SOFT MATERIALS AT THE CENTER FOR HIERARCHICAL MATERIALS DESIGN

Juan de Pablo, University of Chicago

October 31, 2016

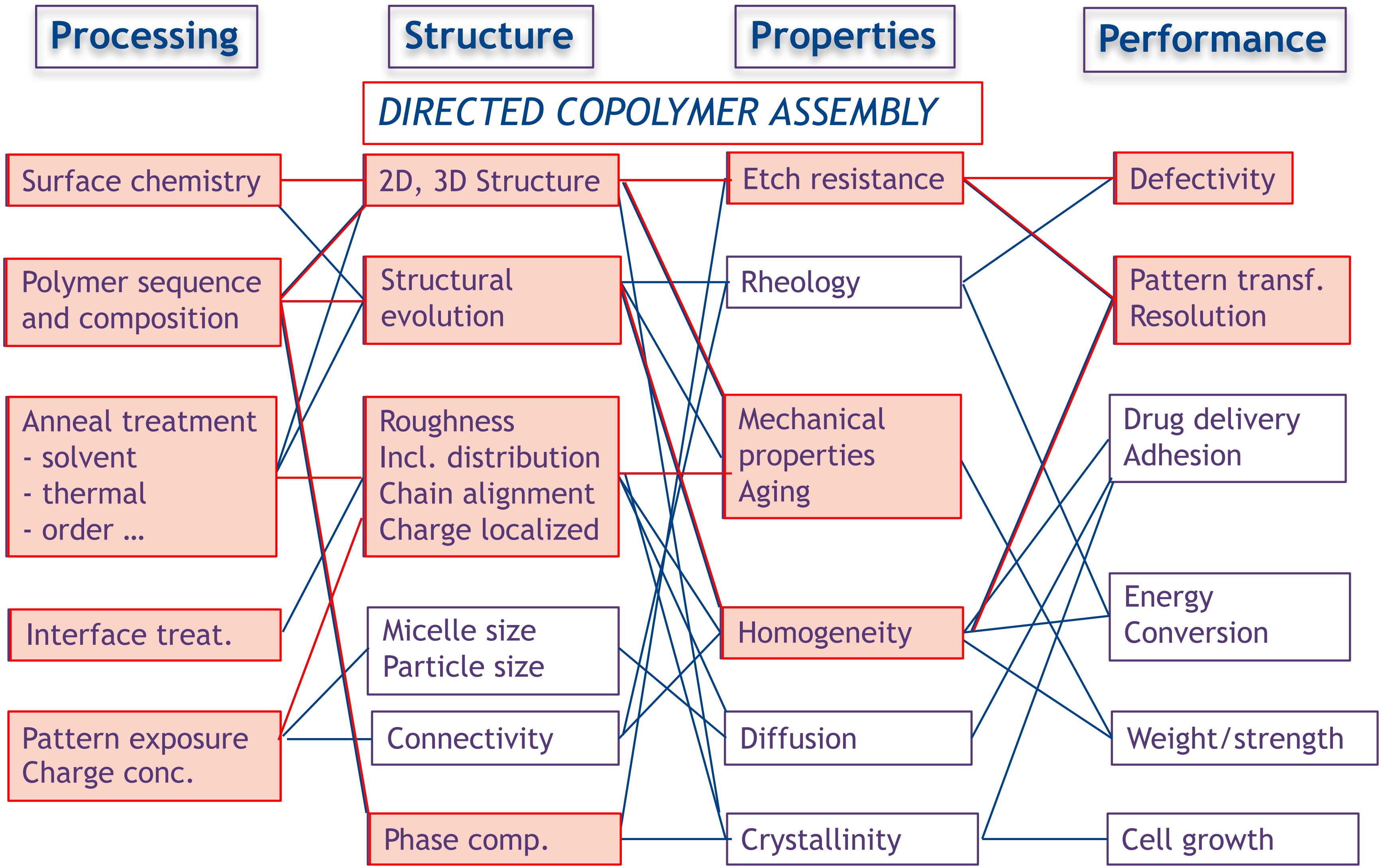
CHiMaD

- Weak interactions, order $k_B T$
- Always evolving, often far from equilibrium
- Often amorphous, difficult to "define"
- One compound can behave very differently
  - linear polyethylene
  - branched polyethylene
- Complicated theoretical descriptions, hard to solve
- Lack of data
- …

HARD VS. SOFT MATTER

CHiMaD

SOFT MATERIALS AT CHiMaD



CALPHAD Method – Metallic Alloys

$$G = G_{id}{}^{\phi} + G_{E}{}^{\phi}$$

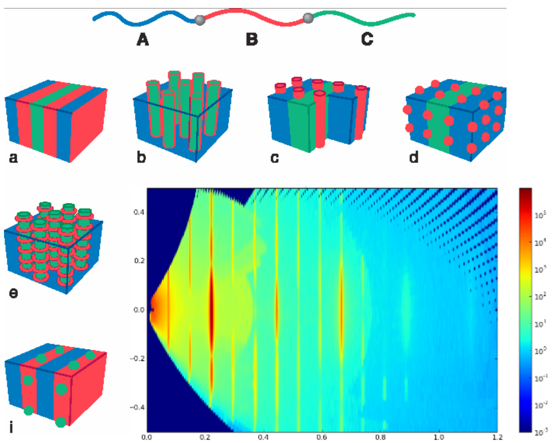
$$G_{id}^{\phi} = \mathrm{R} \cdot \mathrm{T} \cdot \sum_{i=1}^{n} x_i \cdot \ln(x_i), \quad i = 1, \ldots, n$$

$$G_{E}^{\phi} = \sum_{\substack{i,j=1 \\ i \neq j}}^{n} x_i x_j \sum_{z=0}^{m} {}^{z}L(x_i - x_j)^{z} + \sum_{\substack{i,j,k=1 \\ i \neq j \neq k}}^{n} x_i x_j x_k L_{ijk} \quad z = 0, \ldots, m$$

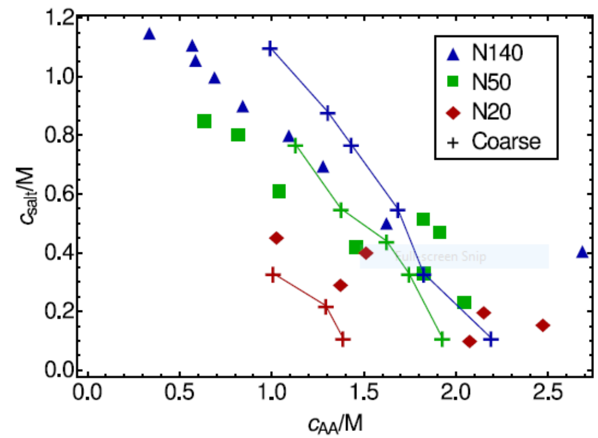
“Modelling of phase diagrams and thermodynamic properties using Calphad method – Development of thermodynamic databases”
A. Kroupa, Computational Materials Science, 66, 3–13 (2013)

A Universal Platform

Multiblocks - DSA

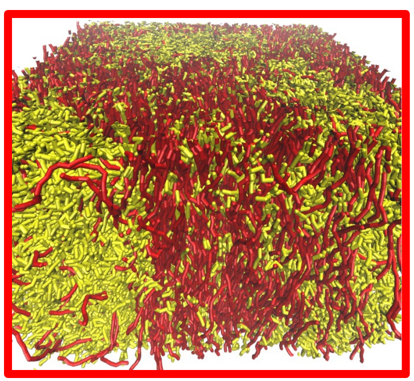


Charged polymers - coacervates

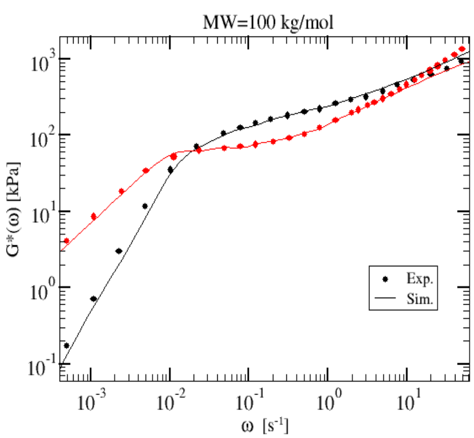


CHiMaD

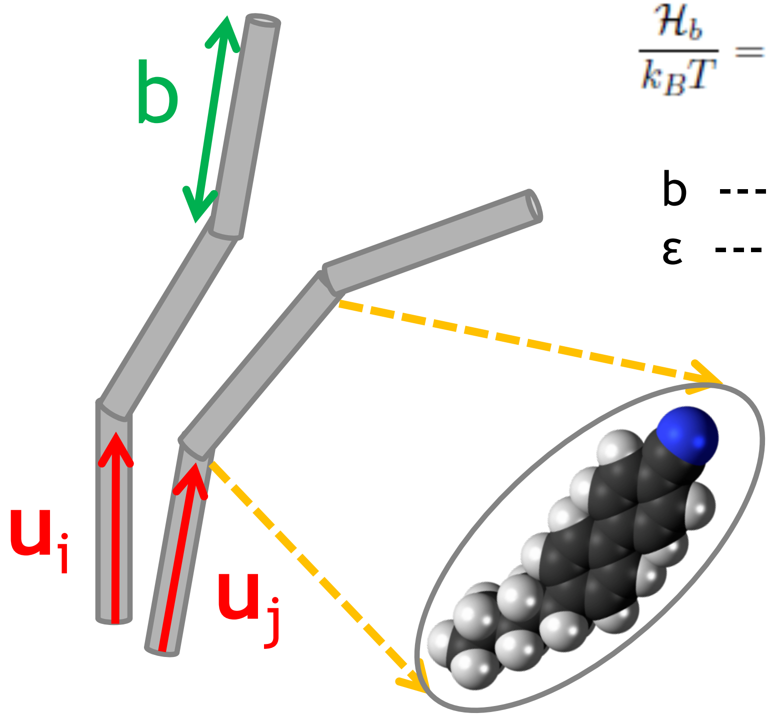
OPVs - Composites



Rheology



OPV Polymers and Liquid Crystallinity - Model



Intra-molecular Interactions: Worm-like chain model

$$\frac{\mathcal{H}_b}{k_B T} = -\varepsilon \sum_{i=1}^{n} \sum_{s=1}^{N-2} \frac{[\mathbf{r}_i(s+2) - \mathbf{r}_i(s+1)] \cdot [\mathbf{r}_i(s+1) - \mathbf{r}_i(s)]}{b^2}$$

b --- bond length

ε --- controls chain stiffness

Inter-molecular Interactions:

segment-segment incompatibility

$$\frac{\mathcal{H}_{nb}}{k_B T} = \rho_o \int_V d\mathbf{r} \left[\boxed{\chi \phi_A(\mathbf{r}) \phi_B(\mathbf{r})} + \boxed{\frac{\kappa}{2} [1 - \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})]^2} \boxed{-\frac{\mu}{3} \mathbf{Q}(\mathbf{r}) : \mathbf{Q}(\mathbf{r})} \right],$$

compressibility

orientational coupling

$$\phi_\gamma(\mathbf{r}) = \sum_{i=1}^{n} \sum_{s=1}^{N_{seg}} \pi_{\gamma,\gamma_{i(s)}} \delta(\hat{\mathbf{r}}_i(s) - \mathbf{r}),$$

$$\mathbf{Q}_{\alpha\beta}(\mathbf{r}) = \rho_o^{-1} \sum_{i=1}^{n} \sum_{s=1}^{N_{seg}} \delta(\hat{\mathbf{r}}_i(s) - \mathbf{r}) \left[\frac{3}{2} \mathbf{u}_{i,\alpha}(s) \mathbf{u}_{i,\beta}(s) - \frac{\delta_{\alpha\beta}}{2} \right]$$

NanoMine

Catherine Brinson, NU

Wei Chen, NU

processing, structure and property parameters for polymer nanocomposite systems

Polymer Design

Juan de Pablo, UChicago

Ian Foster, UChicago

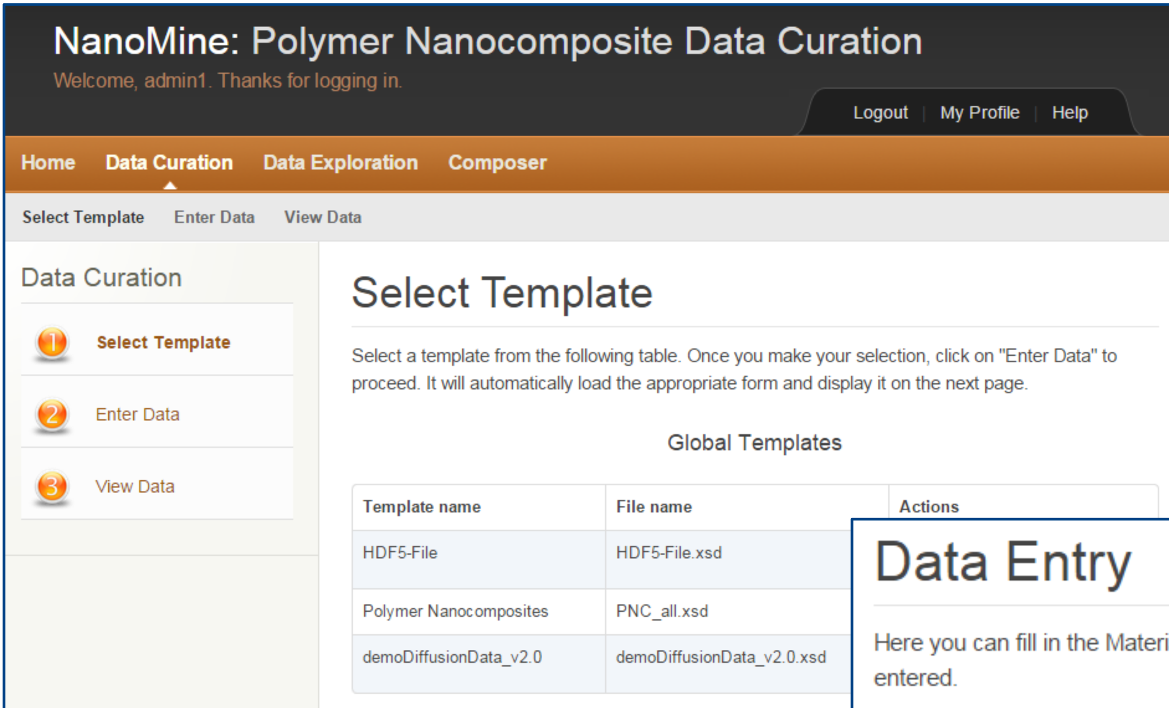
Paul Nealey, UChicago

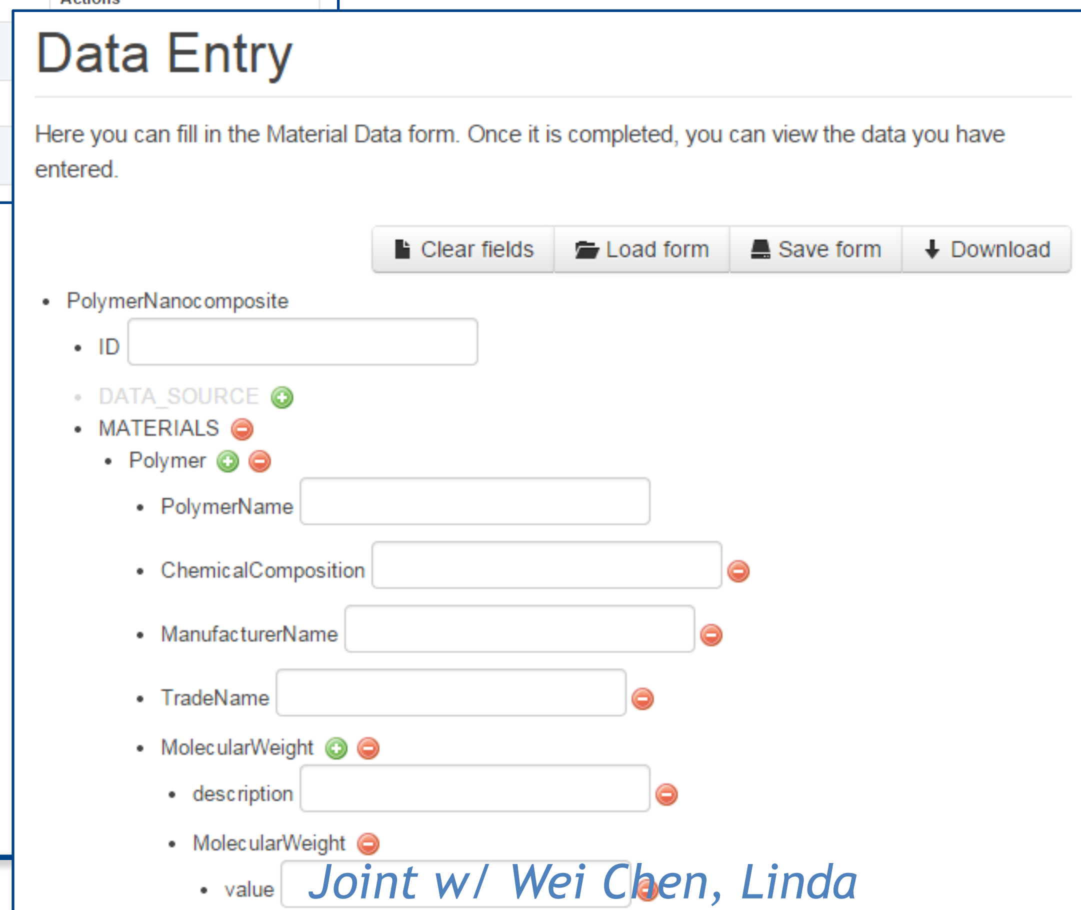
Heinrich Jaeger, UChicago

characteristic properties for design of polymer blends and copolymers for engineering applications

TOOL DEVELOPMENT
DATABASES

DataBase



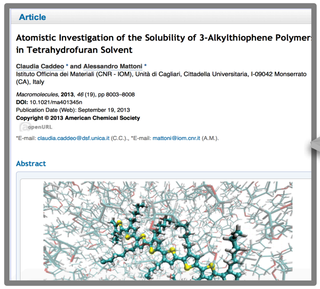


- Data curation: literature and lab,
- automation,
- smart query tools,
- visualization tools

Joint w/ Wei Chen, Linda

PPDB: Method (1)

- Automated knowledge extraction from text, equations, tables and figures.



Title: Sub-5 nm Domains in Ordered Poly(cyclohexylethylene)-block-poly(methyl methacrylate) Block Polymers for Lithography

Authors: Justin G. Kennemur, Li Yao, Frank S. Bates, and Marc A. Hillmyer

Date Published (Web): February 11, 2014

DOI: 10.1021/ma4020164

Abstract: A series of poly(cyclohexylethylene)-block-poly(methyl methacrylate) (PCHE-PMMA) diblock copolymers with varying molar mass (4.9 kg/mol ≤ Mn ≤ 30.6 kg/mol) and narrow molar mass distribution were synthesized through a combination of anionic and atom transfer radical polymerization (ATRP) techniques. Heterogeneous catalytic hydrogenation of α-(hydroxy)polystyrene (PS-OH) yielded α-(hydroxy)poly(cyclohexylethylene) (PCHE-OH) with little loss of hydroxyl functionality. PCHE-OH was reacted with α-bromoisobutyryl bromide (BiBB) to produce an ATRP macroinitiator used for the polymerization of methyl methacrylate. PCHE-PMMA is a glassy, thermally stable material with a large effective segment-segment interaction parameter, χeff = (144.4 ± 6.2)/T - (0.162 ± 0.013), determined by mean-field analysis of order-to-disorder transition temperatures (TODT) measured by dynamic mechanical analysis and differential scanning calorimetry. Ordered lamellar domain pitches (9 ≤ D ≤ 33 nm) were identified by small-angle X-ray scattering from neat BCPs containing 43-52 vol % PCHE (fPCHE). Atomic force microscopy was used to show ~7.5 nm lamellar features (D = 14.8 nm) which are some of the smallest observed to date. The lowest molar mass sample (Mn = 4.9 kg/mol, fPCHE = 0.46) is characterized by TODT = 173 ± 3 °C and sub-5 nm nanodomains, which together with the sacrificial properties of PMMA and the high overall thermal stability place this material at the forefront of "high-χ" systems for advanced nanopatterning applications.

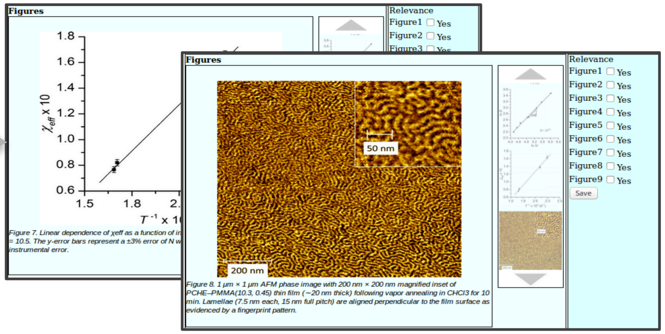


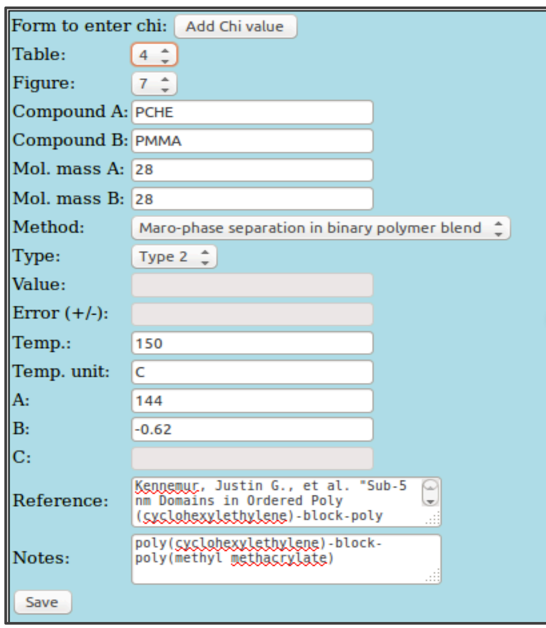
Table 4. χeff(T) Coefficients for Various Lithographic Patterning Block Copolymers Calculated to a Reference Volume of 118 Å3

BCP[a]	α	β	χeff (150 °C)	ref[b]
PCHE-PMMA	144	-0.162	0.178	this work
PS-PDMS	32.6	0.033	0.110	75
PS-PLA	57.4	-0.061	0.075	47
PS-PI	59.1	-0.071	0.069	47
PtBS-PMMA	41.2	-0.044	0.053	47
PS-PEO	29.8	-0.023	0.047	67
PS-PMMA	3.49	0.022	0.022	47

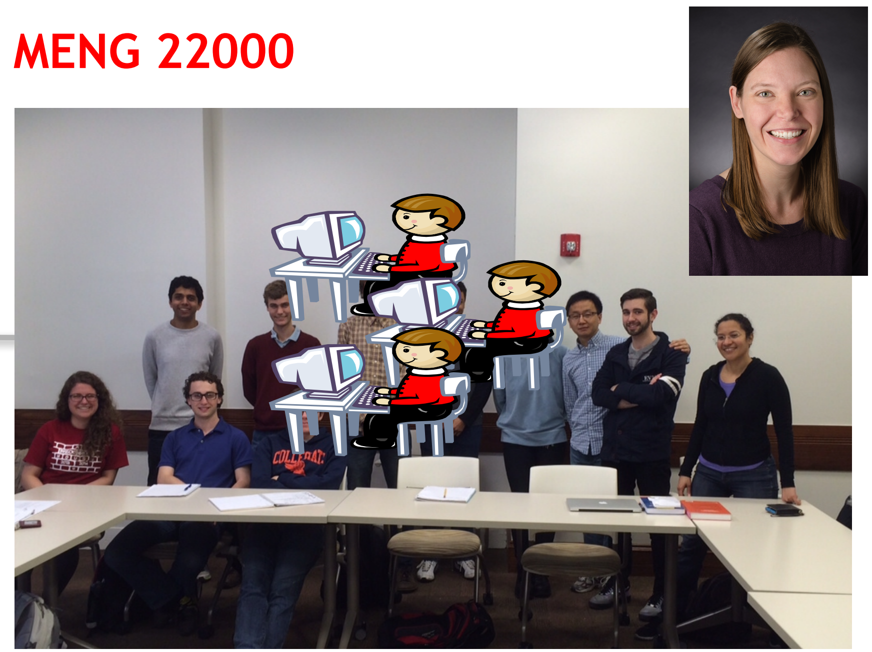
Roselyne Tchoua (CI)

PPDB: Method (2)

- Leverage knowledge from crowd-sourced *experts* to aid classification and knowledge extraction.



MENG 22000

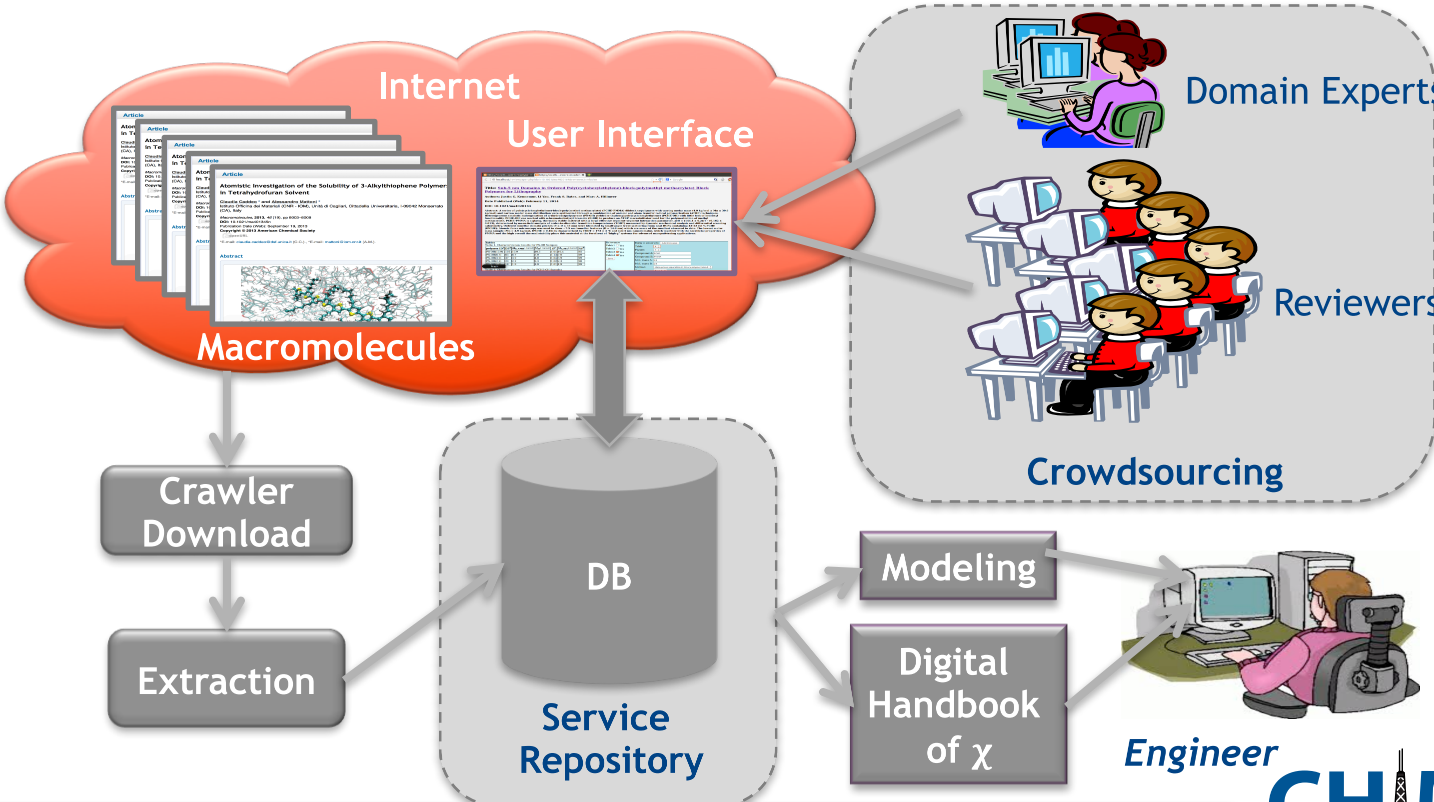


Roselyne Tchoua (CI), Debbie Audus (NIST), Jian Qin (IME), Mladen Rasic(IME)

CHIMaD

PPDB: Method (3)

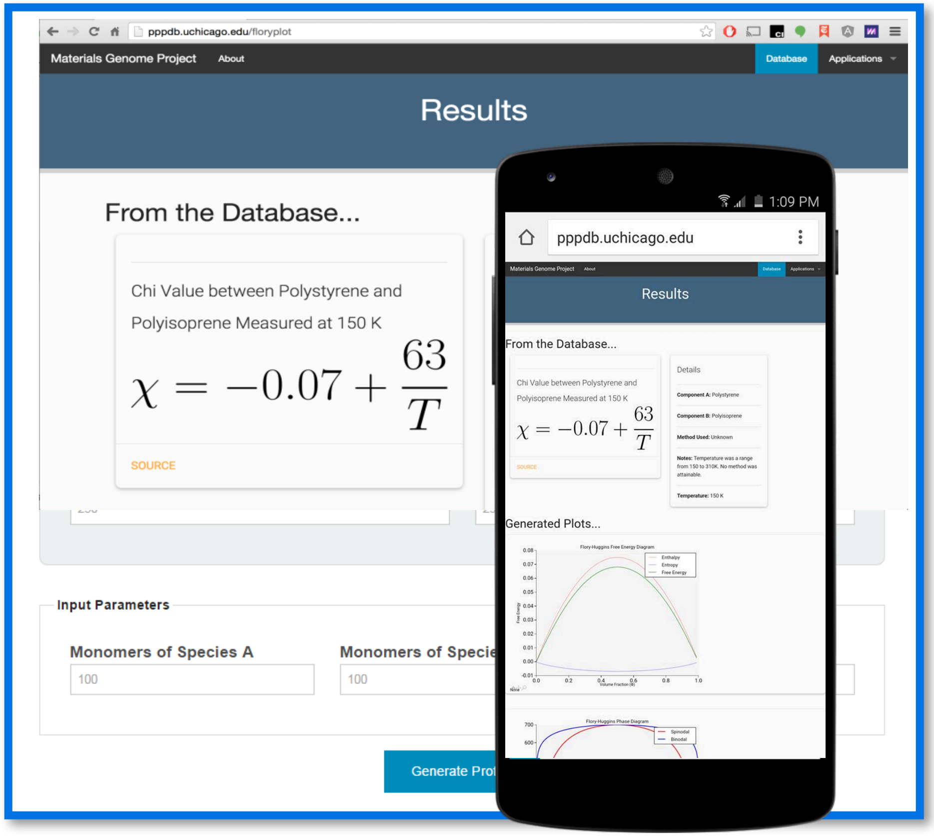
- Create a curated database for a range of polymer properties & present molecular engineers with *approved* relevant data for materials design. Port to other materials/properties.



CHiMaD

Available Tools

- All applications on the site now run natively on mobile devices.
- Interactive Output from the database, obtain chi value, system details, method, and source of chi value.
- Interactive phase diagrams, free energy plots, data points, etc.



Input screen for generation of Lattice Cluster Theory phase diagram with semiflexibility.

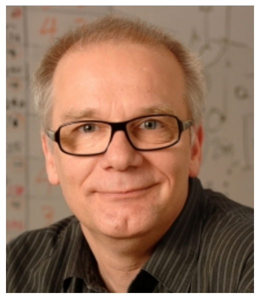
CHiMaD

Paul Nealey,
UChicago

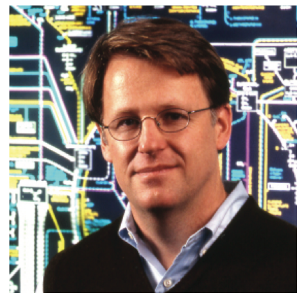
Juan de Pablo,
UChicago

Steven Sibener,
UChicago

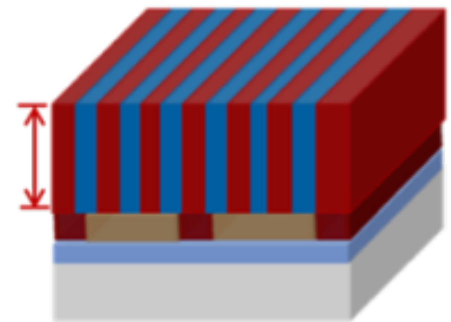
Luping Yu,
UChicago



Heinrich Jaeger,
UChicago



Ian Foster,
UChicago



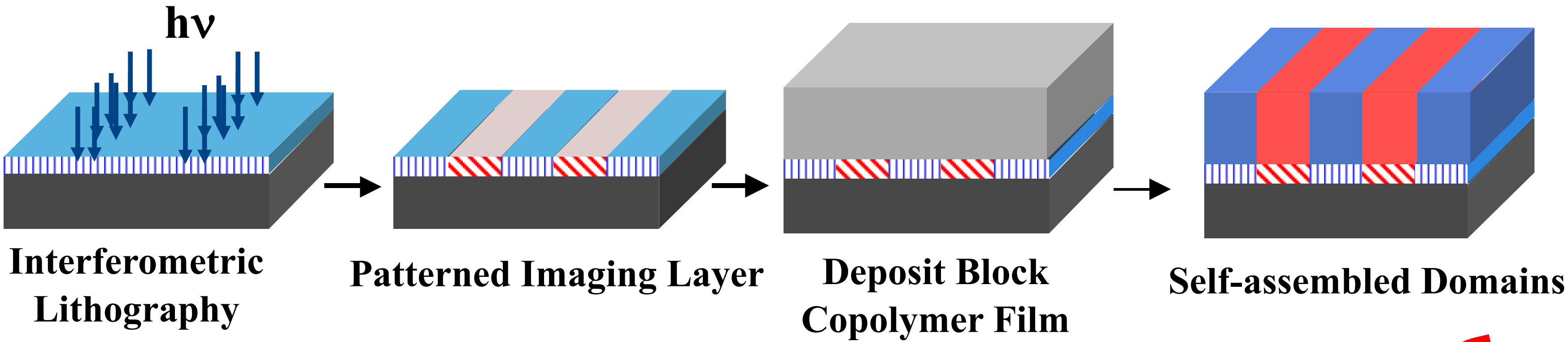
DIRECTED SELF-ASSEMBLY OF BLOCK COPOLYMERS

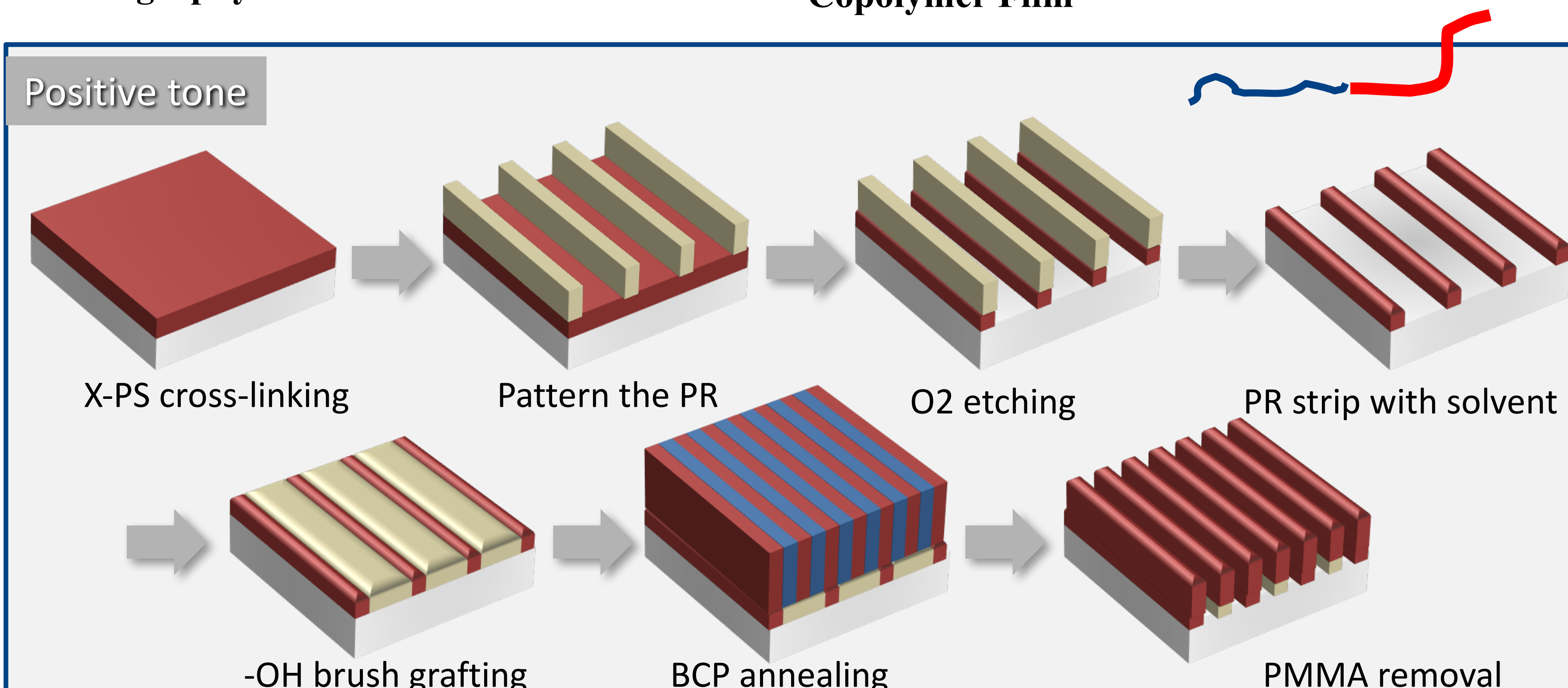
to revolutionize nanomanufacturing. the interest and exponential growth in research activity and expenditure is driven by the semiconductor industry.

Intel, Mentor Graphics, Global Foundries, IMEC

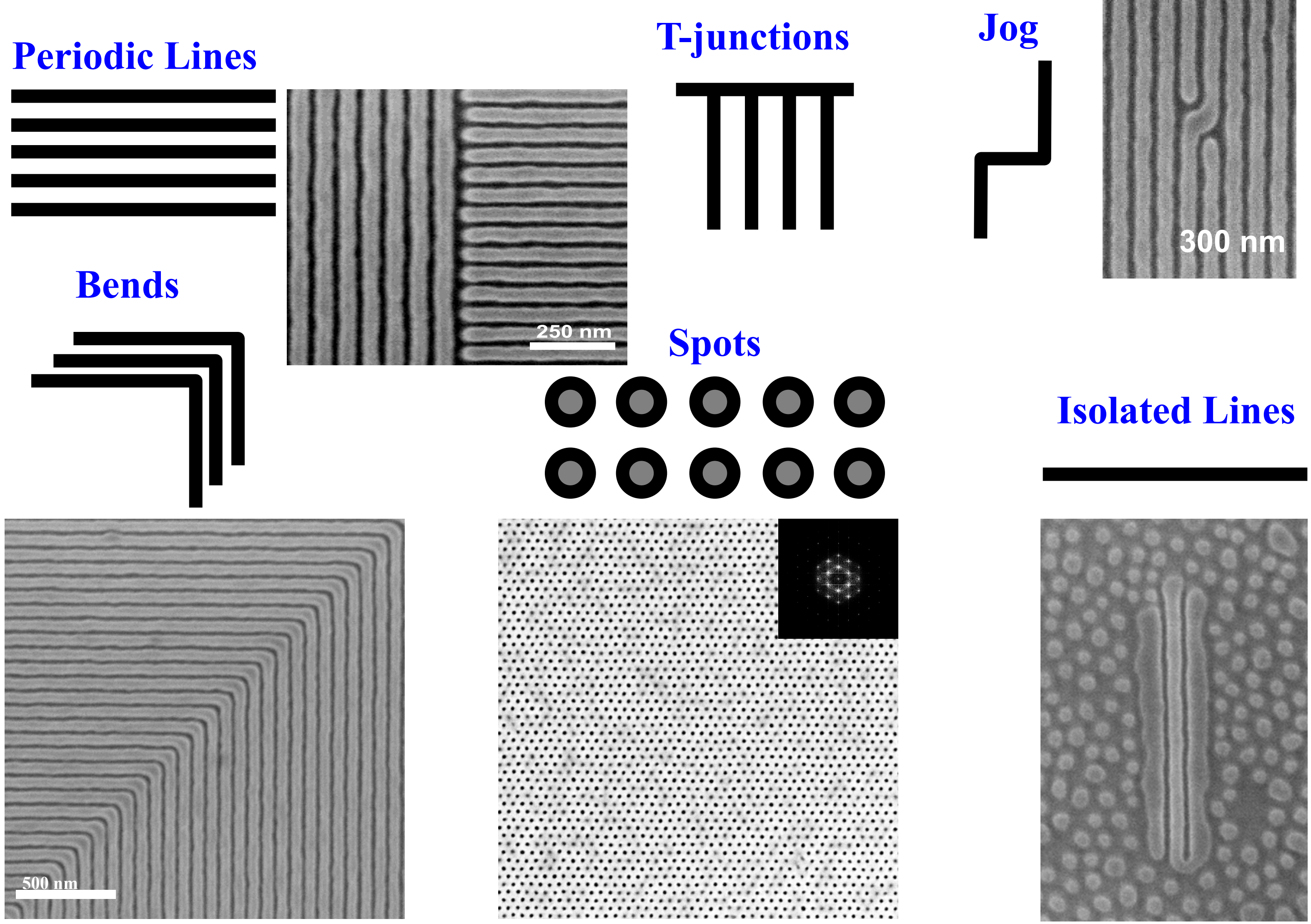
CHIMaD

Directed self-assembly of block copolymers on lithographically defined nanopatterned substrates





Directed assembly of essential features for the fabrication of integrated circuits as defined by representatives from the microelectronics industry

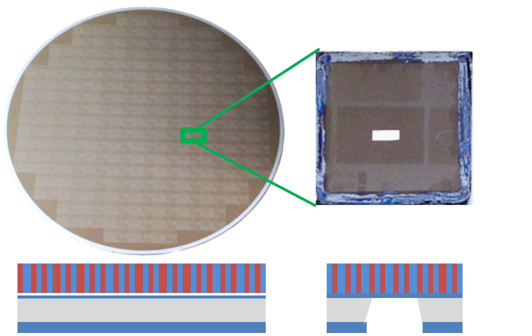


DIRECTED SELF-ASSEMBLY OF BLOCK COPOLYMERS

DESIGN GOALS

- *Materials and processes for sub 10 nm lithography*
- *Scaling to 5 nm resolution*

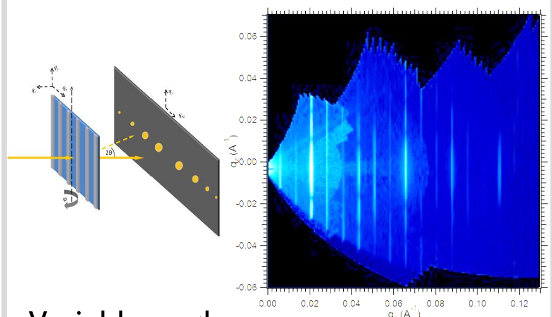
Relevant samples from industrial partners



300mm Wafer

Coupon with back-etched membrane

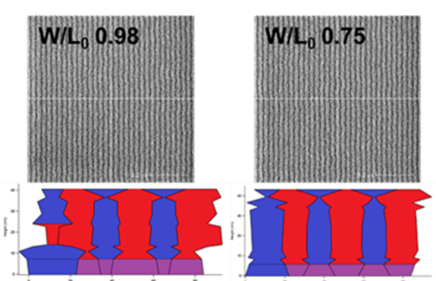
Resonant Soft X-ray Scattering (RSoXS)



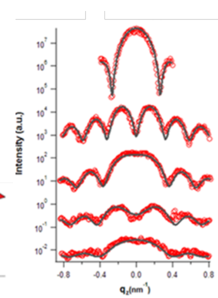
Variable angle transmission measurement

Reconstruct Q_x-Q_z map

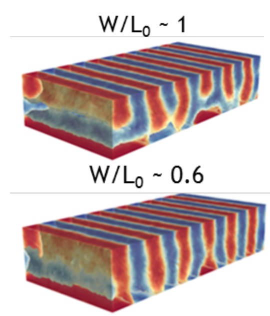
In-film structures revealed



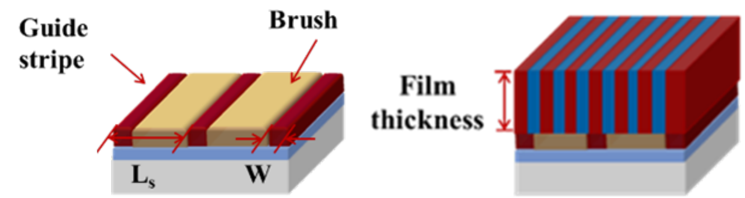
Fit to experiment



Couple to molecular simulation



Input parameters: Pattern characteristics (W/L_0, $\gamma_{interfacial}$) Polymer properties (χ, N, γ)

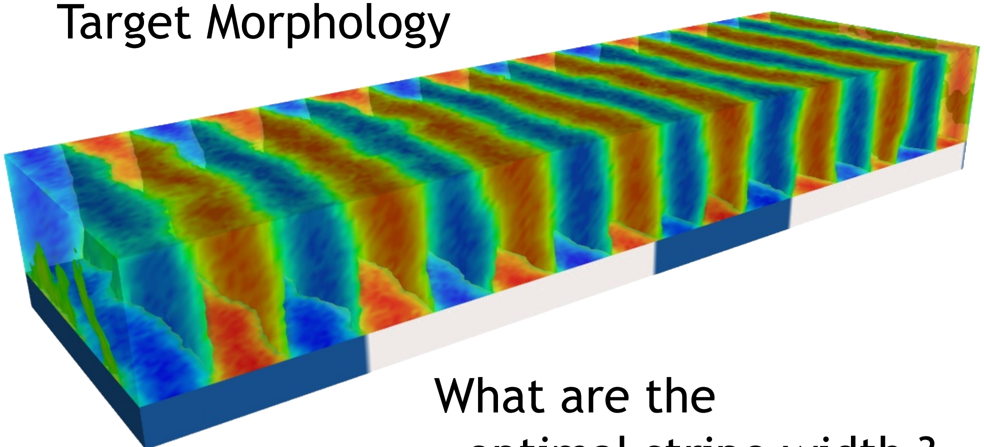


- Enable widespread use of DSA nanotechnology.
- Need to establish proven manufacturing-relevant materials and processes to realize sub 10 nm resolution, and scaling to 5 nm.
- Standard metrology cannot be used to develop and validate predictive models or prototypical systems.
- Objective: develop fully 3D metrology tools of DSA structures based on RSoXS
- Experiments are performed on samples fabricated by industrial partners
- Results are quantitatively compared with those of molecular simulations
- Intimate coupling with advances in models, materials design, and processing.

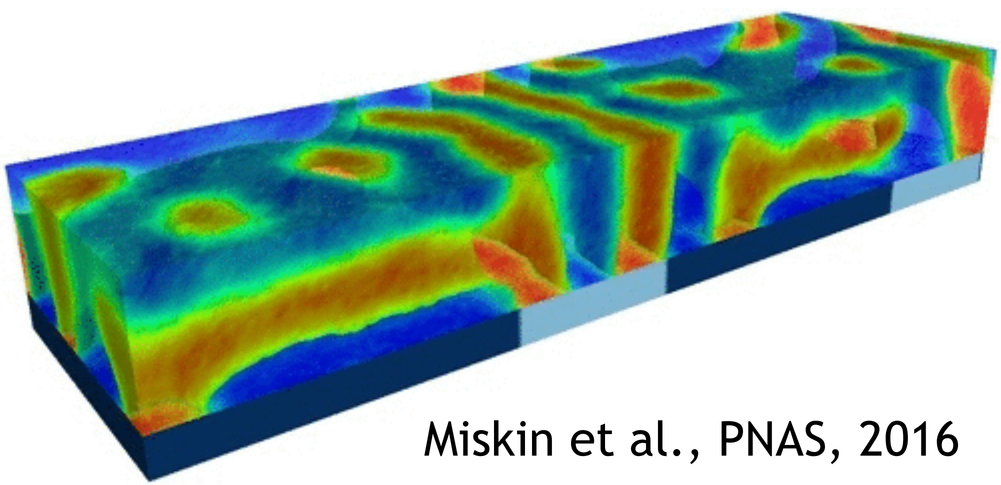
CHiMaD

4X density multiplication

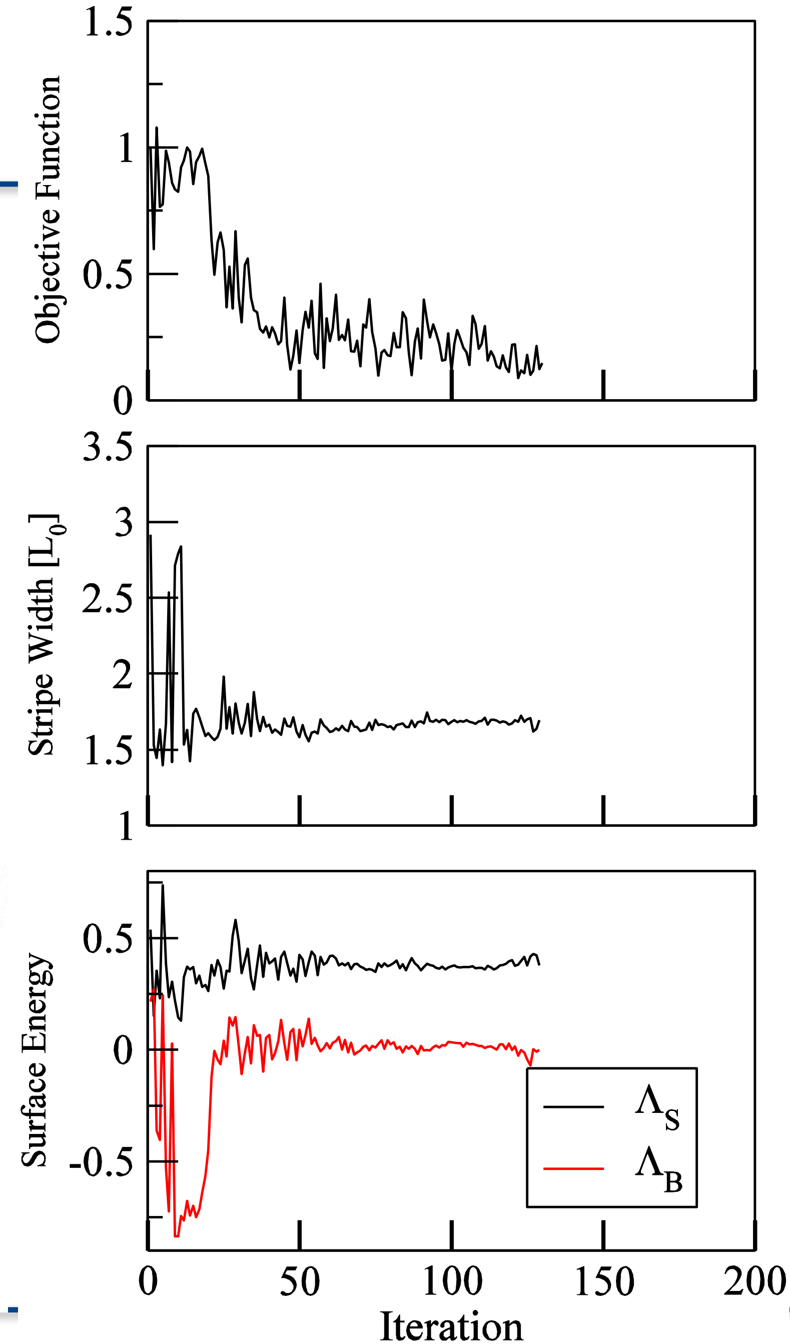
Target Morphology



What are the
- optimal stripe width ?
- pattern characteristics ?

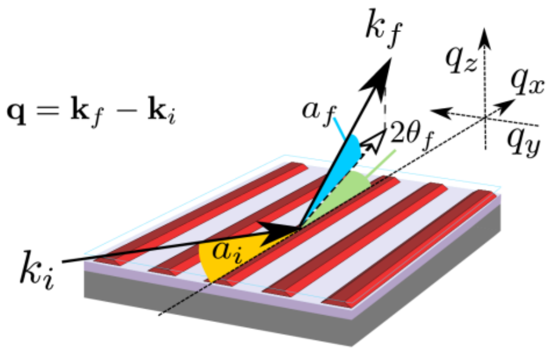


Miskin et al., PNAS, 2016

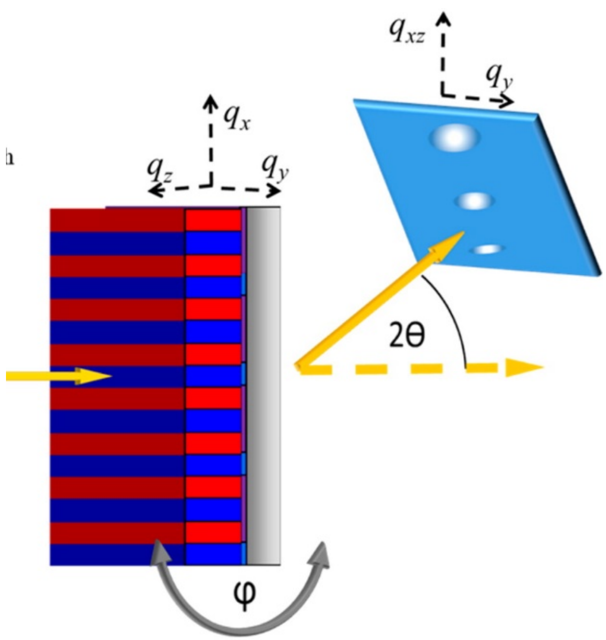


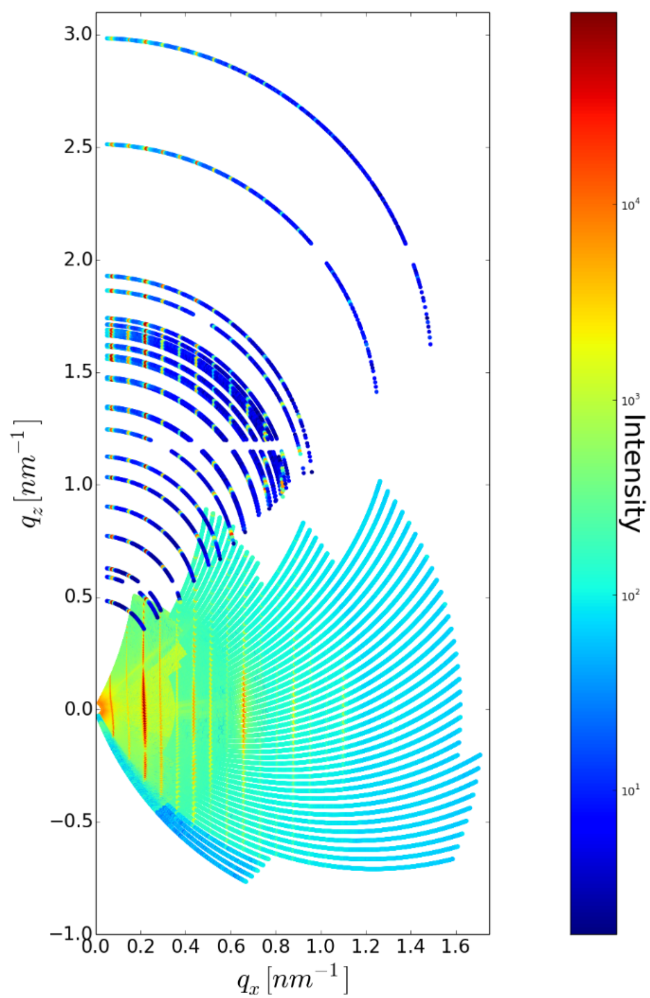
GISAXS and CDSAXS

GISAXS



CDSAXS



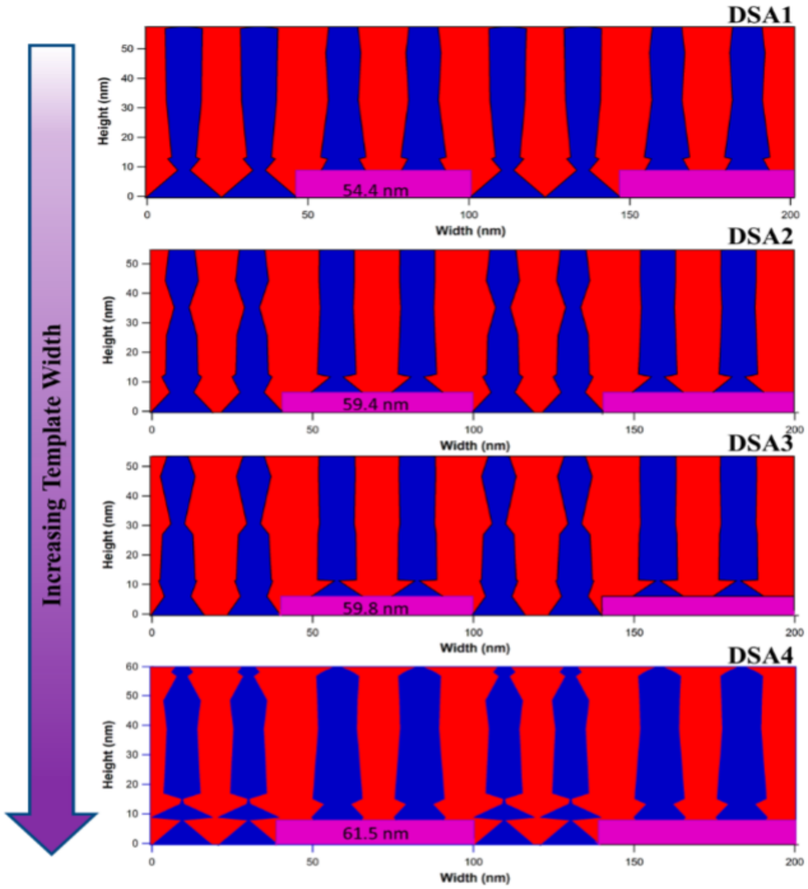


Sunday et al., *ACS Nano*, 2014

CHMaD

Traditional Interpretation

Candidate morphologies constructed from simple geometric shapes



- Treated as a geometric problem

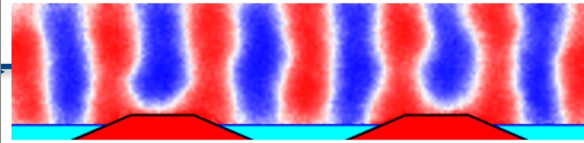
- Average shape described as
combinations of simple patterns

Sunday et al., *ACS Nano*, 2014

CHiMaD

Scattering from Simulations

Thermodynamic and Boundary Conditions

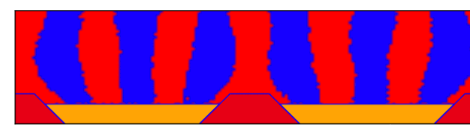


Morphology from Molecular Simulations

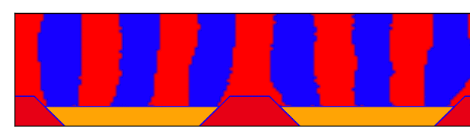
Calculate Fourier Transform of Shape with no interface

Convolute Interfacial Width:
$\sigma = f(\chi N)$

Add the fluctuation of interface

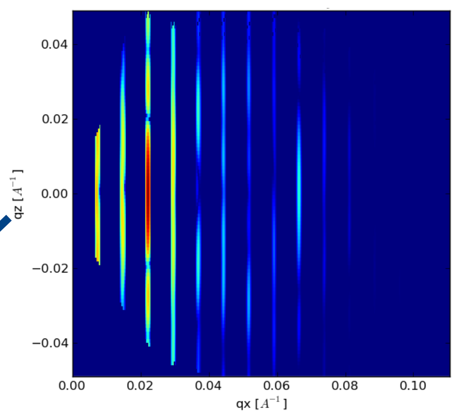


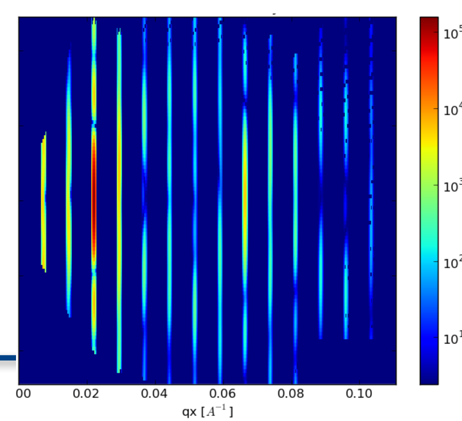
Low χ material: High Fluctuations



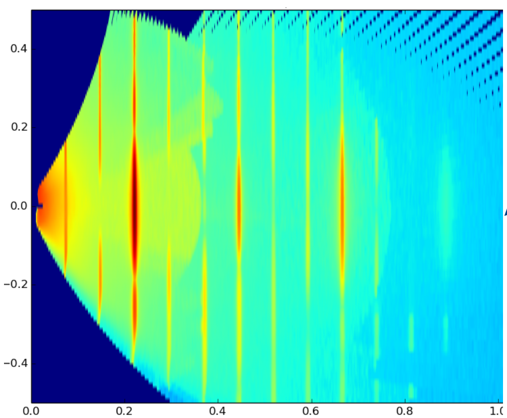
High χ material: Low Fluctuations

Scattering from Simulations





Evolutionary Optimization to select Input Parameters



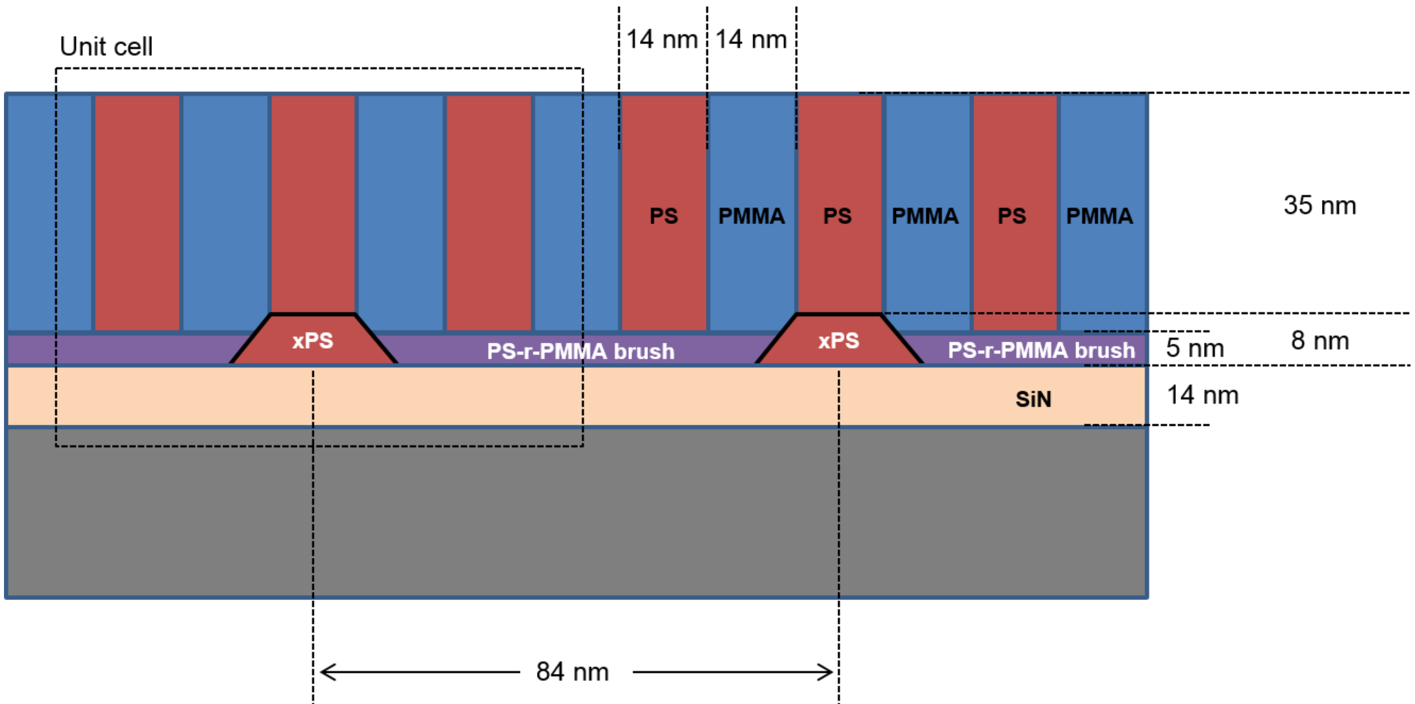
Experimental Data

Khaira et al., submitted, 2016

DOE Grand Challenges Rep.

CHiMaD

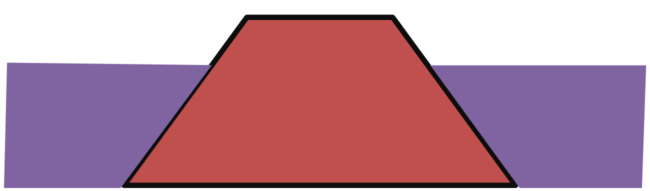
Directed Self-Assembly on Chemical Patterns



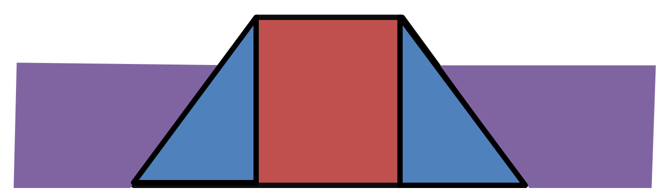
- 3X density multiplication of block copolymer of periodicity 28 nm

Types of Chemical Patterns

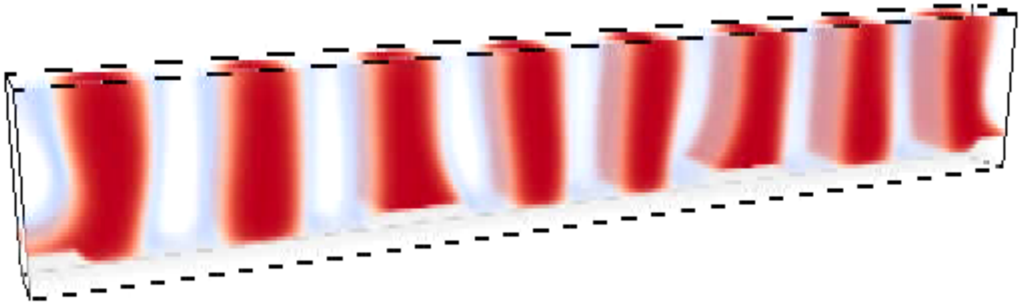
Two Toned: xPS is totally preferential to PS

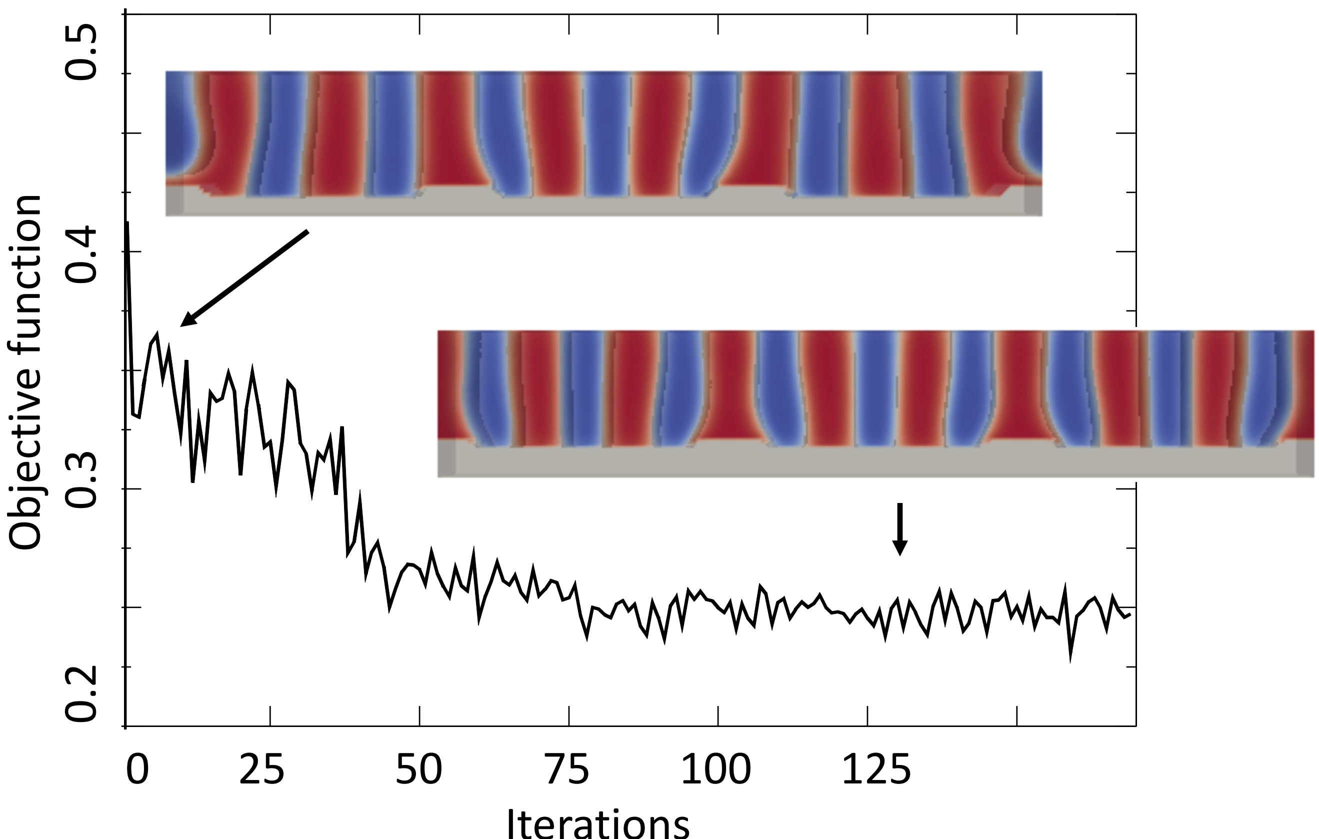


Three-Toned: Top of xPS is preferential to PS while side walls are PMMA preferential



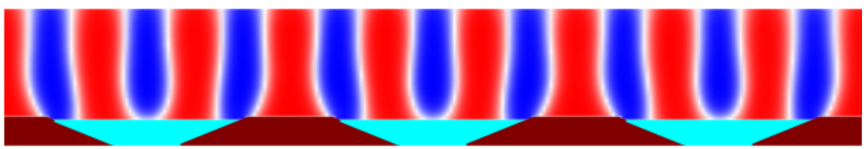
Optimization Results

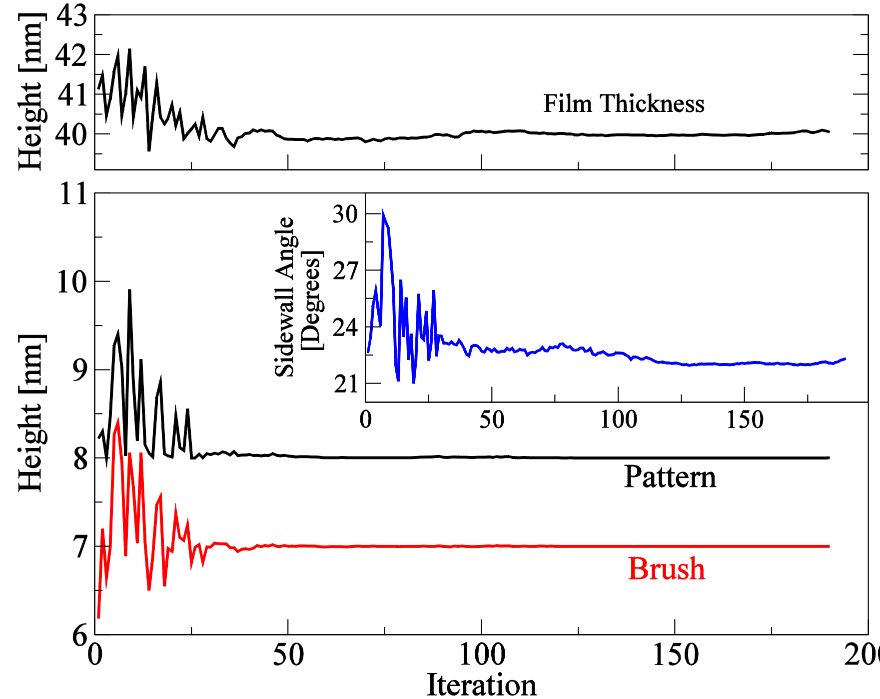


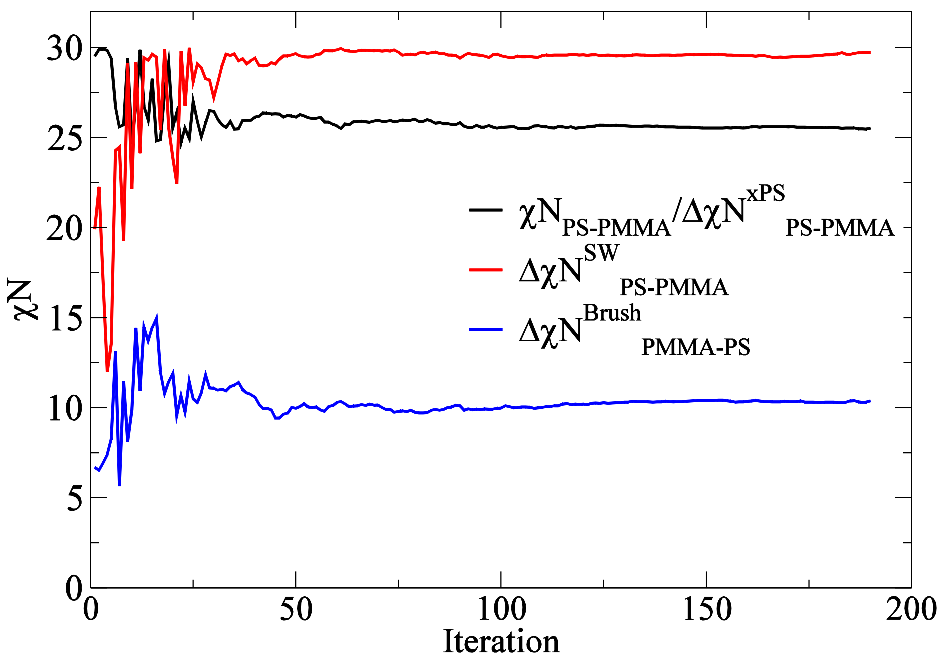


Optimization Results

- W/L0 ~ 0.93
- Approximately 1.5 nm height difference between xPS and backfill brush

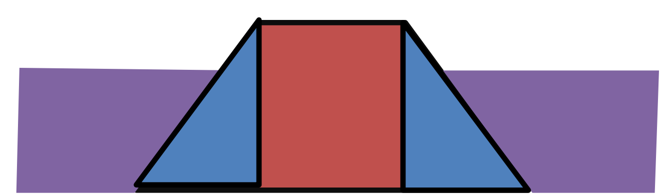




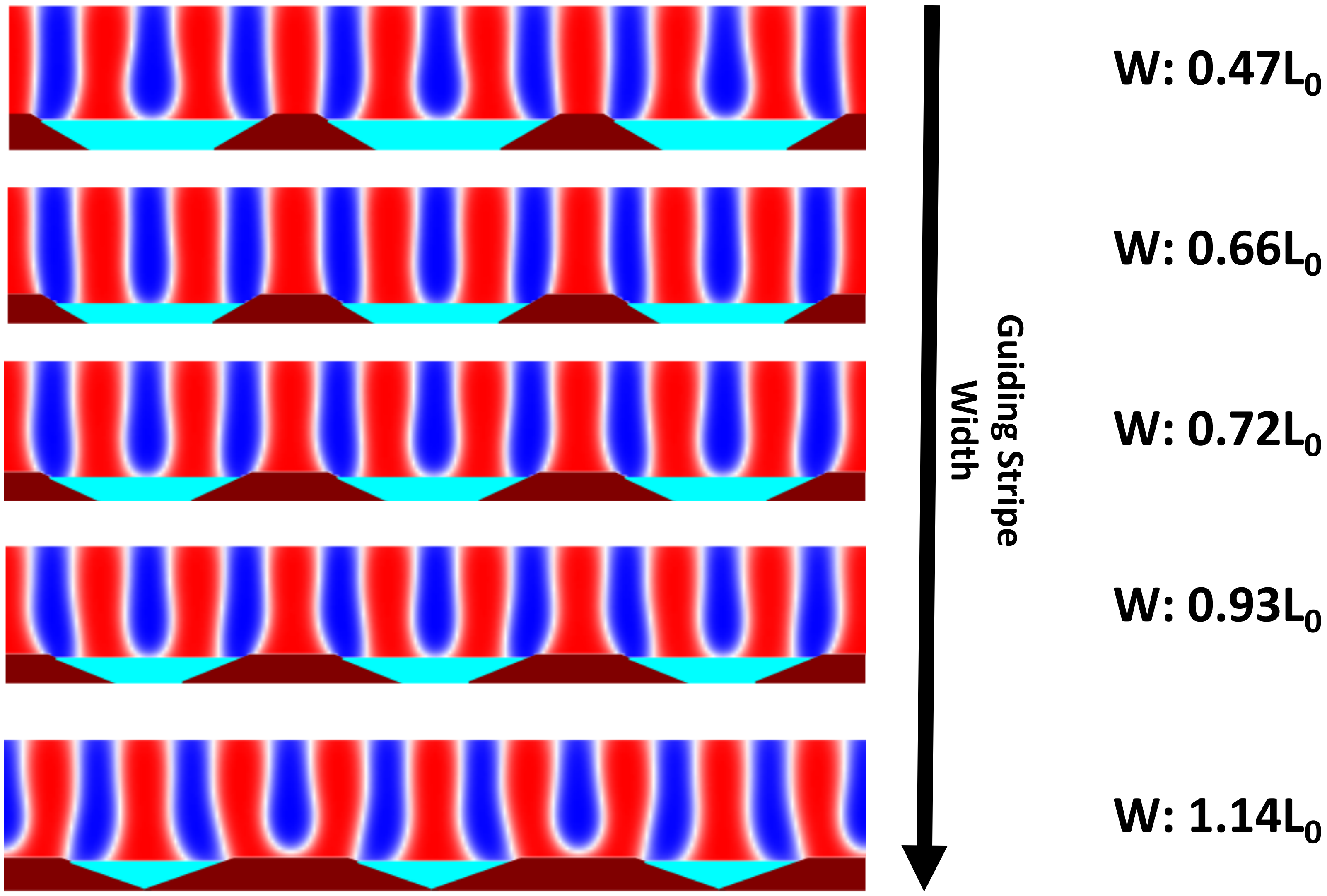


Difference in χN between top of xPS and sidewalls suggests three-toned pattern

Three-Toned: Top of xPS is preferential to PS while side walls are PMMA preferential



Morphology for Different Stripe Widths

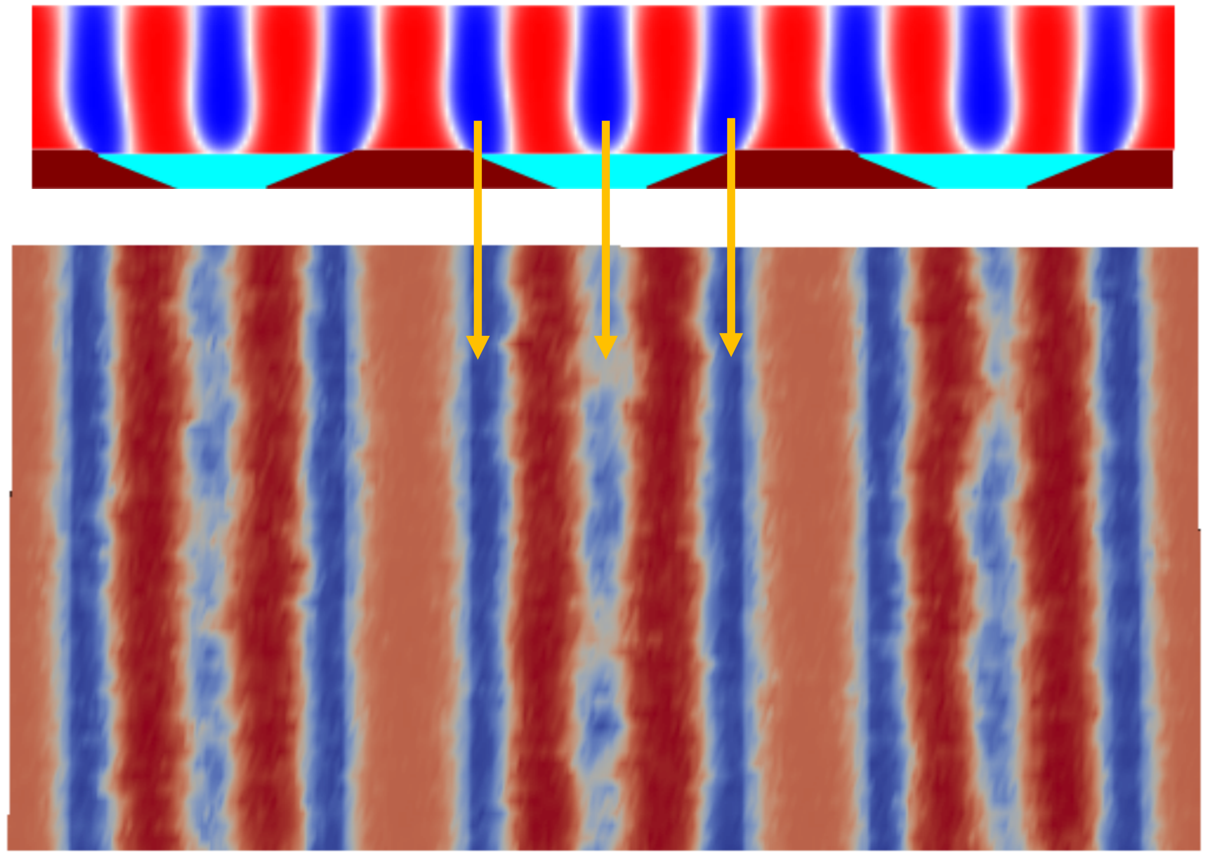


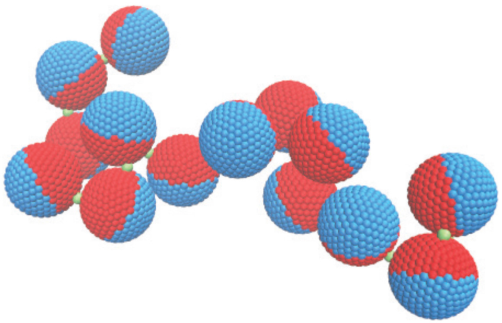
CDSAXS, TEM & GISAXS
$W=1.14L_o$

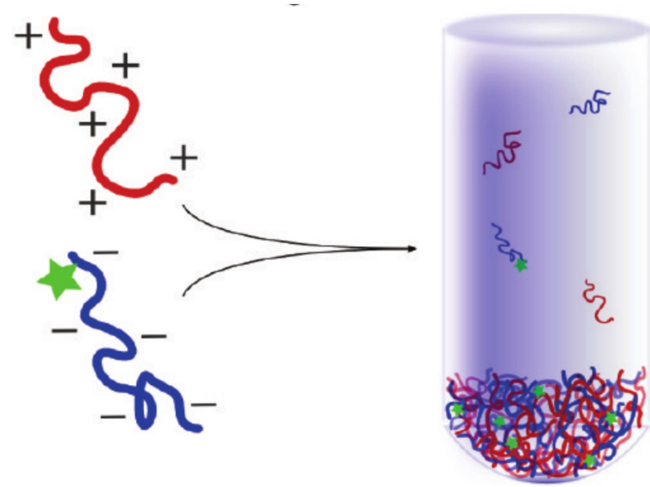
CDSAXS

TEM

GISAXS







Matthew Tirrell, UChicago

Juan de Pablo, UChicago

Monica Olvera de la Cruz, NU

Erik Luijten, NU

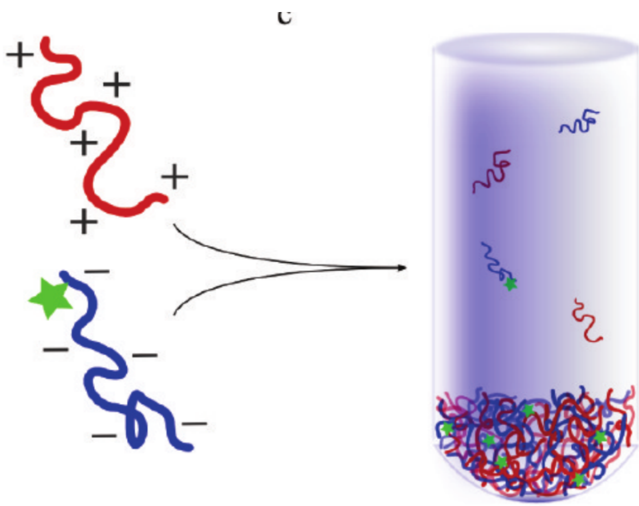
CHARGE DRIVEN ASSEMBLY OF SOFT MATTER

to develop new materials based on multi-valent ionic interactions. This direction is significant because it can yield new types of self-assembled structures. knowledge of the as-yet unexplored phase behavior of polyelectrolyte complexes is scientifically significant and technologically relevant.

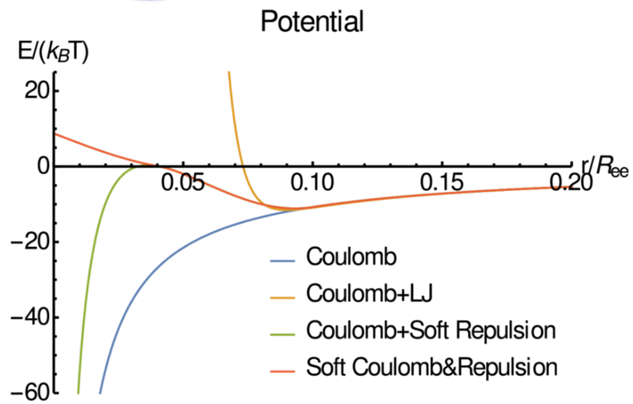
Solvay, Mars, Dupont --- ***Startup***

CHIMaD

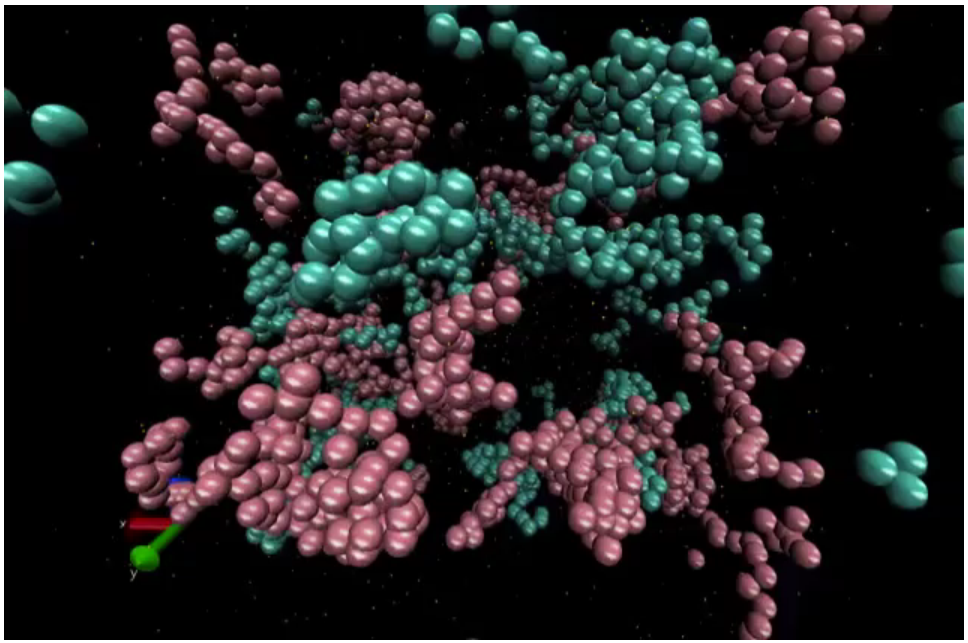
Coarse-grained MD for Coacervate



- molecular dynamics
- bead-spring chain
- soft repulsion (TICG)
- soft Coulomb short range
- Ewald Sum long range
- constant dielectric permittivity
- salt beads



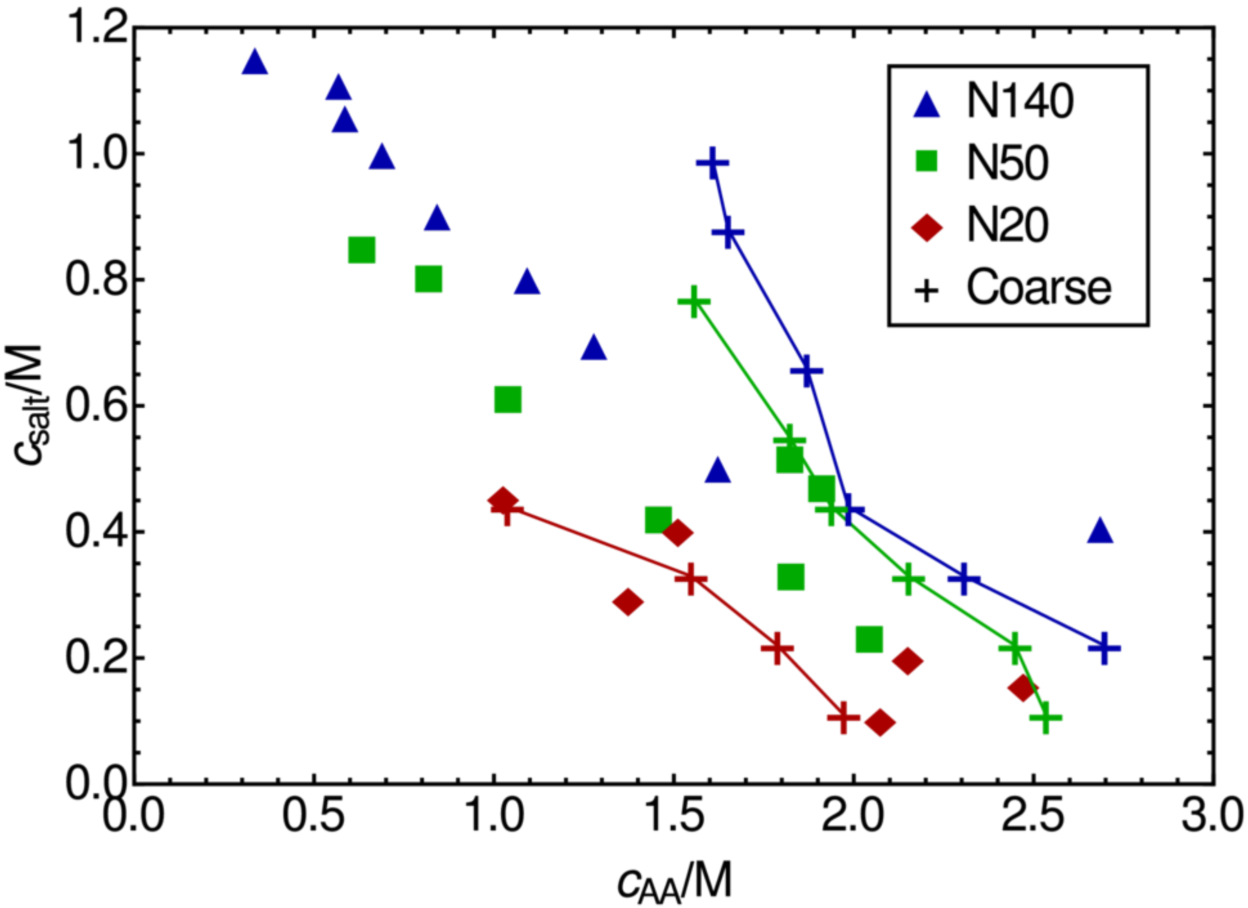
Self Assembly



- PAA & PDMAEMA 1 : 1 ratio, concentration 0.11M
- Length unit $R_{ee} = 10.2nm$,
- 50 beads per chain,
- 71.6 polymer beads per R_{ee}^3
- Coulomb strength parameter Bjerrum length $\lambda_B = \frac{e^2}{\epsilon_r k_B T} = 0.7nm = 0.09R_{ee}$
- Runs on GPU with HOOMD

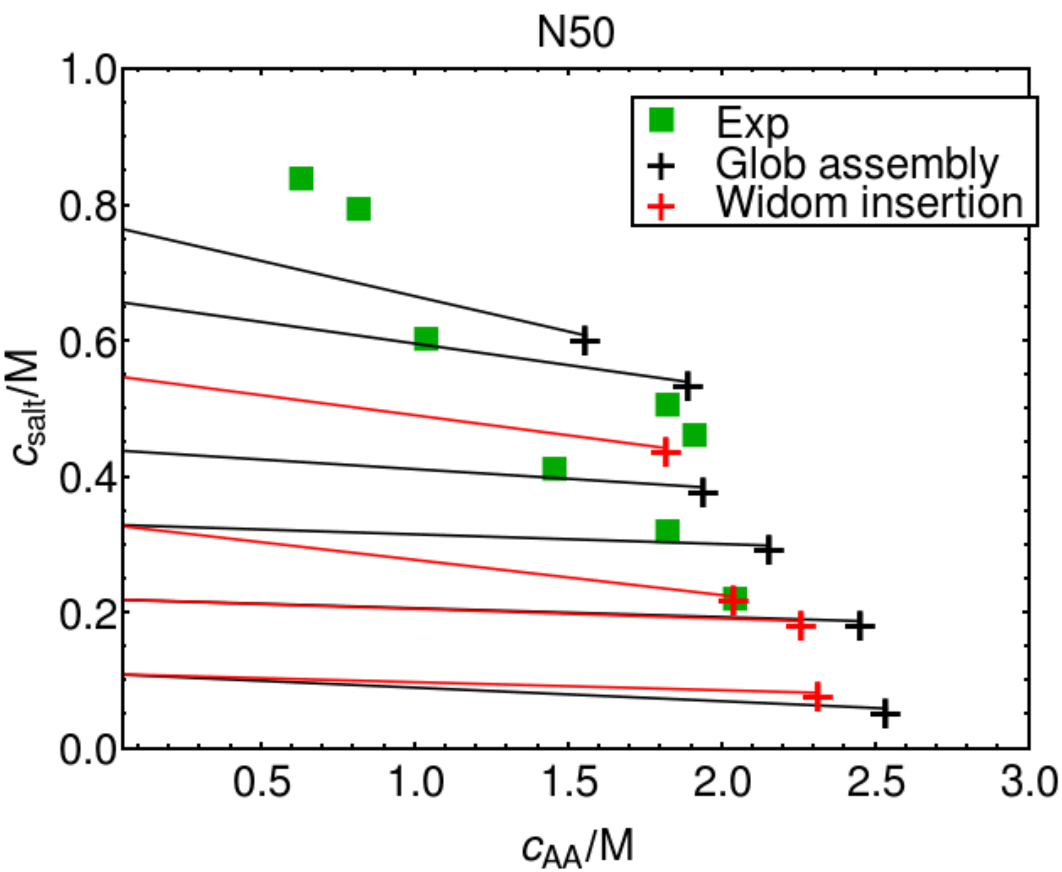
E. Spruijt, A. H. Westphal, J. W. Borst, M. A. Cohen Stuart, J. van der Gucht, *Macromol.*, 2010.

Self Assembly Phase Diagram



E. Spruijt, A. H. Westphal, J. W. Borst, M. A. Cohen Stuart, J. van der Gucht, *Macromol*., 2010.

Phase Diagram

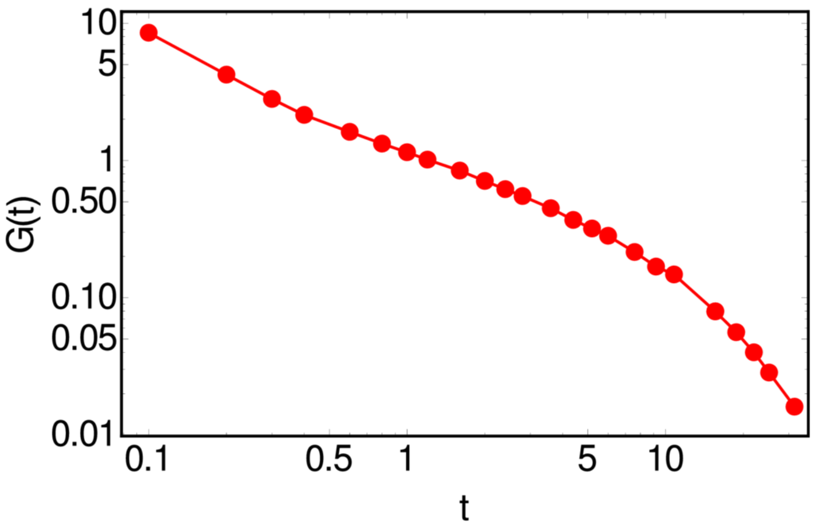


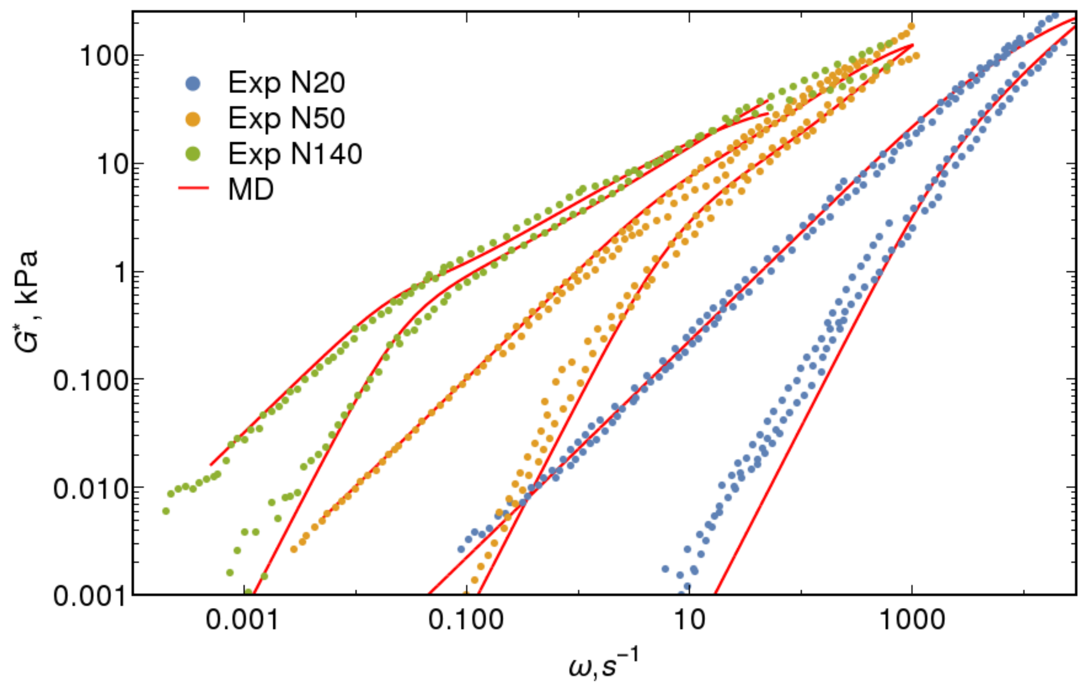
E. Spruijt, A. H. Westphal, J. W. Borst, M. A. Cohen Stuart, J. van der Gucht, *Macromol.*, 2010.

Rheology

Stress autocorrelation

$$G(t) = \langle \tau_{xy}(t')\tau_{xy}(t'+t) \rangle$$

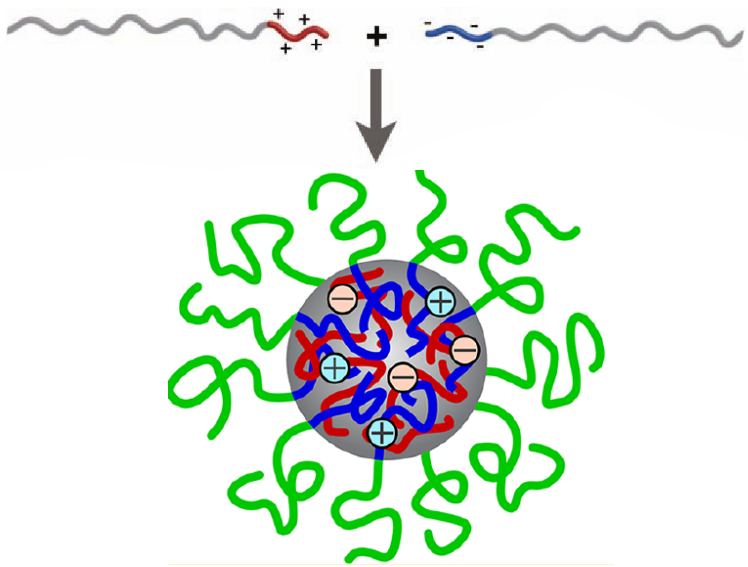


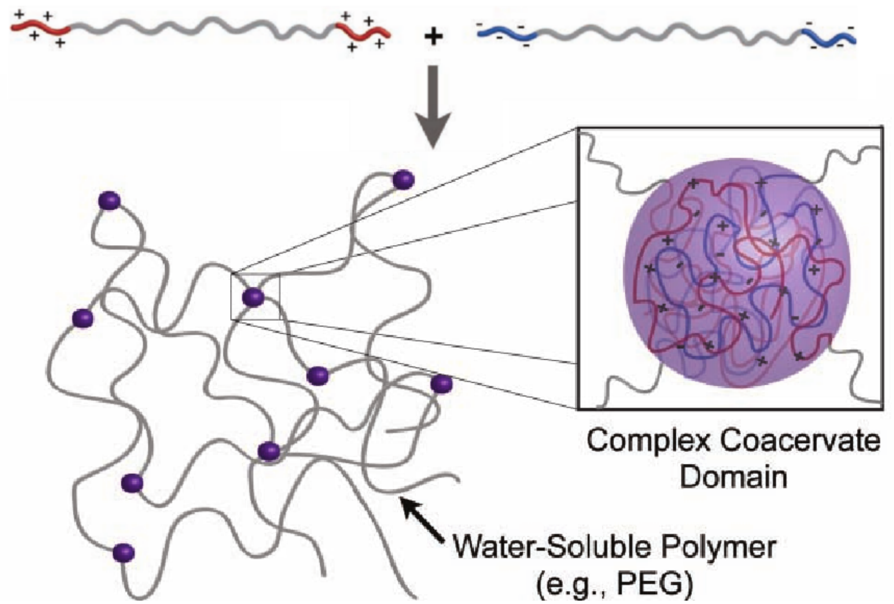


E. Spruijt, M. A. Cohen Stuart, J. van der Gucht, *Macromol.*, 2013.

Coarse-grained TICG for charged copolymers

PAGE-PEO diblocks/PAGE-PEO-PAGE triblocks



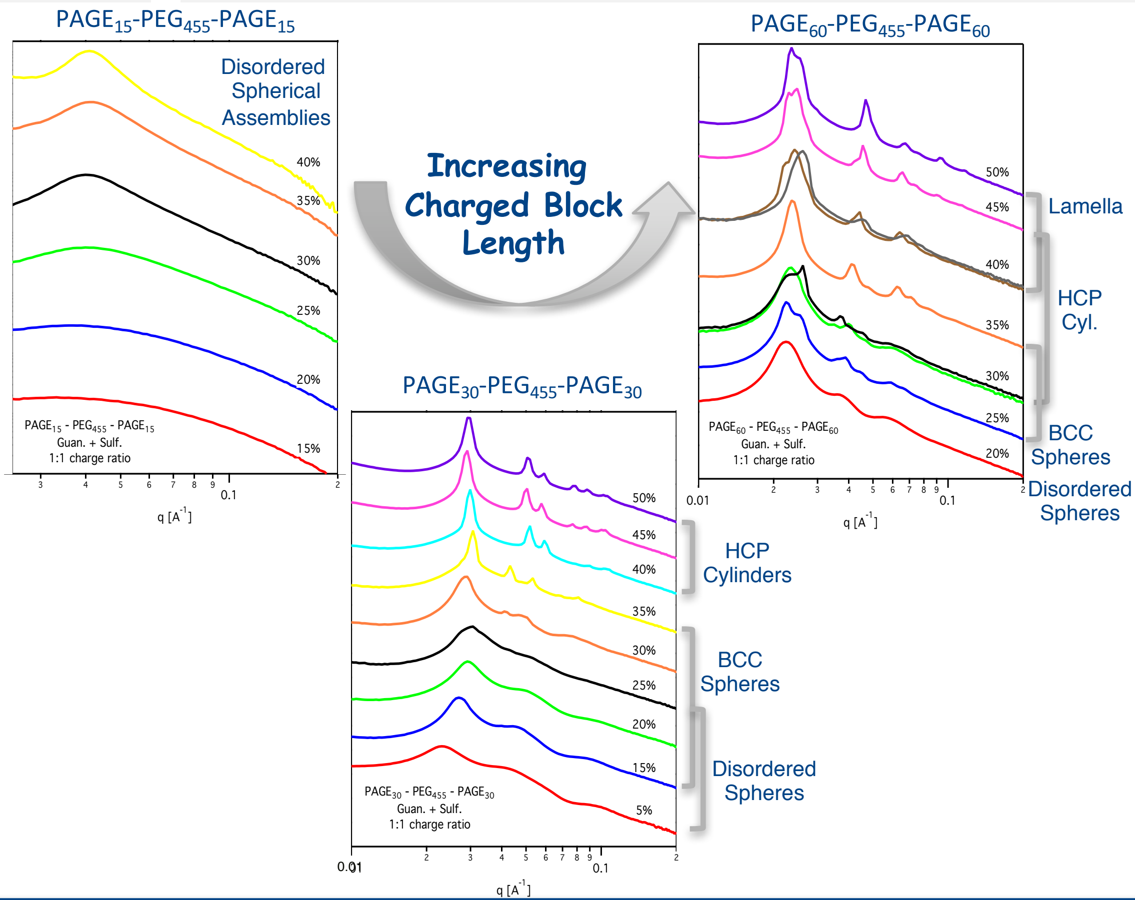


van der Kooij et al., J. Langmuir 48 (2012); Hunt et al., J. Adv. Mater. 43 (2011);

Materials Driven by Charge Complexation

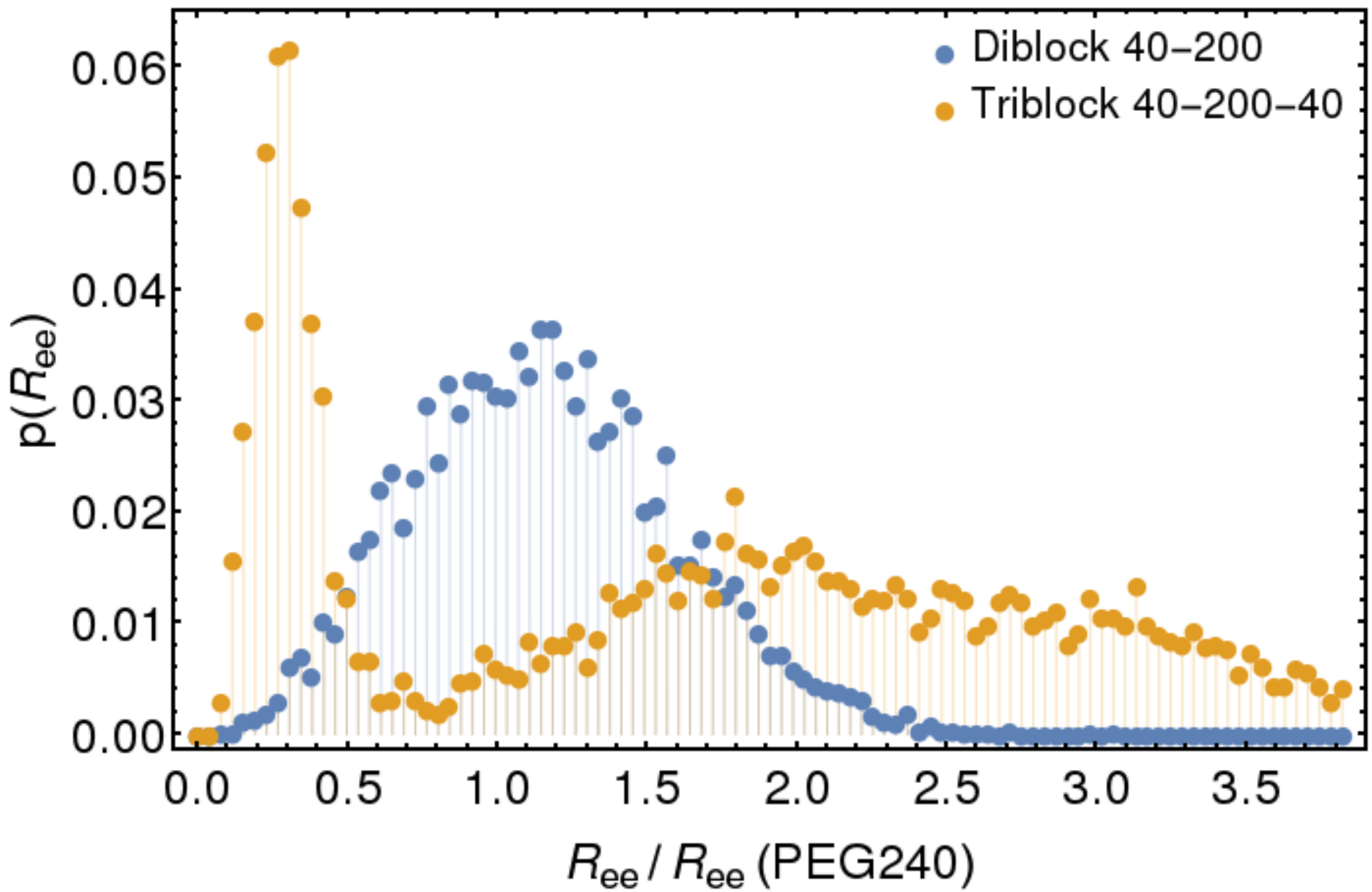
DESIGN GOALS

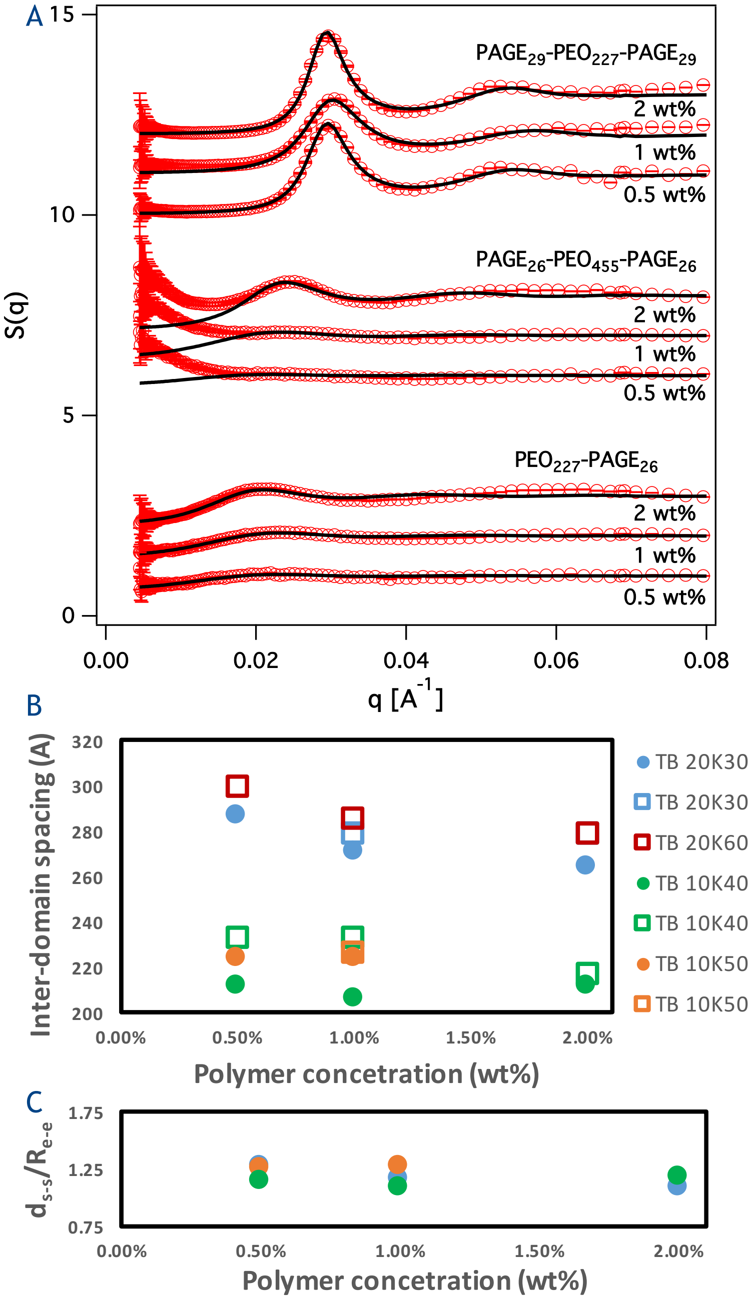
- *Control hydrogel bulk structure by varying lengths of molecular constituents and polymer loading*
- *Tune hydrogel sensitivity to salt and pH by varying block lengths*
- *Combination of salt, pH and macromolecular structure gives tissue-matching tunable moduli*
- *Extension to polypeptide materials with desired biocompatibility and biodegradability envisioned*

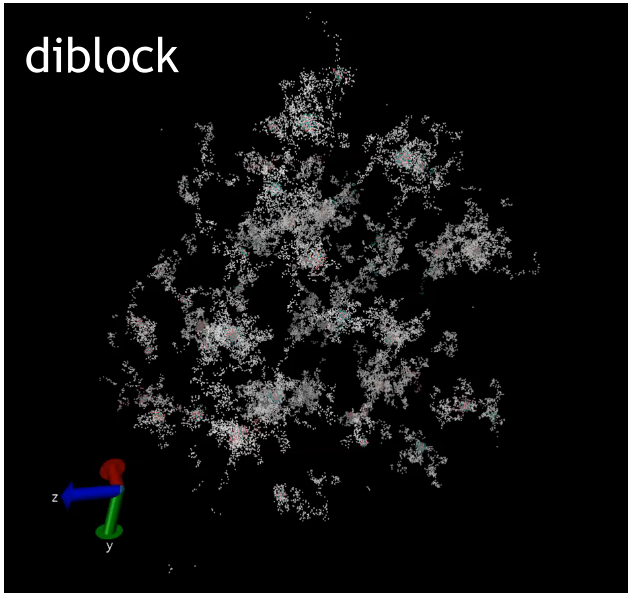


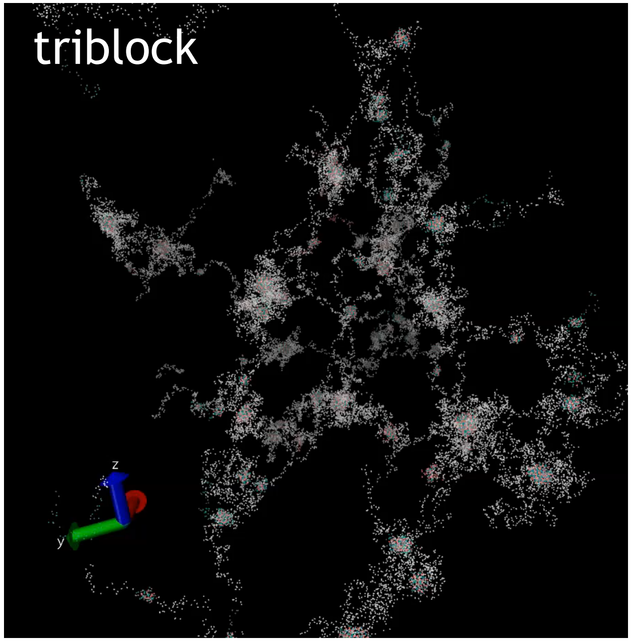
- Electrostatically cross-linked hydrogels obtained from mixing aqueous solutions of $A^{+}BA^{+}$ and $C^{-}BC^{-}$ triblock copolymers.
- Polyelectrolyte complex (PEC) domains serve as tunable cross-links. Micelles are the artificial "atoms" in these self-assembled structures
- The ratio of charged:neutral block size determines
  - Size of the PEC domains
  - Aggregation number
- Polymer loading dictates the PEC domain arrangements.
- Combining block size ratio and polymer loading variations allow for tunable mechanical properties

End-to-end distribution




A
PAGE29-PEO227-PAGE29
2 wt%
1 wt%
0.5 wt%
PAGE26-PEO455-PAGE26
2 wt%
1 wt%
0.5 wt%
PEO227-PAGE26
2 wt%
1 wt%
0.5 wt%
S(q)
q [A^-1]
0.00 0.02 0.04 0.06 0.08
0 5 10 15
B
Inter-domain spacing (A)
320 300 280 260 240 220 200
0.00% 0.50% 1.00% 1.50% 2.00%
Polymer concetration (wt%)
TB 20K30
TB 20K30
TB 20K60
TB 10K40
TB 10K40
TB 10K50
TB 10K50
C
d s-s/R e-e
1.75 1.25 0.75
0.00% 0.50% 1.00% 1.50% 2.00%
Polymer concetration (wt%)


diblock
z
y


triblock
z
y

CHiMaD

- Directed assembly of multiblock copolymers
- Complex coacervation
- Liquid crystalline polymers – OPV materials
- Polymer nanocomposites

Towards a universal platform that enables data analysis, data base population, and rational materials design

Education & Outreach

- Industrial partnerships
  - Intel, Mentor Graphics, Global Foundries
  - Dupont, DOW Corning, Good Year
  - Solvay, Polyera, Mars
- SPIE DSA Course
- Museum of Science and Industry
- Chicago Collegiate Scholars Program

CHiMaD

Impact Adsorption and Dissipation

Sid Nagel, UChicago

Heinrich Jaeger, UChicago

Juan de Pablo, UChicago

- Aaron Forster (NIST)
- Chelsea Davis (NIST)
- Chris Soles (NIST)
- Michael Riley (NIST)

International Workshop on Impact Mitigation

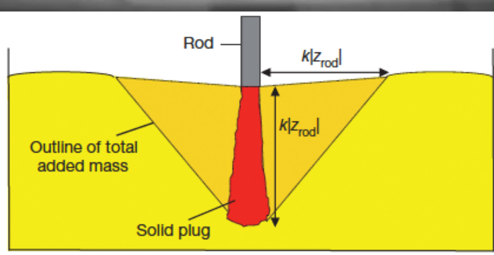
August 8, 2016, U. Chicago

Seed Groups

Dense suspensions ‘by design’ for effective impact energy dissipation

Problem: Want material that conforms to arbitrary and possibly evolving surfaces and can dissipate large amounts of impact energy

Rod impacting @ 1 m/s



Proposed solution: ***Dense suspensions of hard particles in liquid***

- liquid-like and highly conforming at low applied stress
- dynamically (& reversibly) transform to solid-like state at large applied stress

Chicago discovery (Nature 487, 2012): Impact-induced dynamic jamming fronts propagate into the suspension, generating a growing solid mass that takes up the impact momentum

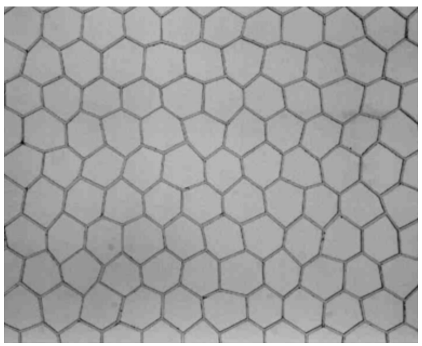
Next steps: impact response by design

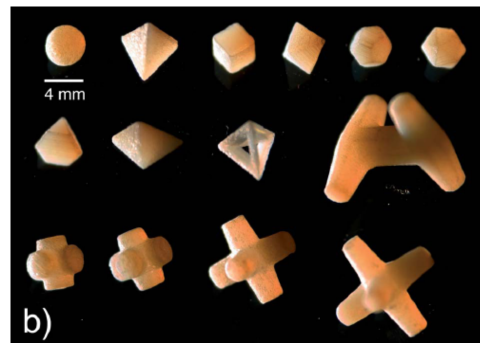
CHiMaD

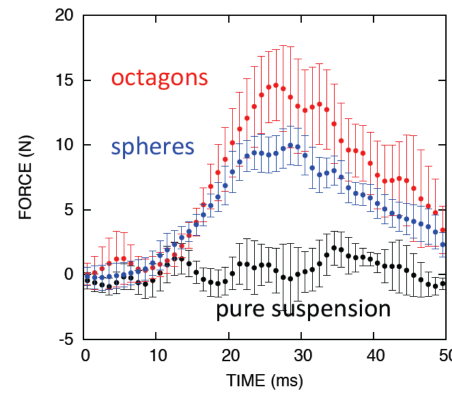
Dense suspensions ‘by design’ for effective impact energy dissipation

Key idea: tailor B/G ratio in solid-like state to optimize energy dissipation

Two-pronged approach:







Dense suspension coupled to cellular network with tuned B/G
➔ Control over wide range of responses

Dense suspension with added designer particles
➔ Optimized dynamic range of response

Network dynamics (Nagel)

Multiscale simulations (de Pablo)

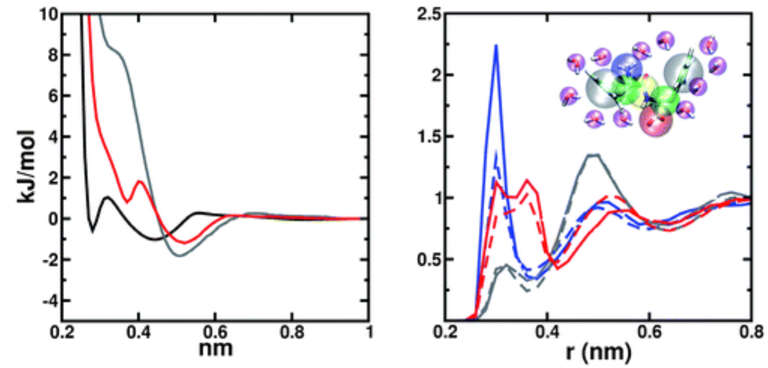
Suspension dynamics (Jaeger)

Systematic Coarse-Graining

Boltzmann inversion

$$U_{\mathrm{an},i+1} = U_{\mathrm{an},i} + f k_{\mathrm{B}} T \ln \frac{p_{\mathrm{an},i} + v}{p_{\mathrm{an,target}} + v}$$

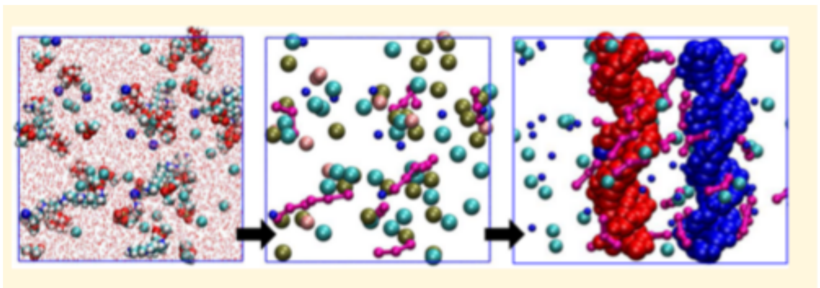
$$U_{\mathrm{nb},i+1}(r) = U_{\mathrm{nb},i}(r) + f k_{\mathrm{B}} T \ln \frac{g_i(r) + v}{g_{\mathrm{target}}(r) + v}$$



Relative entropy

$$S_{\mathrm{rel}} = \sum_{\nu} p_{\mathrm{AA}}(\nu) \ln\left(\frac{p_{\mathrm{AA}}(\nu)}{p_{\mathrm{CG}}(M[\nu])}\right) + S_{\mathrm{map}}$$

$$S_{\mathrm{rel}} = \beta\langle U_{\mathrm{CG}} - U_{\mathrm{AA}}\rangle_{\mathrm{AA}} - \beta(A_{\mathrm{CG}} - A_{\mathrm{AA}}) + S_{\mathrm{map}}$$

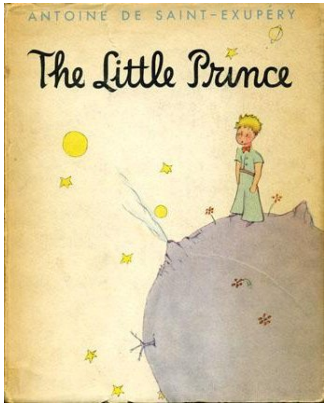


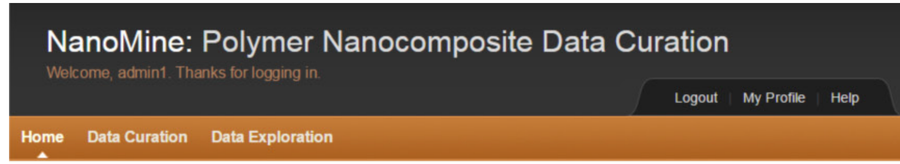
Faller et al., 2009, 2015
Carmichael & Shell, JPCB, 2012
Hinckley & de Pablo, JCTC, 2015

Rely on *Effective* Models

"Perfection is achieved, not when there is nothing more to add, but when there is nothing left to take away."

Antoine de Saint-Exupery, *Vol de Nuit*, 1900-1944





Catherine Brinson, NU

Wei Chen, NU

Sinan Keten, NU

Juan De Pablo, UChicago

Erik Luijten, NU

POLYMER MATRIX COMPOSITES

to develop a "materials informatics initiative" including integrated databases, curation, visualization, and analysis tools to relate macroscale polymer composite behavior to chemical constituent and kinetic behavior, and linking these resources to further development of high-performance modeling and predictive tools

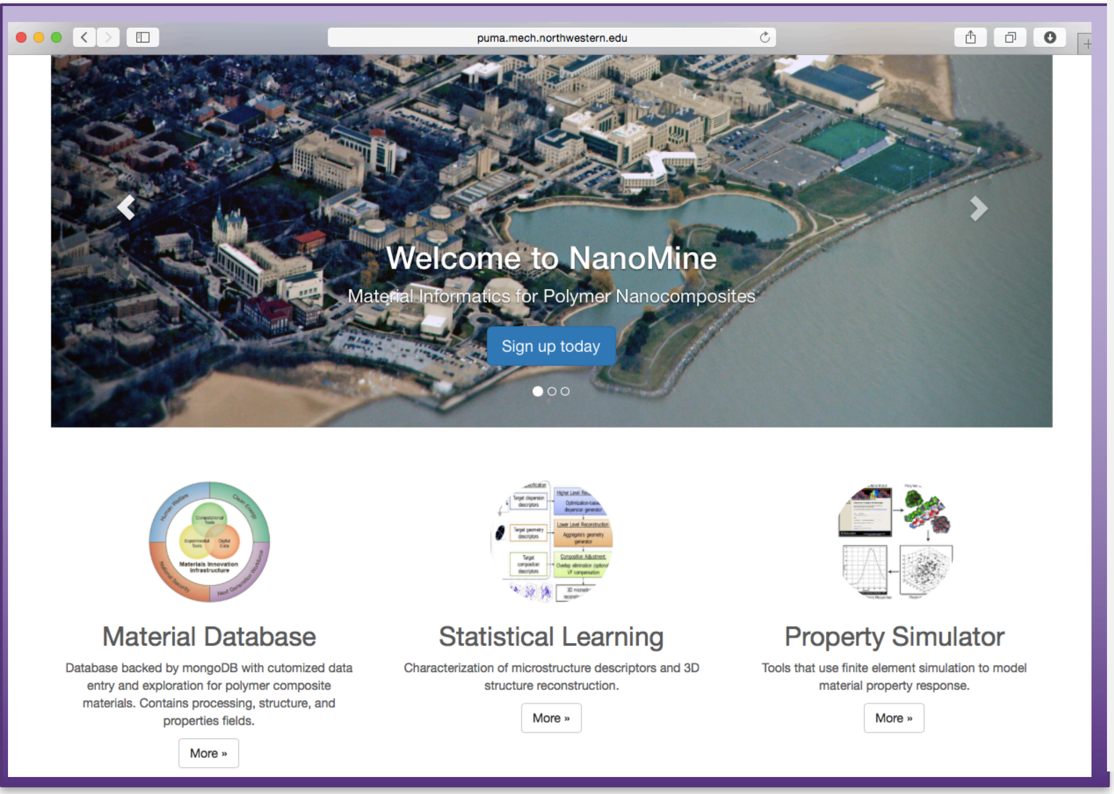
Owens Corning, Good Year

CHIMaD

POLYMER MATRIX COMPOSITES

DESIGN GOALS

- *Short term: Cellulose-polymer nanocomposites with optimized interphase behavior for high modulus/diffusion resistance*
- *Short term: DBs/Models/tools to predict interphase properties and diffusion/modulus of the system*
- *Long term: develop databases, models and tools to enable prediction of hierarchical com- posite behavior based on constituent components and processing*

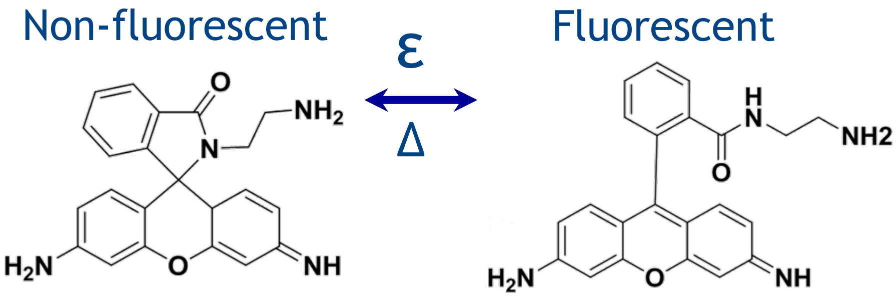


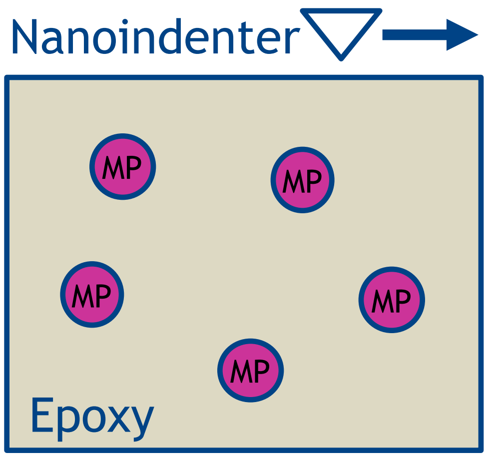
The database system "NanoMine" was created for polymer nanocomposite material systems, including:

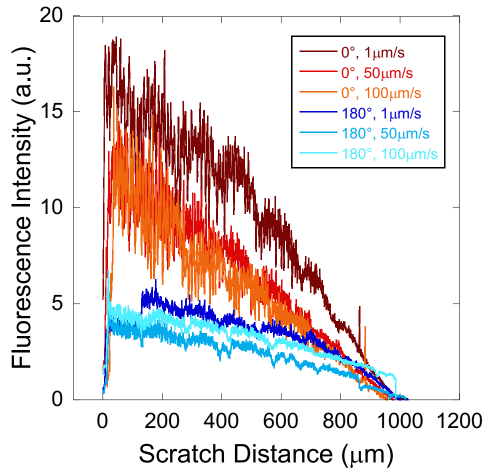
- Curated data from literature in an open source, searchable database, based on Materials Data Curator developed at NIST
- Statistical/machine learning-based methods and tools, eg for identifying the key microstructure descriptors
- Material property simulators for prediction of macroscopic properties using data from DB, predicted microstructures

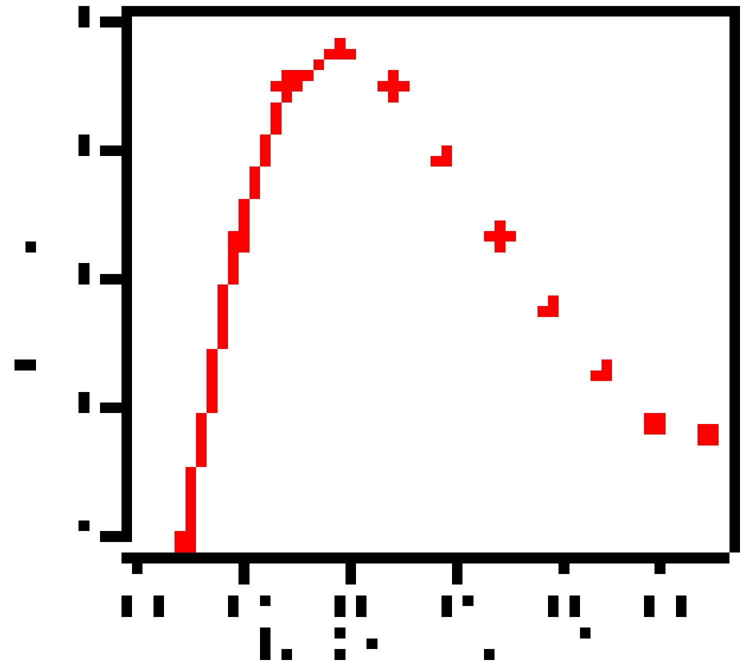
Additional tools and resources being developed. Interphase data and predictions being added based on molecular modeling efforts and local characterization experiments in Use Case.

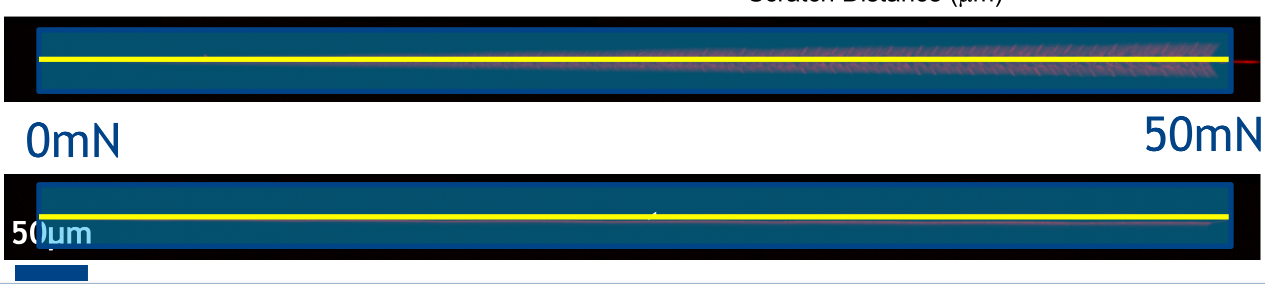
Mechanoresponsive Damage Sensing

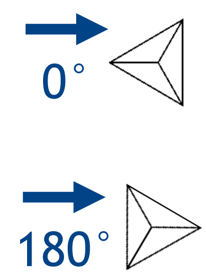








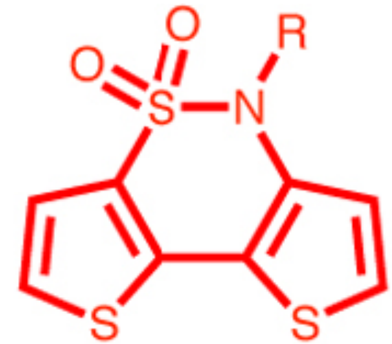




Constrained Geometries for Simulating External Force (COGEF)

CHiMaD

Gilman, Phelan, Woodcock, Wang, Davis, Khare



Luping Yu,
UChicago

Juan de Pablo,
UChicago

Giulia Galli,
UChicago

Tobin Marks,
NU

ORGANIC BULK HETEROJUNCTION POLYMER SOLAR CELLS

bulk heterojunction organic solar cells (OSCs) represent an alternative solar energy harvesting system. New polymers and theoretical methods developed will deepen our understanding in structure/property relationship and push the performance of OSCs towards commercial applications.

Polyera

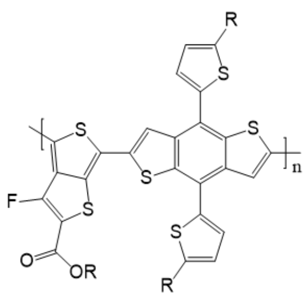
CHIMaD

ORGANIC BULK HETEROJUNCTION POLYMER SOLAR CELLS

DESIGN GOALS

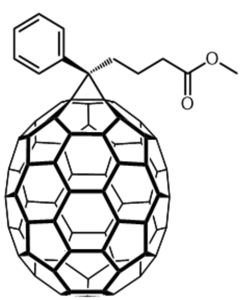
1. Develop OPV solar cells with high efficiency, low cost and long term stability.
2. Establish structure/property relationship via synthesis, physical characterization, theoretical investigation and device engineering to guide further explorations of new and more efficient materials.

PTB7-Th:PID2:PCBM Ternary OPV System

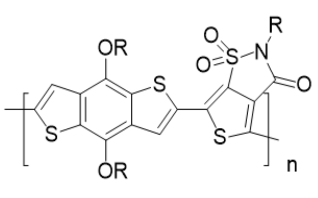


R=2-ethylhexyl

PTB7-Th

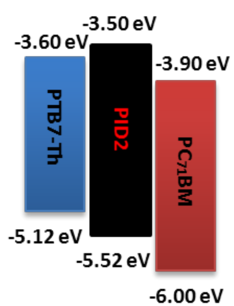


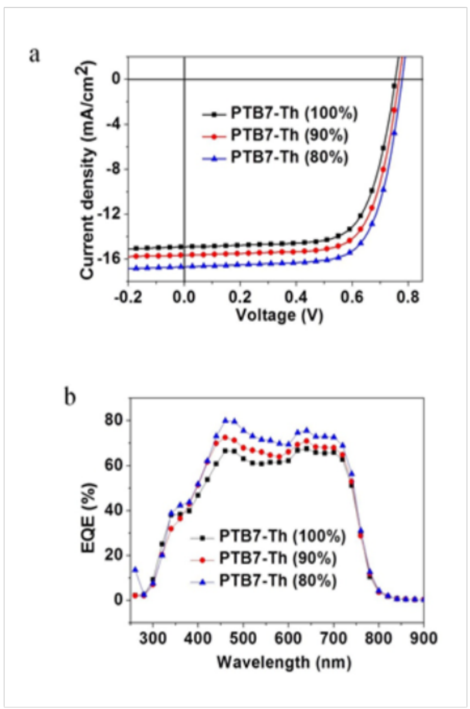
$PC_{71}BM$



R= 2-ethylhexyl

PID2





L. Lu, et al., Nat. Commun., in press.

Insert

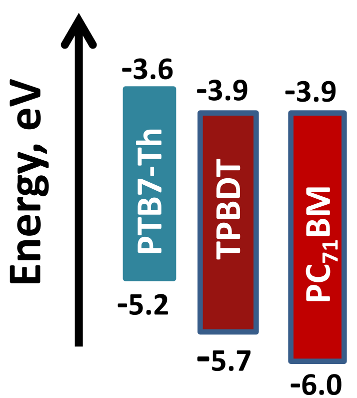
- New polymers with varied band gaps were synthesized either as electron donor or acceptors.
- Ternary OPV solar cells were developed that exhibit high efficiency and large enhancement.
- New methods are being developed to modify the the generic molecular dynamics force field method to fully describe the aromatic semiconducting polymers.
- Electronic properties of these polymers are modelled based on sophisticated quantum mechanical calculation.
- Collaborations with NIST scientists are on-going via sample exchanges and teleconferences.

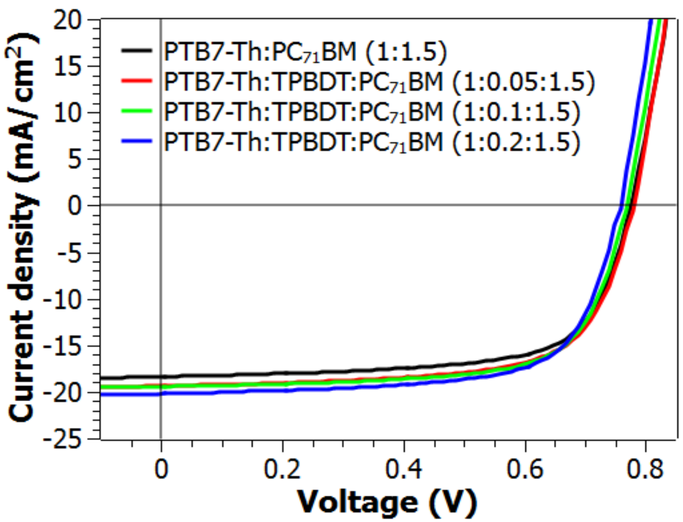
CHIMaD

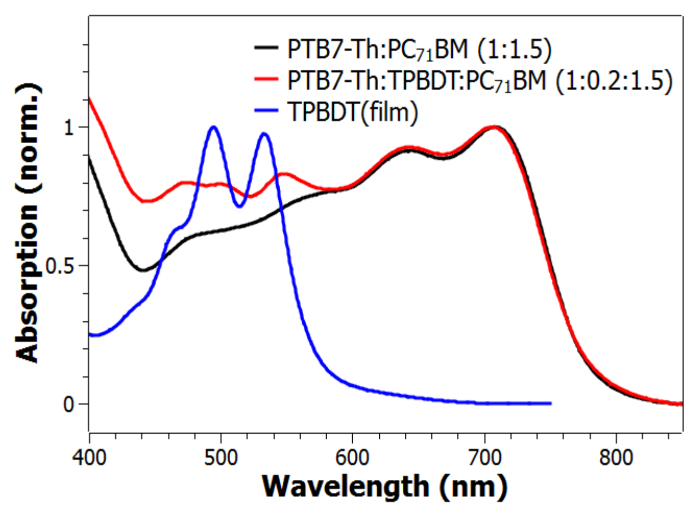
Ternary OSC with PTB7-Th and Two acceptors

Inverted device architecture: ITO/ZnO/PTB7-Th:TPBDT:$PC_{71}BM/MoO_3$/Ag

Active layer	V_{oc}, (V)	J_{sc}, (mA/cm^2)	FF, (%)	PCE, (%)	Highest PCE, (%)
PTB7-Th:$PC7_1BM$ (1:1.5)	0.77±0.01	18.1±0.1	67.9±0.7	9.5±0.1	9.8
PTB7-Th:TPBDT:$PC7_1BM$ (1:0.05:1.5)	0.77±0.01	18.7±0.2	67.2±0.2	9.8±0.1	10.2
PTB7-Th:TPBDT:$PC7_1BM$ (1:0.1:1.5)	0.76±0.01	19.4±0.2	68.3±0.8	10.1±0.1	10.3
PTB7-Th:TPBDT:$PC7_1BM$ (1:0.2:1.5)	0.77±0.01	19.6±0.4	67.7±0.2	10.1±0.2	10.5

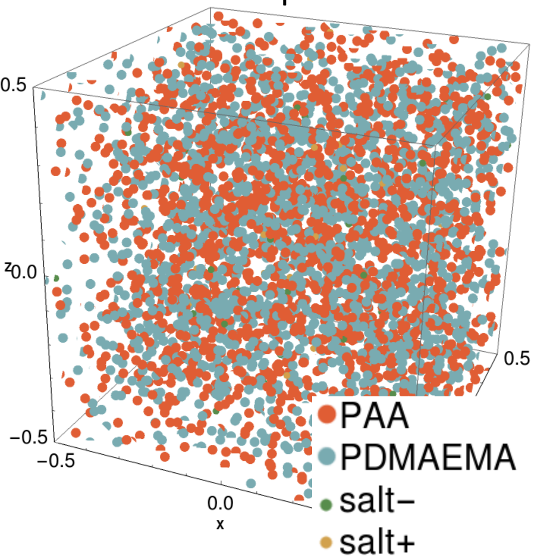






Validation of coacervate density from self-assembly

Coacervate phase simulation



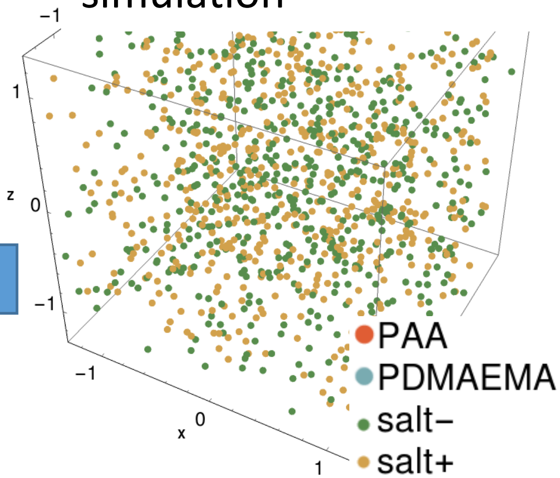
Adjust polymer and salt concentration to match chemical potentials and pressure

$$P_{coac}(\varphi_{polymer}, \varphi_{salt}) = P_{water}$$

$$\mu^{i}_{coac}(\varphi_{polymer}, \varphi_{salt}) = \mu^{i}_{water}$$

i – {salt+/-, water}

Water phase simulation



Calculated with Widom insertion method $\frac{(\mu-\mu_0)}{k_B T} = -\ln\langle exp(-\Delta E_t)/k_B T\rangle_{NVT}$