Nanotechnology & Self-Assembly

Today's Agenda

Part 1.

(1) What is Nano & Nanotechnology?

(2) Some History about Nanotechnology

(3) Why "Nanoscale" matter?

(4) Benefit & Application of Nanotechnology

Part 2.

(1) Manufacturing Nanomaterials (Top down & Bottom up)

(2) Self-assembly & Self-assembled systems

(3) Self-assembly through force balance

(4) General scheme for self-assembly process

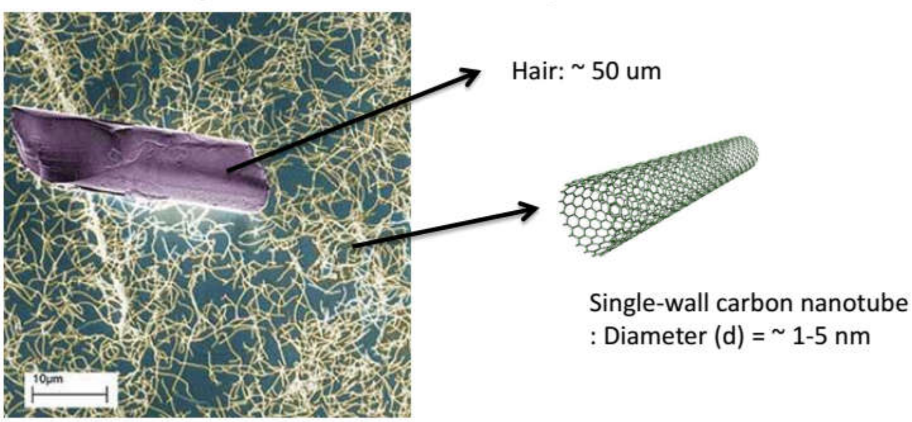
Part I

What is Nano?

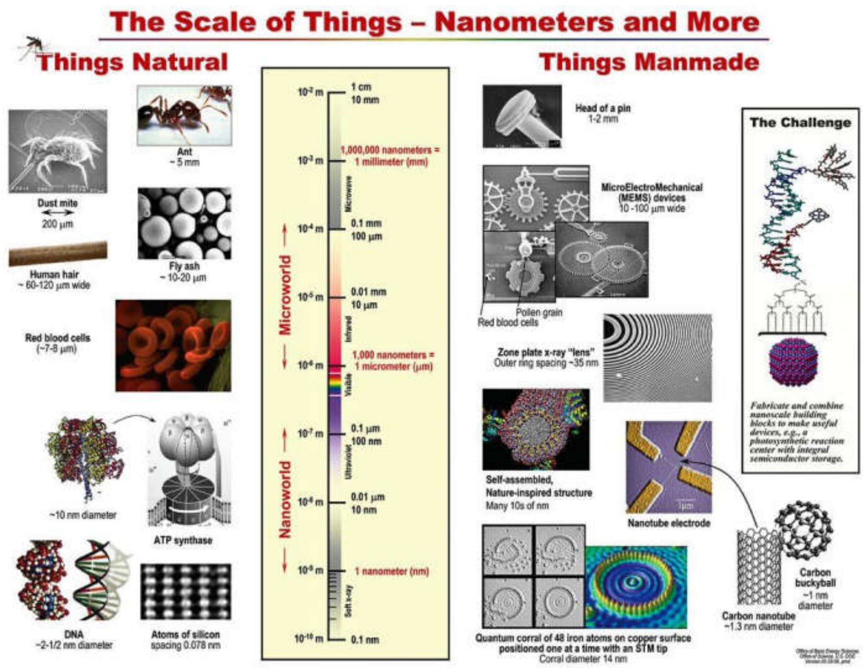
"Nano": A Greek word for "dwarf"

1 nm = 10^{-9} m

Human hair fragment and a network of single-walled carbon nanotubes



http://www.nanowerk.com/nanotechnology/introduction/introduction_to_nanotechnology_1.php



http://www.asu.edu/clas/csss/NUE/img/Scale-of-Things.jpg

What is Nanotechnology?

- ***Nanotechnology*** *is the understanding and control of matter at dimensions between approximately 1 and nanometers, where unique phenomena enable novel applications.*
- *...Nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale.*

- National Nanotechnology Initiative (NNI)

What is Nanotechnology?

- *Unusual physical, chemical, and biological properties can emerge in materials at the nanoscale. These properties may differ in important ways from the properties of bulk materials and single atoms or molecules*

- Nanotechnology R&D is directed toward understanding and creating improved materials, devices, and systems that exploit these new properties.

Some History of Nanotechnology

◆ ***Introducing "Nano" to the World***

"Nanotechnology": First introduced in 1959 by Richard Feynman (Nobel Prize in Physics, 1965) at the American Physical Society (APS)
"There's Plenty of Room at the Bottom"

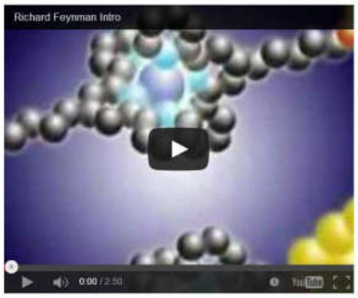
He asked:

1) Why can't we write the entire 24 volumes of the Encyclopedia Britannica on the head of a pin?

2) Why can't we manipulate materials atom by atom?

3) Why can't we control the synthesis of individual molecules?

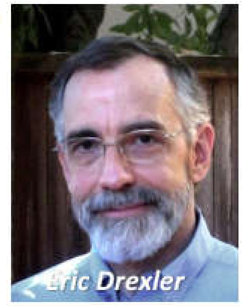
4) Why can't we build machines to accomplish these things?



https://www.youtube.com/watch?feature=player_embedded&v=eKj5IAmy9Wk

Some History of Nanotechnology

- **The term "Nanotechnology"** was first used by Eric Drexler (*another pioneer of nanotechnology*) in his book "*Engines of Creation: The Coming Era of Nanotechnology*" ***(1986)***



"Molecular Assemblers"

: devices capable of positioning atoms and molecules for precisely defined reactions in almost any environment

- A co-founder of **The Foresight Institute (1986)**

➔ To increase public awareness and understanding of nanotechnology concepts and implications

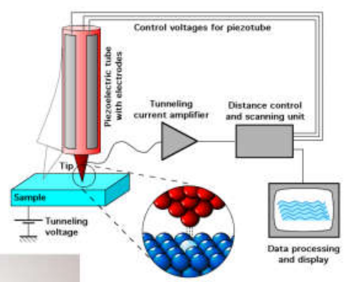
FORESIGHT INSTITUTE®
advancing beneficial nanotechnology

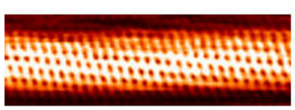
Growth of Nanotechnology was enabled by…

- **Two major breakthroughs** (in the 1980s)

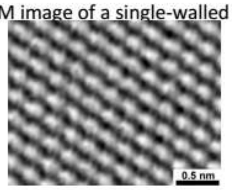
1) Invention of Scanning Tunneling Microscope (STM, 1981)

- By Gerd Binnig & Heinrich Rohrer (at IBM Zürich)
- Unprecedented visualization of individual atoms and bonds
- Novel Prize in Physics (1986)
- Manipulated individual atoms (1989)





An STM image of a single-walled CNT



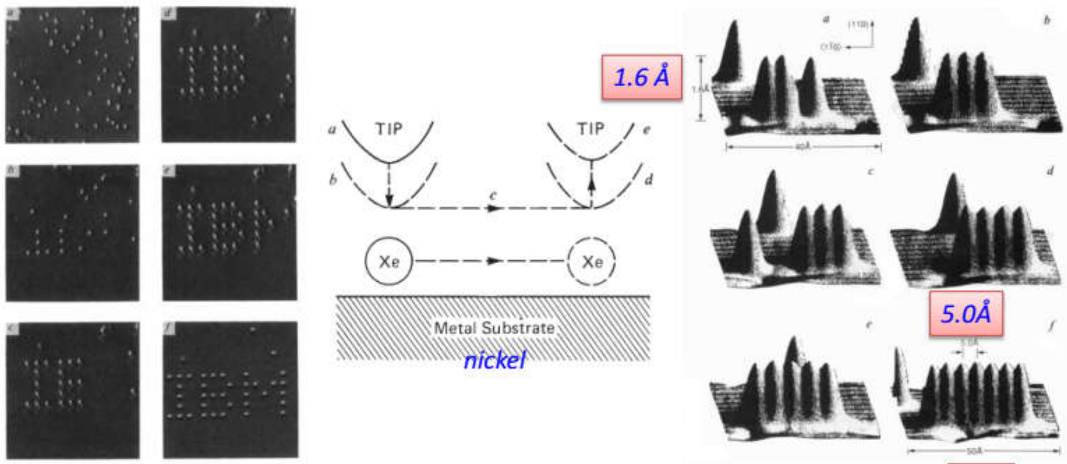
A graphite surface at an atomic level

- lateral resolution: 0.1 nm
- depth resolution: 0.01 nm

https://en.wikipedia.org/wiki/Scanning_tunneling_microscope

Positioning Single Atoms with a STM

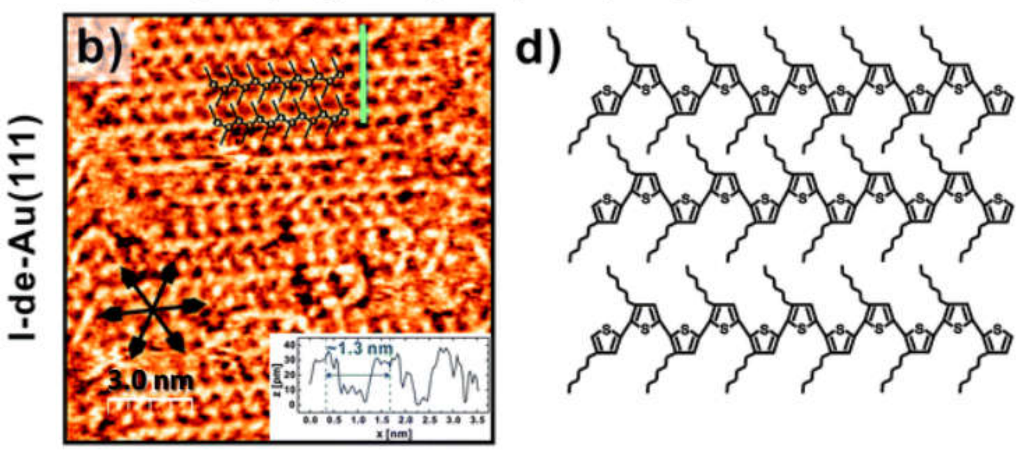
We can manipulate materials atom by atom



D.M. Eigler and E.K. Schweizer, *Nature,* **1990**, 344, 524-526

By the way, STM can also image some polymers

STM image of poly(3-hexylthiophene) on gold surface



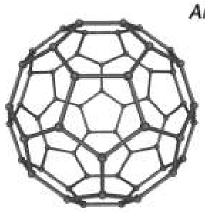
Y Lee et al. Nanoscale, **2013**, **5**, 7936-7941

Only conductive polymers

- **Two major breakthroughs** (in the 1980s)

2) **<u>Fullerenes</u>** (one of the first nanomaterials) were discovered in 1985

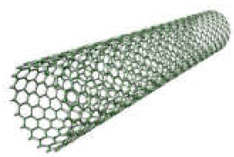
- By Harry Kroto (UK), Richard Smalley, and Robert Curl (US, Rice University)
- Received Novel Prize in Chemistry (1996)
- molecule of carbon in the form of a hollow sphere, tube, and many other shapes
- Produced by laser vaporization of graphite under an helium gas (the first method)
- Hydrophobicity, 3 dimensionality, electronic configuration:



Buckminsterfullerene C_{60}, (<u>buckyball</u>)

- Diameter : ~1nm

Architect "Richard Buckminster Fuller"



Carbon nanotubes

(<u>buckytube</u>)

- Diameter : ~1-5 nm

C_{60} in solution

(Ex) aromatic solvents

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One of the leading universities for nanotechnology research and education

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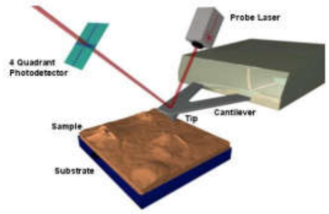
Advance of Nanotechnology is also enabled by…

- **New tools for nanoscale characterization**

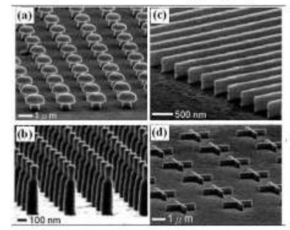
  Ex) Atomic force microscopy (AFM)



http://education.mrsec.wisc.edu/nanoquest/afm/

- **New capabilities for fabricating nanoscale structure**

  Ex) e-beam lithography



Adv Mater, 2003, 15, 49

- **Computational access to large systems of atoms and long time scales**

  Ex) Supercomputer

molecular structure of six polymer NPs

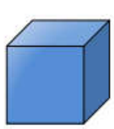
http://web.ornl.gov/info/ornlreview/v37_2_04/article06.shtml
https://en.wikipedia.org/wiki/Titan_(supercomputer)

What's the BIG deal about something so SMALL?

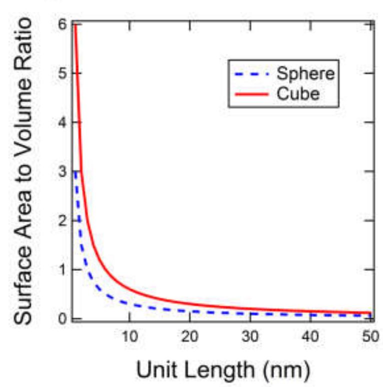
- Materials behave differently at the nanoscale.
- It's not just about miniaturization.
- At this scale---it's all about Interfaces (or interfacial area)

- Surface-area-to-volume-ratio (SA:V)

$$\mathrm{SA:V} = \frac{4\pi a^2}{\frac{4}{3}\pi a^3} = \frac{3}{a}$$



$$\mathrm{SA:V} = \frac{6a^2}{a^3} = \frac{6}{a}$$

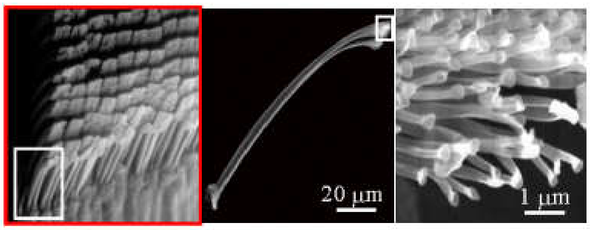


The smaller dimension, the larger interfacial area & shape also matters

Interaction	Example	Energy (kJ)
Ion-Ion	$Na^+ Cl^-$	400-4000
Covalent Bonds	H-H	150-1100
Ion-Dipole	Na^+ HCl	40-600
Dipole-Dipole	HCl HCl	5-25
Dipole-Induced Dipole	HCl O_2	2-10
London Dispersion	N_2 N_2	0.05-40

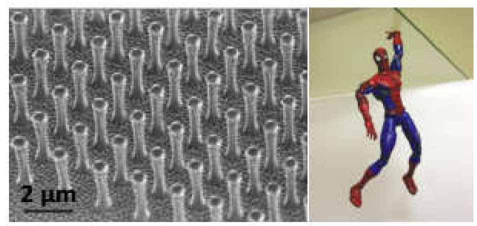
Van der Waals (VDW) Forces ← (Dipole-Dipole, Dipole-Induced Dipole, London Dispersion)

Gecko's Foot: create billions of weak VDW forces



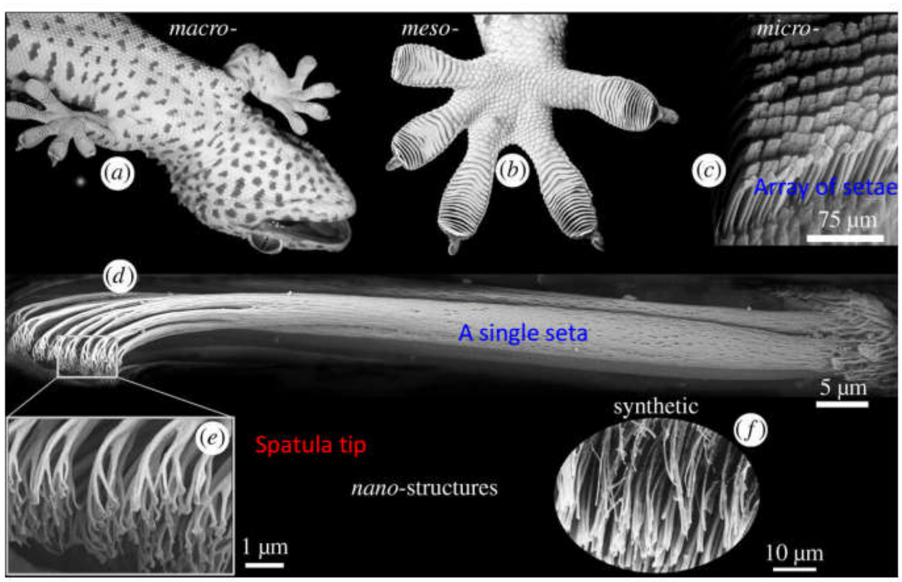
K. Autumn, Nature, 405, 681 (2000)

Artificial Gecko's Foot



A.K. Geim, Nature Mater., 2, 461 (2003)

Why SA : V ratio matters?



Structural hierarchy of the gecko adhesive system.

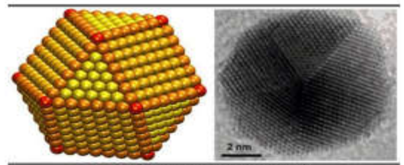
K. Autumn, *Phil. Trans. R. Soc. A* (2008) 366, 1575–1590

What's the BIG deal about something so SMALL?

❖ **Chemical Reactivity** of Gold (Au)

(1) Gold (Au) in bulk scale

- Inert materials (no corrosion or tarnished)
- Not useful as a catalyst for chemical reaction



http://www.redorbit.com/

(2) Gold (Au) at **nanoscale** (~5 nm)

- Can act as a catalyst (e.g, CO_2 ➔ CO)

- Smaller the nanoparticle
  ➔ the larger the proportion of atoms at the interface
  ➔ the larger the proportion of atoms at the corners of crystals

- Much larger % of gold atoms exist on the surface & the corners (vs. surface of bulk gold)

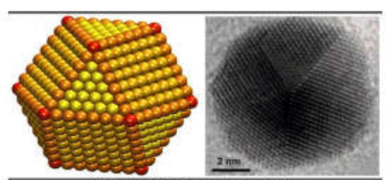
➔ chemically more reactive ➔ allows for catalysis

What's the BIG deal about something so SMALL?

❖ **Melting at temperature**

(1) Gold (Au) in bulk scale

: Tm = ~ 1064 °C



http://www.redorbit.com/

(2) Gold (Au) nanoparticles (~2.5 nm)

❖ **It is due to…**

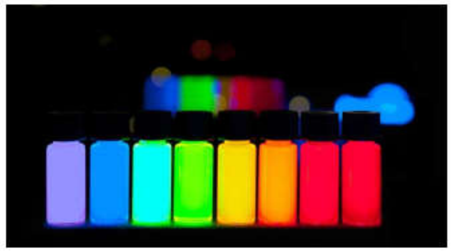
- Again, much larger % of gold atoms on the surface & the corners

➔ (Au nanoparticles): Larger No. of atoms are exposed to heat
➔ the bond between atoms can easily be broken down

➔ Smaller the particles ➔ the lower Tm

What's the BIG deal about something so SMALL?

❖ **Quantum dots**



https://en.wikipedia.org/wiki/Quantum_dot

Size Matters!

Ex) Color depends on particle size
Quantum dots 3.2 nm in diameter have blue emission
Quantum dots 5 nm in diameter have red emission

Benefits of Nanotechnology

"The power of nanotechnology is rooted in its potential to transform and revolutionize multiple technology and industry sectors, including aerospace, agriculture, biotechnology, homeland security and national defense, energy, environmental improvement, information technology, medicine, and transportation.

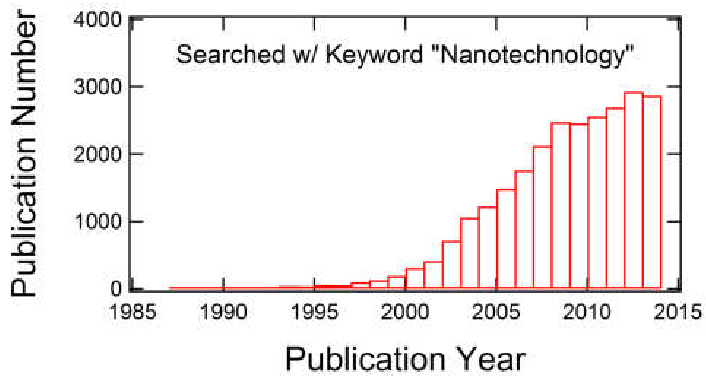
- National Nanotechnology Initiative

"Nanoscience will change the nature of almost every human-made object in the next century"

- National Science and Technology Council, 2000

Nanotechnology: Extensively Studied

Various specialized journals:
Nature Nanotechnology, Nano Letters, ACS Nano, etc.



Searched at Web of Science

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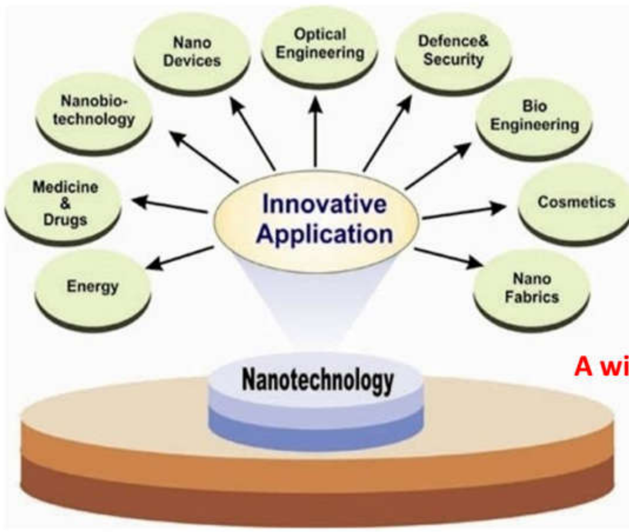
Nanotechnology Applications

4/28/2017 24

Nanotechnology Applications

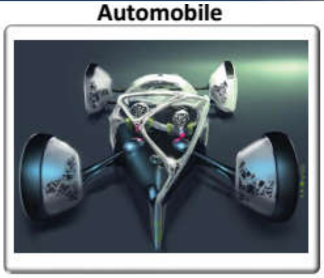


A wide range..

Khan, *Orient. J. Chem.* **2013**, 29, 1399-1408

Nanotechnology Applications

Automobile



Nanocomposites for lighter and stronger materials

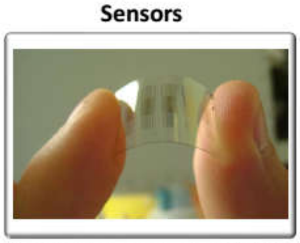
Sporting goods

SiO2 nanoparticles
For high strength, and light weight

Functional Coating

TiO2 nanoparticles
For Self-cleaning properties

Sensors



Chemical sensors made with CNTs
Can detect explosives

Cosmetic

TiO2 + ZnO nanoparticles
: protection from UV w/o producing a thick residue

Food Packaging

Clay nanoparticles
For reducing O_2 permeability

http://news.stanford.edu/news/2009/september21

These are mostly Nanoparticles based…

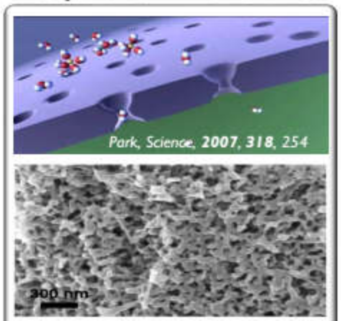
Then, what about polymers..?

(Q) Polymers are Nanomaterials?

Maybe…but..

We are mostly interested in "nanostructure" of polymers

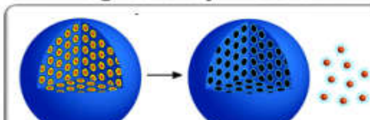
Separation membranes



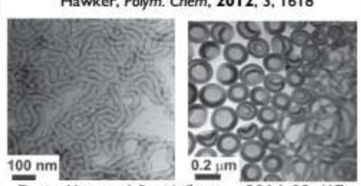
Hillmyer *J. Am. Chem. Soc.* **2010**, 132, 8230

- *Pore size, porosity,*
- *Surface area*

Drug-delivery micelles



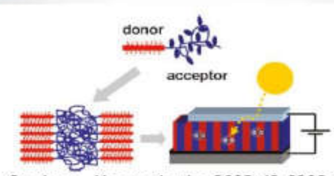
Hawker, *Polym. Chem*, **2012**, 3, 1618



Davis, *Macromol. Rapid. Commun* **2014**, 35, 417

- *Shape, size*
- *Surface functionality*

Organic solar cells



Segalman, *Macromolecules*, **2009**, 42, 9205

- *Morphology*

(Domain size, connectivity orientation)

- *Interface*

❑ *Next-Generation Polymeric Materials*

Synthesis & Characterization → ***Direct & Manipulate Nanoscale Assembly*** → ***Understand Dynamics & Interactions***

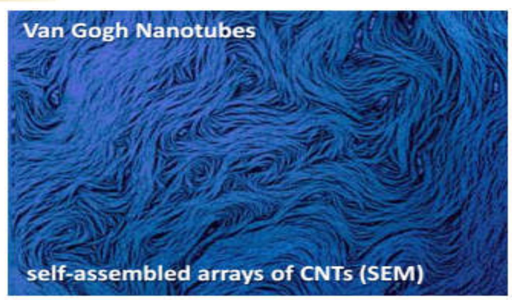
How to make "nanostructured" polymer?

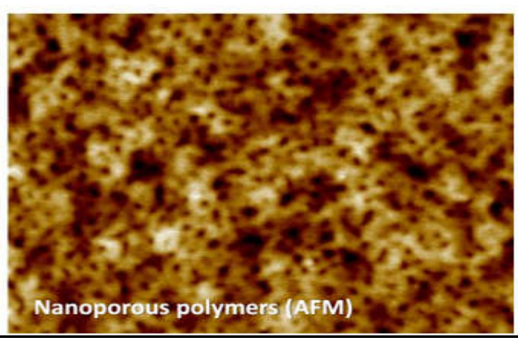
"Self-Assembly or Self-Organization"

(bottom-up approach)

:Governed by different intermolecular interactions

Nanotechnology Images





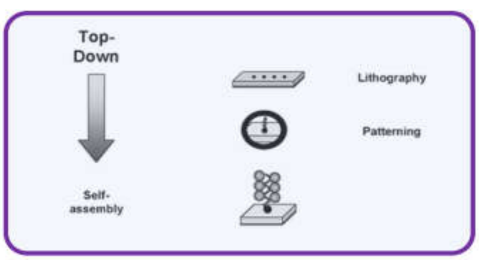
Part 2

Manufacturing Nanostructured Materials

Top down approach

fabricate nanostructured materials via etching away bulk material until the desired (micro or nano) structure is obtained.

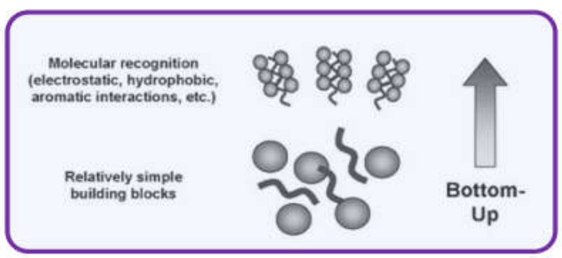
- Conventional Lithography
  - Photo, e-beam
- Unconventional Lithography
  - Nanoimprint, soft



Bottom up approach

build nanostructured materials using nanometer sized building blocks (atoms, molecules, monomers), and putting them together piece by piece until the overall macroscopic device is constructed.

- Supramolecular chemistry
- Synthetic methods (chemical or biological)
- Surface science
  - Self-assembled monolayers
  - Langmuir Blodgett films



E Gazit, *Chem. Soc. Rev.*, **2007**, 36, 1263

(Top down) Photolithography

(1) Prepare wafer

(2) Spin coat photoresist (PR)

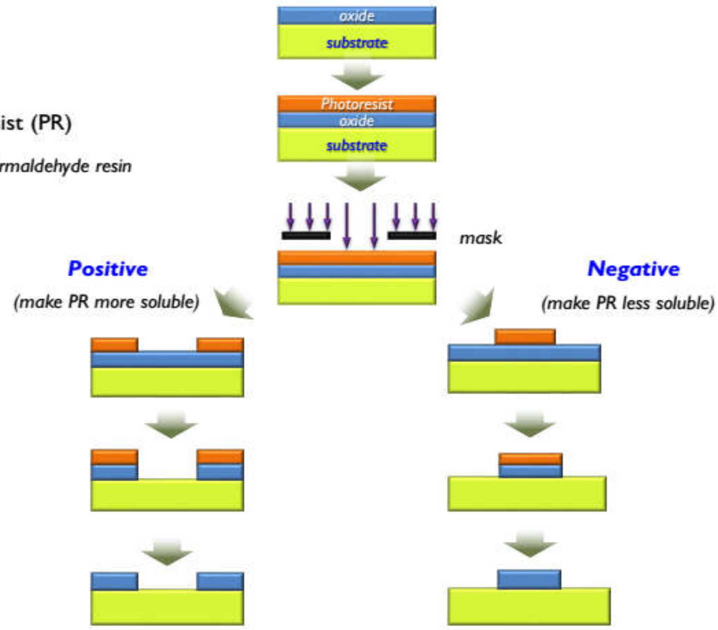
ex) PMMA, phenol formaldehyde resin

(3) Expose UV

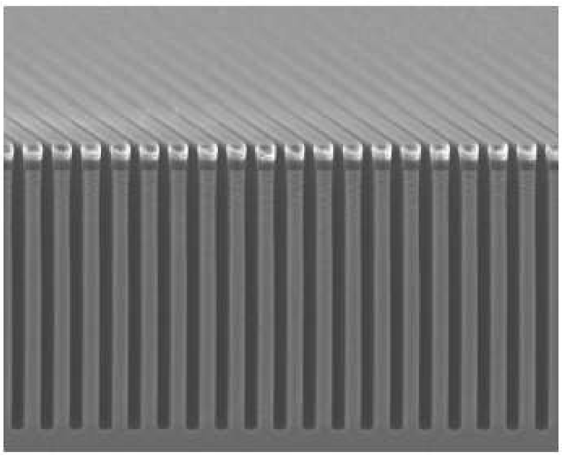
(4) Develop

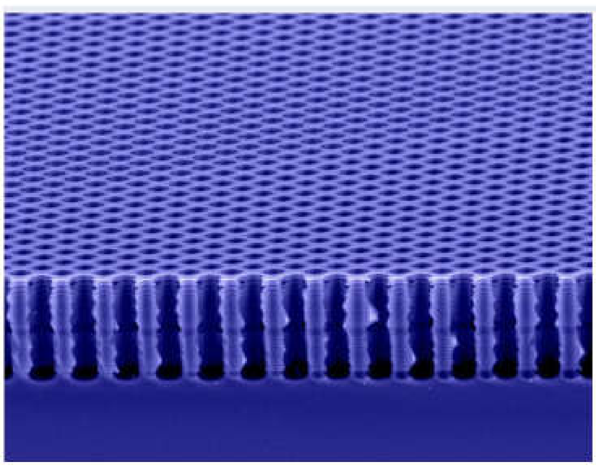
(5) Etch
: remove oxide layer

(6) Strip
: remove PR layer



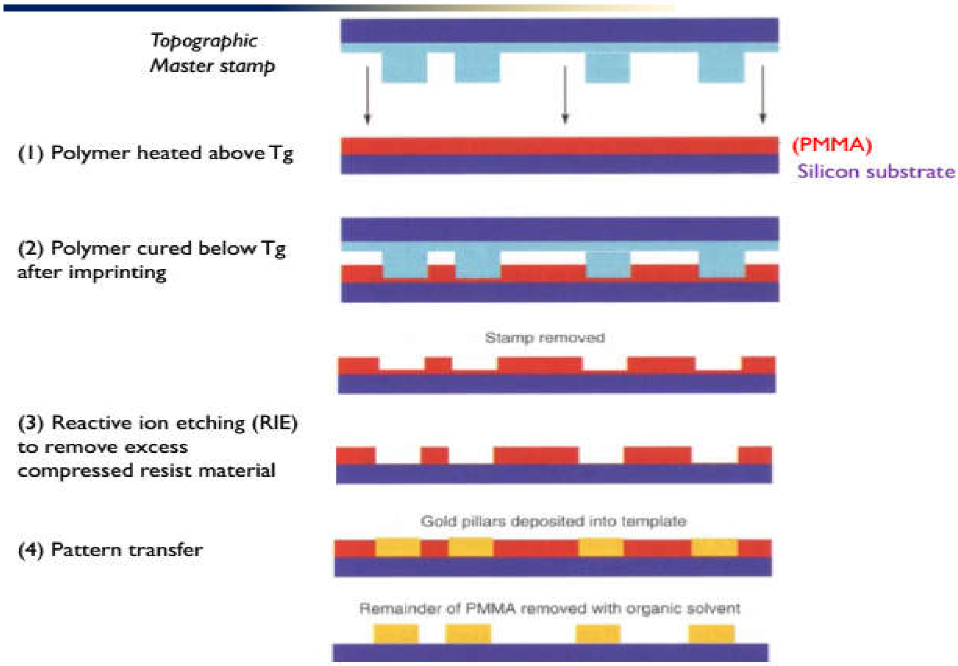
(Top down) Photolithography



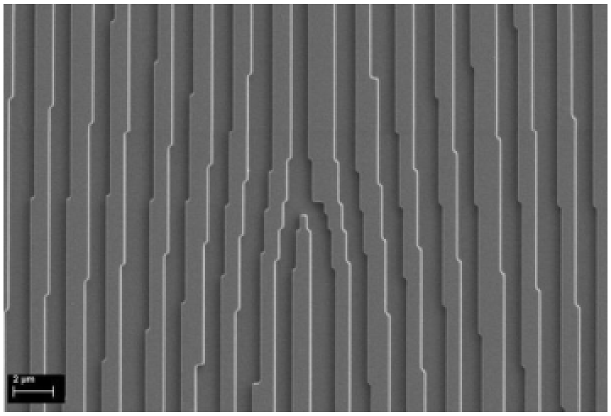


http://www.psi.ch/lmn/grating-fabrication

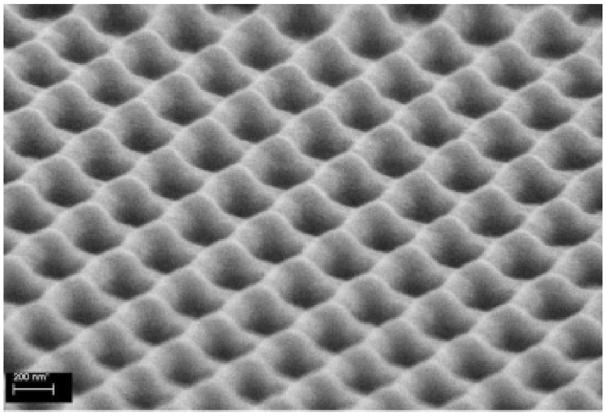
(Top down) Nanoimprint lithography



(Top down) Nanoimprint lithography

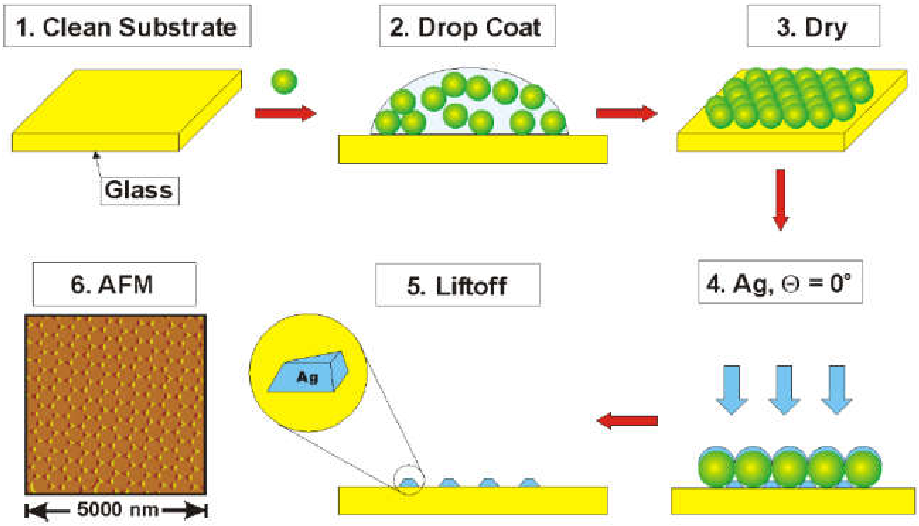


SEM image of a corrugated grating structure



a patterned surfaces showing an anti-reflective structure patterned on a flexible substrate

(Top down) Nanosphere lithography



Mark Hersam (2005), "Introduction to Nanometer Scale Science & Technology," https://nanohub.org/resources/179.

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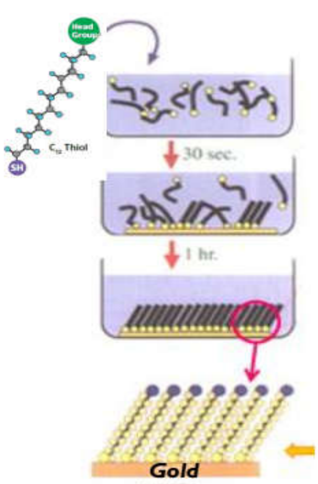
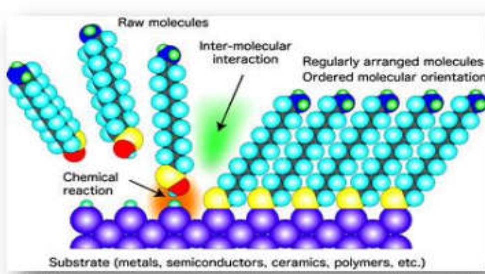
(Bottom up) Self-Assembled Monolayer (SAM)

Ex) organic molecules having -SH end groups on the Gold (Au) surface



http://nano.quimica.unlp.edu.ar/research/sams.php



http://www.mtl.kyoto-u.ac.jp/english/laboratory/nanoscopic/nanoscopic.htm

- ❖ **Molecular Interactions involved…**
- Covalent interactions (-SH and Au surface)
- Repulsive interactions (other electrons surrounding S)
- Attractive interactions (VDW interactions among alkyl chains)
  - **Reason for Tilt :** to maximize VDW interactions

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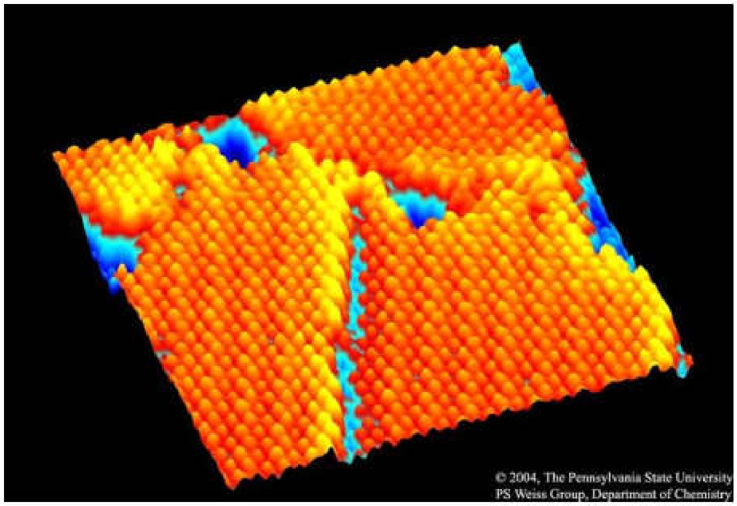
(Bottom up) Self-Assembled Monolayer (SAM)



A STM image (15 nm x 15 nm) of a self-assembled monolayer of n-decanethiolate on Au {111}. The individual molecules closely pack into a hexagonal array.

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Hybrid approach (Top-down + bottom-up)

- Templated Self-assembly of block copolymers

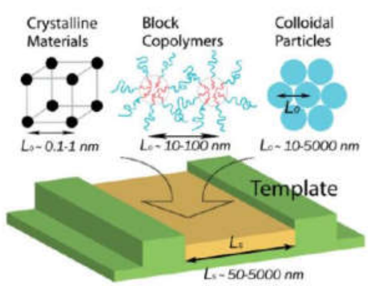
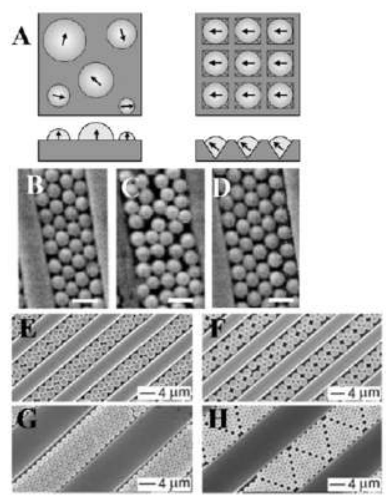


Figure 1. Illustration of some types of TSA systems. Characteristic lengths (L_0) of crystalline materials, block copolymers, and colloid assemblies and the characteristic length (L_S) of the template are indicated.

E. L. Thomas, *Adv Mater*, **2006**, 18, 2505



Molecules can self-assemble (bottom up), guided by the periodic patterns (or templates) fabricated by lithographic methods (top-down)

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What is the self-assembly (SA)?

❑ **Self-assembly**

- spontaneous association of molecules into defined three-dimensional (3D) geometry under a defined condition.

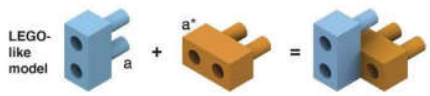
- "Self" : building units come close together
- "Assembly": form aggregates

Building units (BU)

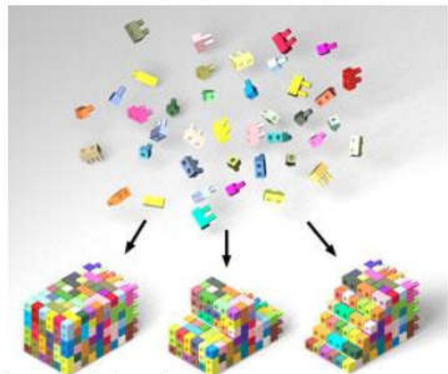
"Self-assembly process"

Spontaneously assemble

❖ Analogy to Lego block



- Simple, diverse, easy to assemble
- Complementary segments

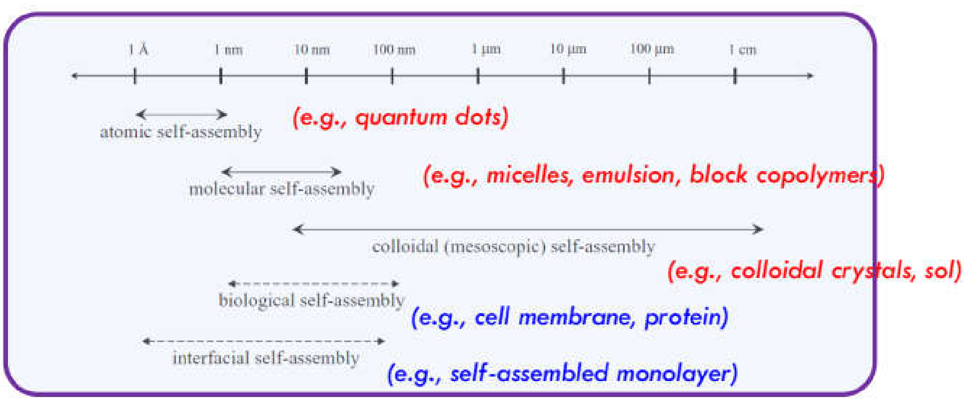


http://theolduvaigorge.tumblr.com/post/36880512253/ulaulaman-lego-and-dna-yonggang-ke-luvena-l
http://www.rsc.org/chemistryworld/2012/11/dna-lego-bricks-origami

Classification of self-assembly

1. By size/nature of building unit:
- Atomic, molecular (traditional), and colloidal

2. By system where is occurs:
- Biological and interfacial



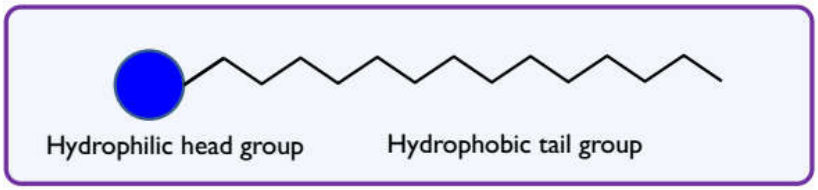
Self-Assembled System: (1) Surfactant micelles

◆ Surfactant: Surface Active Agent

1) Compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants.

2) Surfactants are composed of a polar head group that is hydrophilic and a nonpolar tail group that is hydrophobic.

i) A surfactant contains both a water-insoluble (or oil-soluble) component and a water-soluble component.
ii) The head groups can be anionic, cationic, zwitterionic, or nonionic.
iii) The tail group can be a hydrocarbon, fluorocarbon, or a siloxane



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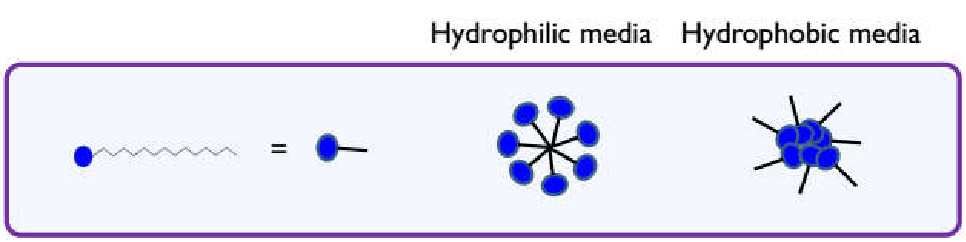
Self-Assembled System: (1) Surfactant micelles

- Surfactant molecules exist in solution as individual molecules at low concentrations.
- **Micelles:** the surfactant molecules saturate the surface and start forming aggregates in solution at higher surfactant concentrations
- **Critical micelle concentration (CMC):** Micelles are formed, once the surfactant exceeds a certain concentration



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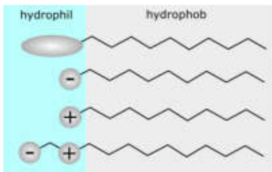
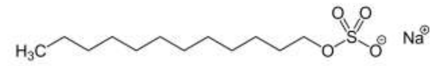
Self-Assembled System: (1) Surfactant micelles

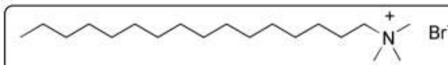


surfactant



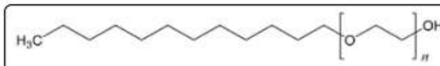
Sodium Dodecyl Sulfate (SDS)
(CMC = 8.2 mM)

(2) Cationic surfactant



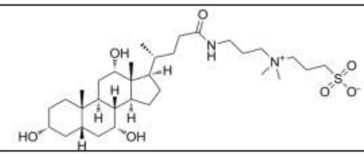
Cetyl Trimethylammonium Bromide (CTAB)
(CMC = 0.89–0.93 mM)

surfactant



Lauryl alcohol ethoxylate

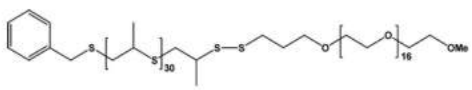
surfactant



3-[(3-Cholamidopropyl)dimethylammonio]-1-propanesulfonate hydrate (CHAPS)
(CMC = 8-10 mM)

Self-Assembled System: (2) Block copolymer in solution

- Amphiphilic nature can be programmed in the block copolymers as well



Formation of polymersome (polymeric vesicle)

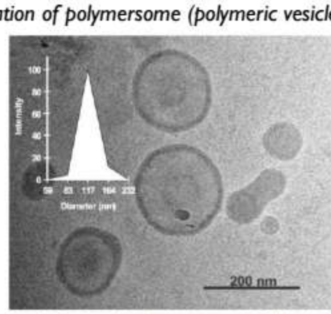
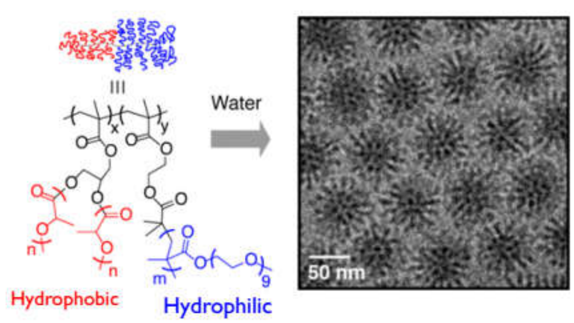


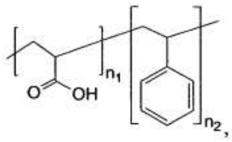
Figure 2. Cryo-transmission electron microscopy (cryo-TEM) analysis of the polymersomes. Cryo-TEM clearly demonstrated mostly monolamellar polymersomes with wall thicknesses around 9 nm. (Inset) Dynamic light scattering (DLS) analysis of the polymersomes, which gave an average size of about 120 nm and a quite narrow polydispersity.

Biomacromolecules, **2007**, *8*, 1966



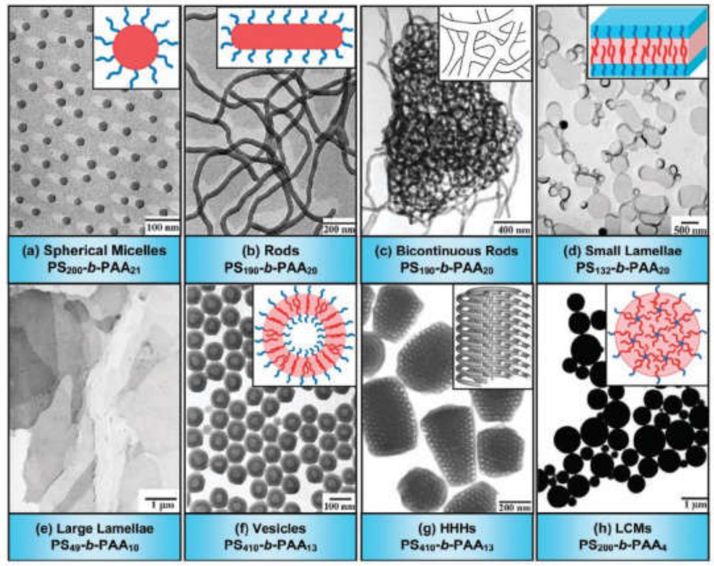
J. Rzayev, J. Am. Chem. Soc., **2014**, *136*, 7762

Self-Assembled System: (2) Block copolymer in solution



PS (x) - b- **PAA** (y)

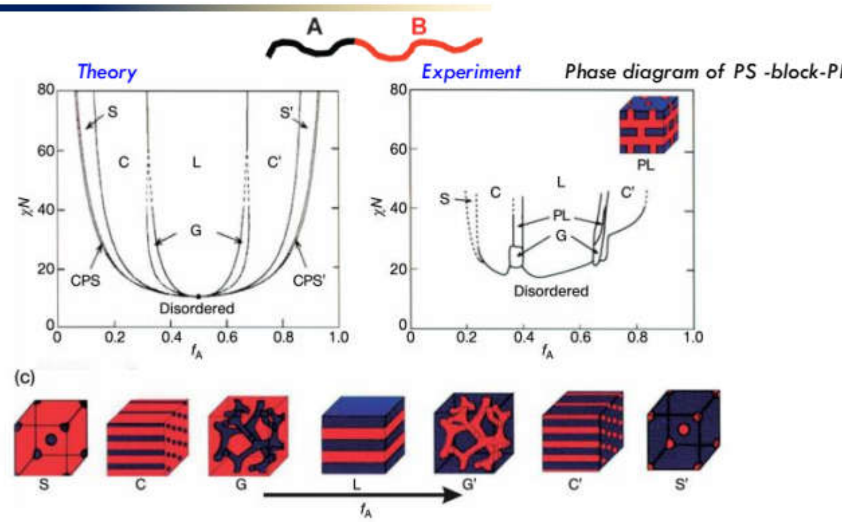
Hydrophobic Hydrophilic



4/28/2017 A. Eisenberg, *Chem. Soc. Rev.* 2012, 41, 5969

Solution morphologies can be tuned depending on compositions, concentration, solvent composition, additives (ions or homopolymers)

Self-Assembled System: (3) Block copolymer in bulk



1) χ = strength of A-B monomer repulsion
2) N = degree of polymerization
3) f_A = volume fraction of polymer A

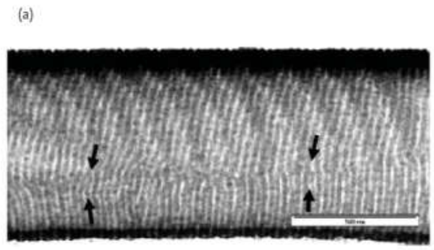
4/28/2017 A. Eisenberg, *Chem. Soc. Rev.* 2012, 41, 5969

Self-Assembled System: (4) Block copolymer thin-films

On thin film, interfacial interactions become significant (e.g., btw substrate and polymers)

(a) PS - b - PMMA
On a neutral substrate

(b) PS - b – PI
on PS-preferential substrate



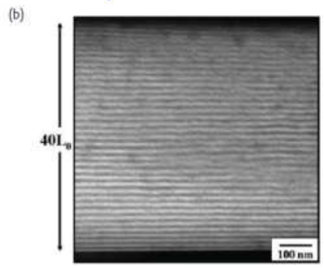
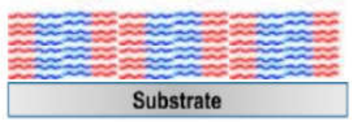
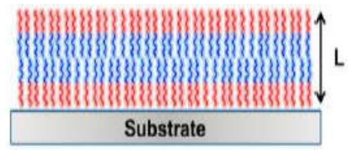


Fig. 2 (a) Cross-sectional TEM image of a ≈ 900 nm thick cylinder-forming PS-b-PMMA film on a neutral substrate surface annealed at 230 °C. Scale bar represents 500 nm. Defect line ≈ 200 nm (6 × L_0) into the film (arrows) indicates where neutral substrate and neutral free surface field effects intersect. Both fields align cylinders perpendicular to the substrate surface. (b) Cross-sectional TEM image of a ≈ 1400 nm thick lamellar PS-b-PI film on a PS-preferential substrate. (a) Reprinted in part with permission from[37] © 2009 American Chemical Society. (b) Reprinted with permission from[37] © 2008 American Chemical Society.

T Epps et. al., *Mater Today*, **2010**, 13, 24



Perpendicular to the substrate



Parallel to the substrate

Self-assembly through Force Balance

- ❖ **Three major forces (or interactions) for self-assembly**

Intermolecular interactions for self-assembly

❑ Major interactions

: relatively **weak** intermolecular or colloidal forces

TABLE 1.1. Representative intermolecular/colloidal attractive and repulsive forces for self-assembly.

Attractive Force	Repulsive Force
Van der waals[a]	Electric double-layer[b]
Solvation	Solvation
Depletion	Hydration
Bridging	Steric
Hydrophobic	
π–π stacking	
Hydrogen bond	
Coordination bond[c]	

(& also Directional force)

Three fundamental segments

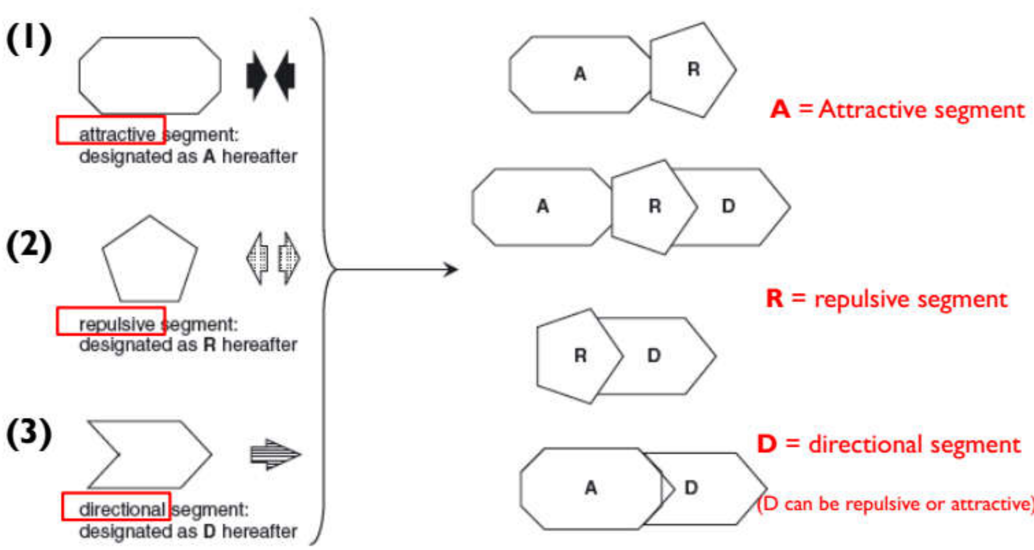


Figure 1-3. Three fundamental segments of self-assembly building units and their possible combinations. Arrows represent the direction of the force between the segments during self-assembly.

Example of Attractive, Repulsive & Directional Segment

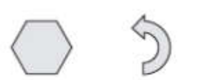
TABLE 1-1. Intrinsic components that can be each of the three fundamental segments. Physical, chemical, and conditional factors that can act as fundamental segments are also shown. A, R, and D refer to attractive, repulsive, and directional segments, respectively.

	Intrinsic Component	Physical Factor	Chemical Factor	Conditional Factor
A	hydrocarbon chain	surface charge	surface thiolation	concentration
	fluorocarbon chain	solvation	surface silylation	evaporation
	hydrophobic surface	physisorption	chemisorption	temperature
	charged atom		surface oxidation	pressure
	charged surface		surface reduction	pH
	structure recognizable group		other surface reactions	
R	bulky group	surface charge		concentration
	charged atom	solvation		temperature
	hydrated atom	desorption		pressure
	charged surface	hydration		pH
D	hydrogen bonding group	electric field	surface thiolation	evaporation
	coordination bonding group	magnetic field	surface silylation	temperature
	structure recognizable group	flow	chemisorption	pressure
	DNA	physisorption	surface oxidation	pH
	biological group		surface reduction	
	Also, π-π interactions		other surface reactions	

❖ **Directional segment**

: (attractive or repulsive) interactions between complementary groups

Two additional segments



asymmetric packing segment

(4) Asymmetric packing segment (AP)

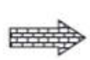
: a segment (within the self-assembly building unit) that induces the packing of the building unit with an asymmetric nature

Ex) many biological and biomimetic self-assembly building units → Chirality

external force-specific functional segment

(5) External force specific functional segment (EF-F)

: a segment (within the self-assembly building unit) that has a functionality whose function is exclusive on a specific signal (or stimulus)



external force-induced directional factor

(+) External force induced directional factor (ED)

: the external fields that impacts on the directionality of entire self-assembly process

Two additional segments

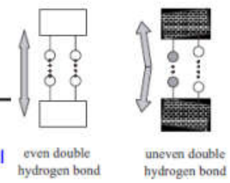
Asymmetric packing segment

External force specific functional segment

External force induced directional factor

TABLE 1-2. Intrinsic components that can be each of the additional segments. Physical, chemical, and conditional factors that can act as additional segments are also shown. AP, EF-F, and ED refer to asymmetric packing segment, external force–specific functional segment, and external force–induced directional factor, respectively.

	Intrinsic Component	Physical Factor	Chemical Factor	Conditional Factor
AP	hydrogen bonding group coordination bonding group asymmetric structure (chirality) structure recognizable group	physisorption	chemisorption	
EF-F	azo group (Sensitive to light) disulfide group (sensitive to catalytic) ferrocenyl group (Sensitive to electrochemical signal) *cis–trans* group charged surface magnetic field-sensitive component electric field-sensitive component			
ED		electric field magnetic field flow epitaxial matching		concentration evaporation temperature pressure pH ionic strength ultrasound UV, visible, laser



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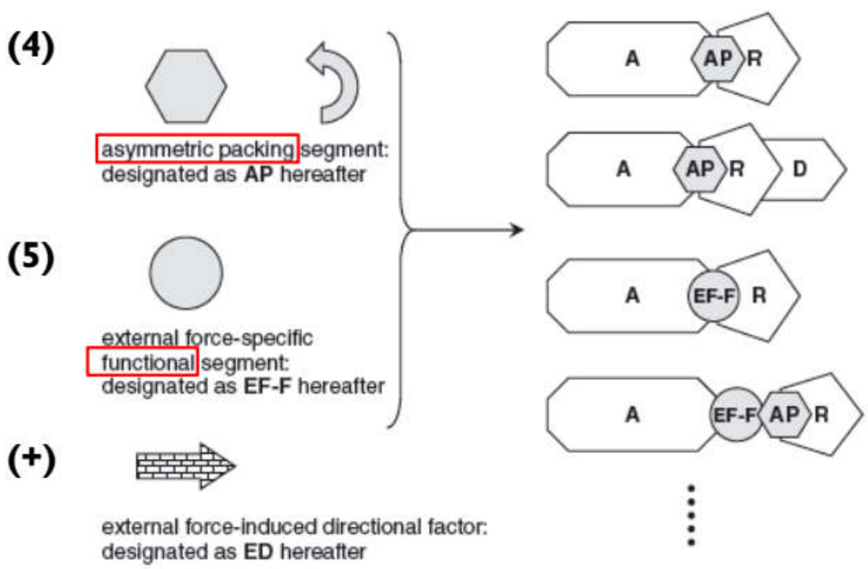
Two additional segments



External conditions

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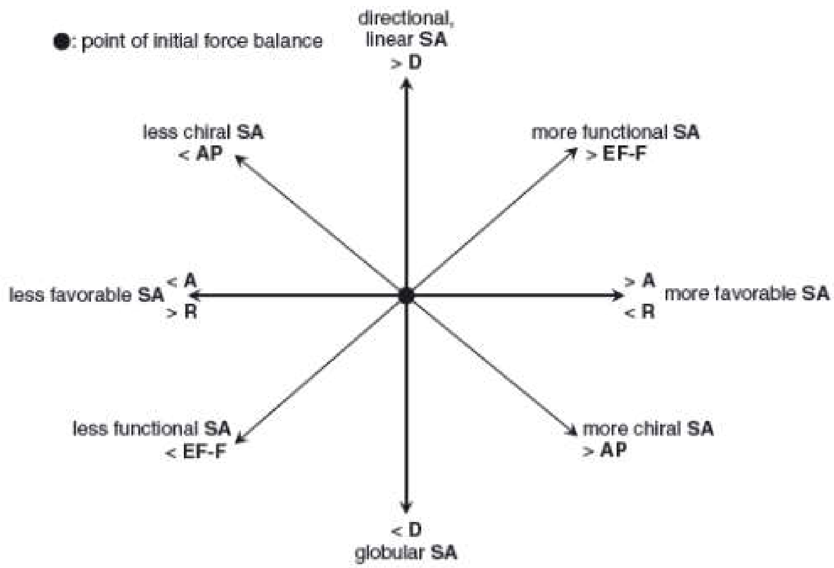
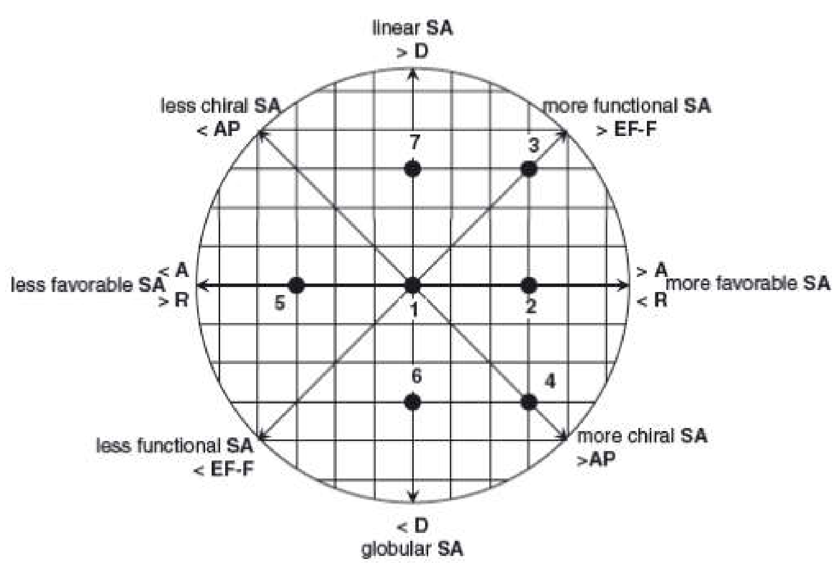
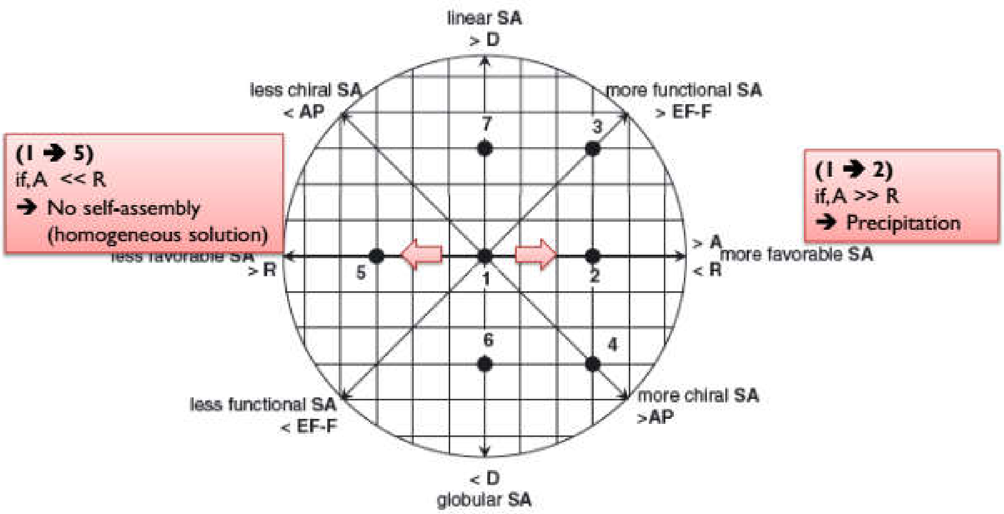
General rules of SA from fundamental and additional segments



Conceptual universal diagram for SA



Conceptual universal diagram for SA



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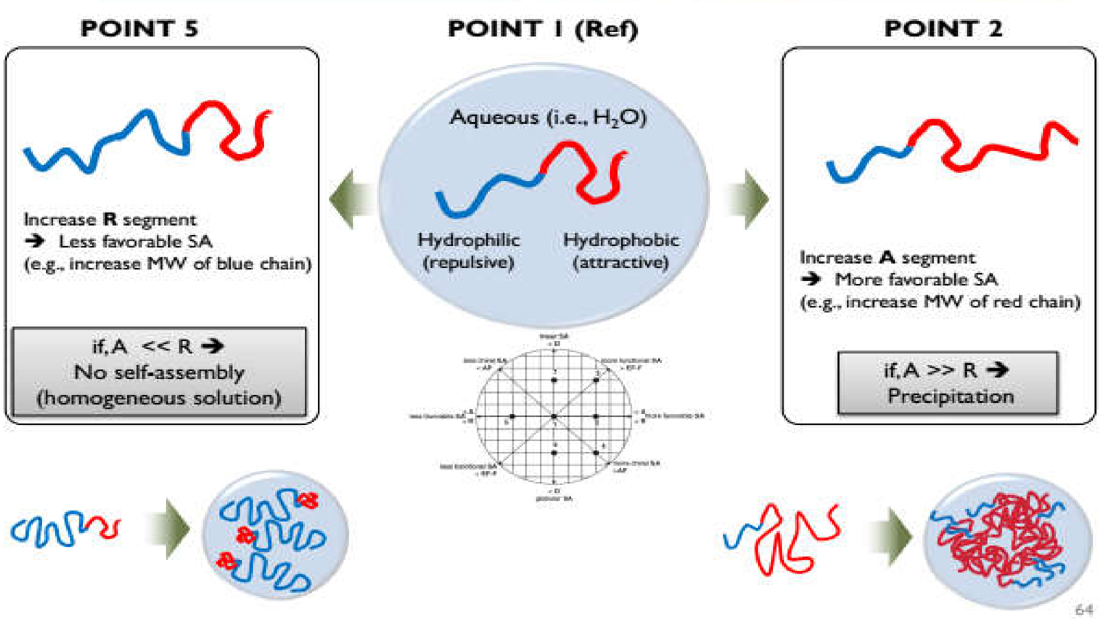
Examples



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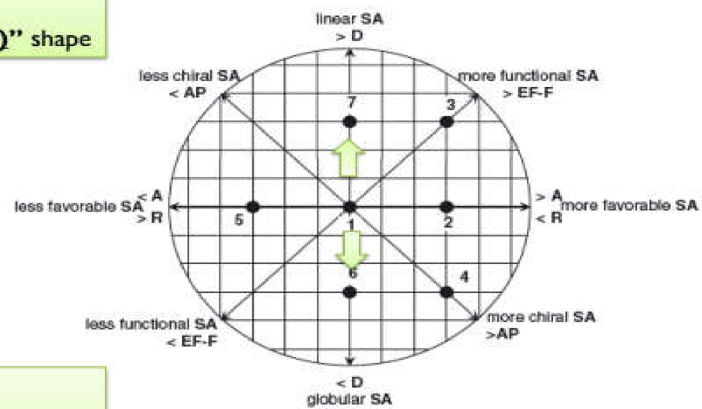
Conceptual universal diagram for SA

(1 → 7)
- CMC : lower (than 1)
- "**Linear (non-spherical)**" shape



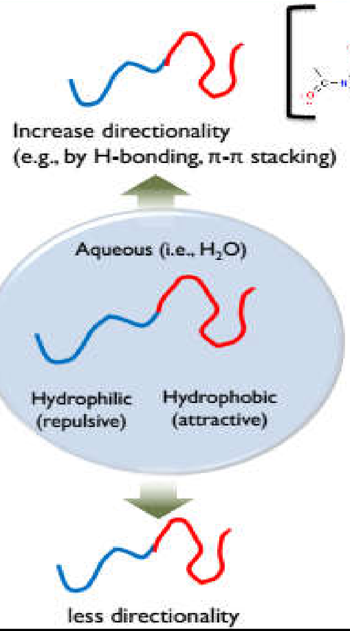
(1 → 6)
- CMC : higher (than 1)
- Aggregation No : smaller
- Size of aggregation: smaller
- "**Globular (spherical)**" shape

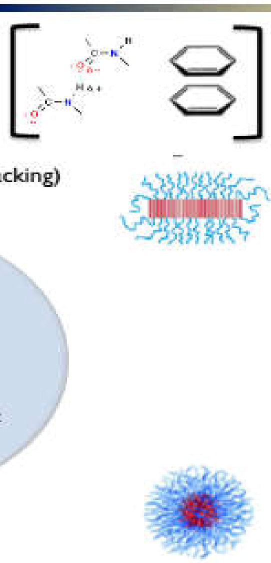
Examples

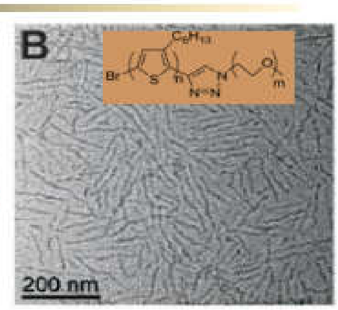
POINT 7

POINT 1 (Ref)

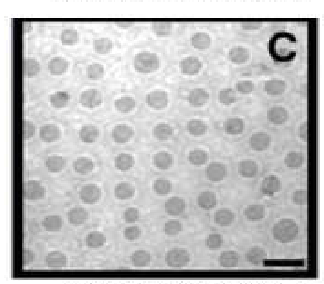
POINT 6







SJ Park, ACS Nano, 2012 6, 2844

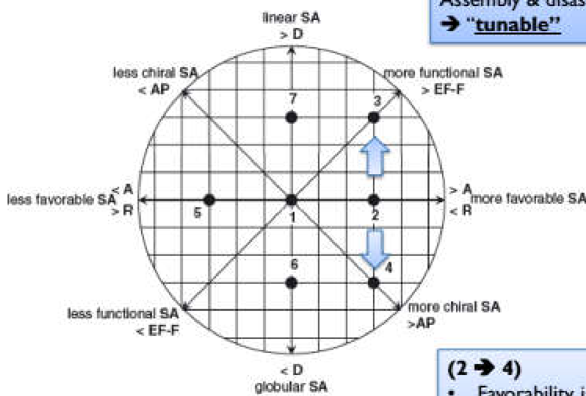


Polym. Chem, 2011, 2, 1018

Conceptual universal diagram for SA

(2 ➔ 3)
- Favorability is impacted by the functional segment
- CMC/ Aggregation No/ Size & shape of Aggregation/ Assembly & disassembly

➔ **"tunable"**



(2 ➔ 4)
- Favorability is impacted by AP segment
- Usually enforces a attractive & directional segment
- Lower CMC
- Higher aggregation No.
- **Diverse and bigger morphologies**

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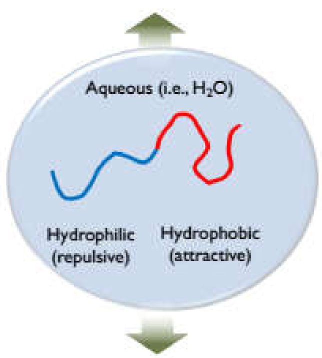
Examples

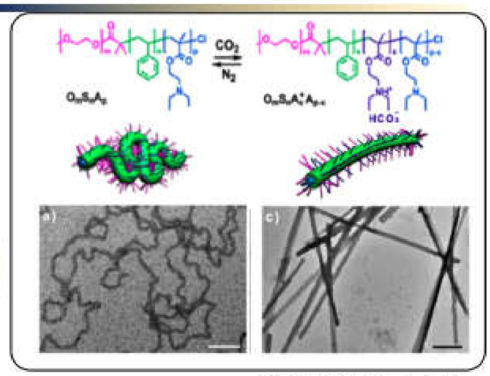
POINT 3 + functionality

POINT 2

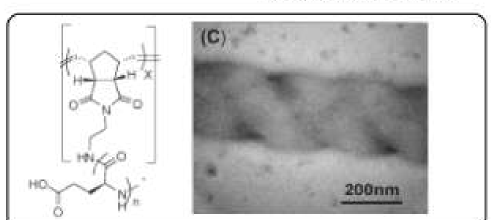


POINT 4 + chirality

PBLG (polybenzylglutamate)
➔ Polypeptide (chiral unit)



Y Zhao, JACS, **2013**, 135, 16300



Y. Lin, *J. Am. Chem. Soc.* **2011**, 133, 12906

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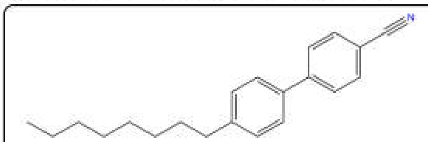
(Q) Identification of force segments

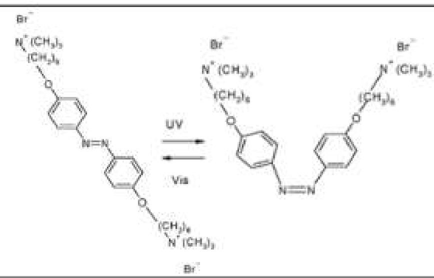
(1) Decyltrimethyl ammonium bromide

(in Water)

(2) 4-cyano-4'-octyl-1,1'-biphenyl (8CB)



(3) 4,4′-bis (trimethylammoniumhexyloxy) azobenzene bromide



More examples can be found in the Section 1.5 of Chapter 1 (Textbook 2, p24-30)

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N. Abbott, *Langmuir* 1999, 15, 4404 69

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Self-assembly (SA): Thermodynamic & kinetic process

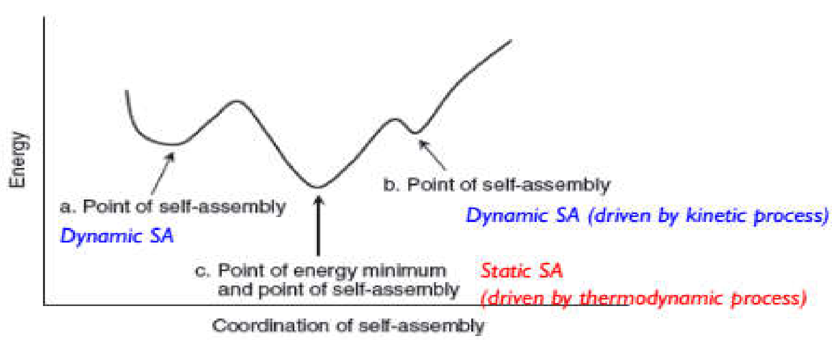

Figure 1-2. The concept of force balance can embrace a wider scope of self-assembly than the energy minimization approach.

- *Self-assembly process can be driven by both thermodynamic process & kinetic process*

1) Thermodynamic equilibrium btw SA building units at the balance point will ensure self-assembly process (bring building units together & hold aggregates with structural integrity)

2) But, Kinetic conditions (i.e., under particular conditions) can also ensure the same aspects of self-assembled aggregates (bring building units together & hold aggregates with structural integrity)

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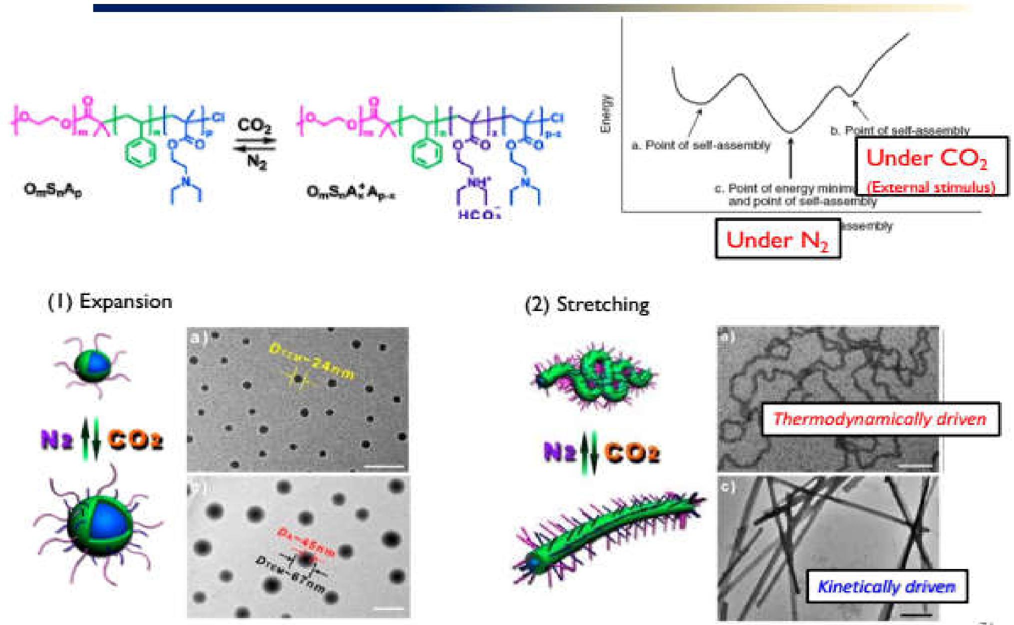
Self-assembly (SA): Thermodynamic & kinetic process



Y Zhao, "CO2-stimulated diversiform deformations of polymer assemblies" JACS, **2013**, 135, 16300

Hierarchical Self-Assembly

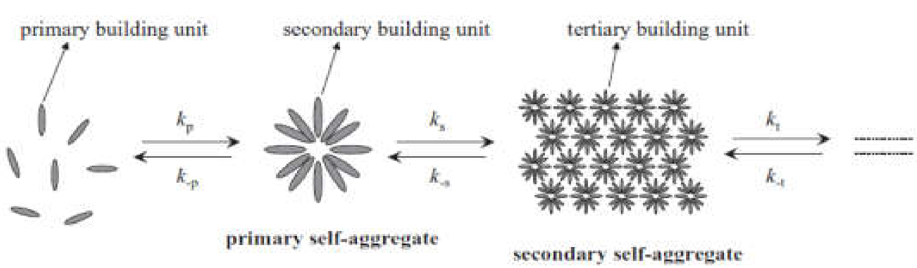
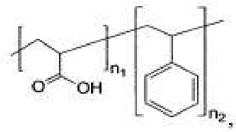


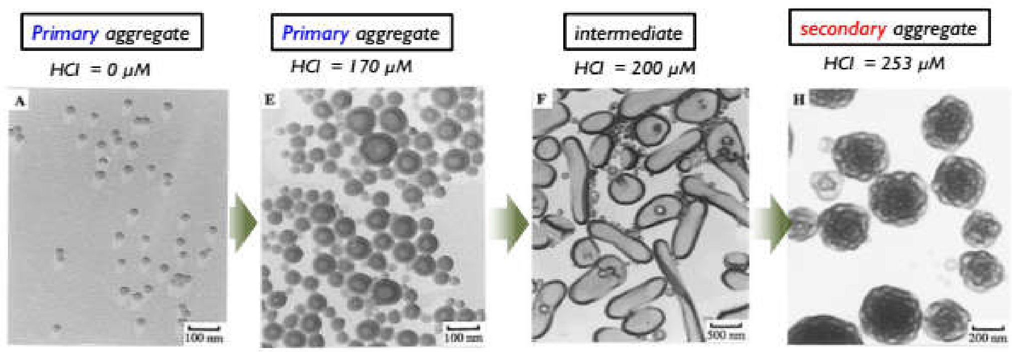
Figure 1.3. General scheme for self-assembly.

→ ***Develop hierarchical structures***

Ex) Formation of secondary aggregates



PS (410) - b- PAA (13)



Individual spherical micelles — *Individual (spherical) vesicle* — *Elongated vesicle* — *Large compound vesicle*

A Eisenberg, *Macromolecules* **1996**, 29, 8805
A. Eisenberg, *Science* **1996**

Summary

1) *Manufacturing Nanostructured Materials:*
   :Top down vs bottom up

2) *Self-assembly through force balance*
   : Balance between Attractive, Repulsive and Directional forces

   - *Attractive segment (fundamental)*
   - *Repulsive segment (fundamental)*
   - *Directional segment (fundamental)*
   - *Asymmetric packing segment (additional)*
   - *Functional segment (additional)*
   - *External force induced directional factor*

3) *Self-assembly can be driven by thermodynamic or kinetic process*

4) *Hierarchical Self-assembly*