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Center for Macromolecular Topology: Center Concept and Summary

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Univ. of Michigan, Univ. of Cincinnati, KAUST/Univ. Athens, Univ. of Tennessee

Associates: Greg Smith, Ron Jones, Jan Ilavsky

Oak Ridge National Lab, National Institute of Standards and Technology, Argonne National Laboratory

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Center Concept

The Center for Macromolecular Topology (CMT) will address the need in the polymer industry to synthetically control, characterize, model and simulate complex macromolecular and nano-architectures for improved mechanical and rheological properties and controlled processing.

Potential CMT Members

ExxonMobil Research and Engineering
P&G
sabic
NIST National Institute of Standards and Technology
lyondellbasell
Argonne National Laboratory
Celanese
Ticona – A Business of Celanese
DuPont
Air Force Research Laboratory
Oak Ridge National Laboratory
Dow
Sandia National Laboratories
Bridgestone Firestone

Analysis of Industry

-Macromolecules make up a large fraction of the output of the US chemical industry

-Branching and chain/network topology can have an important impact on properties, especially rheological performance and processing.

-Quantification and understanding of chemical routes to complex chain topology is an area of need since in many cases common analytic techniques are not sufficient

-An effort in this area requires coordination between synthetic chemists, rheologists, modelers, simulators and analytic scientists.

-A coordinated effort between industry, academics and national labs is the best approach to target the technical needs.

-Targeted areas: Long chain branching in polyethylene, cyclization in polysiloxanes, transesterification in polyesters, residual vinyl reactivity in polystyrene, hyperbranched polymers, elastomers, gels.

Grand Challenge

To develop methods to measure and manipulate chain (and nano-) topology to optimize processing and properties.

If successful, the project would, for example, allow specific molecular topologies to be identified that would enhance processing with little or no reduction in properties. To do this, we would need to show how to enhance extensional rheology while not affecting or improving crystal/amorphous structure and orientation.

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Activities of the Center

-Center will fund projects targeting the interests of the Industrial Advisory Board (5 proposed)

-Center organized access to characterization facilities, deuteration of materials, TREF facility for polyethylene, services for routine samples such as filled polymers

-Access to services provided by Associate Members through in-kind contributions such as specialized processing, characterization and synthesis capabilities

-Symposia, short courses, recruitment, reports on research, exclusive license to IP, independent consulting and contract research associated with center activities, software development

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Organization

The Center will initially have two sites:

University of Michigan:
Rheology, Synthesis, Experimental Interface Studies, Colloids, Synthesis, Modeling, Simulation

University of Cincinnati:
Scattering, Synthesis, Simulation, Modeling

Affiliate Sites:
University of Tennessee, University of Athens, KAUST, Oak Ridge National Laboratory, National Institute of Standards and Technology, Argonne National Laboratory, Eclipse Film Technology

Organization

An Industrial Advisory Board (IAB):
Full Members: $75,000/year at 10% IDC with a two year commitment. IAB Suggests Projects from Center Fees, suggests bylaws, organization, membership fee rates, suggest approval of Associate Members. Membership fee paid to one of the two sites.

Center Wide Panel:
Associate Members & Full Members: Suggest Projects for 10% IDC and NSF funded startup projects (~$45,000 total funds).

Other administrative structure seen in the diagram that follows.

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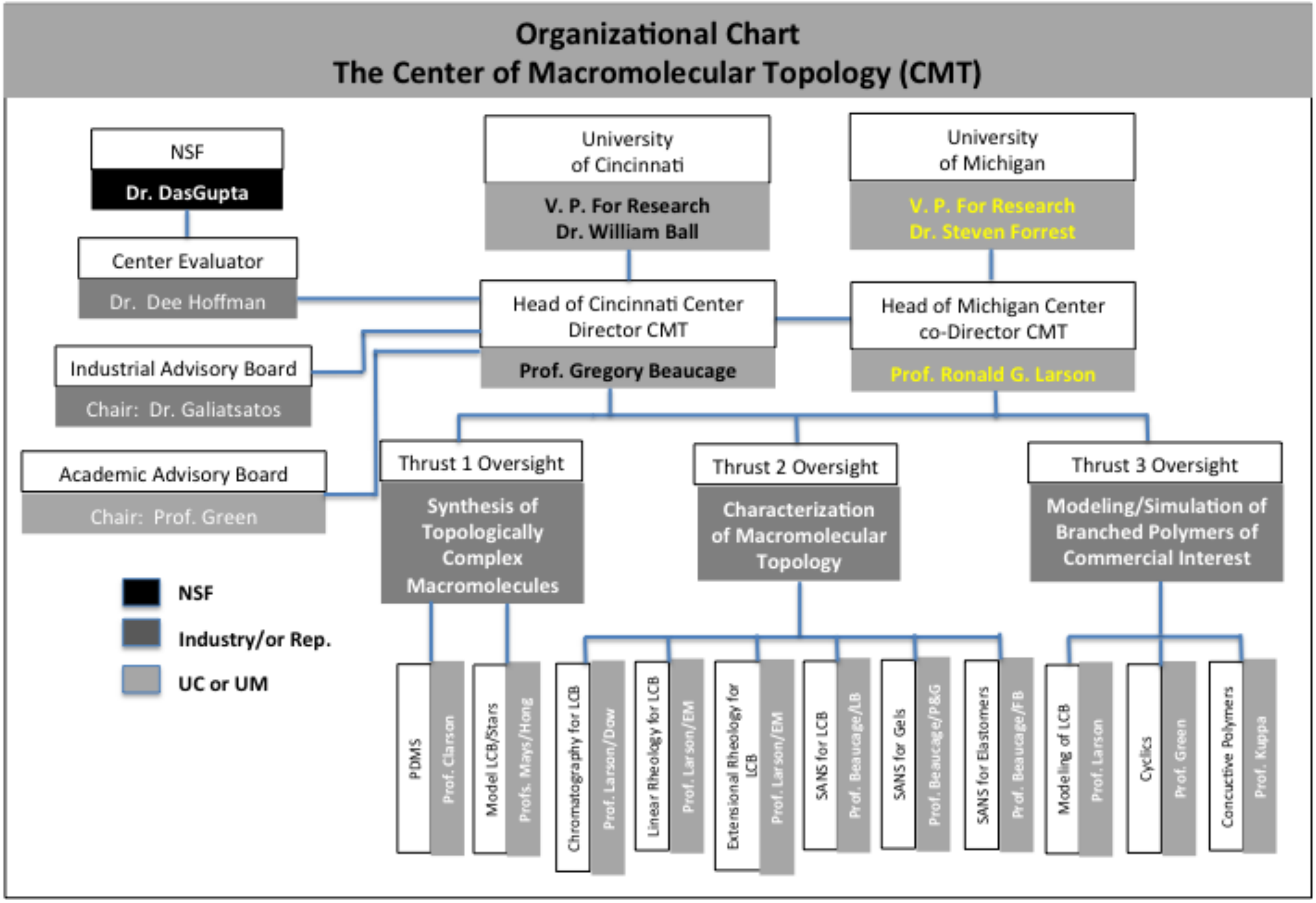
Organization



Potential Members

University of Cincinnati

***Procter & Gamble, Phase & Colloid Science Analytic Division (First Membership)**
***LyondelBasell Industries**
***Dupont, Experimental Station, Wilmington, DE**
***Oak Ridge National Laboratory**
***Bridgestone/Firestone**
***Eclipse Film Technologies**
***ThreeBond Corporation**
*Avery Dennison Corporation
*SABIC Americas
DSM Hybrane Division
Goodyear Tire & Rubber
Goodrich Tire
PPG Industries
Nova Chemicals
Ashland Chemicals
Ticona Coporation
PolyOne Corporation

University of Michigan

***ExxonMobil, Baytown, TX (First Membership)**
***Dow Chemical, Freeport TX**
***Air Force Research Laboratory**
***Procter & Gamble Materials Science & Technology (Second Membership)**
***Myaterials**
***Dow Corning Corporation**
*ExxonMobil, Research & Engineering Co. (Second Membership)
*Procter & Gamble, Baby Care Division (Third Membership)
*Sandia National Laboratory
Michigan Molecular Institute
3M Corporation
Soldier Research, Development and Engineering Center (NSRDEC) U. S. Army Natick, MA
Total Petrochemicals
ChevronPhillips

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5 Projects
Potential Supporters
Research Sites

Each Project is described in the executive summaries and in separate Power Point slides

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Project 1 Controlling Polymer Rheological Properties Using Long-Chain Branching

Dupont	Cincinnati
LyondellBasell	Michigan
ExxonMobil	ORNL/CNMS/Tennessee
Dow	NIST Consortium
Nova	
Celanese	
Procter & Gamble	

Project 2 Adsorption, Adhesion, and Topology of Linear and Branched Macromolecules on Curved and Flat Surfaces

AFRL	Cincinnati
Bridgestone	Michigan
Procter & Gamble	ORNL/CNMS/Tennessee

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Project 3 Effect of Branching on Flow-Induced Crystallization and Crystalline Orientation

Dupont	Cincinnati
LyondellBasell	Michigan
ExxonMobil	ORNL/CNMS/Tennessee
Dow	Argonne National Lab
Nova	
Celanese	
Procter & Gamble	

Project 4 Gel Structure, Molecular Aggregation/ Agglomeration and Gelation in Colloidal Fluids

Procter & Gamble	Cincinnati
Bridgestone	Michigan
Others	ORNL/CNMS/Tennessee
	NIST Consortium

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Project 5 Network/Reinforcing Filler Mechanical Response

Bridgestone
ExxonMobil
Dow
Procter & Gamble
AFRL

Cincinnati
Michigan
Argonne National Lab

Future Projects

-Network Conductive Polymers for PV
-Software Development for Rheological Analysis
-Synthesis of Topological Systems for Coatings
-Two-Dimensional SAXS/DMA for Reinforcing Fillers
-Model Polymers for Topological Studies

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Short Courses, Conferences
Targeted Strategy Groups

Structure and Rheology of Molten Polymers
Ron Larson & Mike Solomon

Scattering Techniques for Topological Structures of Complex Macromolecules
Greg Beaucage, Mike Solomon

Simulation Methods for Prediction of Properties in Branched Polymers
Ron Larson, Vikram Kuppa

Synthetic Mechanisms for Chain Branching in Polyolefins
Ron Largon, Jimmy Mays

Long Chain Branching in Polyethylene Strategy Group

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Center Service Contracts

Rheological Measurements of Commercial Polymer Melts

Interpretation of Rhelogical Data

Rheological Training

Rheological Software

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Potential Center Associate Members:

ORNL, Argonne, NIST, Eclipse

Oak Ridge National Laboratory: Neutron Scattering, Synthesis of Model Materials, Other Characterization Facilities

Argonne National Laboratory: Advanced Photon Source: X-ray Scattering

National Institute of Standards and Technology: Neutron Scattering, Other interactions with the Polymer Division

Eclipse Film Technologies: Polymer processing facilities, MDO, processing equipment for in situ SAXS

Relationship with other Centers

Consortium for Soft Material Manufacturing at NIST.

IRC at University of Leeds (and other UK Universities)

CNMS ORNL, Scattering Centers at NIST, Oak Ridge, Argonne

NSF Role

Each site requires a minimum of $150,000/year from Membership Fees and 3 Members. (One member can be an Associate Member.) NSF requires 10% indirect charges on membership fees.

NSF will contribute $60,000/year per site with 56% indirect charges. (Net $109,100) This could go towards center wide projects. NSF will also pay $20,000 to Cincinnati for administration.

NSF provides avenues to other funds:
International Travel Supplements for Centers ($25,000), IGERT, REU, academic center grants.
Funds for industrial participants to travel to foreign centers or to have extended stays at university sites or national labs.

NSF audits/certifies the center operations.

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Center for Macromolecular Topology: Capabilities

Laboratories of Ronald Larson Greg Beaucage, Rick Laine, Steve Clarson, Peter Green, Vikram Kuppa, Mike Solomon, and Jude Iroh, Jimmy Mays

Univ. of Mich., Univ. of Cincinnati, Univ. of Tennessee

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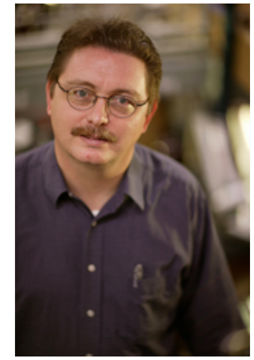
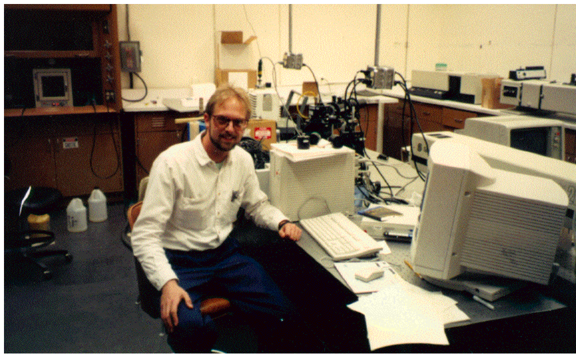
The faculty


Jimmy Mays, UT


Greg Beaucage,UC


Steve Clarson,UC


Jude Iroh, UC


Vikram Kuppa, UC


Peter Green,UM


Rick Laine, UM


Ron Larson, UM


Mike Solomon,UM

Equipment & Facilities

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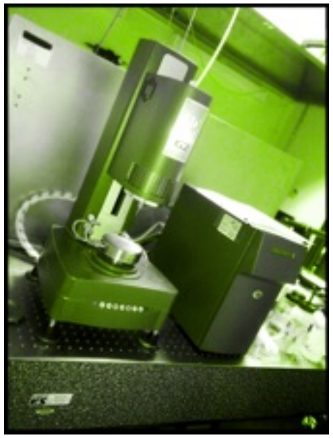
Rheometers

- ARES AR-G2 rheometer (low stress)
- TA Instruments ARES rheometer
- AR 1000 constant stress rheometer
- Assessment of impact of changing
- Ubbelohde viscometry



Solomon/Larson lab

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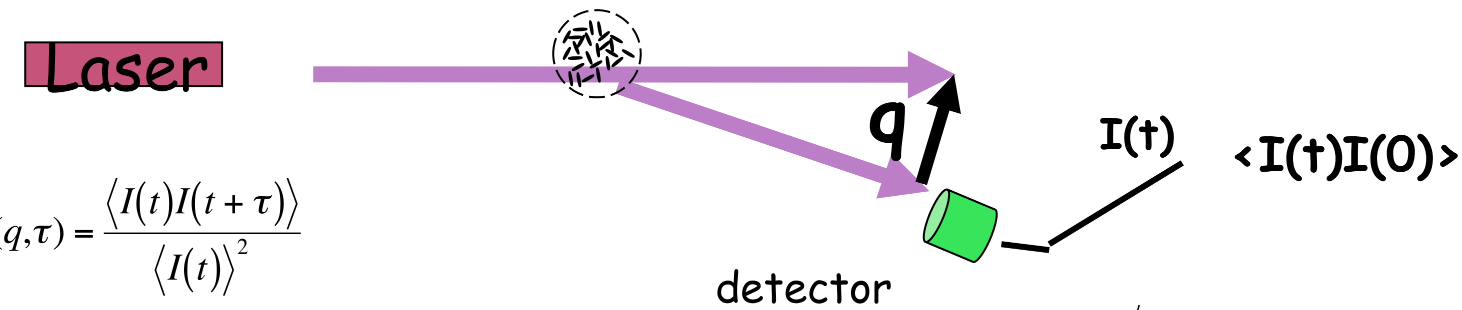
Collective dynamics by means of dynamic light scattering

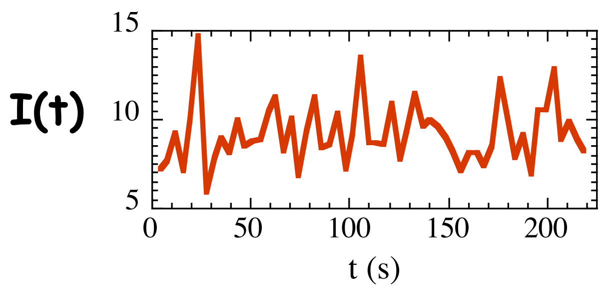


$$g_2(q,\tau) = \frac{\langle I(t) I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$

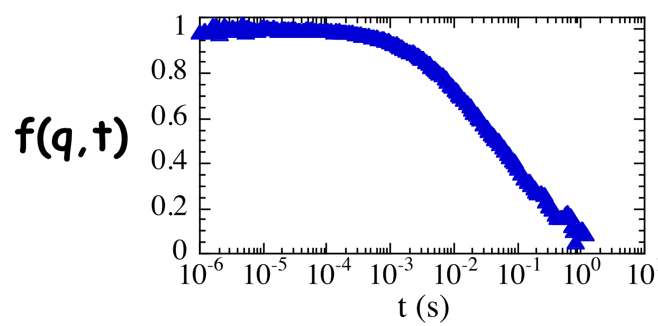
$$g_2(q,\tau) = 1 + \beta \left| f(q,t) \right|^2$$

$$f(q,t) = \frac{1}{N}\left\langle \sum_{i,j} \exp(i\mathbf{q} \bullet \left[\mathbf{r}_i(0) - \mathbf{r}_j(t)\right] \right\rangle$$

Scattering Intensity



Dynamic Structure Factor



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Special methods for non-ergodic samples: Pusey and van Megen, 1989

$$5 \le q \le 25 \mu m^{-1}$$

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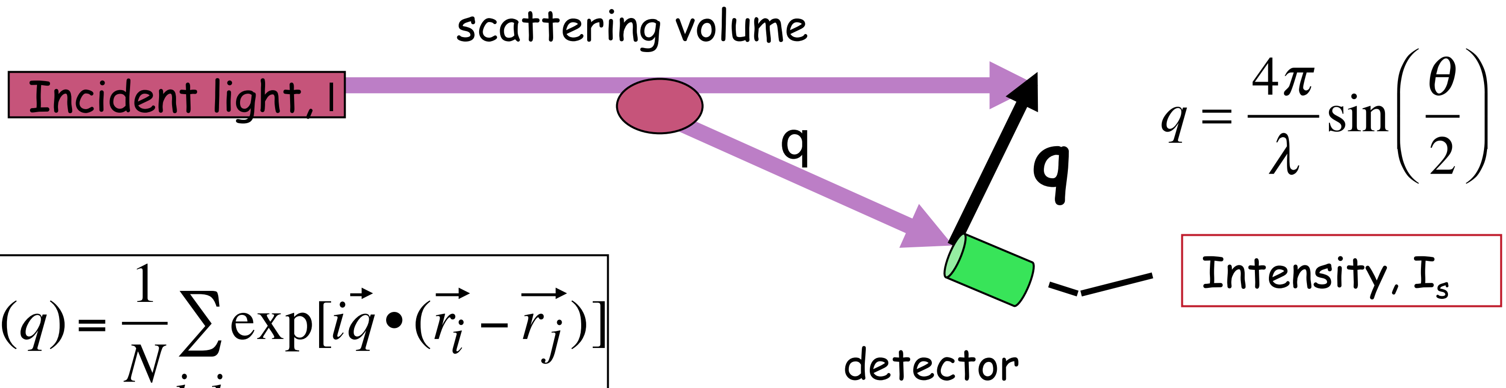
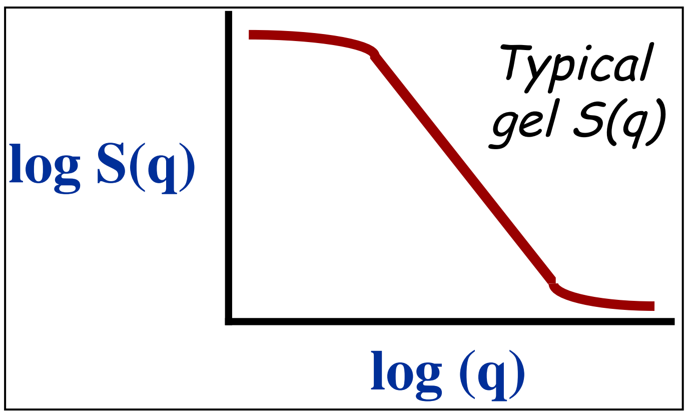
Structure from Scattering

Structure factor, S(q), depends on particle configuration



$$q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

$$S(q) = \frac{1}{N}\sum_{i,j}\exp[i\vec{q}\bullet(\vec{r}_i - \vec{r}_j)]$$



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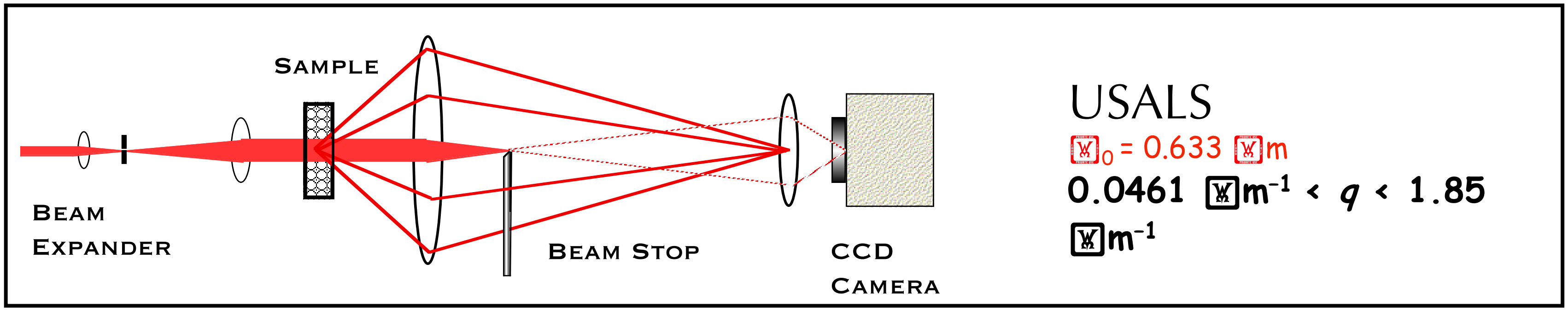
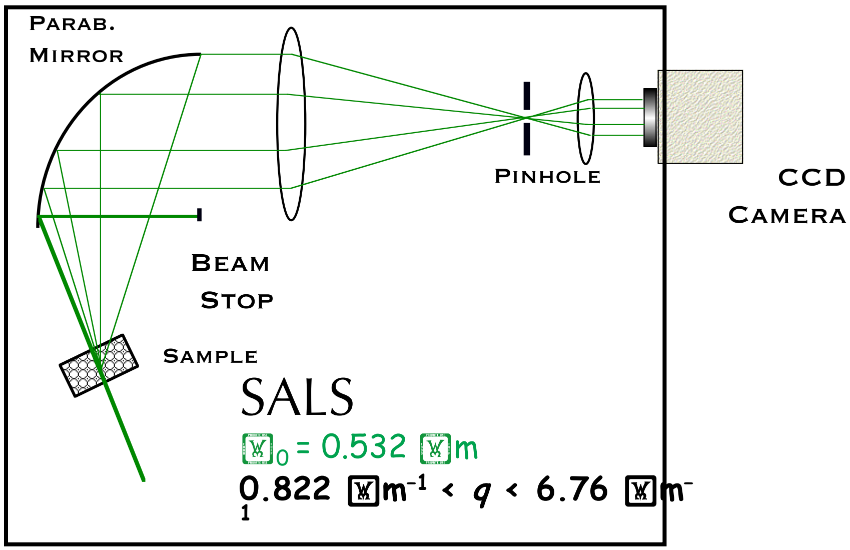
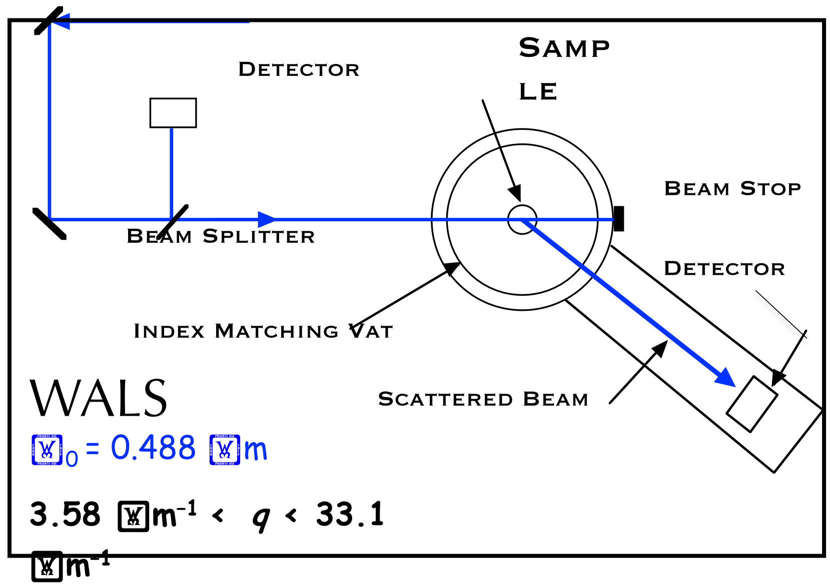
I_s	**~**	**rP(q)S(q)**
q:		*scattering vector*
r:		*density*
P(q):		*form factor*
S(q):		*structure factor*

Light scattering detects structure on scales from ~20 nm to ~ 20 mm

Static Light Scattering







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In house Pinhole and Bonse-Hart X-ray Scattering Cameras and Static Light Scattering Facilities

In house X-ray reflectivity, spectroscopic elipsometry and a variety of other surface analysis techniques

Access to the Advanced Photon Source (ANL) for USAXS (See poster by Jan Ilavsky attending)

Access to NIST Neutron Scattering Center (Ron Jones attending)

Access to ORNL Neutron Scattering Facilities (Greg Smith attending)

Center for Nanophase Materials Science at ORNL (Jimmy Mays, M.S. Rahman (attending & poster), Greg Smith/Mussie Alemseghed (both attending))

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Leica TCS SP2 Confocal Laser Scanning Microscope

- Excitation wavelengths : a blue Argon/Argon-Krypton laser (458/488nm), a green laser (543nm), and a red Helium-Neon laser (633nm).
- Detectors: wavelengths between 400 - 850nm
- Image resolution: up to 4096 x 4096
- Image speed up to 3 frames per second at 512 x 512 pixels.

Solomon/Larson/… lab

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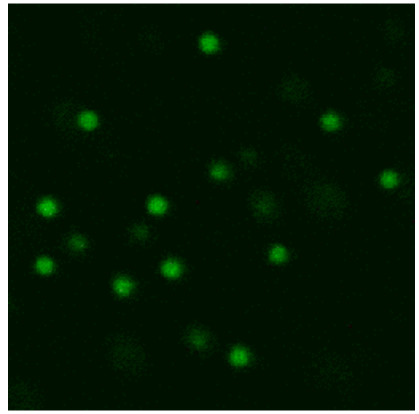
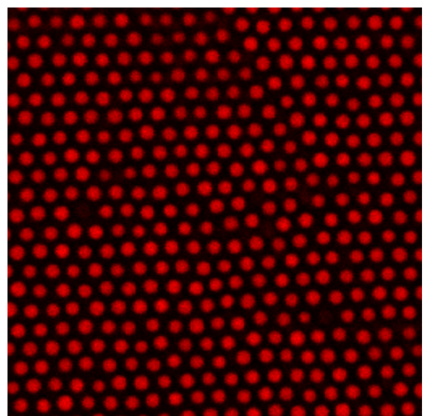
Particle Imaging

Brownian Motion



$$\lim_{t \to \infty}\left\langle r^2(t)\right\rangle = 6D_s^L(\phi)t$$

Pair potential interactions



$$U(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{2\alpha} - \left(\frac{\sigma}{r}\right)^{\alpha}\right)$$

1 nm ***10 nm*** ***100 nm*** ***1 µm*** ***10 µm***

molecular ***granular***

(slide from Solomon group)

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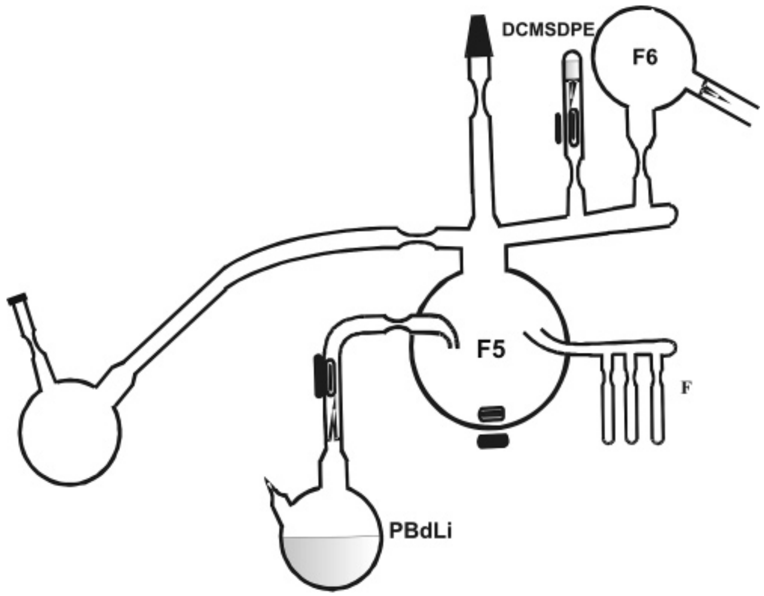
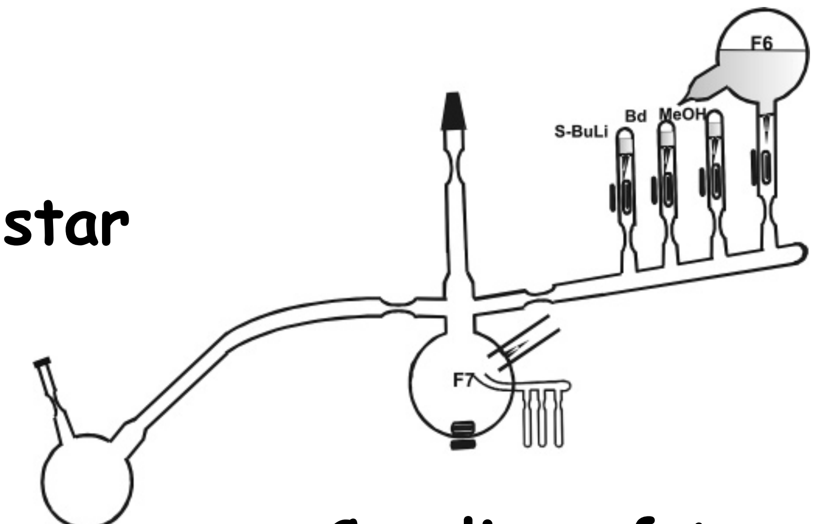
Polymer Synthesis



Synthesis of star



Mays lab

Coupling of two arms

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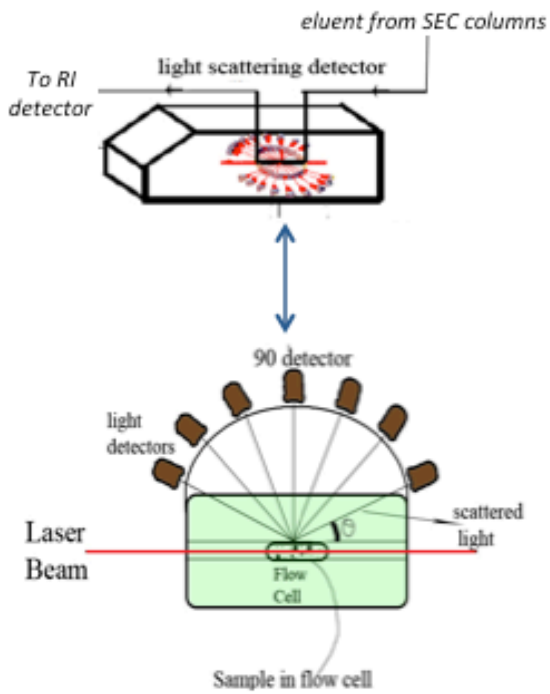
Size exclusion chromatography

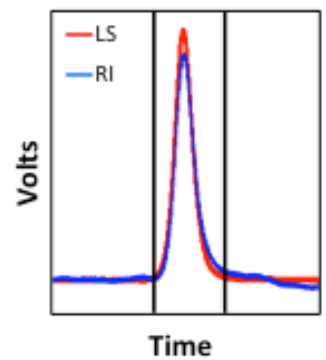
Determination of M_w distribution

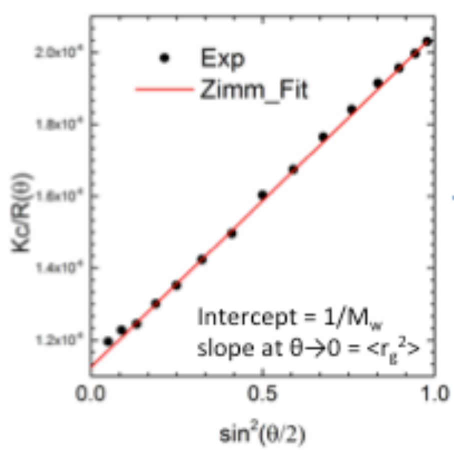
SEC+MALLS



Angle dependent scattering is recorded

MALLS: Multi-angle laser light scattering (Wyatt DAWN EOS)
RI : differential refractometer (Wyatt Optilab DSP)
SEC Columns : Waters Ultrahydrogel 2000,250
Mobile Phase : 0.1M NaNO3





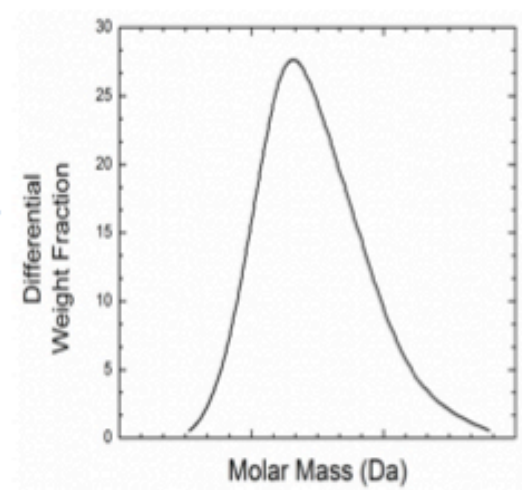
LS ≡ polymer size
RI ≡ concentration

Intensity of scattered light and molar mass is related by the Zimm Equation[1]

$$\frac{Kc}{\Delta R_\theta} = \left(\frac{1}{M_w} + 2A_2c\right)\left(1 + \left(\frac{16\pi^2\eta_0^2 \sin^2(\theta/2)}{3\lambda^2}\right)\langle R_g^2\rangle\right)$$

$$K = \frac{4\pi^2\eta_0^2(dn/dc)^2}{N_A\lambda^4}$$

dn/dc = differential refractive index increment (=0.162 mLg^{-1})



[1] B. H. Zimm, Journal of Chemical Physics 16, 1099 (1948)

Temperature Gradient Interaction Chromatography (TGIC)

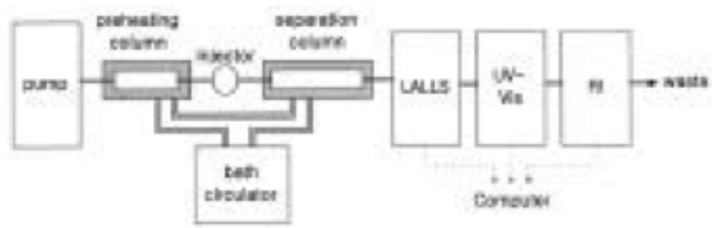
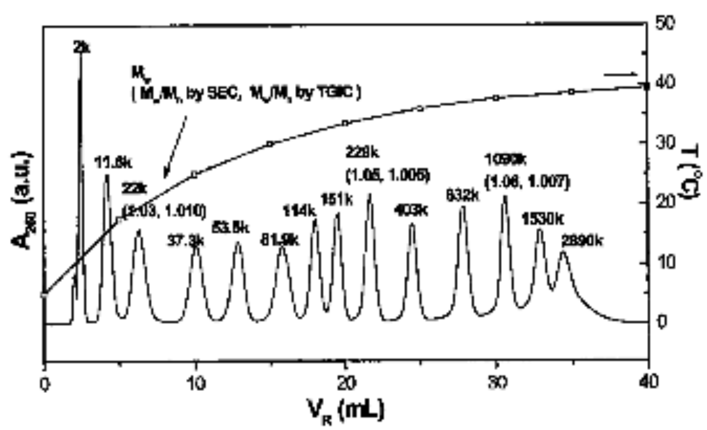


Figure 1 *Schematic diagram of TGIC apparatus.*



from group of Taihyun Chang, Pohang Univ., Korea

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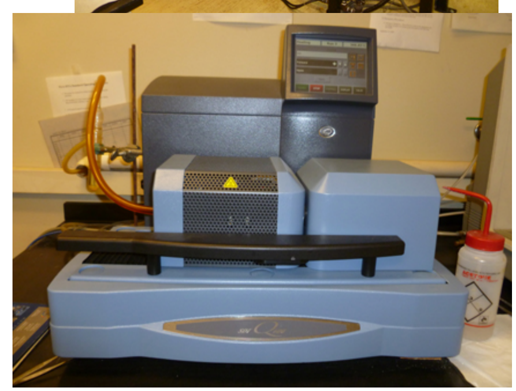
Processing/analysis Equipment

- **Cold and hot Isostatic Presses**
- **Burnout and sintering furnaces**
- **Differential scanning calorimetry / thermal gravimetric analysis**
- **Dilatometers**
- **Extruders and Lab Scale Film Blowing**







Laine lab

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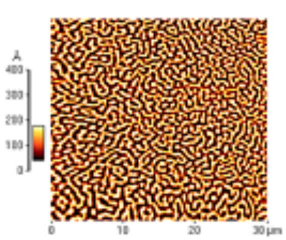
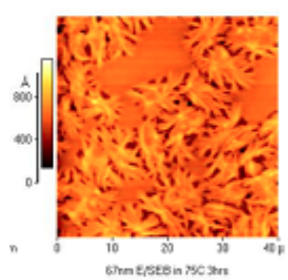
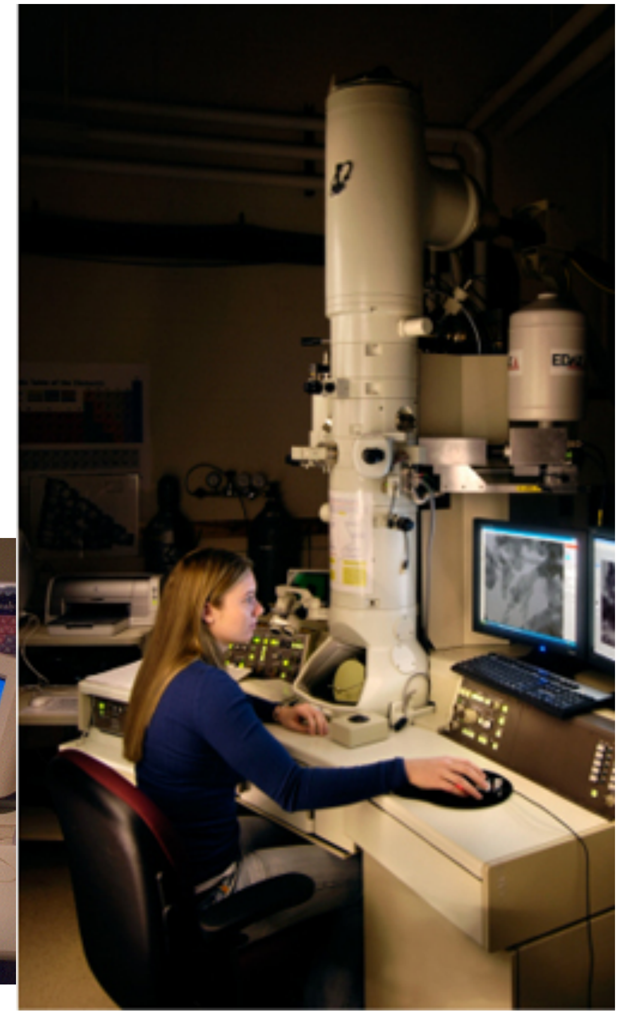
Electron Microbeam Analysis Laboratory

- Scanning electron microscopy
- Transmission electron microscopy
- Atomic force microscopy
- Focused Ion beam
- X-ray diffraction and SAXS







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Computational Capabilities: Kinetic Modeling

Reaction kinetics of LCB PE using single-site catalyst

$$P_{x,n} + M \xrightarrow{k_p} P_{x+1,n}$$

monomer addition

$$P_{x,n} + D^{=}_{y,m} \xrightarrow{k_{LCB}} P_{x+y,n+m+1}$$

addition of unsaturated chain

$$P_{x,n} + CTA \xrightarrow{k_{CTA}} D^{+}_{x,n} + P_{1,0}$$

generation of dead structured chain

$$P_{x,n} \xrightarrow{k\beta} D^{=}_{x,n} + P_{1,0}$$

β-hydride elimination

Monte Carlo probabilities

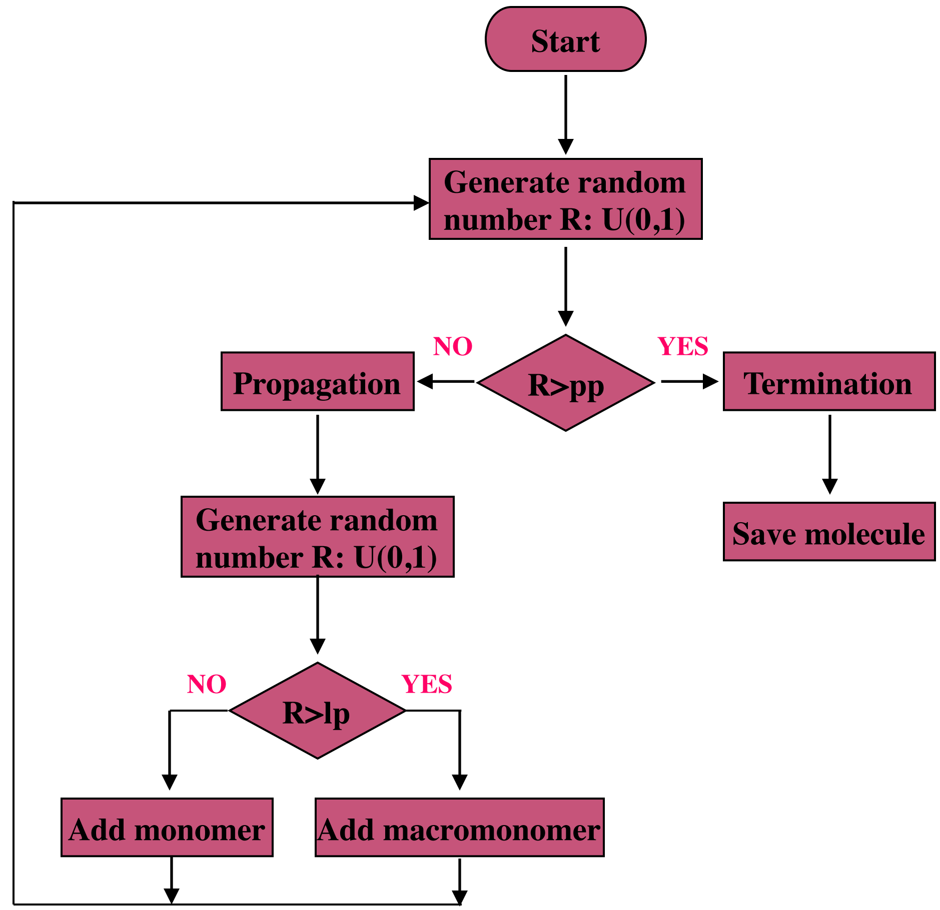
$$pp = \frac{R_p + R_{LCB}}{R_p + R_{LCB} + R_T}$$

propagation probability

$$lp = \frac{R_p}{R_p + R_{LCB}}$$

monomer selection probability

Algorithm for Monte Carlo simulation of LCB PE using single-site catalyst



Costeux et al., *Macromolecules* (2002)

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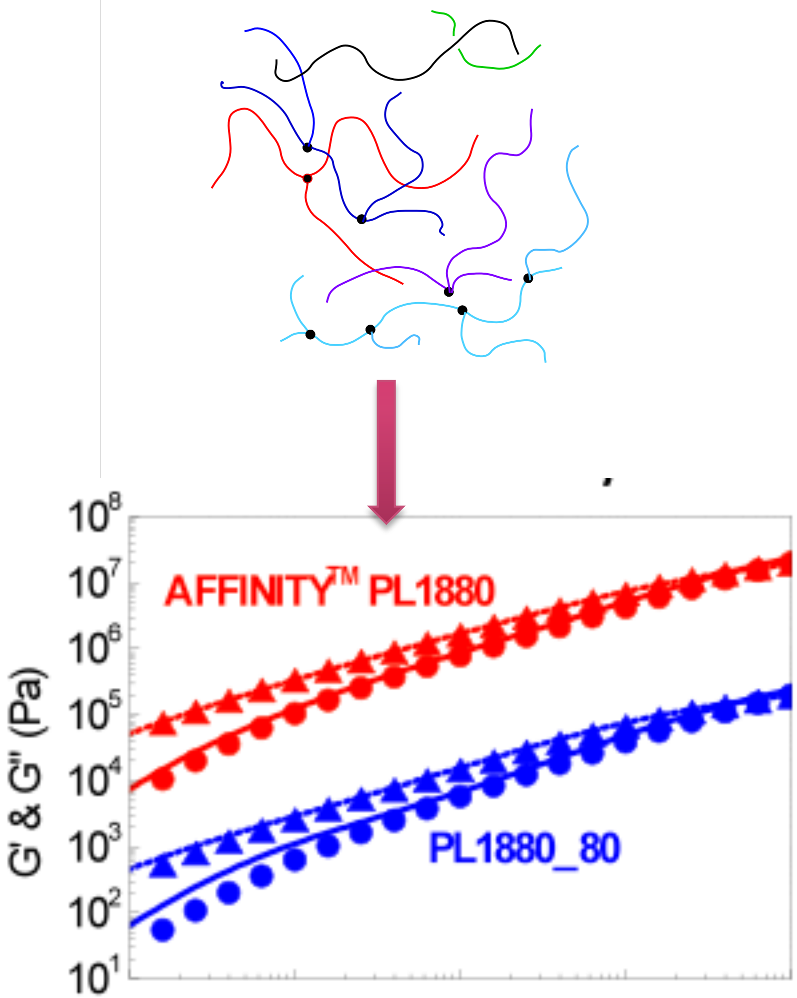
Computational Capabilities: Model of Polymer Linear Rheology



- A complex commercial branched polymer is represented by an ensemble of up to 10,000 chains, all with different molecular weights and branching structures.
- The ensemble is generated from a combination of GPC characterization, knowledge of reaction kinetics, and rheology.
- The ensemble is fed into the "Hierarchical Code," and a prediction of the linear rheology (G' and G") emerges.

Larson et al., (2001, 2006, 2011)

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Computational Capabilities: Molecular Simulations

atomistic & coarse-grained simulations of polymers, surfactants, etc.