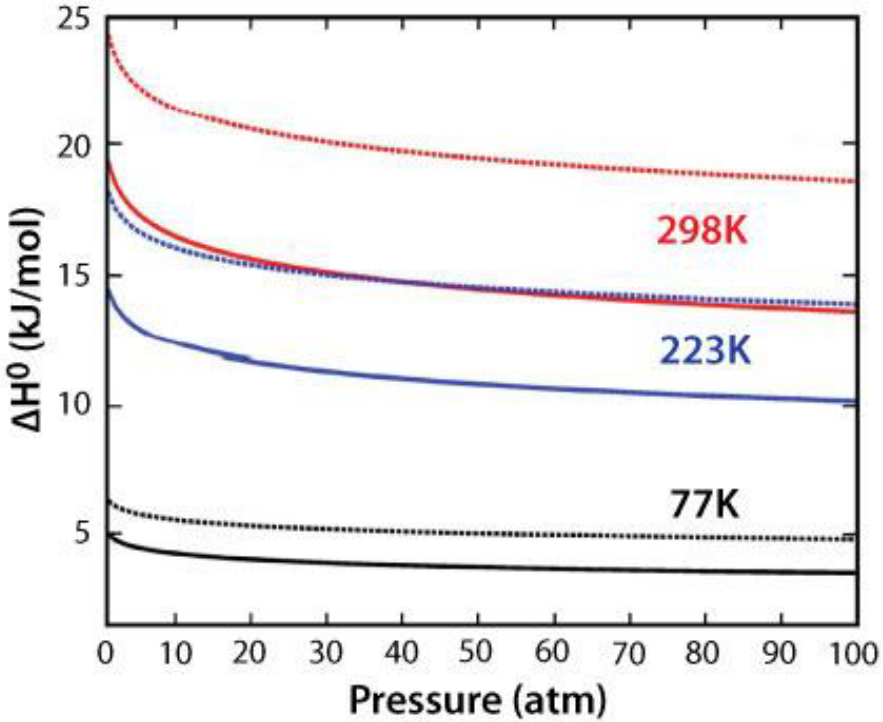
- **Porous Polymer Network (PPN) can offer high surface area (>4000 m^2/g)**
- **Polymers also offer good mechanical and thermal stability**
- **But low H_2 binding energy (<10 kJ/mol)**

Relevance: Optimal sorbent material

Binding Energy

Bhatia and Myers 2006

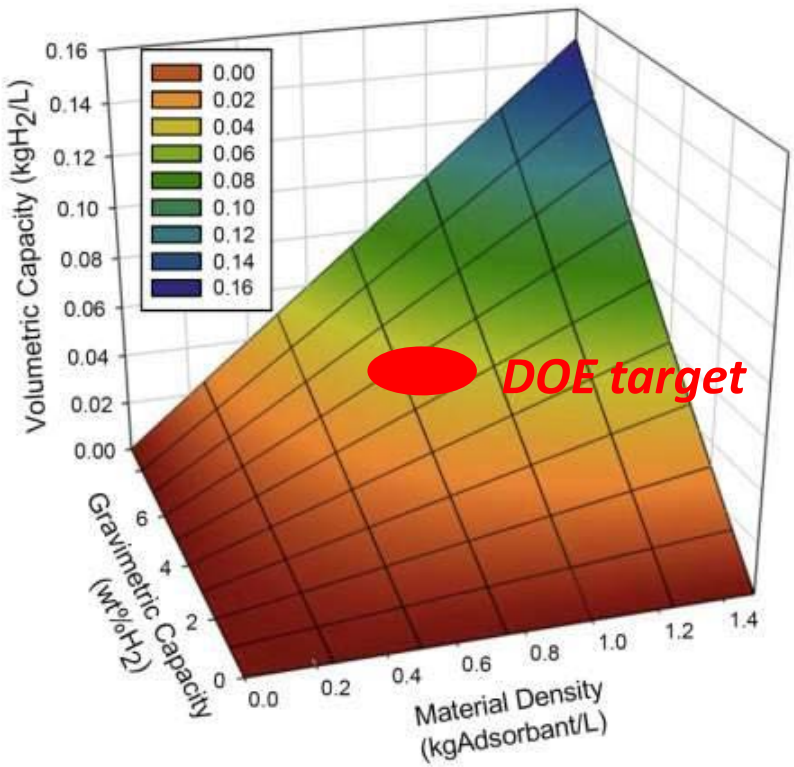
dotted lines ΔS=-10R
solid lines ΔS=-8R



ΔH: 15-25 kJ/mol

Bulk Density

Argonne National Laboratory



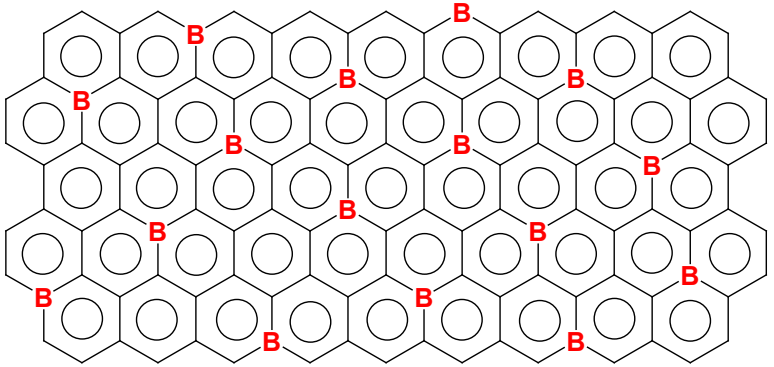
Bulk material density: >0.6 g/cm³

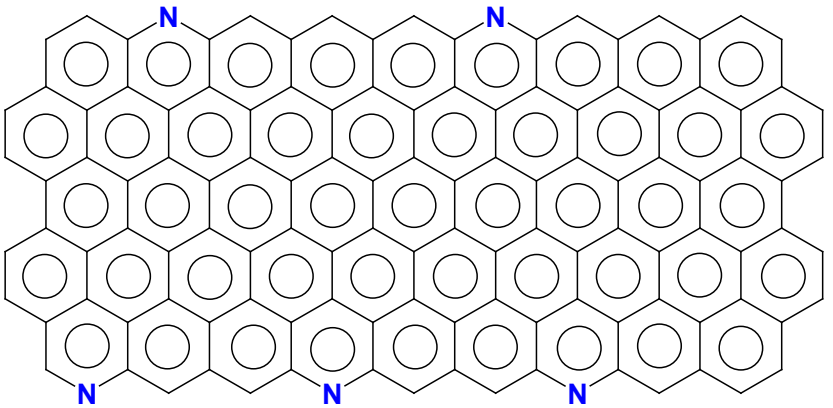
Practical H_2 storage at ambient temperature and pressure <100 bar

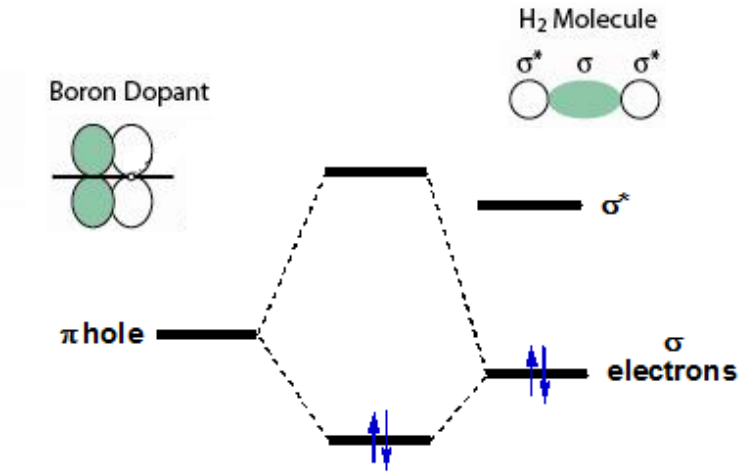
PENNSTATE

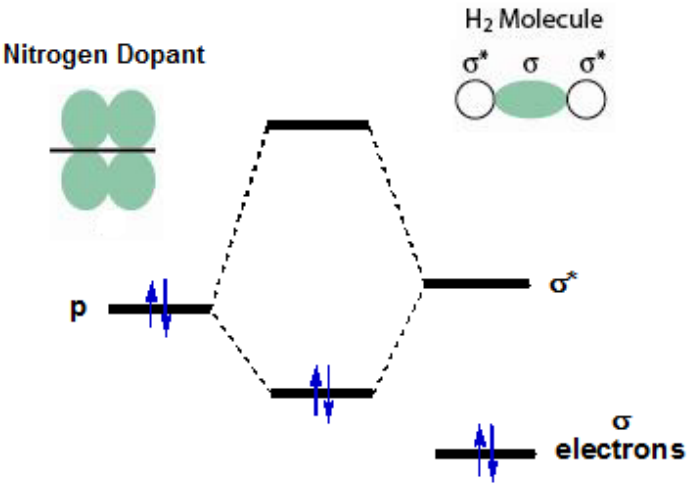
HyMARC

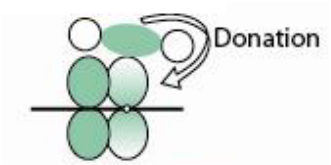
Relevance: Increase H_2 binding energy









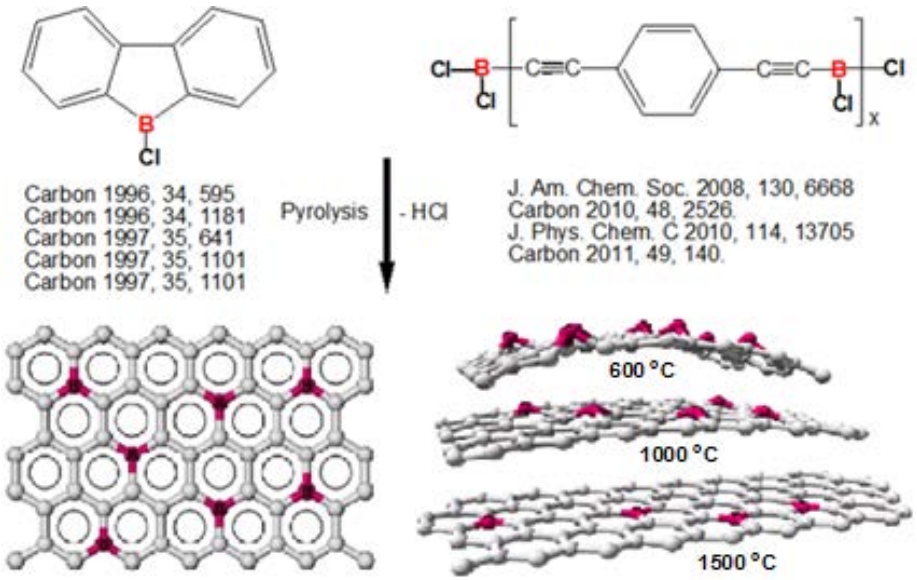


NREL led H_2 Sorption Center of Excellence (HSCoE) 2005-10

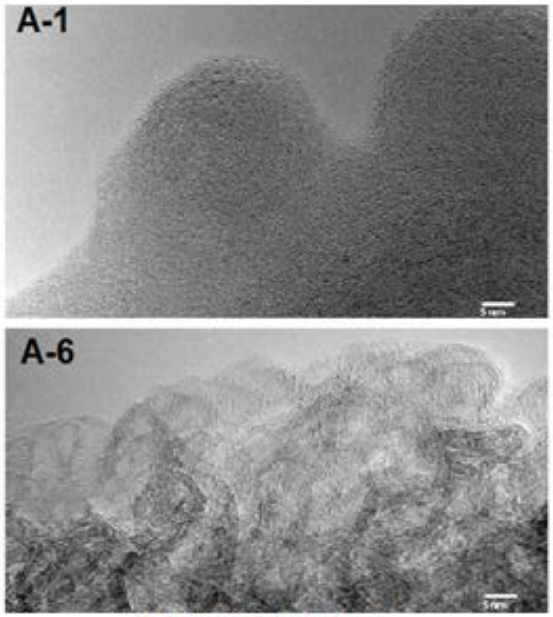
PENNSTATE

HyMARC

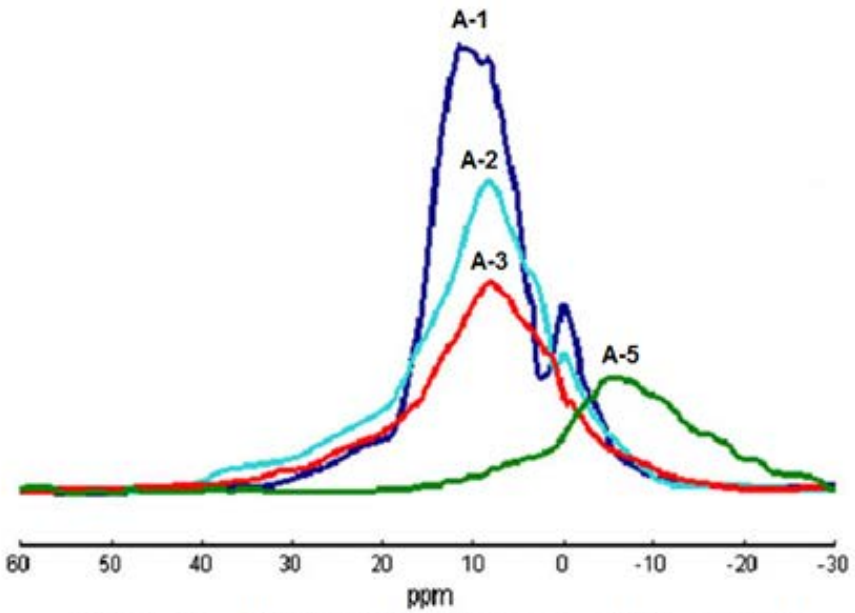
Relevance: Synthesis of BC_x by Precursors



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

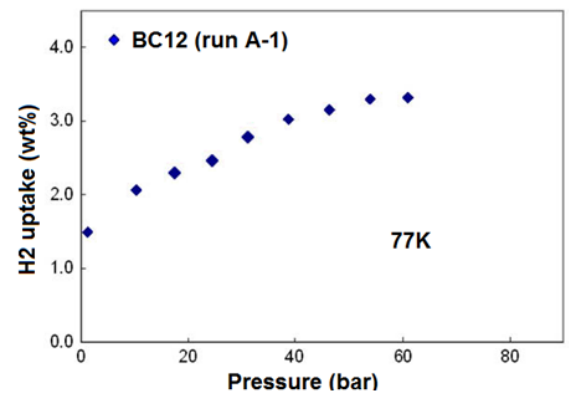


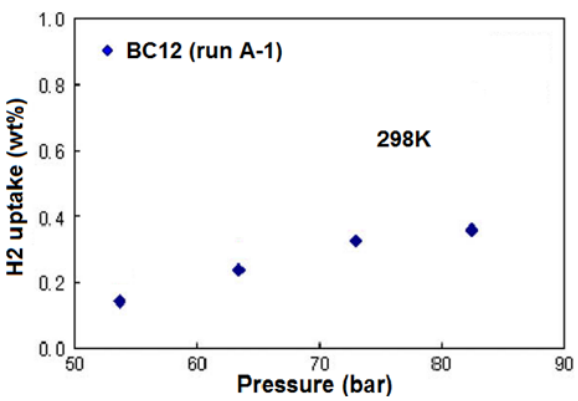
Solid state (MAS) 11B NMR spectra of BCx materials

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

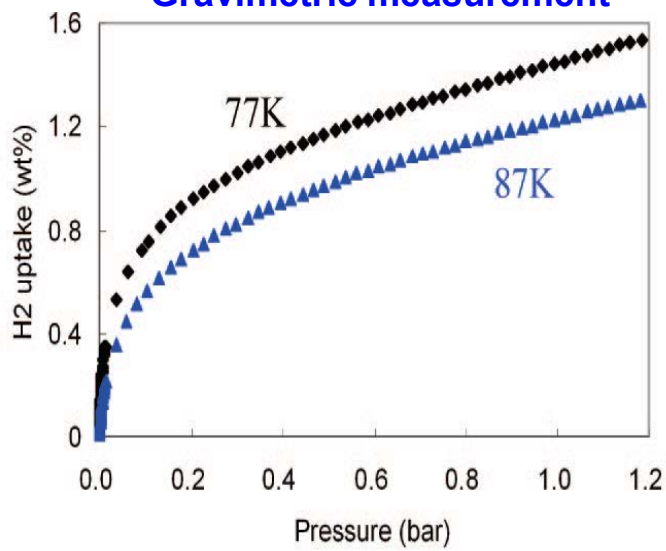
Volumetric measurement





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

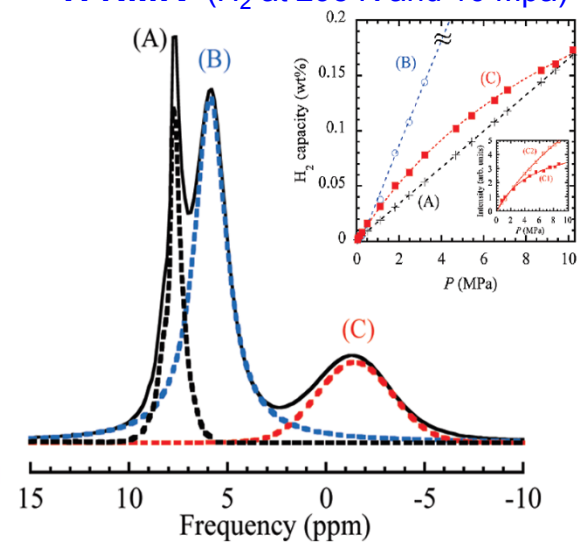
Gravimetric measurement



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

PENNSTATE

HyMARC

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.

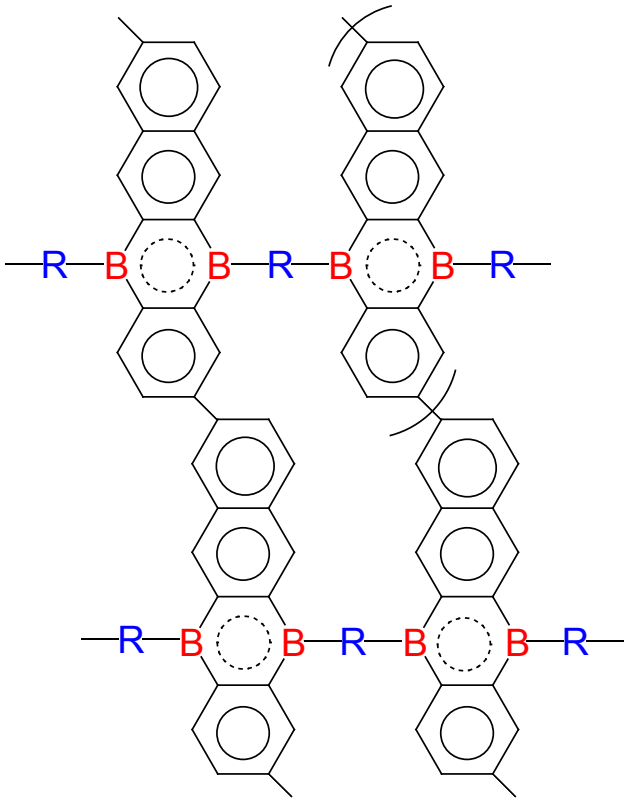
PENNSTATE

HyMARC

Approach: Two New B-containing Polymer Networks

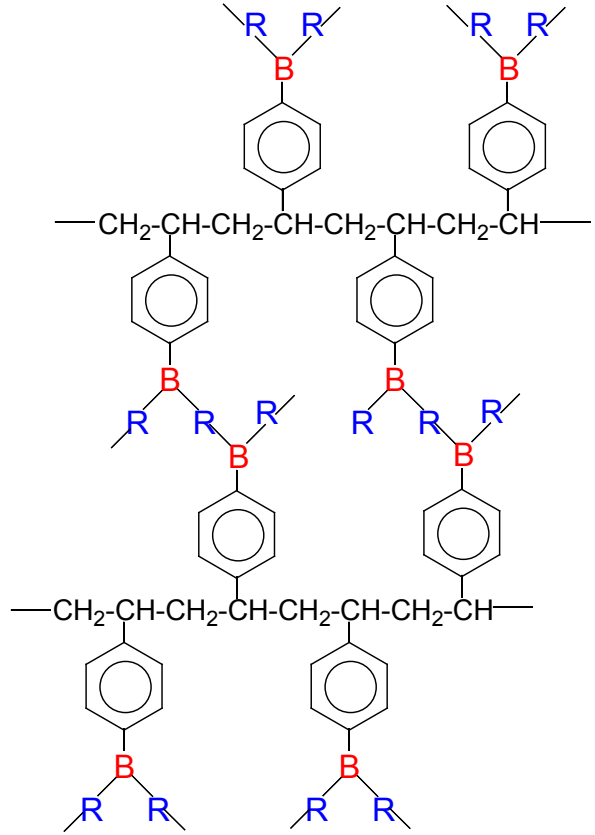
Condensation Mechanism

(A)

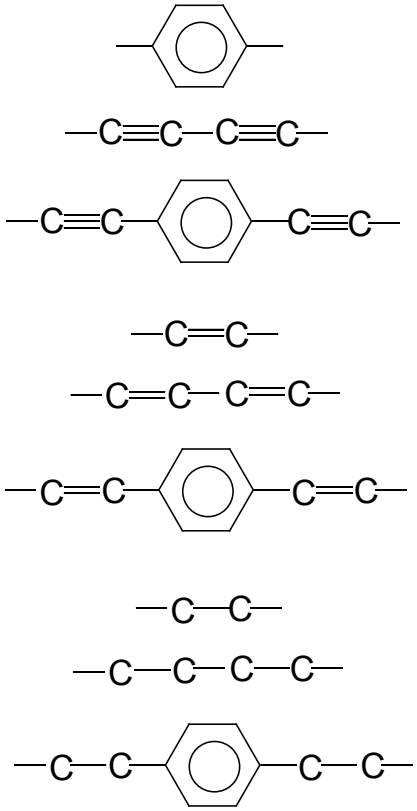


Addition Mechanism

(B)



R Spacers:

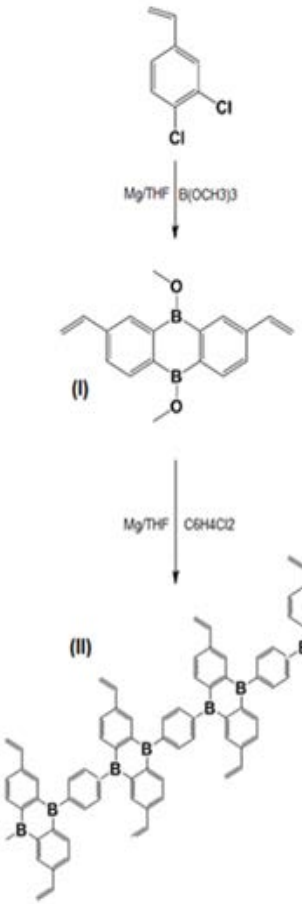


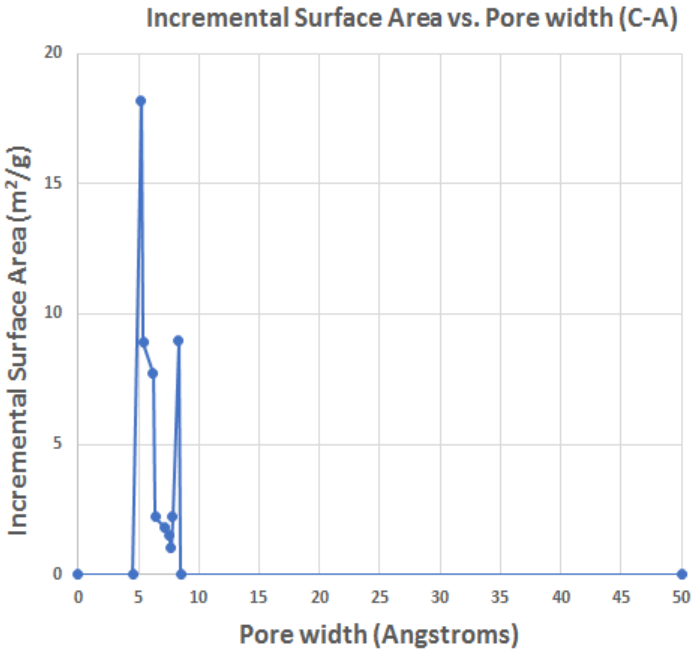
Organoborane moiety with suitable acidity (correlative ^{11}B chemical shift to H_2 binding energy)

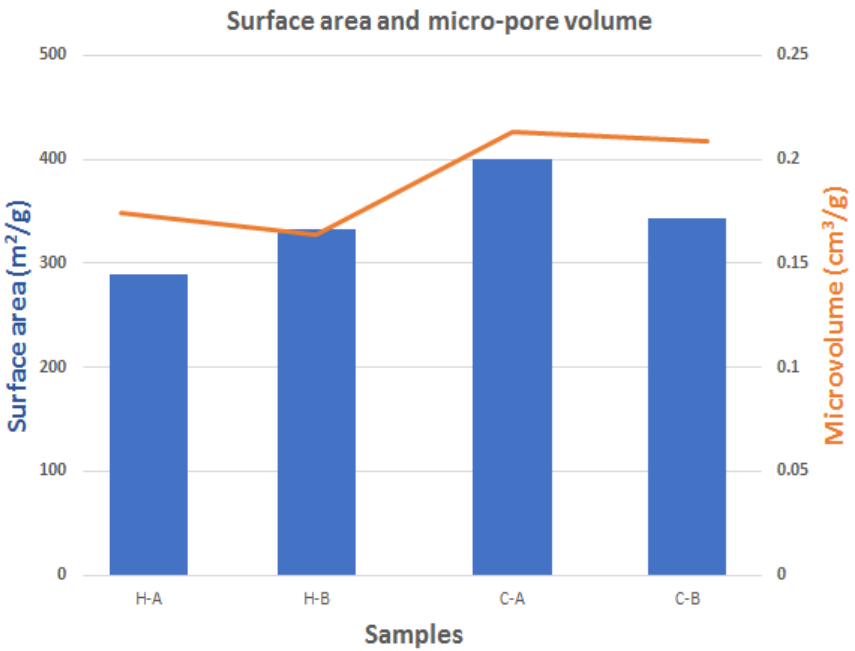
PENNSTATE

HyMARC

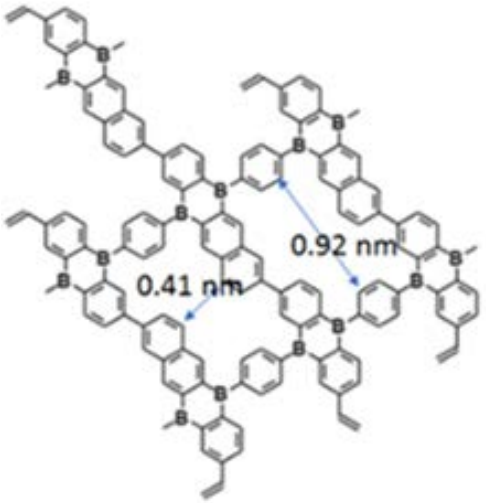
Accomplishments - Condensation mechanism; 2,6-divinyl-9,10-methoxyboraanthracene monomer

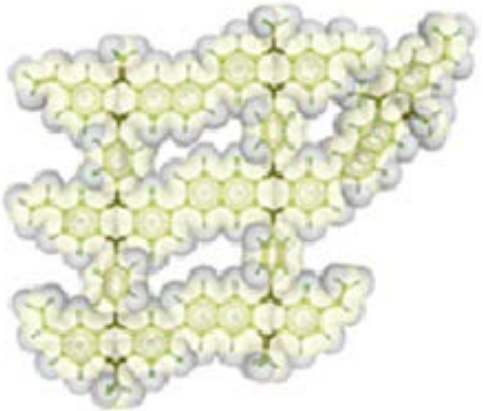






Bulk density= 0.95 g/cm³



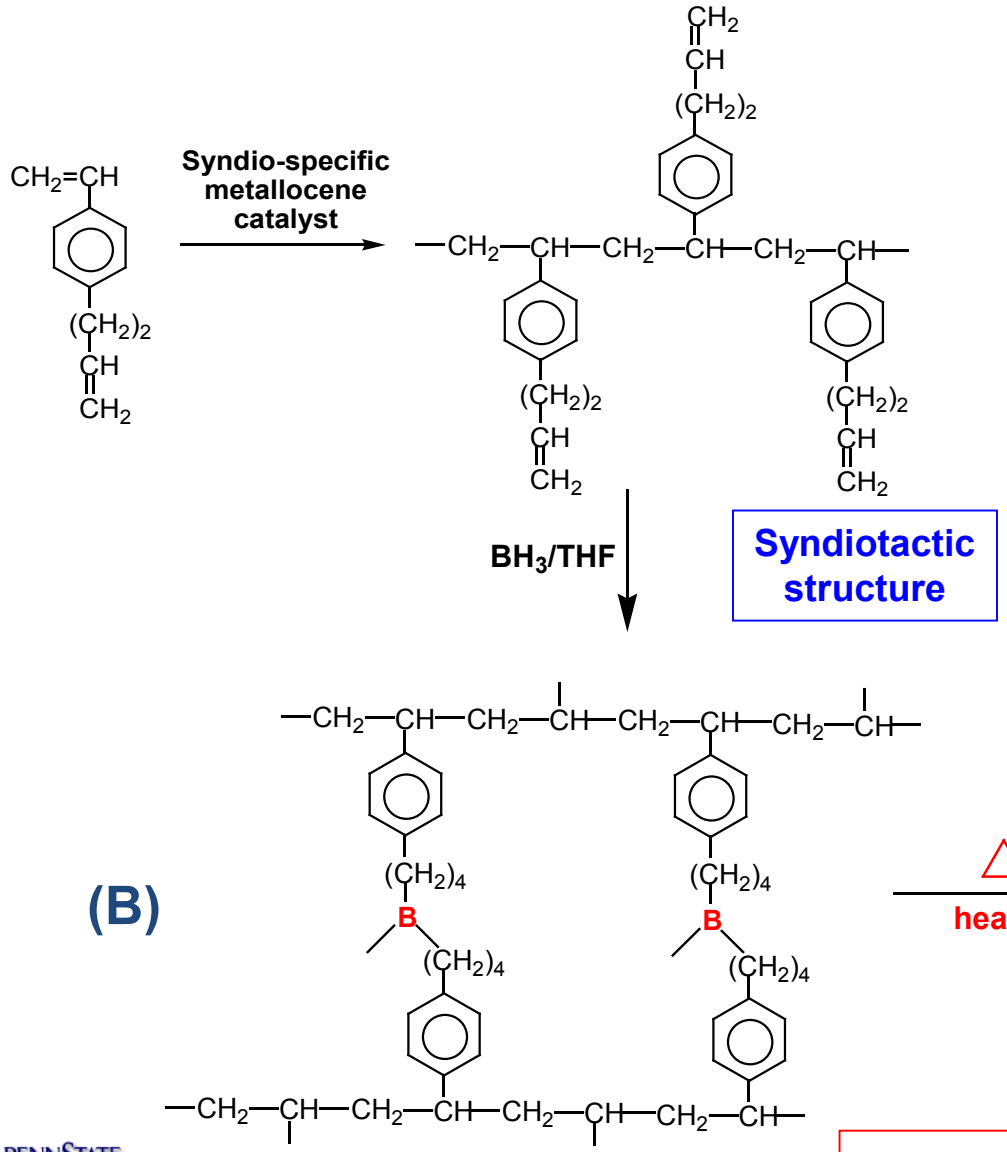


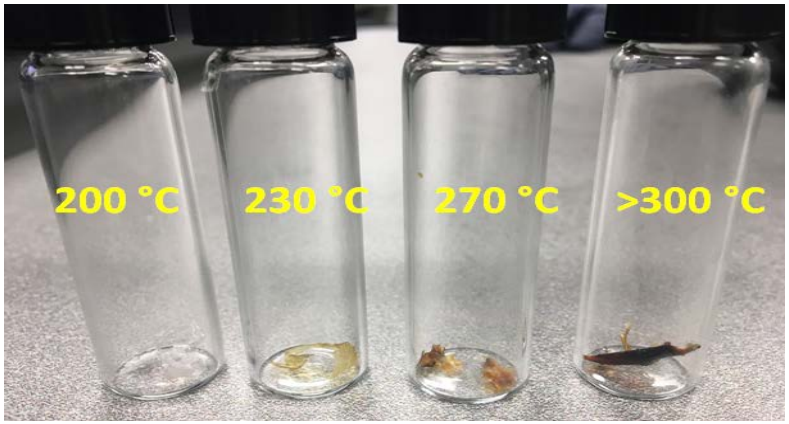
(A)

PENNSTATE

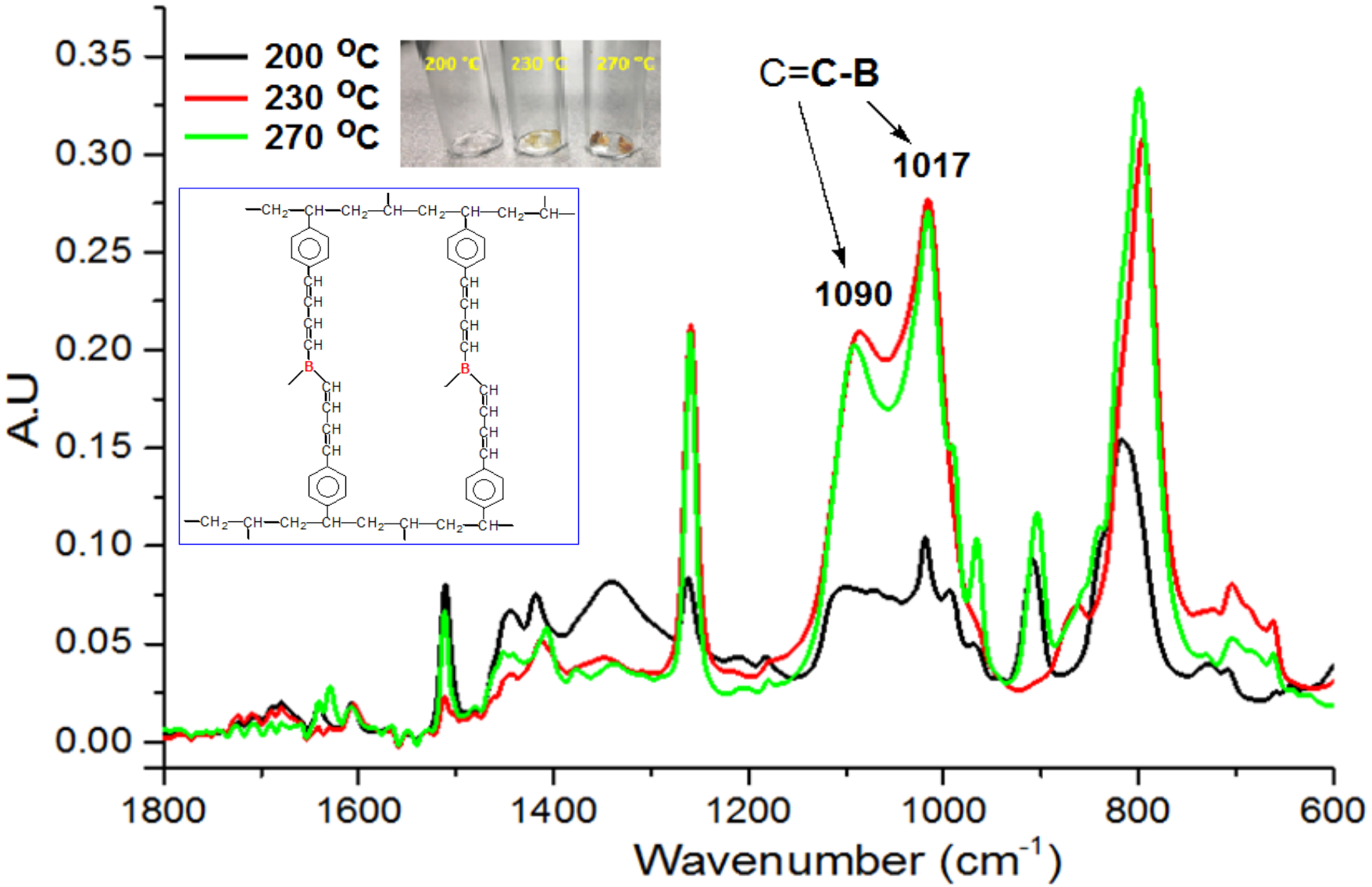
HyMARC

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





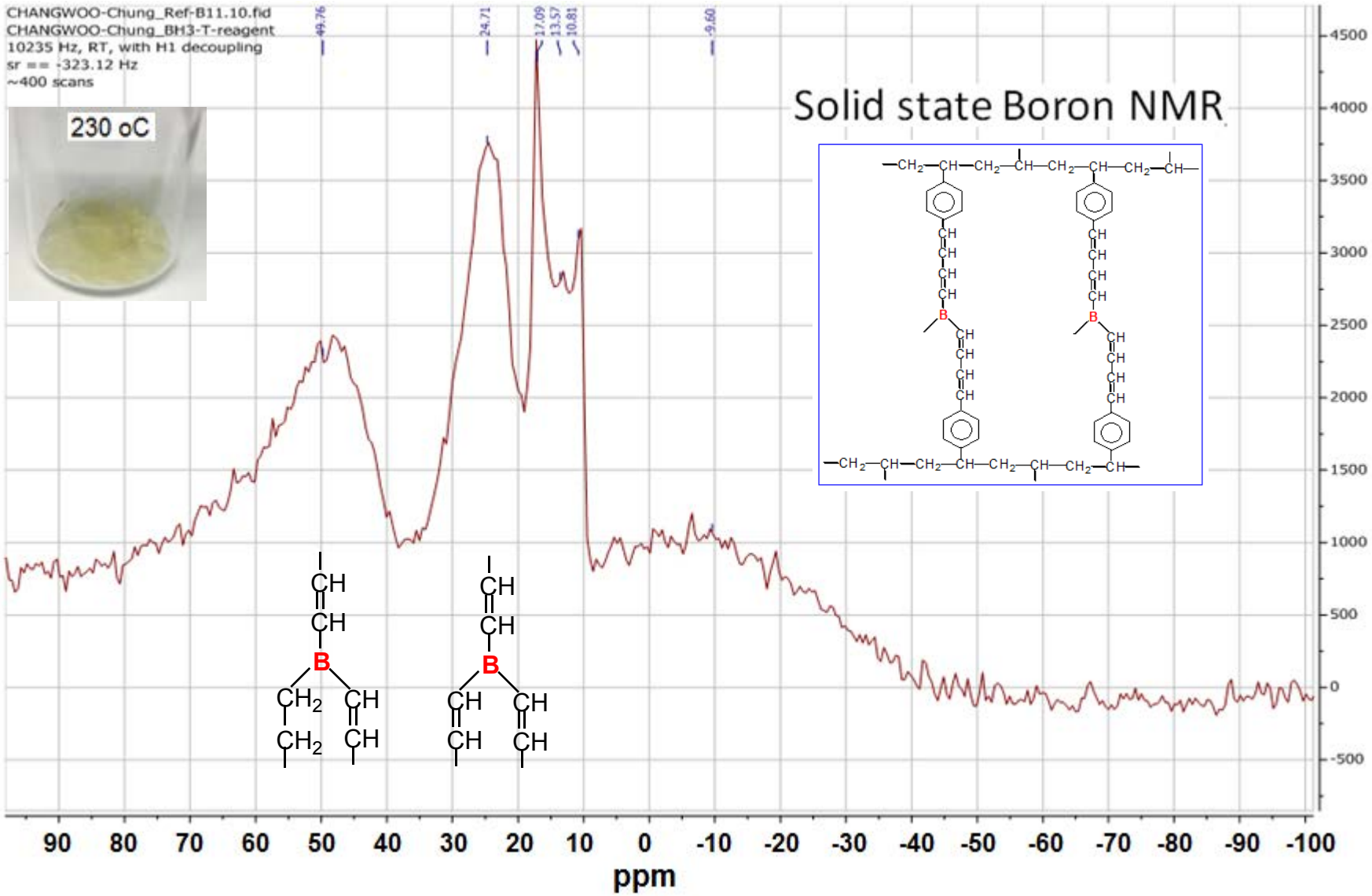
Accomplishments: FTIR spectrum of B-PBS polymer



PENNSTATE

HyMARC

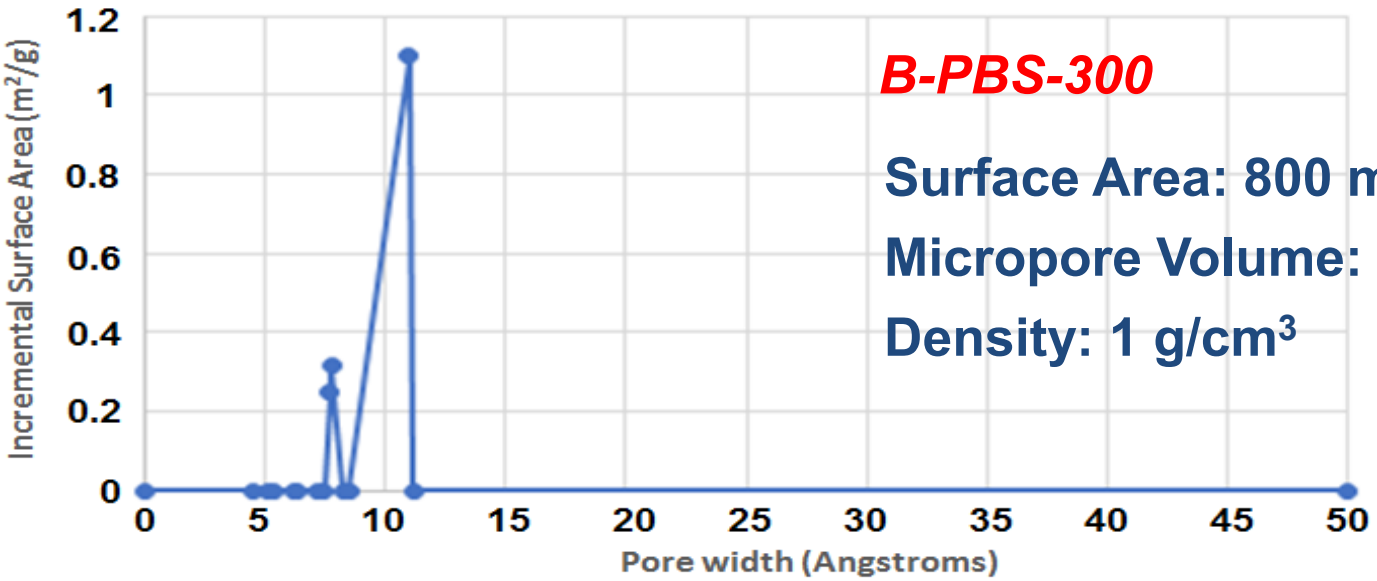
Accomplishments: MAS ^{11}B NMR spectrum of B-PBS polymer



PENNSTATE

HyMARC

Accomplishments: Pore Structure of B-PBS polymers

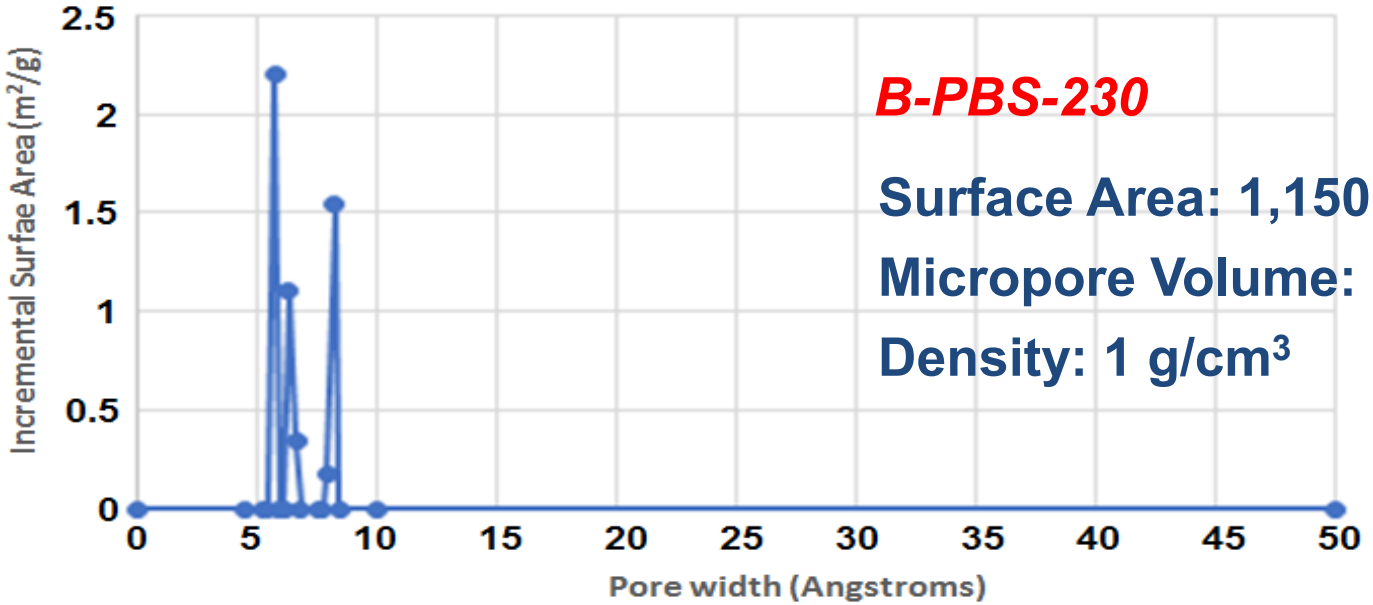


B-PBS-300

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

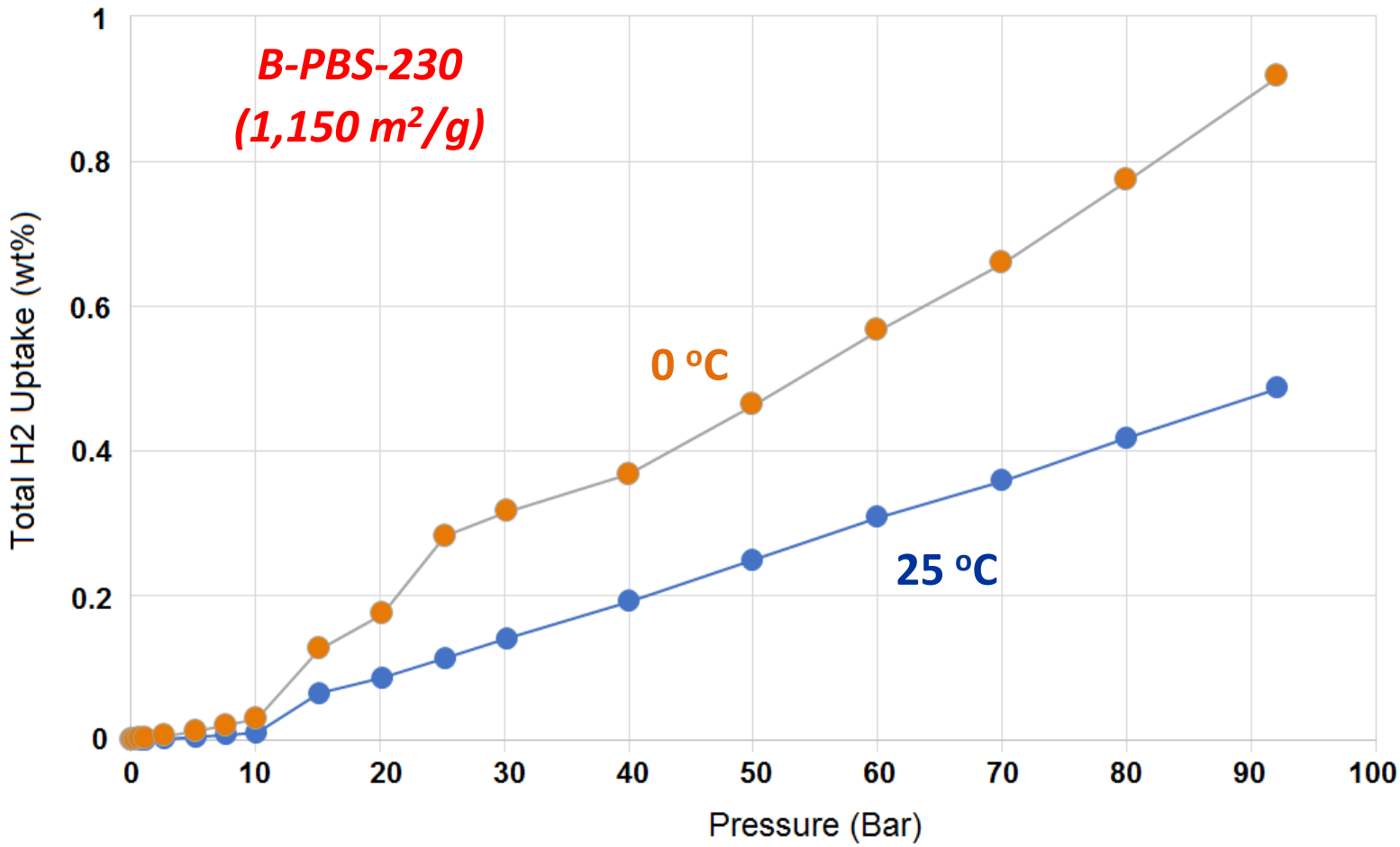
Micropore Volume: 0.75 cm^3/g

Density: 1 g/cm^3

PENNSTATE

HyMARC

Accomplishments: H_2 Adsorption Isotherm



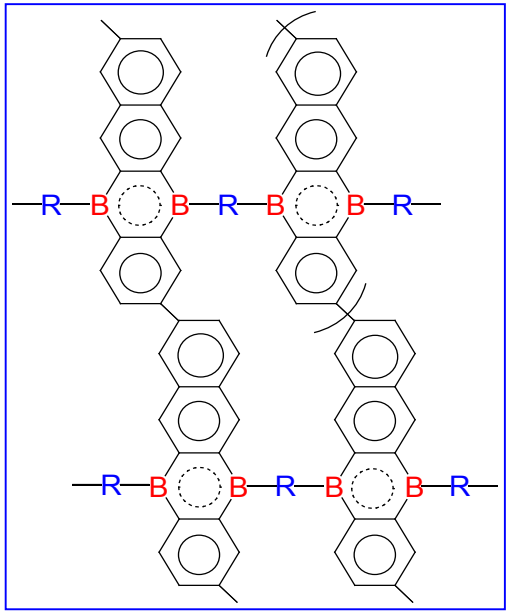
H_2 adsorption was measured at Sandia National Labs (Dr. Vitalie Stavila)

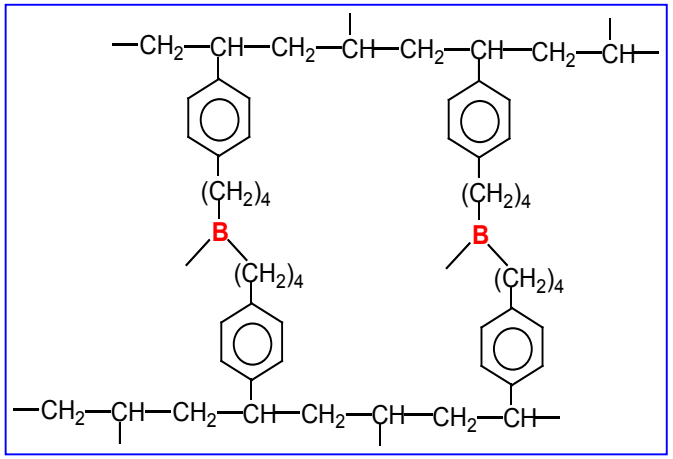
PENNSTATE

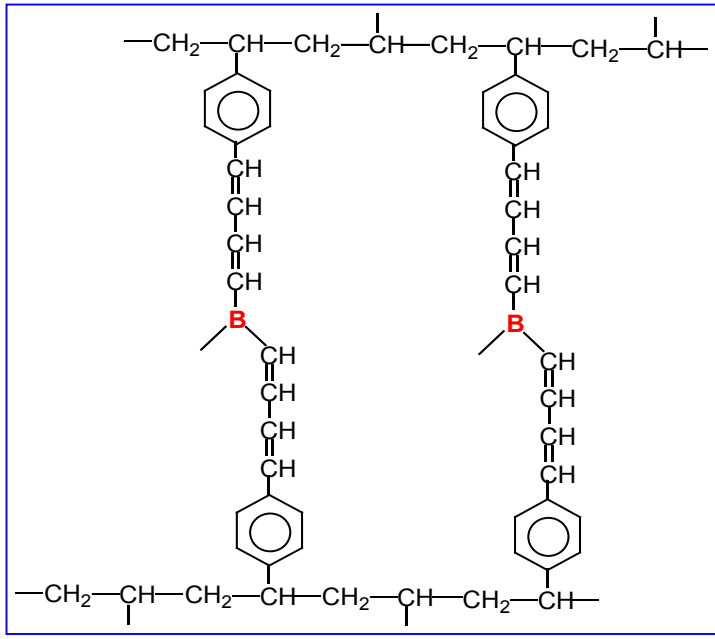
HyMARC

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.**





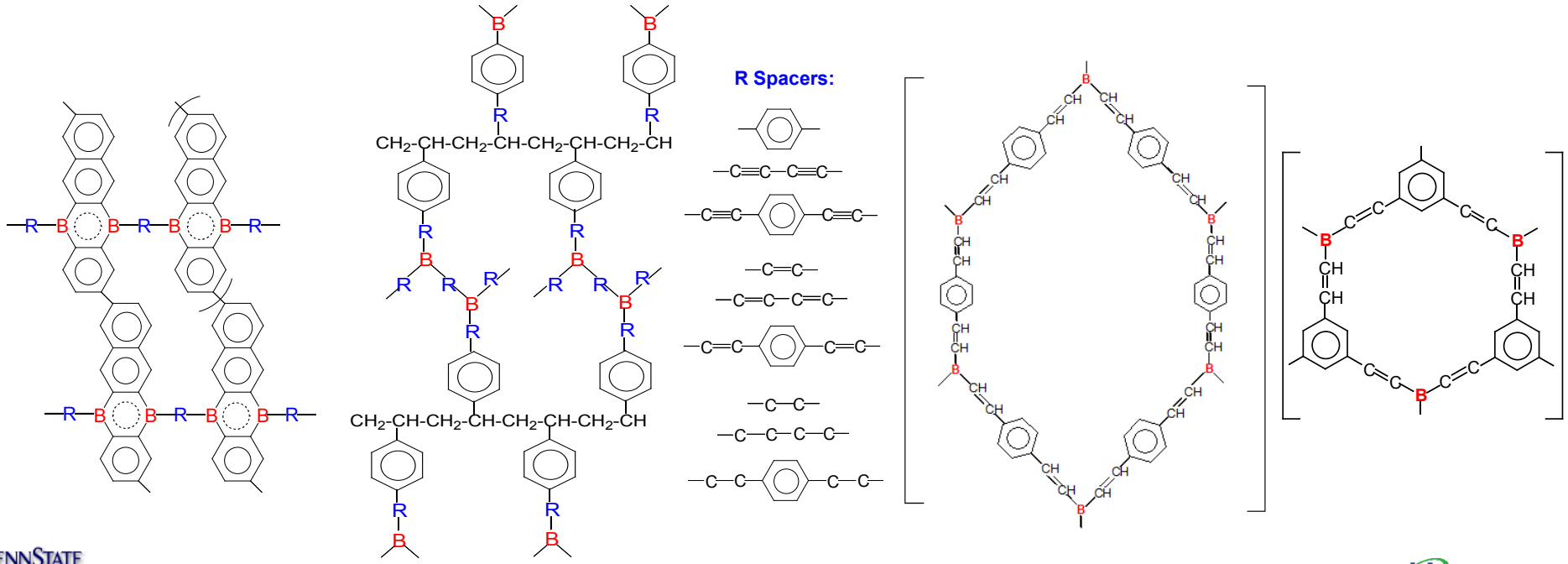


PENNSTATE

HyMARC

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.**



PENNSTATE

HyMARC

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.

PENNSTATE

HyMARC