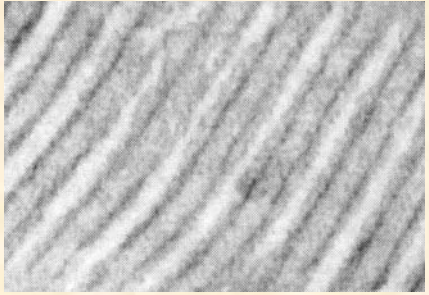
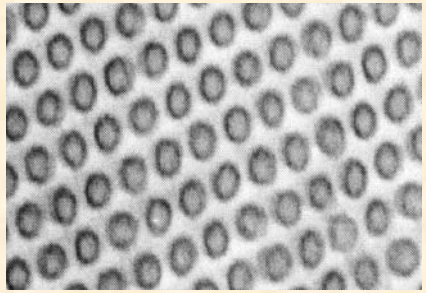




Synergism Between Macromolecular Complex Systems Research at CNMS and SNS HFIR

AB A_2B

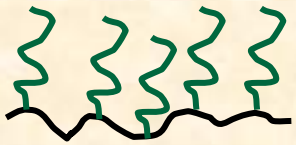
$A_3A'B$

Jimmy W. Mays and Phillip F. Britt

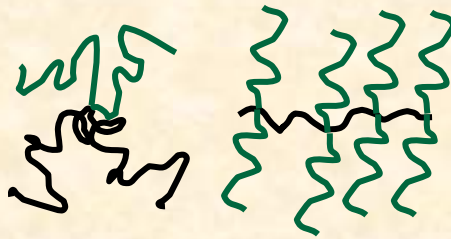
Scientific and Operational Leaders

SNS HFIR User Meeting

October 11-13, 2005



comb



A_2B_2 centipede

www.cnms.ornl.gov

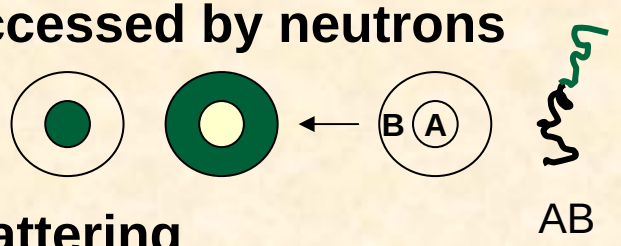
Office of Basic Energy Sciences • Serving the Present, Shaping the Future •

CNMS Oak Ridge National Laboratory Center for Nanophase Materials Sciences

Office of Science U.S. DEPARTMENT OF ENERGY

Neutron Scattering in Macromolecular Materials

- **Neutron scattering has played a major role in the understanding of the conformation (or structure) and dynamics of polymers and copolymers in the bulk solid and in solution for almost 35 years**
  - **Length (0.1-10^5 Å) and time scales (μs-fs) accessed by neutrons**
  - **Capability of manipulating contrast by H-D substitution (without changing structure)**



- **Examples of information gained by neutron scattering**
  - **Molecular conformation of bulk polymers, polymer blends, and copolymers**
  - **Molecular weight, radius of gyration, and conformation of a single molecule in dilute or concentrated solution**
  - **Polymer-polymer thermodynamics**
  - **Morphology of block copolymers in solution and solid state**
  - **Polymer chain behavior in deformation, shear, extrusion, etc**
  - **Interface structure and depth profile of polymers**
  - **Conformational changes upon swelling or stretching of networks**
- **Need for well defined deuterated small molecules and polymers**

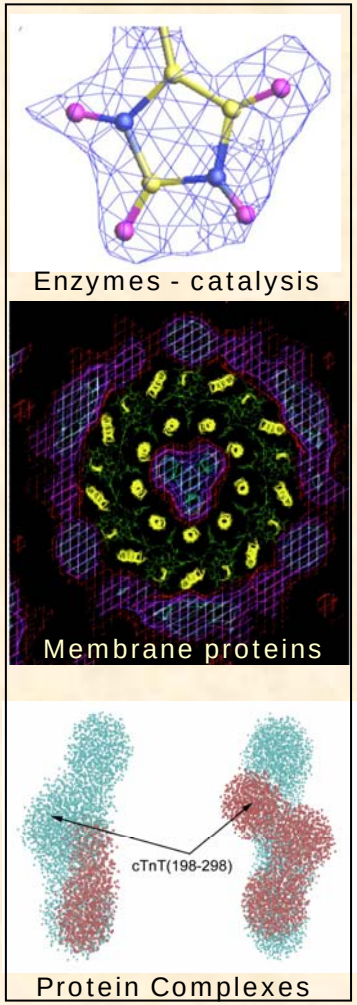
Research in Macromolecular Science at CNMS

- ***Scientific Grand Challenge***
  - **To design and control the nanoscale organization of macromolecular materials to achieve novel functionality**

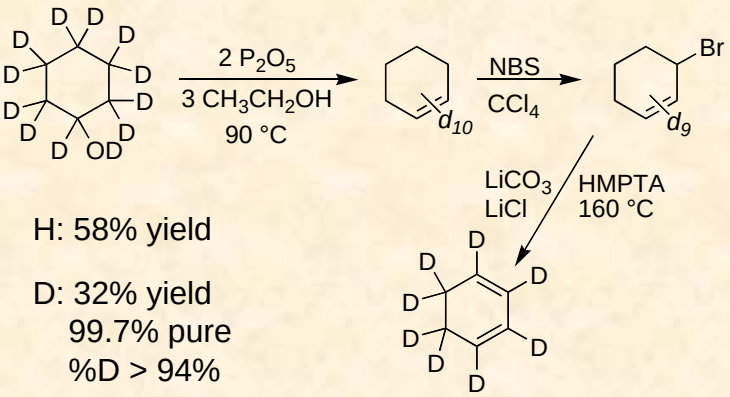
- **"One Stop Shop" for all of your polymer needs: design, synthesis, deuteration, characterization, and TMS**
- **Synthetic tool box for the synthesis and characterization of small molecules (monomer), polymers, and biomaterials**
- **Unique anionic synthetic techniques for the preparation of well-defined polymers and complex polymer architectures (such as stars, combs, and hyperbranched polymers) that are only available in a few groups in the world**
- **Expertise in directed self-assembly of molecules**
- **Emerging synthetic capabilities in preparation of novel polymer architectures based solely or in part on amino acids**
- **Unique capabilities in SWNT chemistry and in preparing and characterizing polymer-carbon nanotube composites**

Unique Deuteration Capabilities Available

- **Two NSF Workshops (2003) recommended deuteration facilities convenient to the beam line**
- **CNMS will provide synthetic staff trained in organic and polymer synthesis for preparation of well defined deuterated small molecules, monomers, and polymers**
- **Center for Structural Molecular Biology at ORNL (Dean Myles, Director) will provide a deuteration laboratory and staff dedicated to *in vivo* H/D labeling of cells, proteins, nucleic acids and other biomolecules**



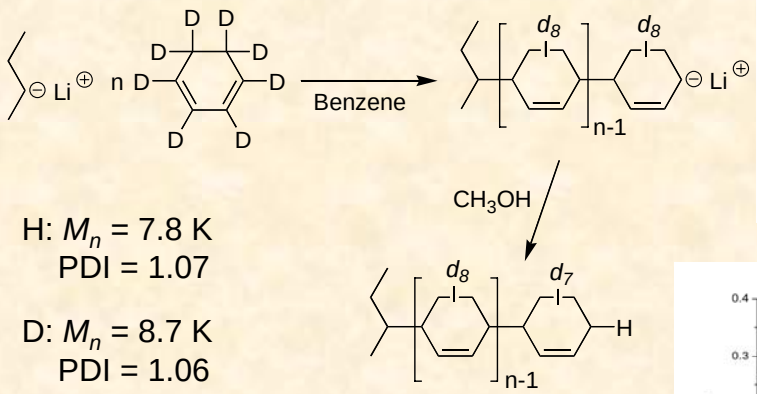
Synthesis of deuterated monomer



H: 58% yield

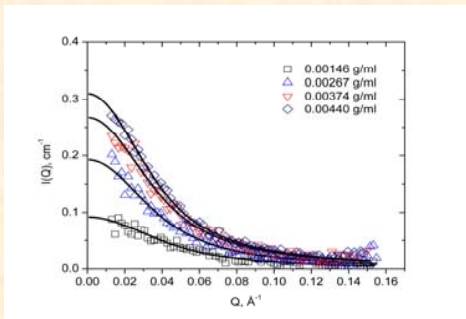
D: 32% yield
99.7% pure
%D > 94%

Synthesis of deuterated polymer



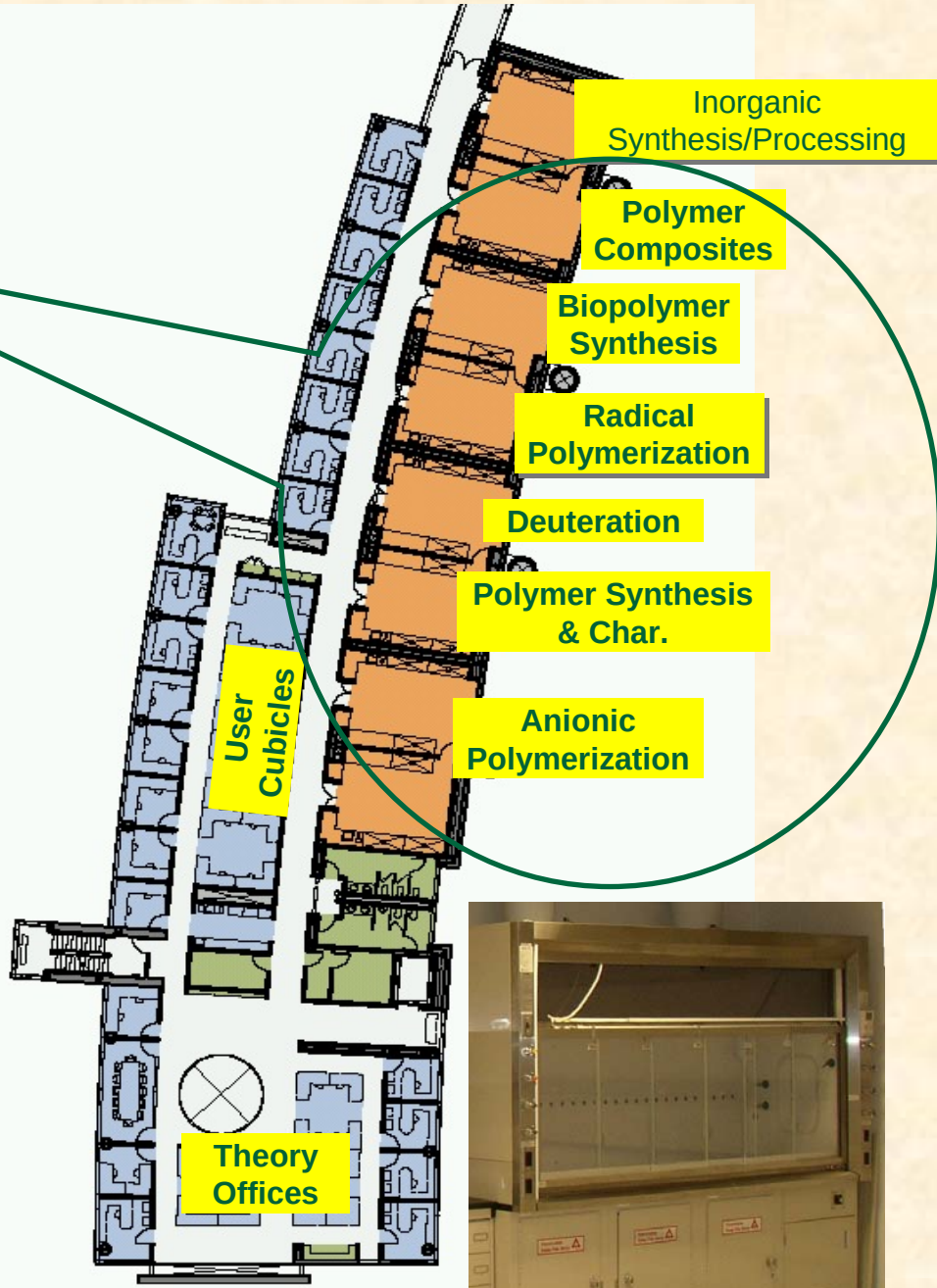
H: M_n = 7.8 K
PDI = 1.07

D: M_n = 8.7 K
PDI = 1.06



Facilities - Third Floor

- **Third floor**
  - **Seven synthetic labs**
  - **Most labs have three hoods:**
    - **8’ benchtop**
    - **8’ walk-in**
    - **10’ walk-in**
  - **GPC characterization**
  - **Glass annealing oven**
  - **Refrigerators/freezers**
  - **Glove box**
- **Second floor**
  - **Three characterization labs**
  - **Instrumentation used in many research themes**



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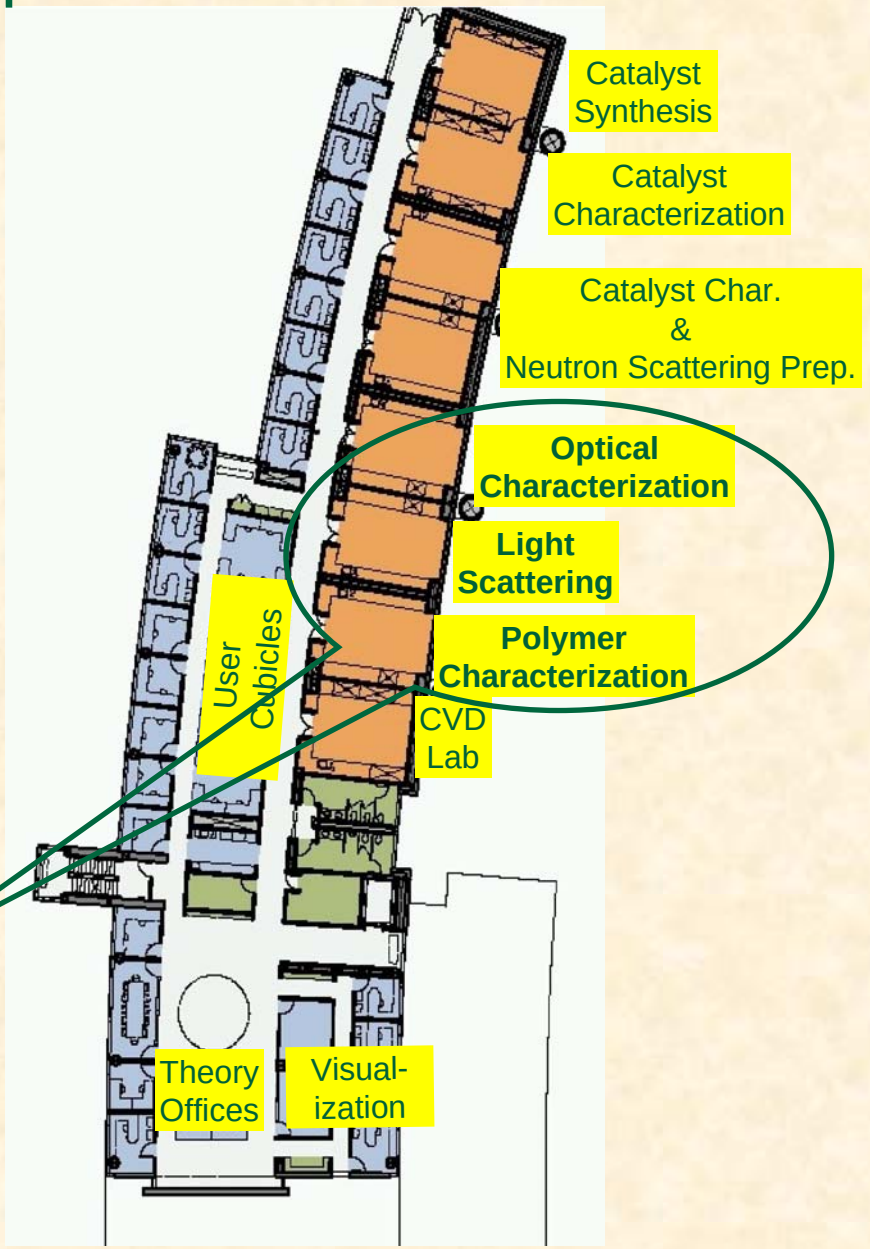
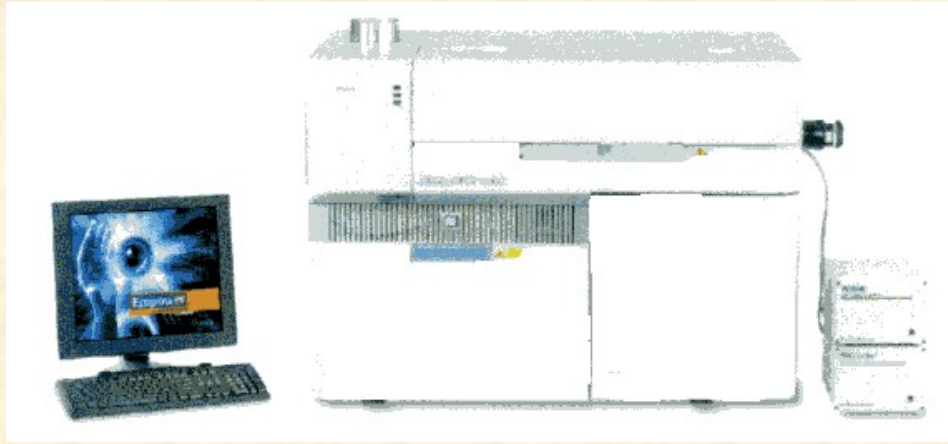
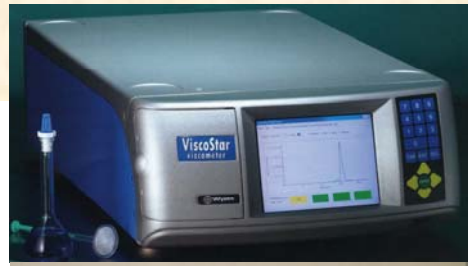
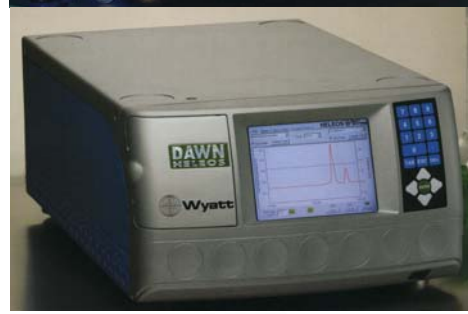


Polymer Characterization Tools

- **Molecular weight characterization**
  - **High temperature Gel Permeation Chromatography (GPC) with refractive index, light scattering, and viscosity detectors**
  - **Room Temperature GPC with refractive index, light scattering, viscosity, and UV-Vis detection for organic and aqueous**



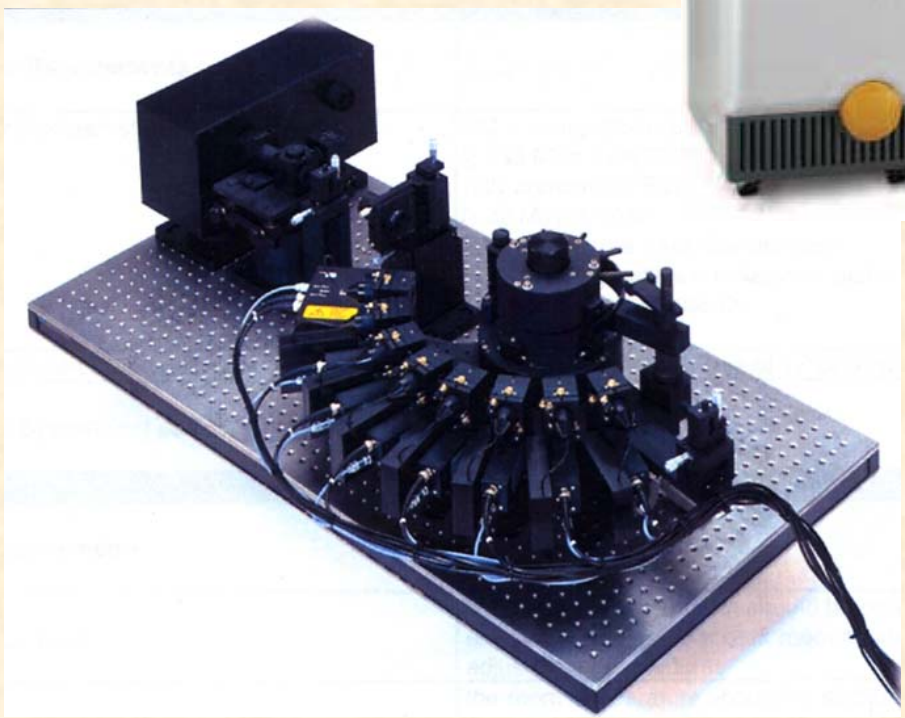




CNMS
Center for Nanophase Materials Sciences

Polymer Characterization Tools

- **Molecular weight characterization (continued)**
  - **MALDI-TOF-MS**
  - **Static and dynamic light scattering**
  - **Membrane osmometry**
  - **NMR (400 MHz) solution and solid-state (Planned 700 MHz NMR)**



Polymer Characterization Tools

- **Thermal properties**
  - **Differential scanning calorimeter (DSC)**
  - **Thermal gravimetric analyzer (TGA)**
  - **Rheometer (Planned FY 06)**
  - **Dynamic mechanical analyzer (DMA, late in 06)**

Polymer Characterization Tools

- **Spectroscopic Characterization**
  - **Fourier transform infrared (FTIR, ATR, photoacoustic, IR microscope)**
  - **Spectroscopic Ellipsometer**
  - **Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) Spectrometer**
- **Other tools at CNMS**
  - **Scanning probes (AFM)**
  - **Electron microscopy (SEM and TEM)**
  - **Neutron scattering**
  - **Theory Modeling and Simulation**

Current Technical Resources

- **Scientific and Operational Leaders**
  - **Jimmy Mays - UT/ORNL Distinguished Scientist - Anionic polymer synthesis**
  - **Phillip Britt - Senior Research Staff, CSD Organic and polymer synthesis, deuteration, chemistry/purification of carbon nanotubes**
- **CNMS Research Staff**
  - **Kunlun Hong - Polymer synthesis (anionic and controlled radical), deuterated monomer synthesis, characterization, and neutron scattering**
- **Postdoctoral Research Associates**
  - **David Uhrig - Anionic polymer synthesis, branched polymers and silane coupling**
  - **Joseph Pickel - Polymer characterization and controlled radical polymerization**
  - **Jamie Messman - Anionic synthesis of polypeptides and biomaterial and ROP**
- **Future resources**
  - **Staff - Synthetic organic chemist (deuteration) and biopolymer chemist**
  - **Postdoctoral - Anionic synthesis and polymer characterization**
  - **Technician - Polymer characterization**

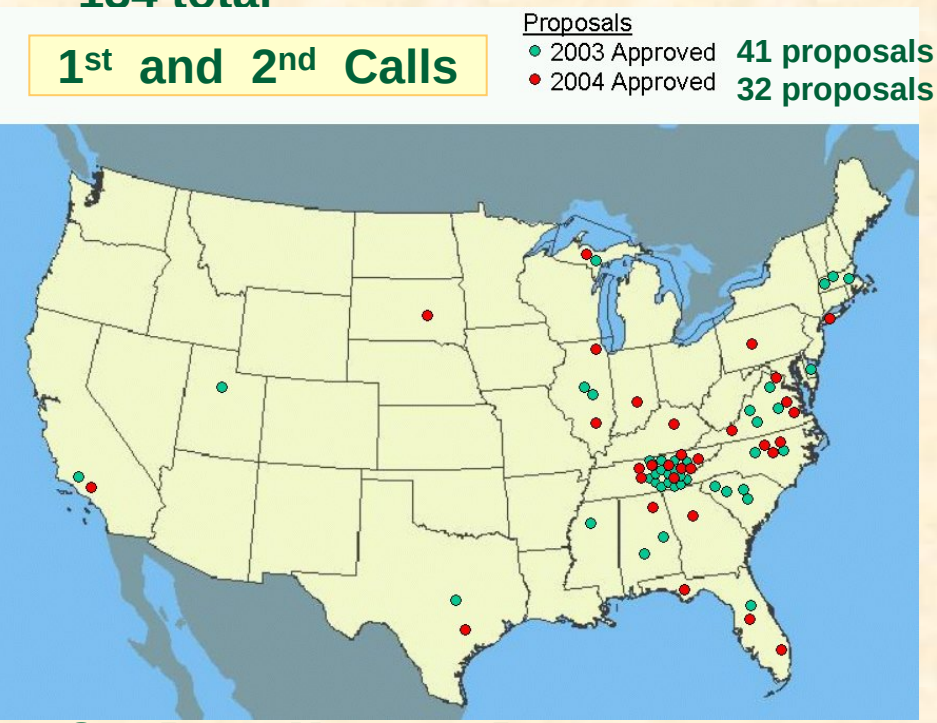
Jump-Start Users in 2004 and 2005

SOURCES OF PROPOSALS

- 96 universities
- 8 industry
- 19 ORNL
  - Some with universities, some partner proposals
- 7 foreign
  - Germany, France, China

134 total

1st and 2nd Calls

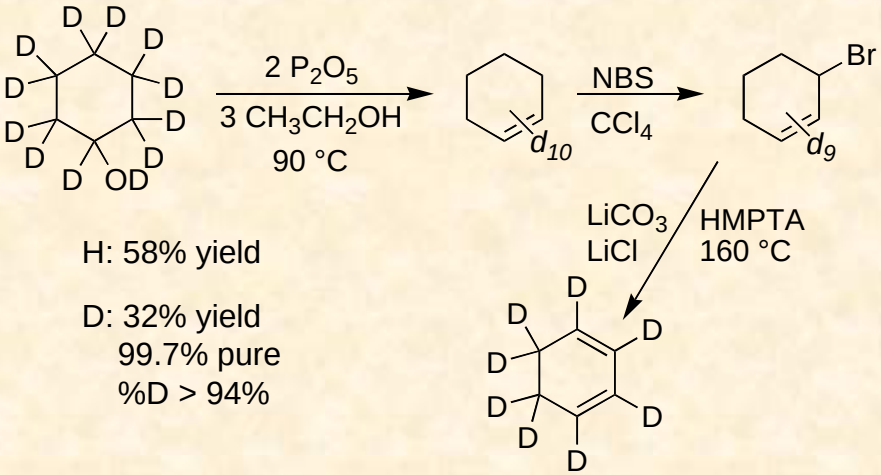


Macromolecular Theme Users

- Received 59 proposals in Macromolecular Complex Systems
- Accepted 20 proposals (33%)
  - 10 anionic synthesis
  - 5 deuterated polymers for neutron scattering studies
  - 10 characterization
- Users from:
  - CEA- Saclay (France), Clemson, Georgia Tech, Institute of Polymer Research Dresden (Germany), Luna Innovations Inc., Michigan Tech, North Carolina State University, Northwestern University, ORNL (3), Rice, University of Florida, University of Alabama Tuscaloosa, University of Massachusetts (3), University of Tennessee, and Virginia Tech
- Progress on 14 projects

Early Success: Neutron Scattering on CNMS Polymers

Synthesis of deuterated monomer



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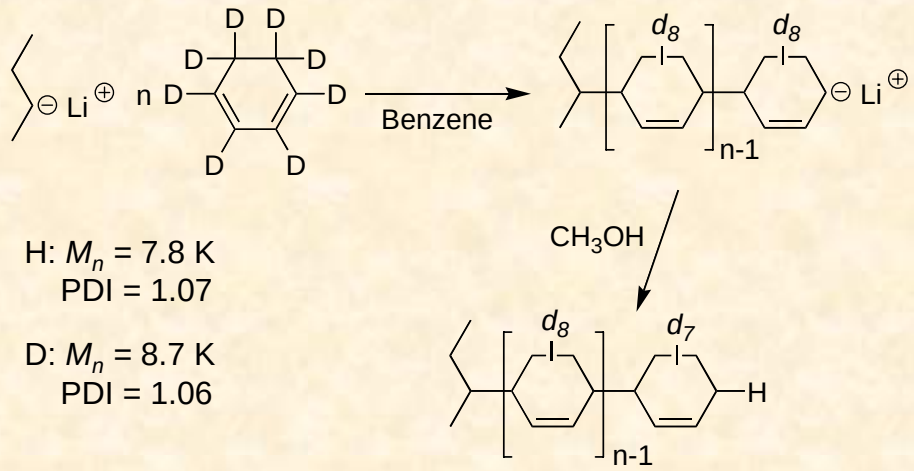
Synthesis of deuterated polymer



H: M_n = 7.8 K
PDI = 1.07

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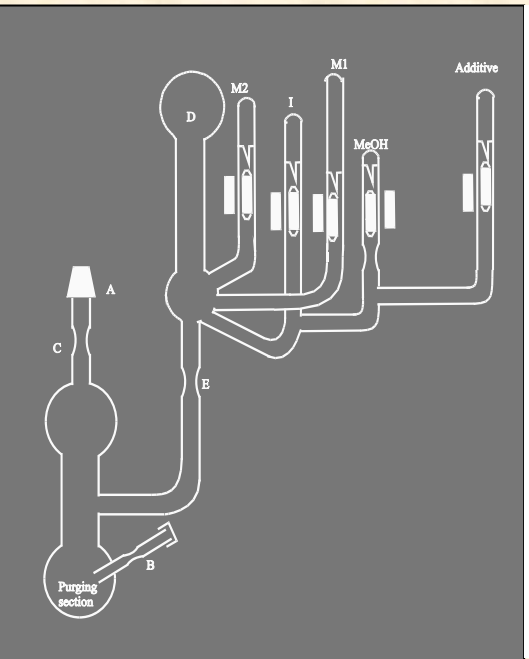
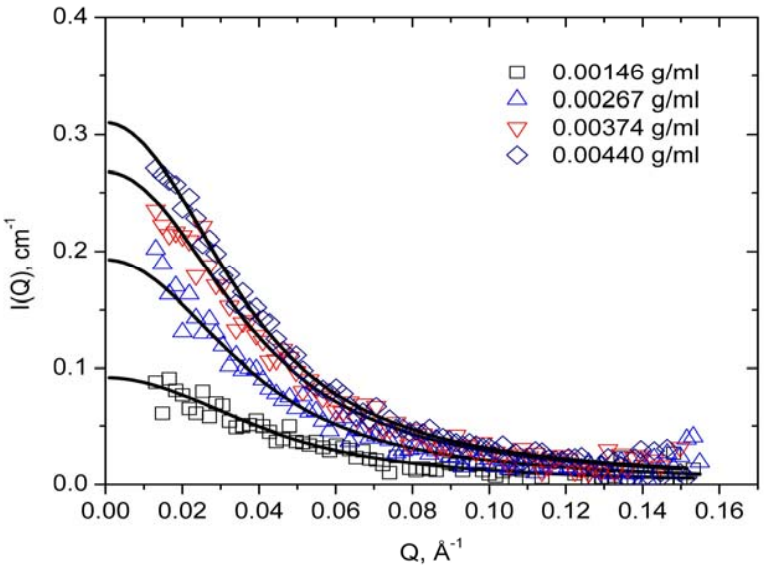
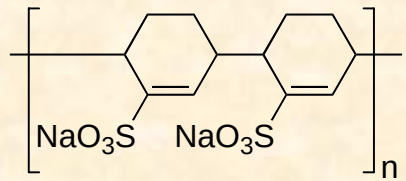
PDI = 1.06

- **Statistical segment length for PCHD 0.83 nm while PS 0.67 nm**

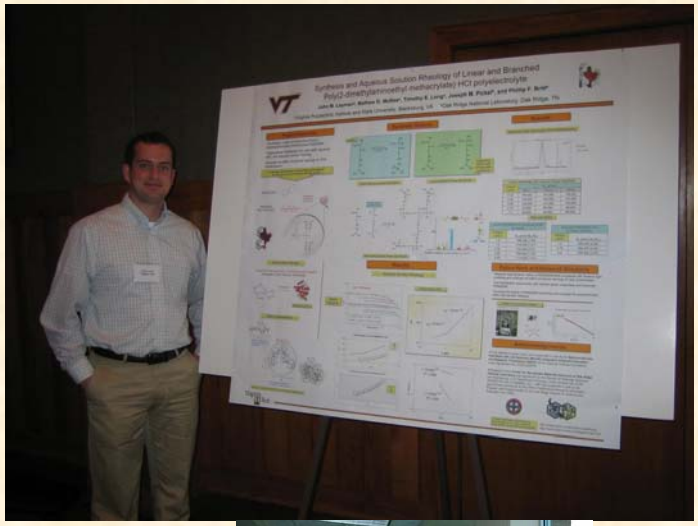


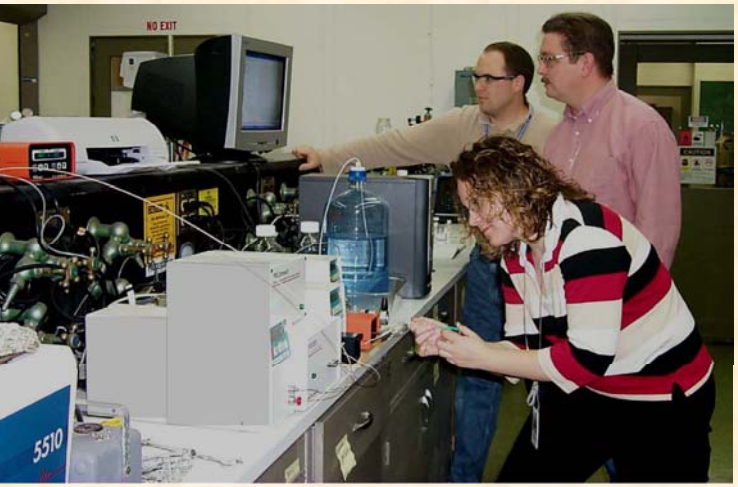


- **Manuscript drafted for publication**
- **Additional SANS studies on sulfonated PCHD**



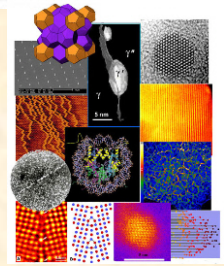
CNMS Users





CNMS Planning Workshops

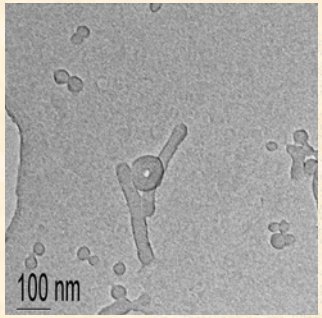
Synthetic and Bio-Inspired Macromolecular Materials

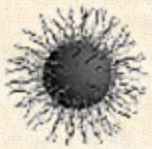


- **Scientific Grand Challenges**
  - To design and control the nanoscale organization of macromolecular materials to achieve novel functionality
- **Key Issues**
  - Design and synthesize complex macromolecular architectures
  - Develop directed self-assembly strategies
  - Understand the effect of nanoscale confinement on structure, dynamics, and properties of macromolecular systems
  - Understand and control the nature of interfaces in nanophase macromolecular systems
  - Generate biological function by hierarchical structures to achieve material properties
  - Develop a theoretical understanding and predictive capabilities to achieve the above

Challenges in Macromolecular Science

- **Structure-Property relationships**

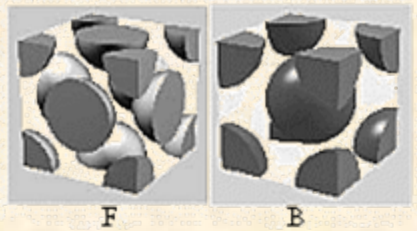




micelle

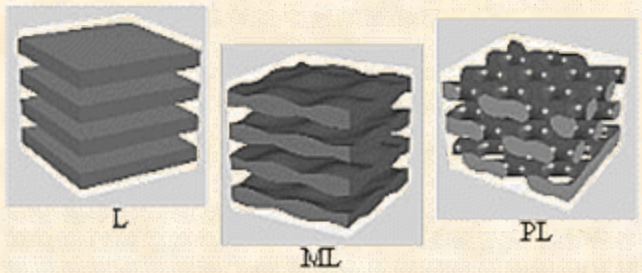
cylindrical micelle

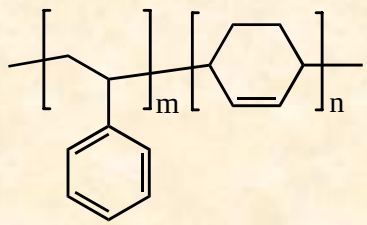
vesicle

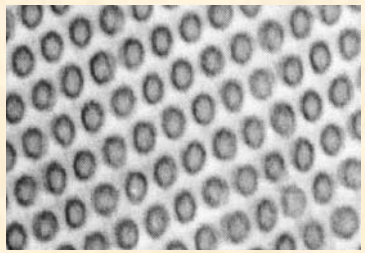


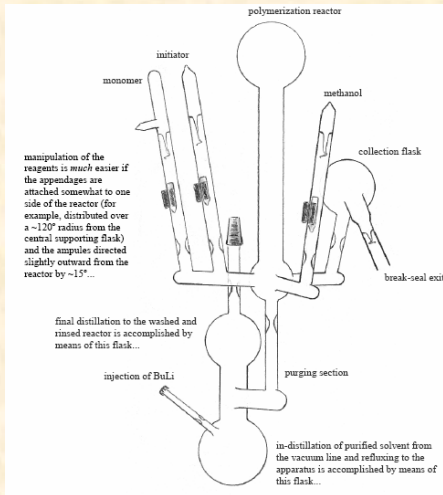
H

gyroid





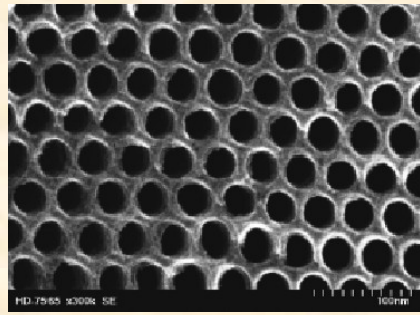


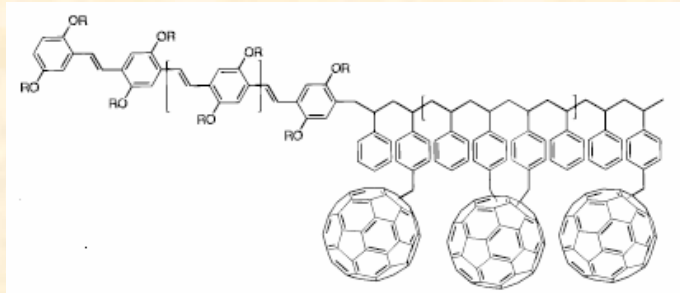


Picture from Förster, S.; Plantenberg, T. *Angew. Chem. Int. Ed.* **2002**, *41*, 688.

Application of Polymers

- **Synthesis of mesoporous carbons for catalyst supports and separations**
- **Solar energy applications**
  - **Photovoltaic devices**
  - **Organic LEDs**
- **Synthesis of multifunctional polymer compositions (strong, lightweight, conductive)**
- **Environmentally responsive polymers (temperature, pH, etc.)**
- **Biocompatible polymers for tissue engineering, drug delivery, coating**





Stalmach, U. et al. *J. Am. Chem. Soc.* 2000, *122*, 5464