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DOE Hydrogen Program

Hydrogen Storage through Nanostructured Polymeric Materials

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DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Arlington VA

June 11, 2008

Project ID ST21

Overview

DOE Hydrogen Program

Timeline

- Project start: July 2007
- Project end: June 2012
- % complete: 20%

Barriers

- Barriers addressed
  - A. System Weight and Volume
  - B. System cost
  - C. Efficiency
  - D. Durability/Operability

Budget

- Total project funding: $2 Million
  - DOE share: $1.88 Million
  - Contractor share: $120 K
- Funding received in FY07
  - $ 200 K
- Funding for FY08
  - $ 616 K

Partners

- Interactions/collaborations
  - U of Chicago
  - DOE HSCoE Members
  - NREL
  - N. Carolina U.
  - Others

Objective

DOE Hydrogen Program

- **To design, synthesize, and evaluate nanostructured polymeric materials (NPM) as new hydrogen storage adsorbents for transportation applications**
- **To support polymer materials development with modeling/simulation and advanced structural characterizations**

Potential Advantages of Polymeric H_2 Adsorbent

- **Polymer surface properties such as specific surface area and porosity can be controlled at molecular level**
- **Polymer-hydrogen can be enhanced through incorporating different functional groups and atomically dispersed metals**
- **Polymers are generally stable under the temperature and humidity required for hydrogen storage application**
- **Polymer can be scaled-up for production with existing industrial infrastructure**

Selected Literature Reports on Polymeric H_2 Adsorbent

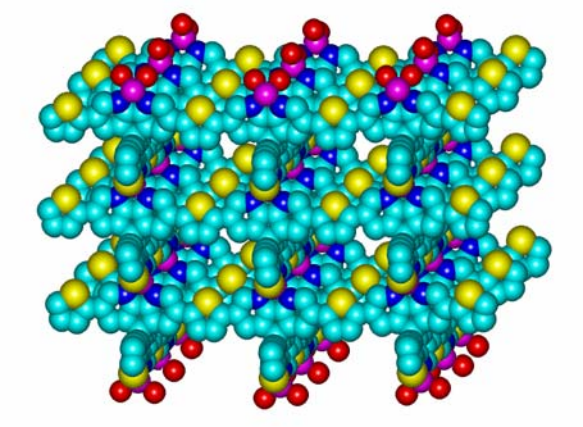
- Cho *et. al. Catal. Today*, **2007** - polyaniline and polypyrrole
- McKeown, *et. al. Angew. Chem. Int. Ed.* **2006** - polymers with intrinsic porosity (PIMs)
- Wood, *et. al. Chem Mater*. **2007** - hypercrosslinked polymers

Approach

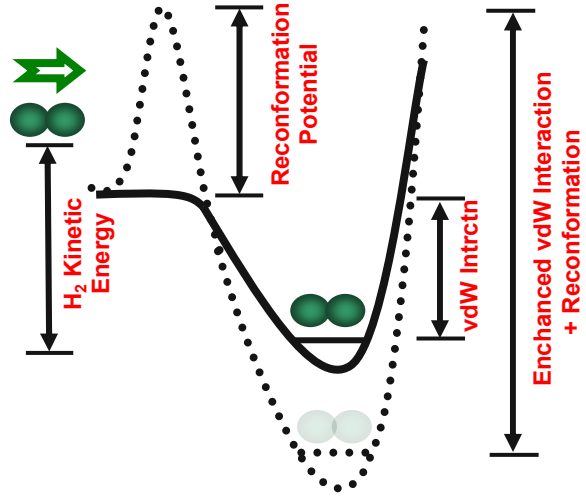
DOE Hydrogen Program

Argonne/U of Chicago Approach to Polymer Design

- We will produce high surface area & narrow pore size through stereo-contorted polymer design
- We will incorporate "metallic" feature to polymer through conductive backbone
- We will improve polymer-H_2 interaction with by Introducing coordinated metal elements and various functional groups through synthetic approach
- We will explore the feasibility of "trapping" hydrogen through semi-rigid framework



An example of ANL/UofC polymer with conductive backbone incorporated with different elements

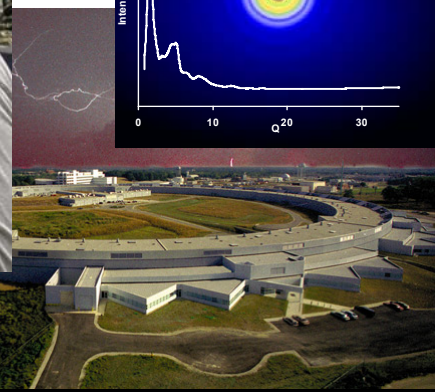


Control surface property and the interaction with hydrogen through design & synthesis at the molecular level!

Approach

DOE Hydrogen Program

New Polymer Exploration (UofC)	Characterization & Optimization (ANL)	Modeling & Simulation (ANL)
■ New polymer synthesis through rational design at molecular level ■ Molecular structure characterization	■ H_2 storage capacity measurement ■ Surface structure characterization ■ Synthesis method improvement	■ H_2-polymer interaction study via *ab initio*, DFTB & MD methods ■ Advanced X-ray characterization



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Progress Summary

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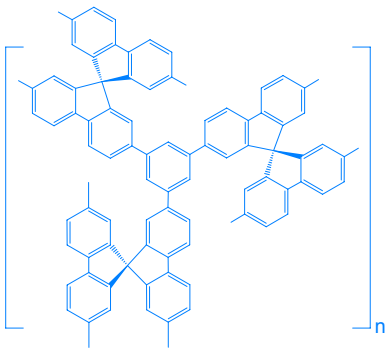
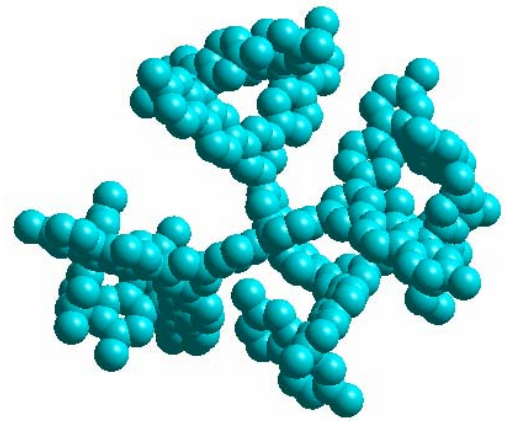
- Three series of porous polymers based on our design principles were successfully synthesized. Two groups showed promising surface properties (U of Chicago)
- Specific surface area and porosity of 11 polymer samples were measured, some of which showed high SSA and narrow pore distribution (Argonne)
- Upgrade of Sievert isotherm apparatus and analysis method were completed. System is now used for high pressure (up to ~75 bar) measurement (Argonne)
- Hydrogen uptake of several polymers were measured at both RT and 77K with pressure up to 75 bars. A carbon molecular sieve (CMS) material was also investigated as the reference material (Argonne)
- Theoretical modeling/simulation study was initiated (Argonne)

Progress – Design & Synthesis of Porous Conjugated Polymers

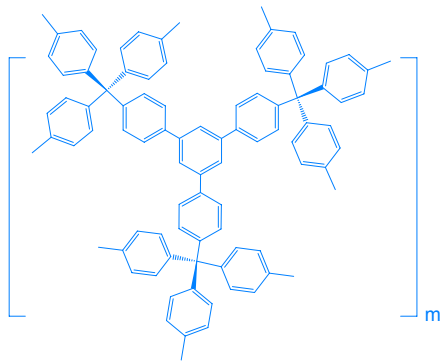
DOE Hydrogen Program

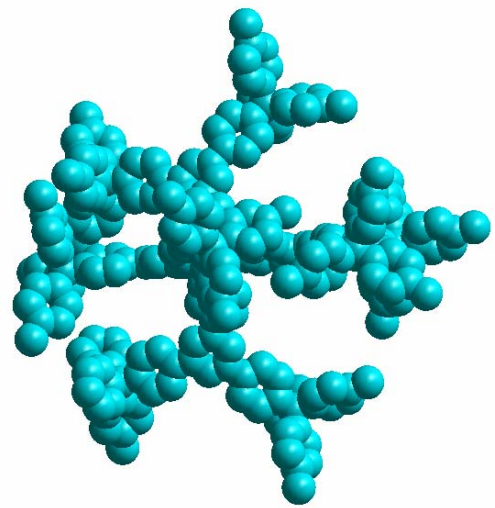
- Seven porous polymers with conjugated aromatic planes were designed and synthesized
- Porosity was created and controlled through cross-linking of monomers with different stereo-contorted structures
- Polymer samples have demonstrated good surface properties and high stability towards heat and moisture





PC1



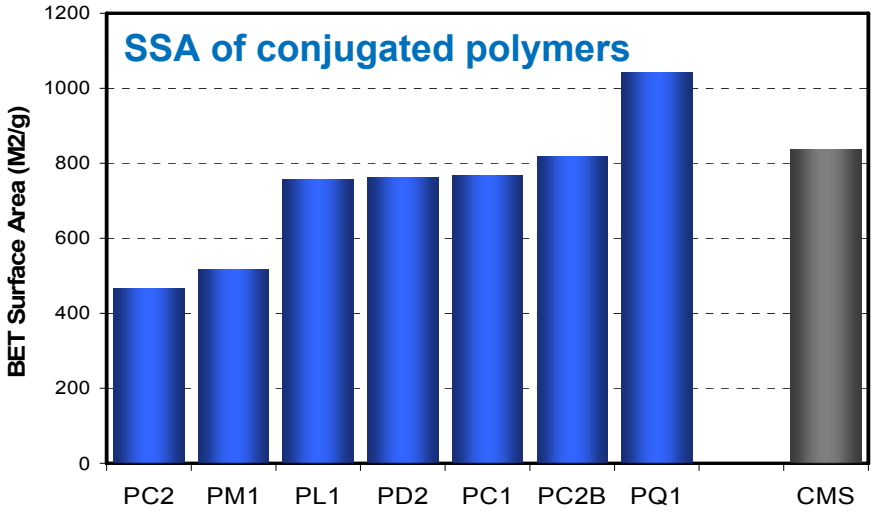


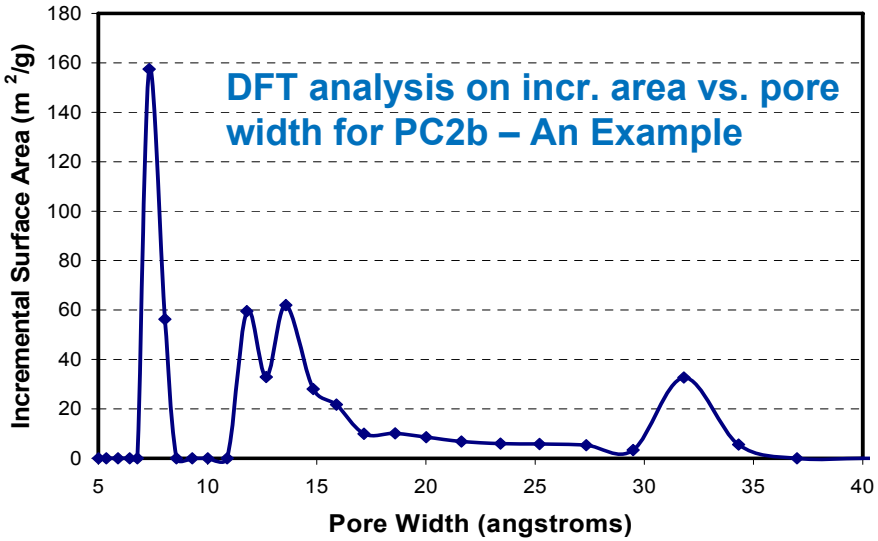
PD2

Proposed Structures of the Selected Examples

Progress – Surface Property Characterization for Conjugated Porous Polymers

DOE Hydrogen Program





N_2-BET Surface Characterization

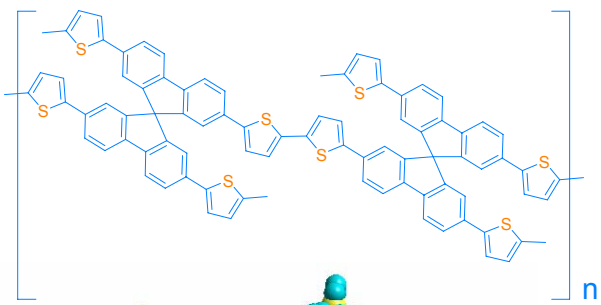
	BET Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Median Pore Diameter (nm)	Density (g/cm^3)
PC2	468	0.265	0.76	0.66
PD2	762	0.425	0.64	0.39
PC1	769	0.427	0.62	0.66
PC2b	818	0.498	0.66	0.66
PQ1	1043	---	---	0.38
PM1	517	---	---	0.42
PL1	758	---	---	0.46
CMS	837	0.423	0.47	0.9

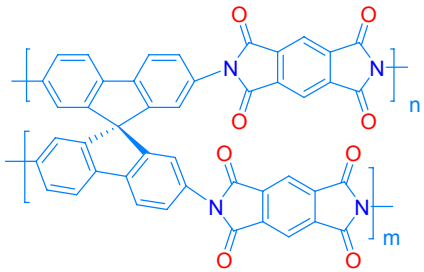
Relatively high surface area and narrow pore distribution can be achieved through rational polymer design. Further improvement is still necessary.

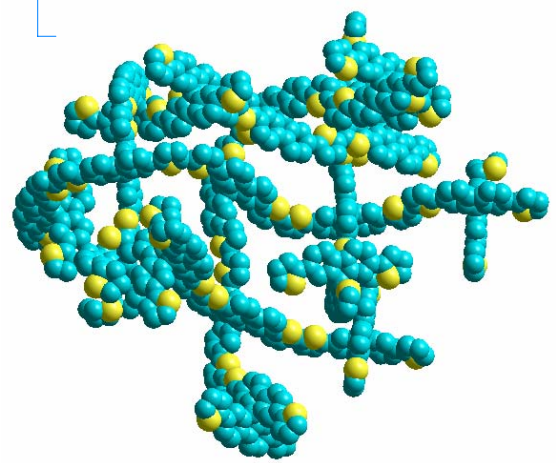
Progress – Design & Synthesis of Polymers with Conductive & Polyimide Backbones

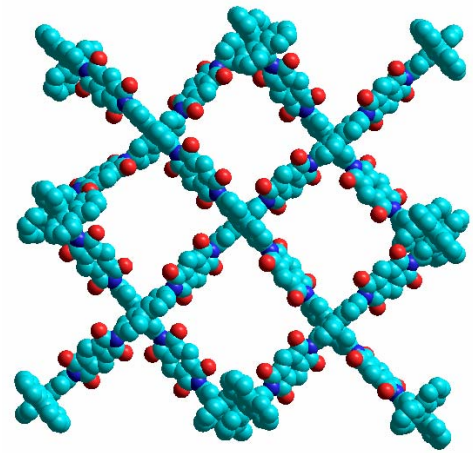
DOE Hydrogen Program

- Five porous polymers with conductive or polyimide backbones were designed and synthesized with the goal of enhancing hydrogen-functional group interaction
- Polymers prepared with spiral core linked by thiophene and bi-thiophene groups demonstrated relatively high surface area and promising pore size distribution
- The surface property of the polymers with imide group were mixed









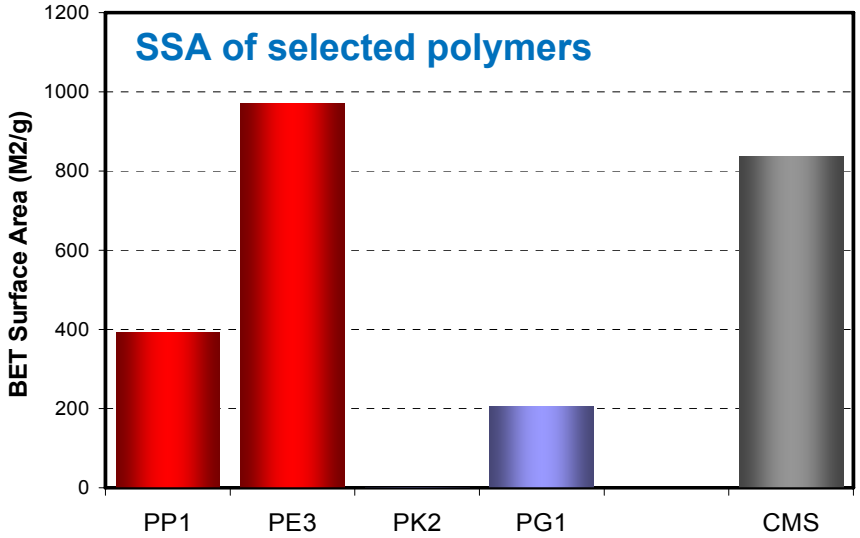
PE3

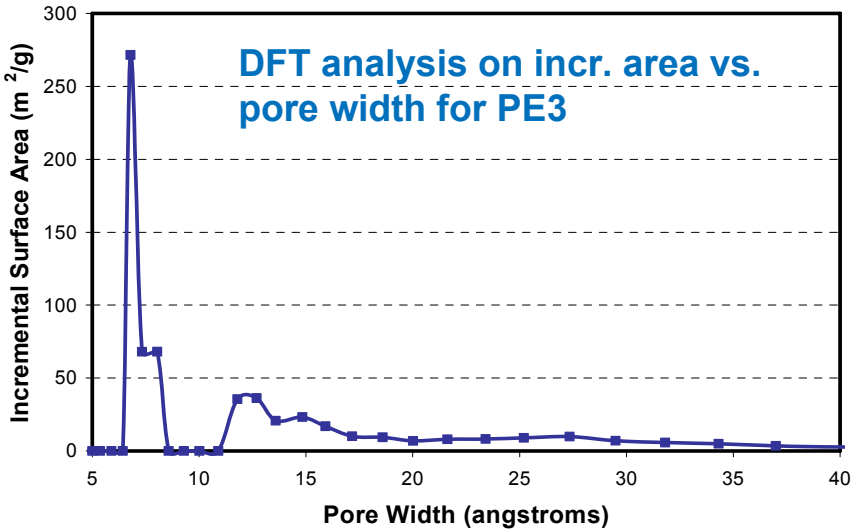
PG1

Proposed Structures of Selected Polymers

Progress – Surface Property Characterization for Polymers Crosslinked with Conductive & Polyimide Backbones

DOE Hydrogen Program





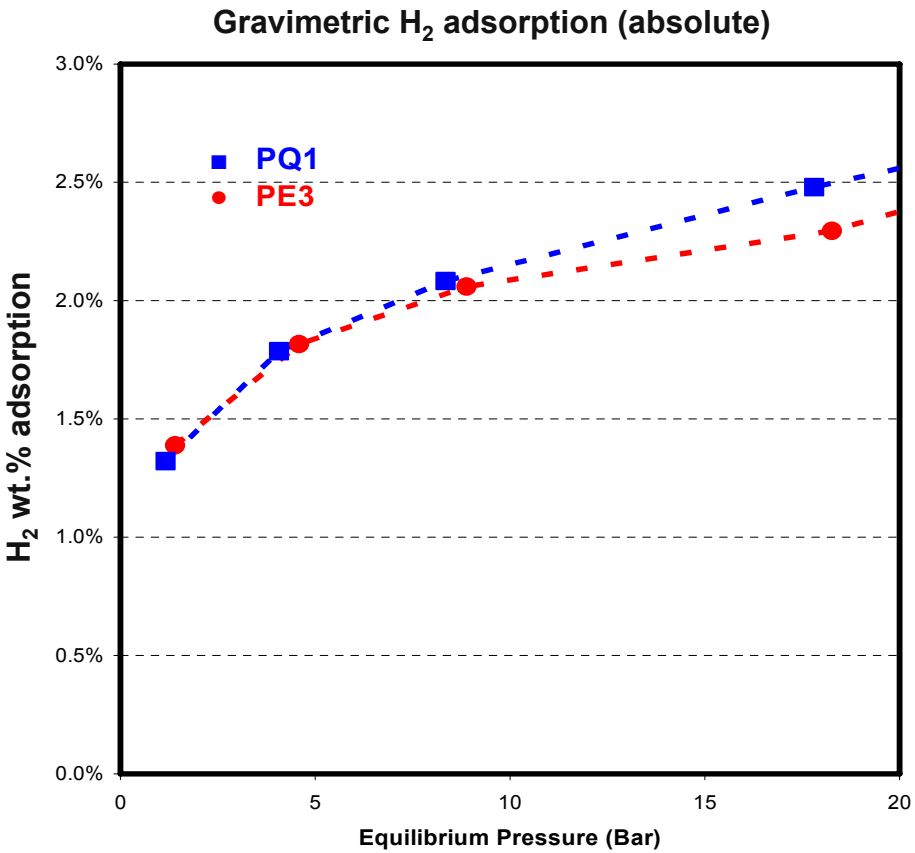
N_2-BET Surface Characterization

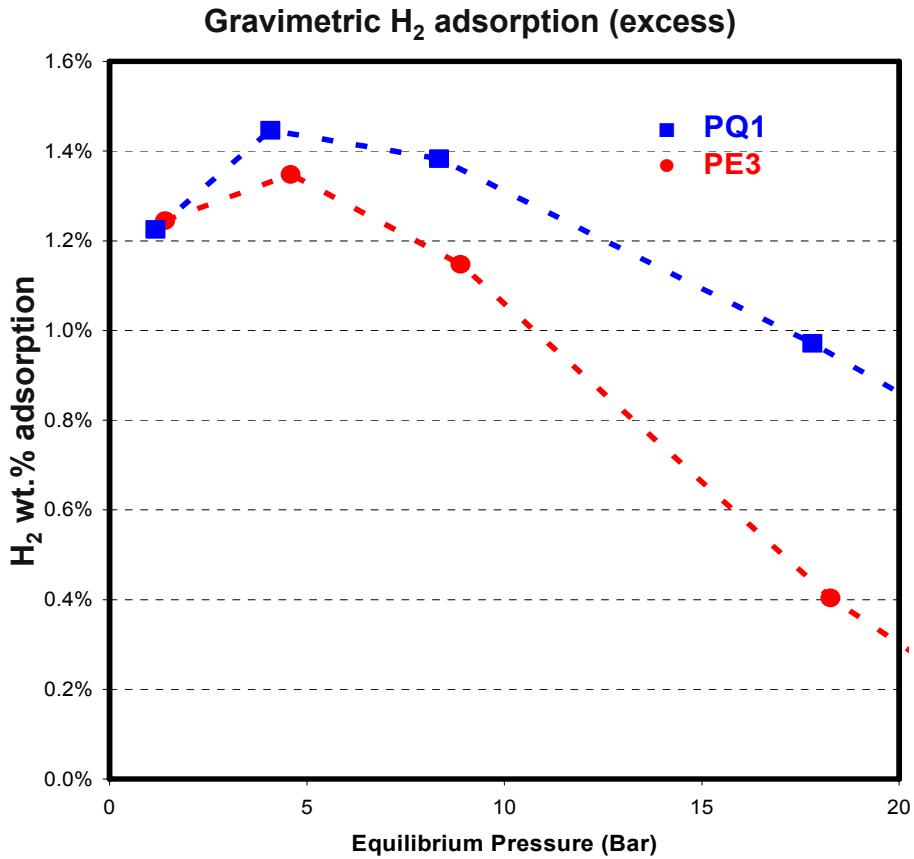
	BET Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Median Pore Diameter (nm)	Density (g/cm^3)
PE3	971	0.575	0.62	0.30
PP1	393	--	--	0.19
PK2	2.1	--	--	0.55
PG1	206	--	--	0.42
CMS	837	0.423	0.47	0.9

The synthesis condition has strong influence on the polymer structures during the condensation reaction

Progress – H_2 Uptake Capacity Measurement at Liquid Nitrogen Temperature

DOE Hydrogen Program





Hydrogen uptake over the polymer surface at 77 K generally follows Langmuir isotherm

Progress – H_2 Uptake Capacity Measurement at Liquid Nitrogen Temperature

DOE Hydrogen Program

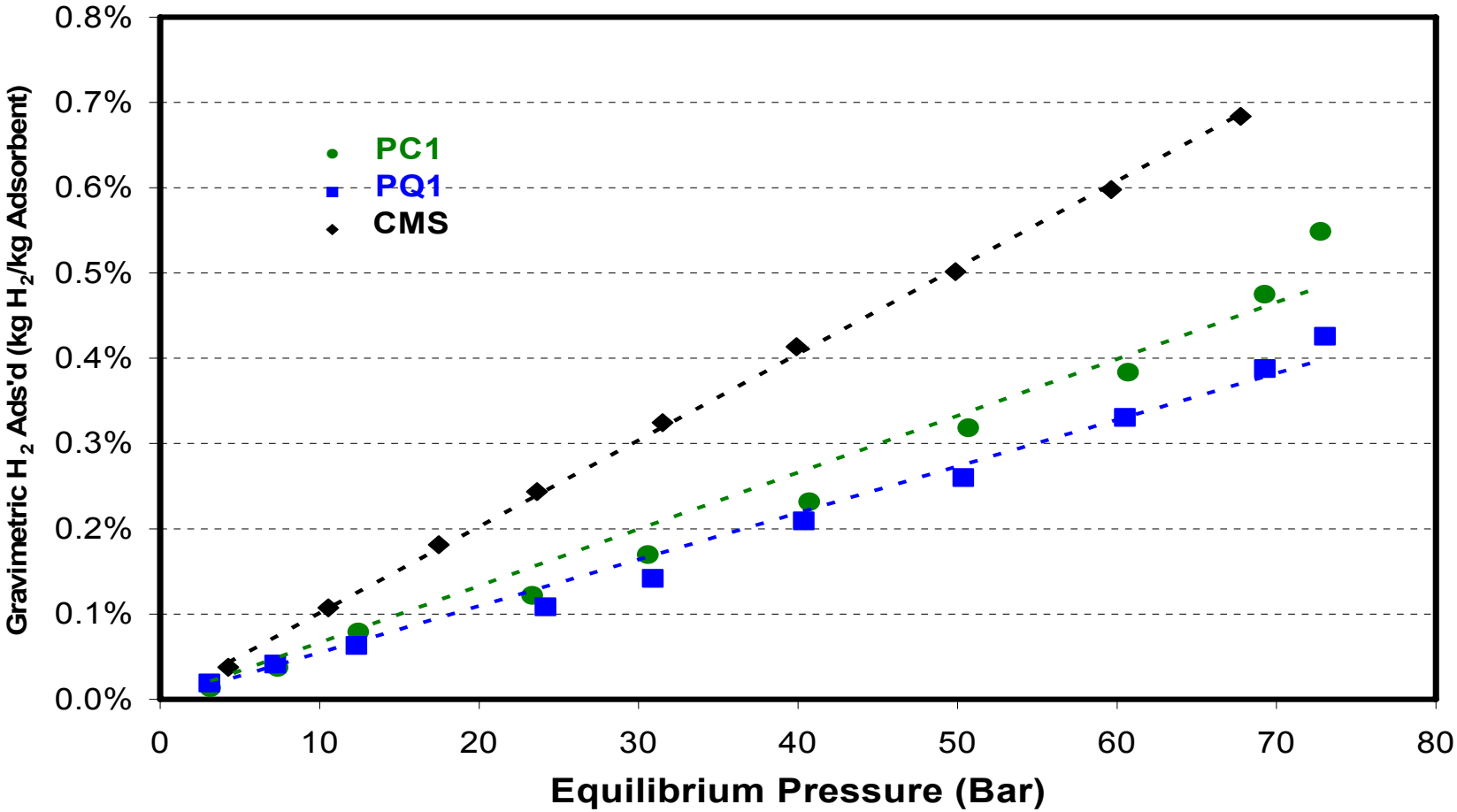
Sample	Gr. Uptake (Absolute)* (kg H_2/kg adsorbent+H_{2ads})	Vol. Uptake (Absolute) (kg H_2/L adsorbent)	Gr. Uptake (Excess) (kg H_2/kg adsorbent+H_{2ads})	Vol. Uptake (Excess) (kg H_2/L adsorbent)	BET SSA (M^2/g)	Modified Chahine Factor
PQ1	2.1%	0.0080	1.4%	0.0053	1043	1.00
PC1	1.7%	0.011	1.2%	0.0079	769	1.11
PD2	1.2%	0.0047	0.5%	0.0020	762	0.77
PE3	2.1%	0.0063	1.2%	0.0036	971	1.06

*** Values in the table represent the measurement taken at a hydrogen pressure of ~ 7 bar**

- Absolute capacities are generally proportional to surface area at 77 K.
- Excess capacities diminish when the storage pressure exceeds 20 bar; significant improvement in adsorption uptake is necessary.

Progress – H_2 Uptake Capacity Measurement at Ambient Temperature

DOE Hydrogen Program



In contrast to CMS, H_2 uptakes of polymers deviate from linear increase as the function of pressure, suggesting a different H_2/adsorbent interaction.

Progress – H_2 Uptake Capacity Measurement at Ambient Temperature

DOE Hydrogen Program

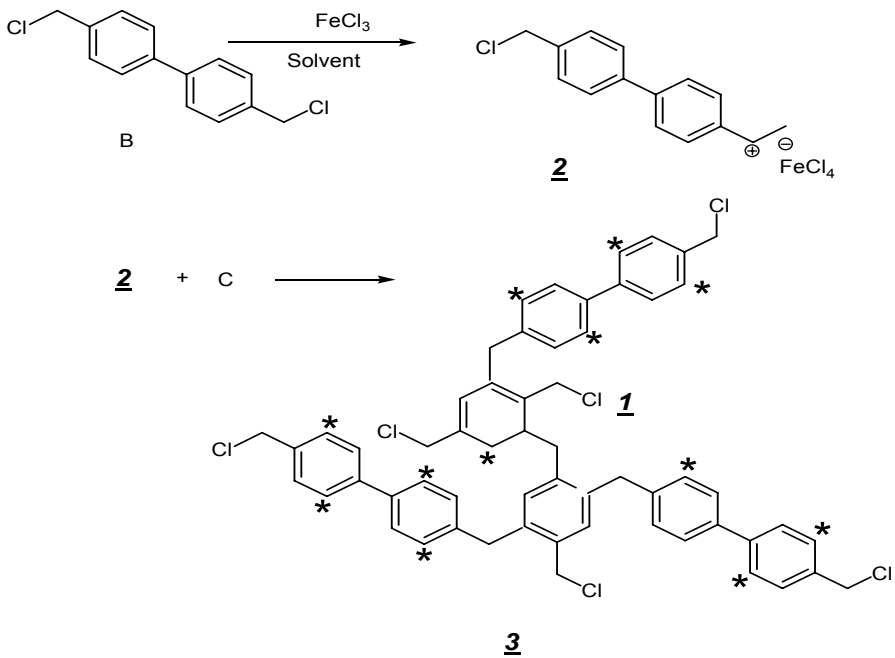
Sample	Sample Mass Tested (gram)	H_2 Gravimetric Uptake @ ~70 Bar ($kg\ H_2/kg\ adsorbent+H_{2ads}$)	H_2 Volumetric Uptake @ ~70 Bar ($kg\ H_2/kg\ adsorbent+H_{2ads}$)
PQ1	0.360	0.43%	0.0016
PC1	0.220	0.55%	0.0036
PD2	0.192	0.66%	0.0026
PE3	0.239	0.45%	0.0014
CMS	0.430	0.54%	0.0049

- No clear correlation between H_2 uptake and surface area is observed
- Major improvements in capacities are necessary to reach the targets

Progress – Investigation of Polymers from Literature

DOE Hydrogen Program

- Three polymer samples were prepared according to literature reports
- High yield was achieved through our modified synthesis process
- Surface characterization and hydrogen storage capacity measurement are underway



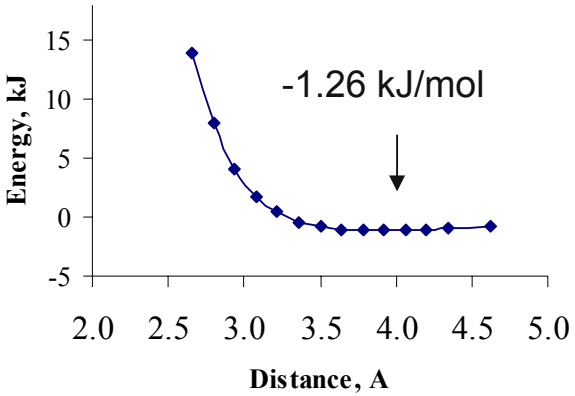
* Potential active sites for alkylation. Activity changes after one of the sites within the aromatic group reacts

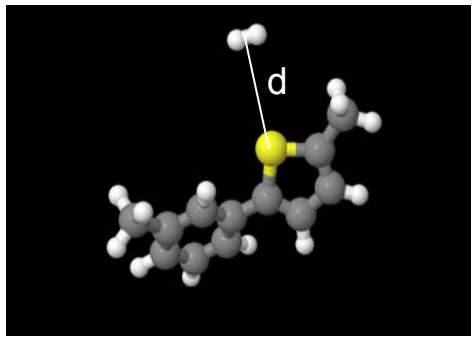
Potential mechanism for polymerization based on report by Wood, *et. al*. *Chem. Mater*. 2007, **19**, 2034-2048

Progress – Computational Modeling of Hydrogen Storage in Polymers

DOE Hydrogen Program

Calculated Structures & H_2 Binding for PE3

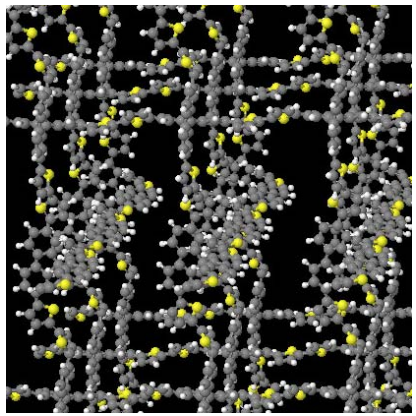




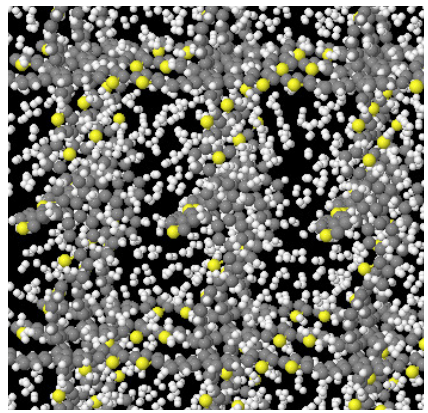
- Structures are optimized at B3LYP and MP2/631G(d) levels
- Hydrogen interaction energies are calculated at MP2/6311+G(2df,p) level

H_2 Binding inside of 3D Polymer Structure

3D cross-linked structure optimized with DFT-PW91



Add H_2



***Ab initio* MD at high H content**

- Local H_2 binding energies over open surface of functional group are low
- Simulation on H_2 distribution, polymer deformation, etc., in 3D space is planned

Milestones

DOE Hydrogen Program

- Complete 1st phase experimental optimization study on TBHTP system **09/07** √
- Complete the initial design and synthesis of one new polymeric system **09/07** √
- Provide one or more polymer samples to a DOE laboratory outside of Argonne for hydrogen storage capacity measurement **01/08** √
- Complete the synthesis of one or more porous polymers reported in the open literature as benchmark materials for the current study **05/08** √
- Complete the surface property characterization and hydrogen storage capacity measurement of the benchmark materials to compare with Argonne/U of Chicago polymers **06/08** →
- Complete first PDF experiments trial on polymer/hydrogen interaction at the Advanced Photon Source **07/08** →
- Initiate theoretical simulation of the interactions between hydrogen and model polymer systems **08/08** →
- Complete design and synthesize two or more new porous polymer materials with targeted hydrogen uptake capacity of 3% at 77 K and 1% at 298 K **08/08** →

Future Work

DOE Hydrogen Program

FY08

- Complete storage measurement and surface property characterization for all the new porous conjugated polymers prepared by U of C team. Derive a preliminary understanding of the molecular structure-capacity relationship
- Complete the storage capacity and structural characterization of the polymers prepared according to the literature report.
- Continue to improve the measurement accuracy of Sievert apparatus for study at higher pressure region (up to 100 bar)
- Initiate preliminary X-ray PDF experiment to probe polymer structure and its interaction with hydrogen under elevated pressure

FY09

- Continue polymer design and synthesis by preparing two additional systems of a) polymers with different main group elements and b) polymers with metal doping
- Optimize synthesis conditions of the best systems to further enhance the surface property and storage capacity.
- Continue computational modeling of hydrogen-polymer interaction and the conformation change at the elevated pressure
- Collaborate with other members of HSCoE in adsorption mechanistic studies (e.g. NMR, neutron, etc.)

Summary

DOE Hydrogen Program

Relevance: Developing the nanostructured porous polymers as new H_2 storage media aimed at meeting DOE performance targets for transportation applications.

Approach: Rational design and synthesis at molecular level supported by surface property/storage capacity measurement, computational modeling and advanced characterization.

Accomplishments:

- Three series of polymeric adsorbents designed and prepared with high surface area and narrow pore distribution.
- H_2 uptakes up to 75 bar studied at both 77K and RT; interesting adsorption behavior observed.

Collaboration: Core team of Argonne and U of Chicago collaborating with HSCoE members.

Future Work:

- Continuous polymer exploration and optimization.
- Improving capacity measurement & mechanistic study at high H_2 pressure.
- Understanding possible conformation change through theory and advanced characterization.