Self-Assembly
to create mesoporous materials

Micelles

Polymers

Liquid Crystals

Outline

1. What are they?

2. What are they useful for?

3. What are some of the theoretical aspects behind these materials?

4. How can we synthetize them?

5. What are the factors affecting their sizes, shapes and their existence ?

What are mesoporous materials?

- Porous materials whose pores are between 2 and 50 nm in diameter.

- Silica based materials first synthesized by scientists at the Mobil Corporation in 1992.

- Non-silica mesoporous materials first reported at UC Santa Barbara in 1994.

Applications

- Molecular sieves

- High surface area catalysts

- Gas sensors

- Dye sensitized photovoltaic solar cells

Micelles

Mesoporous materials are templated by amphiphilic molecules.

- An **amphiphillic molecule** has a hydrophillic (water loving) head and a hydrophobic (water loathing) tail.

- *Surfactant* *is* an amphiphilic molecule with a tendency to adsorb onto free surfaces and interfaces and to aggregate to form micelles

- **Micelle** is an <u>association</u> of amphiphillic molecules.

- **Mesoporous structures** are created by the ordered packing of micelles.

- Small molecules $M_w \approx 100\text{-}1000$

Courtesy of Brian Eggiman

Questions to be answered about micelles

What are amphiphylic molecules?

Why do micelles form?

What factors determine the shape and size of the micelles?

What determines their packing geometry?

What are their properties?

How can we used them?

Why do amphiphiles form micelles?

- Gibb's Free Energy (ΔG) is a thermodynamic quantity which predicts the spontaneity of a reaction. (A decrease in Gibb's Free Energy indicates a spontaneous reaction)

- Water molecules create structure by forming hydrogen bonds with one another.

- The hydrophobic tails of individual amphiphiles placed in solution force water molecules to associate in a particular way. This decreases the entropy (ΔS) of the system.

- When the hydrophobic tails associate to each other (form micelles) in order to minimize their interaction with water molecules they increase the entropy of the system.

$$\Delta G = \Delta H - T\Delta S$$

- An increase in entropy, decreases Gibb's Free Energy of the system therefore the reaction will occur spontaneously.

Temperature Effects

(a) Gas (dispersed) → Liquid (condensed)

under Van der Waals attraction forces

(b) Polymer gels (dispersed) → Collapsed

polymer gel (condensed)

under rubber elasticity (entropy change), counter ions osmotic pressure, and electrostatic repulsive forces

(c) Colloidal particles (dispersed) →

self-assembled colloidal crystals and super lattice structures

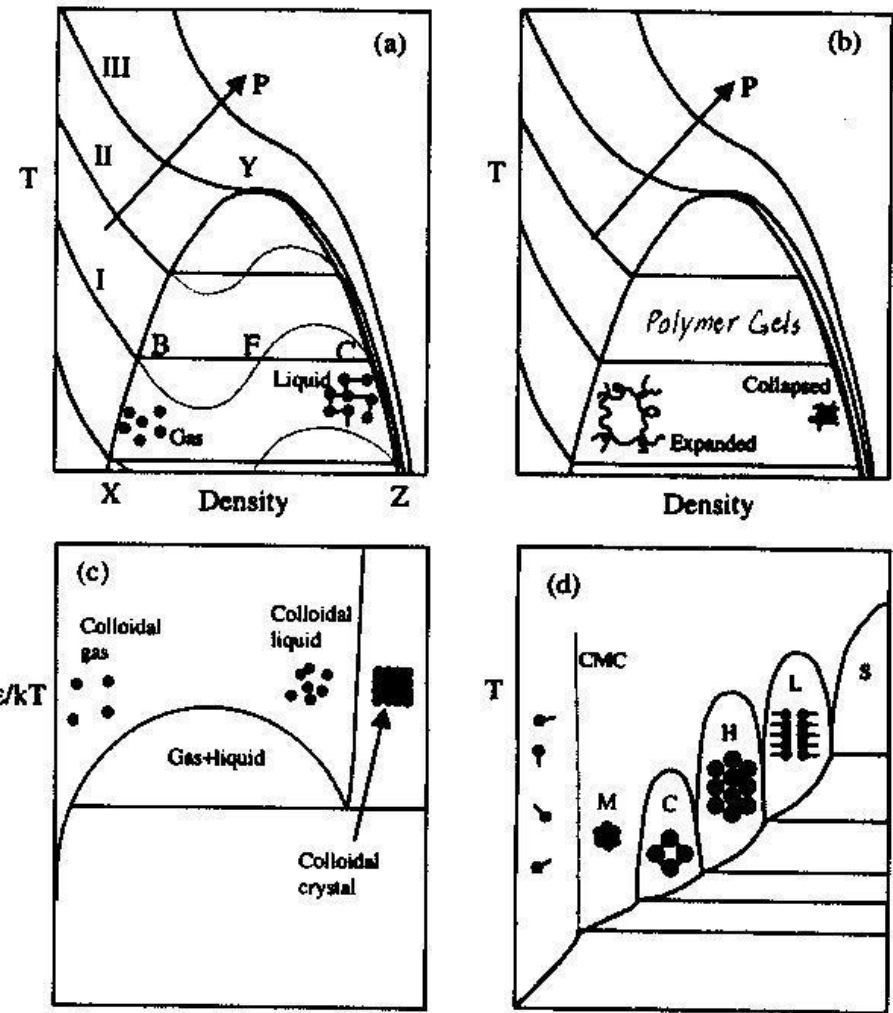**(d) Surfactant packing transition**

cubic, hexagonal, lamellar, solid

FIGURE 2.4. Phase diagrams of several systems showing the transition from dispersed states to condensed states. (a) Gas-liquid phase transition. (b) Swelling-deswelling in polymer gels. (c) Consolidation of colloidal crystals. (d) Surfactant phase diagrams. In Fig. 2.4(d) M, C, H, L, S represent micelles, cubic phase, hexagonal phase, lamellar phase, and solid phase respectively. Figures 2.4(a) and (b) are redrawn after Refs. 9, 10. Figure 2.4(c) is redrawn after Ref. 13. Figure 2.4(d) is redrawn after Ref. 16.

Self-Assembled Structures vs. Temperature
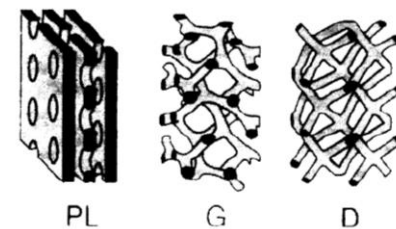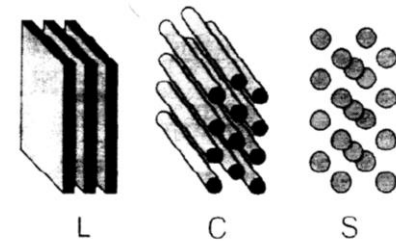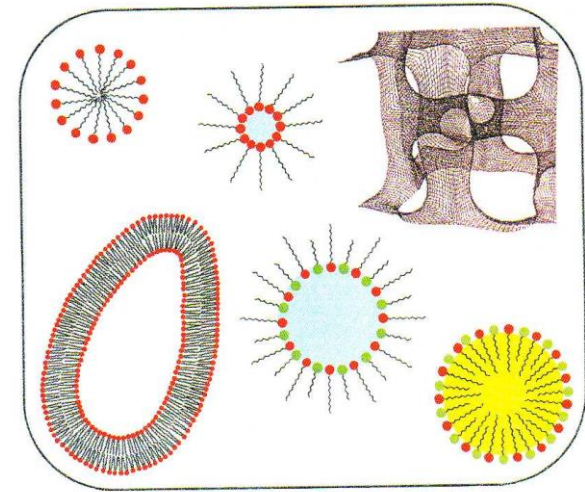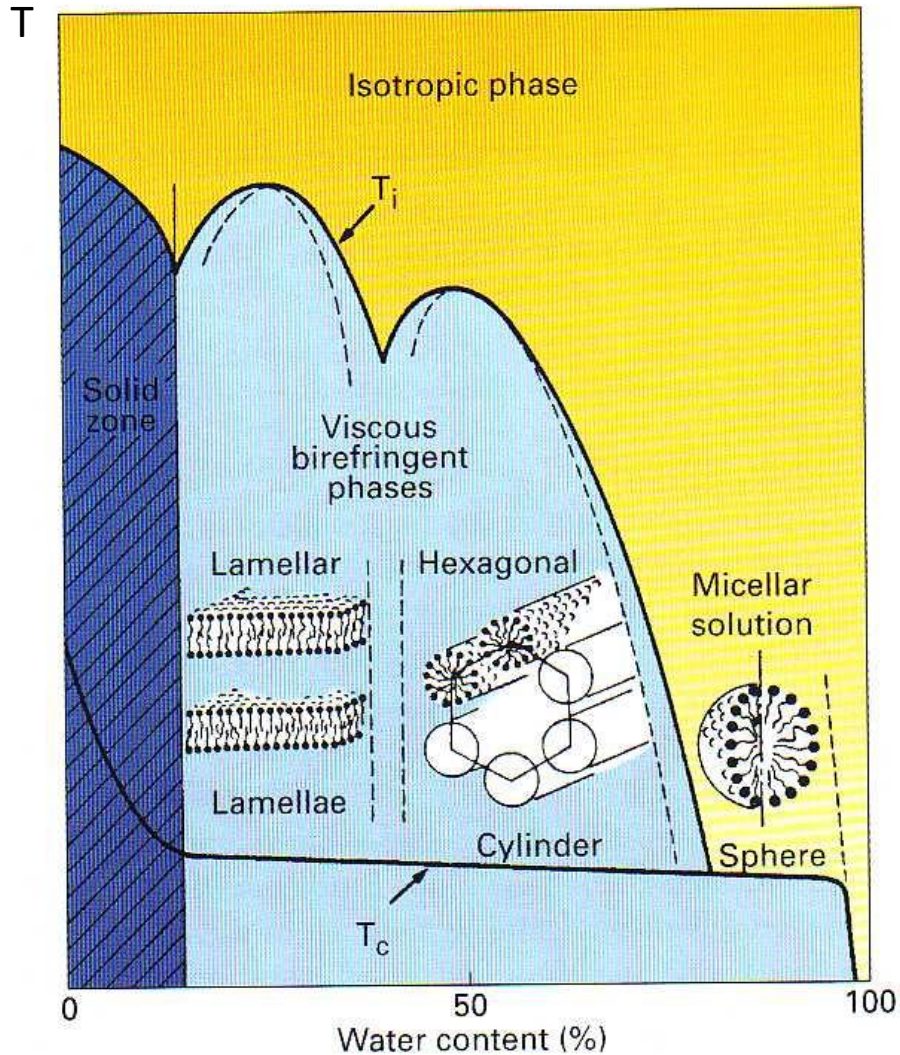
Surfactant concentration effects
keeping constant other variables

Cubic Phase

Lamellar Phase

Hexagonal Phase

Rod-like Micelles

Spherical Micelles
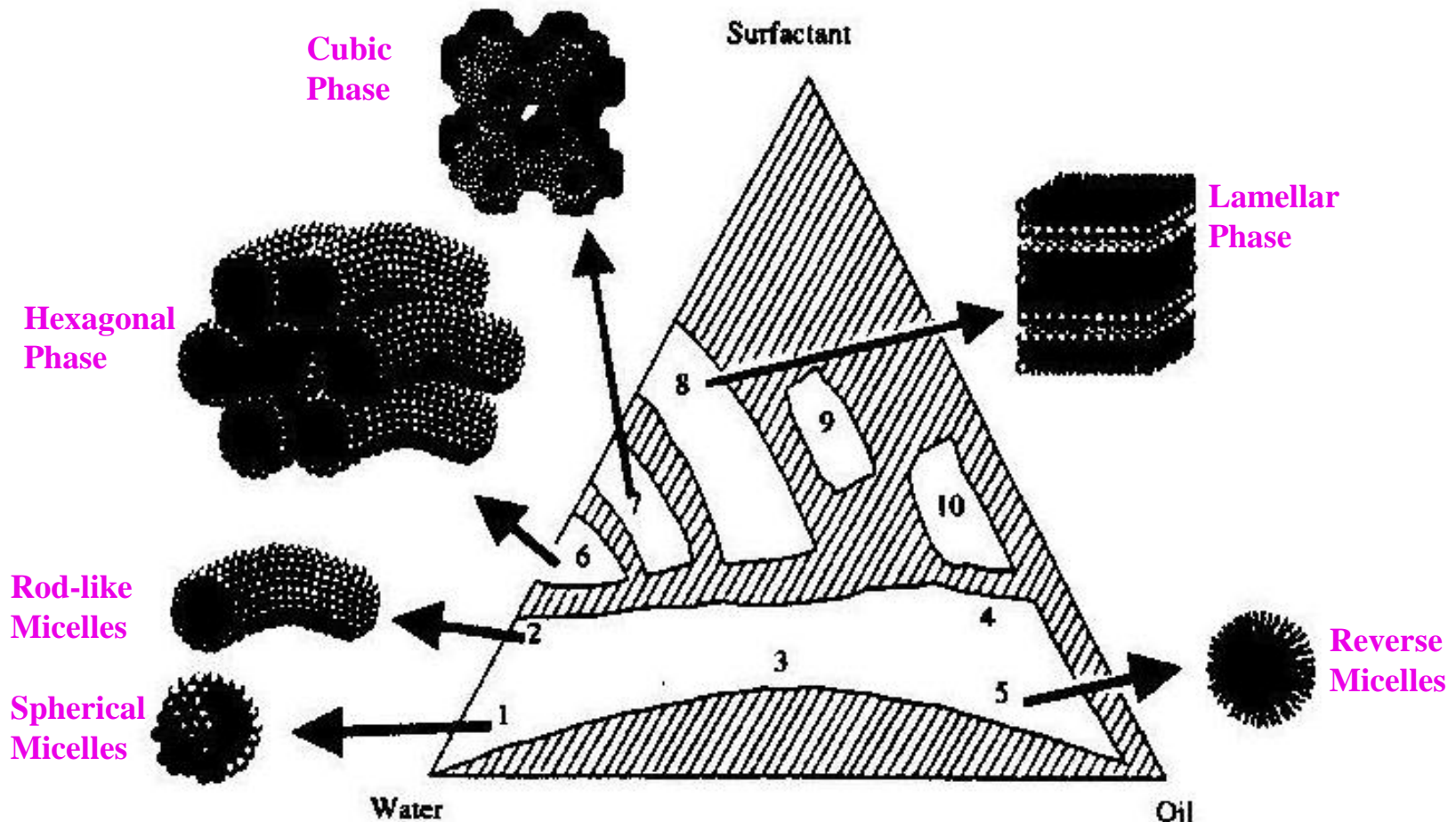
Reverse Micelles

Surfactant

Water

Oil

FIGURE 2.6. Schematic phase diagrams of surfactant-water-oil systems. 1. Spherical micelles. 2. Rod-like micelles. 3. Irregular bicontinuous phase. 4. Reverse cylindrical micelles. 5. Reverse micelles. 6. Hexagonal phase. 7. Cubic phase. 8. Lamellar phase. 9. Reverse cubic phase. 10. Reverse hexagonal phase (Derived from Refs. 18 and 19 with permissions from the publishers).

Increase Surfactant Conc.: spherical micelles → rod-like micelles → cubic → lamellar
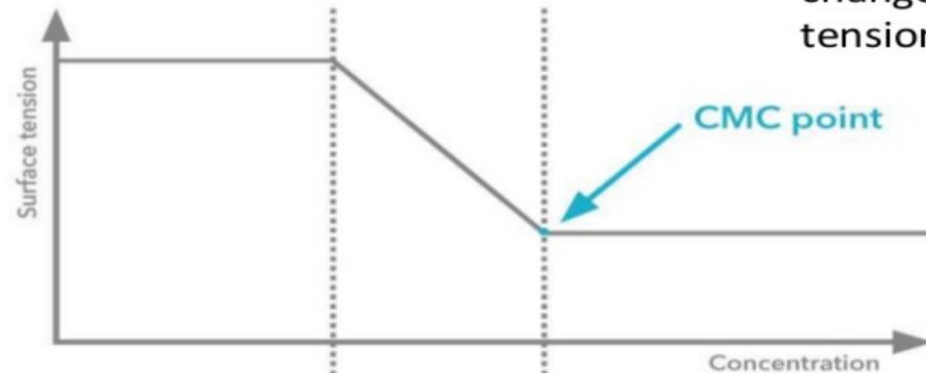
Structure, also depends on:
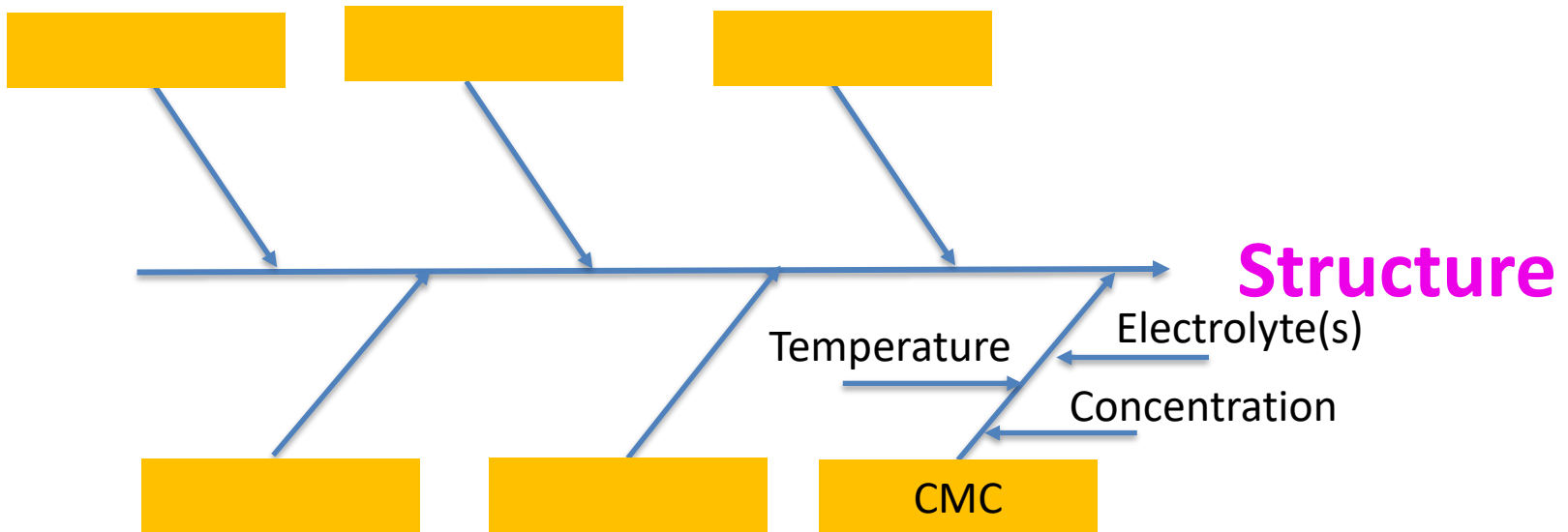
Critical Micelle Concentration

Micelles are formed at the critical micelle concentration (CMC) and at that concentration some of the properties have an inflection point:
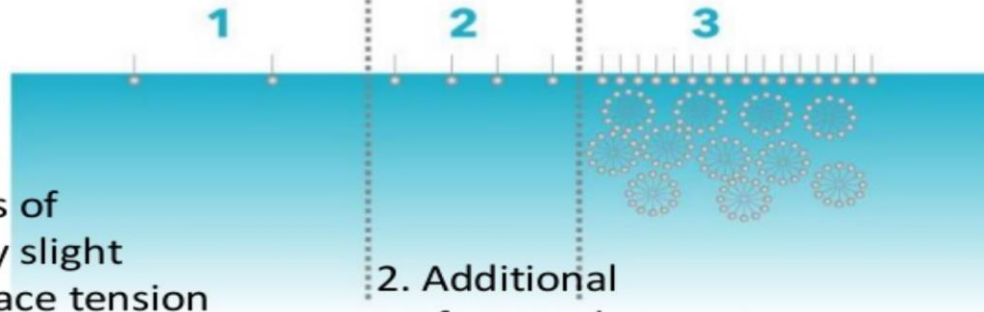
- Surface tension

- Conductivity

- Turbidity

Surface tension

3.Surface becomes fully loaded, no further change in surface tension.

CMC point

Surface tension

Concentration

1   2   3

1. At very low concentrations of surfactant only slight change in surface tension is detected.

2. Additional surfactant decreases surface tension
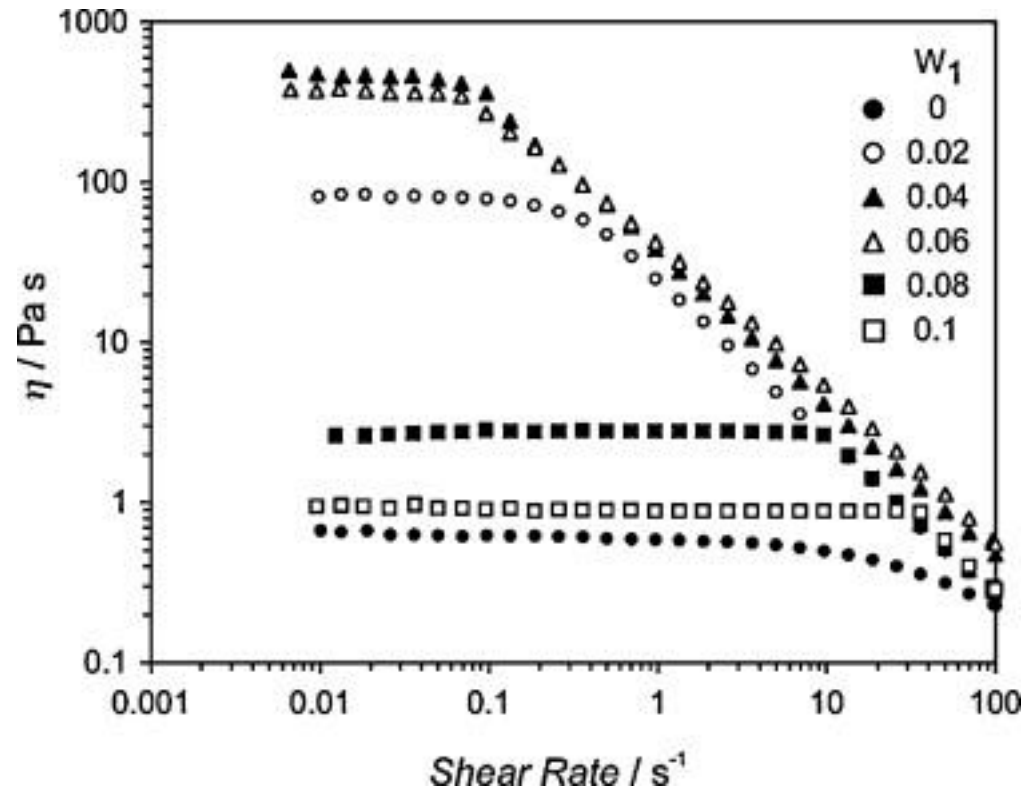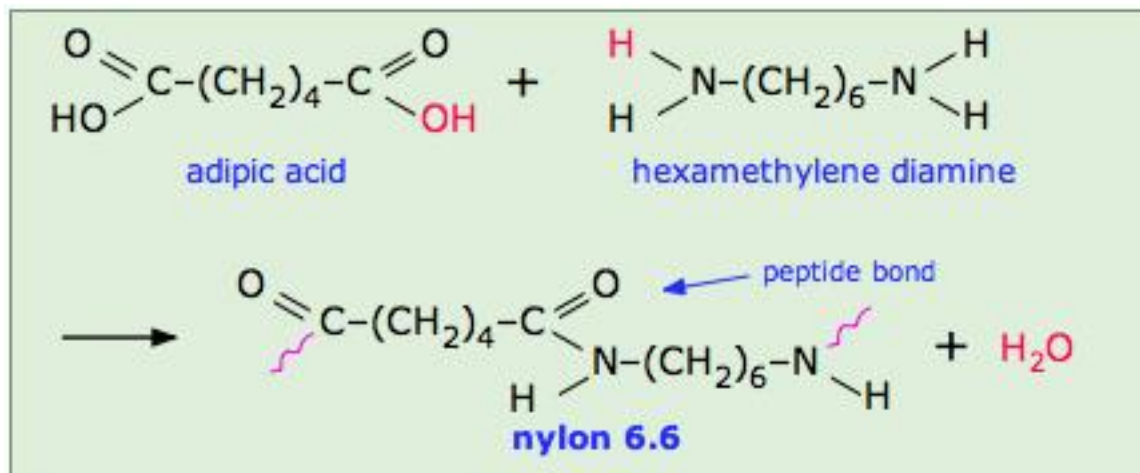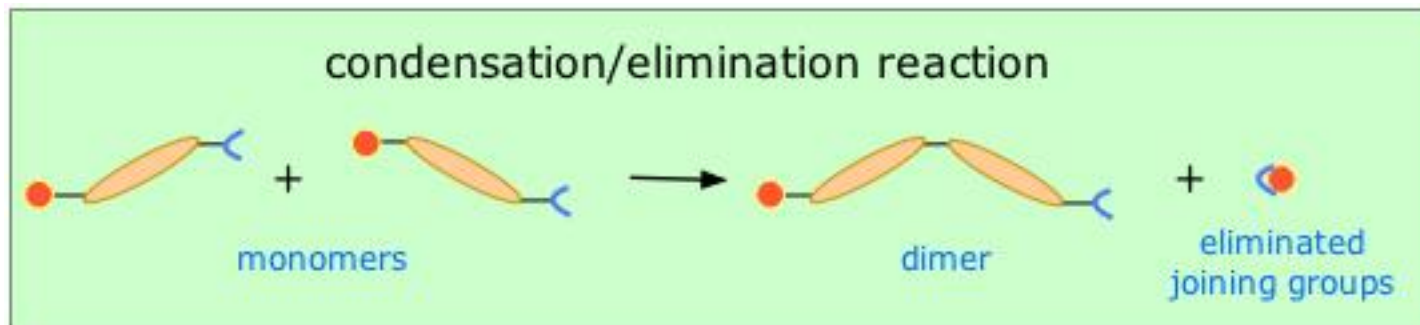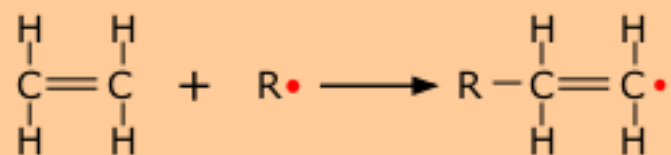
Critical Micelle Concentration

Fig. 1. A plot of viscosity for micellar solutions of the water/C_{16}SE/LA system at 30 °C against shear rate at various weight fractions of LA in total amphiphiles (W_1) is shown. Weight fraction of water in the whole system is fixed at 0.9. Sucrose monopalmitate (C_{16}SE lauric acid (LA)
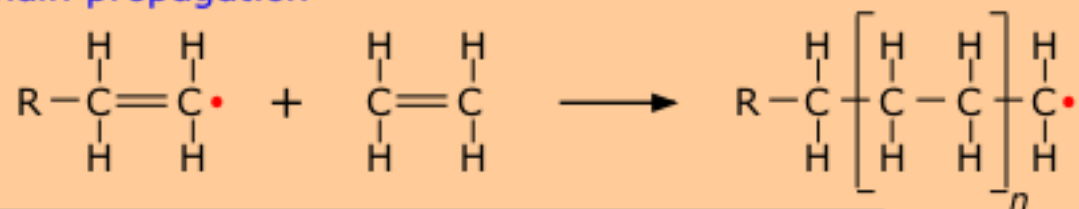
Polymers

Condensation

chain initiation

$$H_2C=CH_2 \ + \ R\cdot \ \longrightarrow \ R-CH_2=CH_2\cdot$$

chain propagation

$$R-CH_2=CH_2\cdot \ + \ H_2C=CH_2 \ \longrightarrow \ R-CH_2\left[CH_2-CH_2\right]_n CH_2\cdot$$

chain termination

$$R-CH_2\left[CH_2-CH_2\right]_n CH_2\cdot \ + \ R\cdot \ \longrightarrow \ R-CH_2\left[CH_2-CH_2\right]_n CH_2-R$$
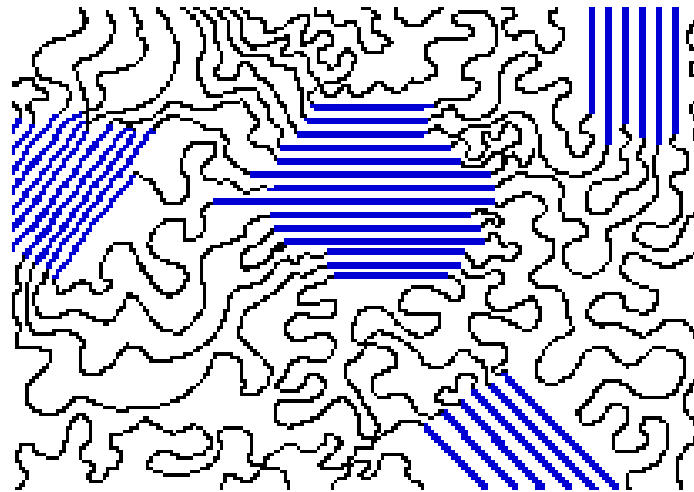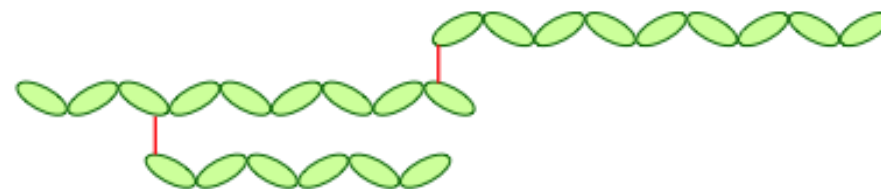
Figure 7.11.3: The crystalline parts of this polymer are shown in blue

branched homopolymer

graft copolymer

Self-assembled Block Copolymer Nanostructures

✓ **Block copolymers are amphiphilic molecules containing distinctively different polymer segments (blocks):**

- polystyrene and poly isoprene block copolymer

- polystyrene and poly butadiene block copolymer

- polyethylene and poly propylene block copolymer

✓ **Different blocks in a single polymer chain are covalently bonded.**

✓ **The phase separation occurs on the nanometric scale, as determined by the dimension of the blocks.**

✓ **Factors: monomer type, composition and molecular size, and molecular configuration.**

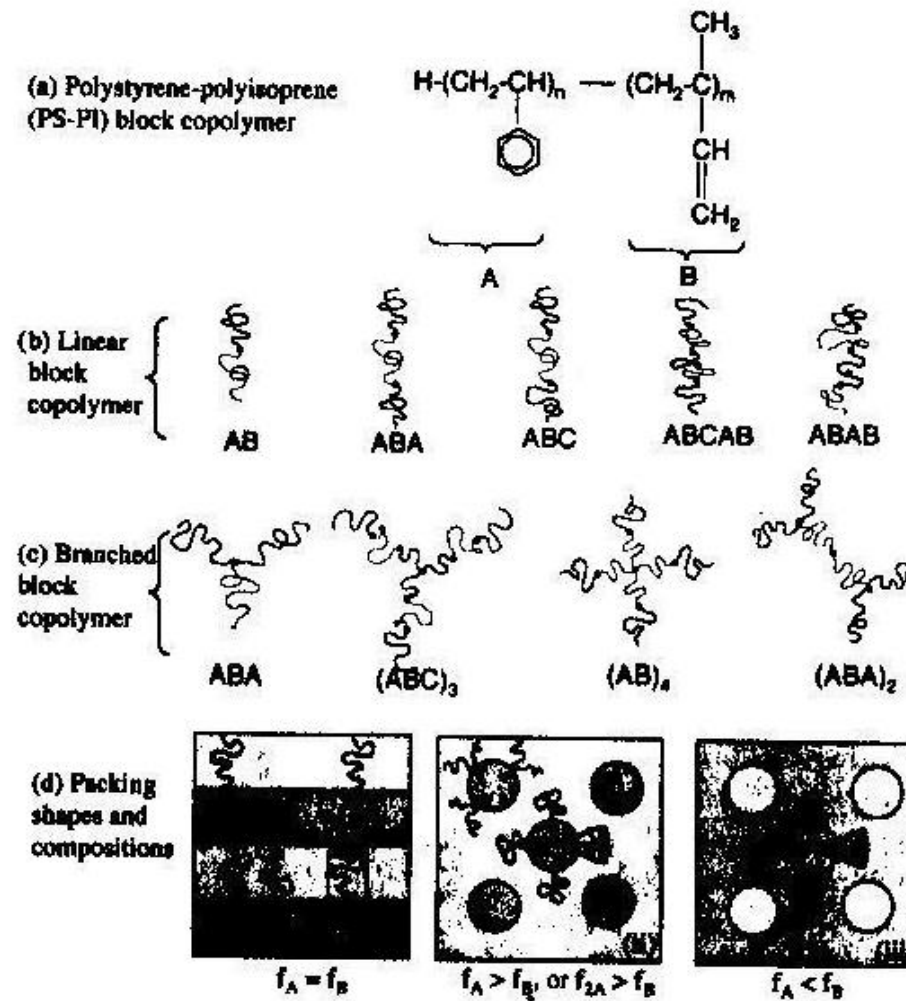## 2.5 Self-assembled Block Copolymer Nanostructures

FIGURE 2.8. Variations of block copolymer configurations and the consequences on the packing geometry of the nanostructural ordering. (a) A common block copolymer, polystyrene-polyisoprene (PS-PI). (b) Linear block copolymers. (c) Branched block copolymers. (d) Packing shapes as a function of the compositions or molecular compositions (redrawn from Ref. 22).

2.5 Self-assembled Block Copolymer Nanostructures

Flory-Huggins segment-segment interaction parameter χ:

$$\chi = \frac{E_{AB} - 1/2\,(E_{AA} + E_{BB})}{k_B T}$$

$\boxed{\chi \rangle 0}$ phase separation is favored

E: Interaction Energy

f = volume fraction

$f_A = f_B$ **→ straight cylinder → lamellar phase**

$f_A > f_B$ **→ cone structure →   B phase dispersed in A phase as spherical micelles**

$f_B > f_A$ **→ cone structure →   A phase dispersed in B phase as spherical micelles**
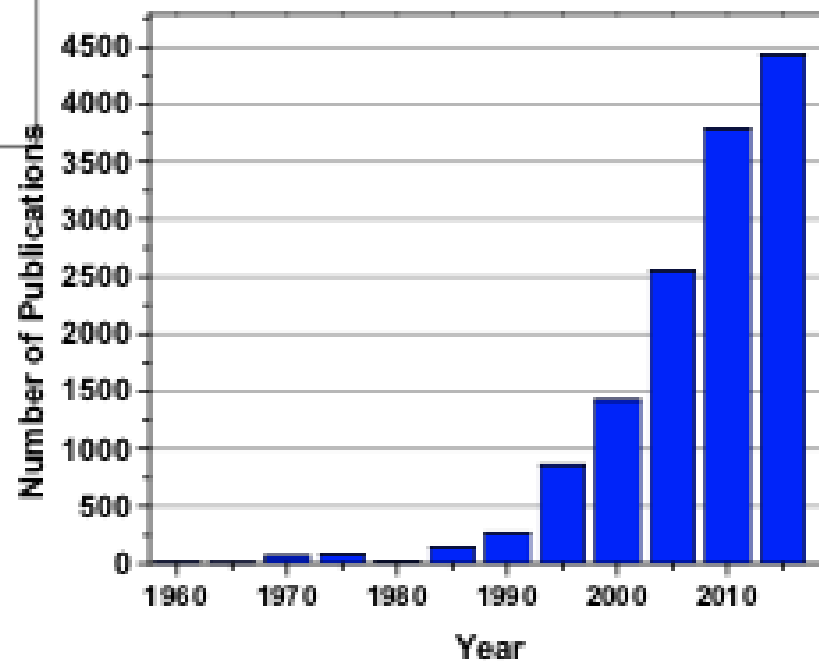
Number of Publications*

Figure 2. The number of publications with block copolymer as topic against year. The data were obtained from Web of Science (2017 Clarivate Analytics).

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[2] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA; wwang41@utk.edu
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[*] Correspondence: jimmymays@utk.edu; Tel.: +1-865-974-0747

Possible BCP Architectures

Linear block terpolymers   "Comb" graft copolymers   "Miktoarm" star terpolymers   Cyclic block terpolymers
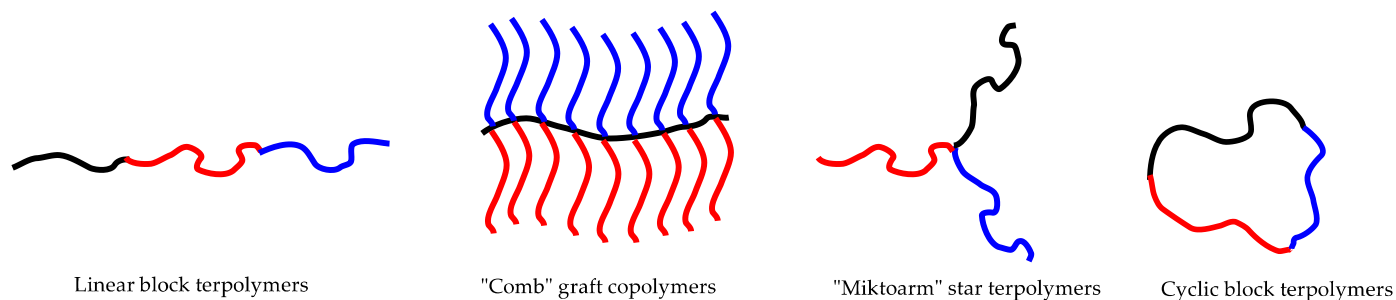
Figure 1. Representative architectures of linear block terpolymers, "comb" graft polymers, miktoarm star terpolymers, and cyclic block terpolymers.

Star block copolymer   Miktoarm Star   Star-b-linear-b-star   "Comb"

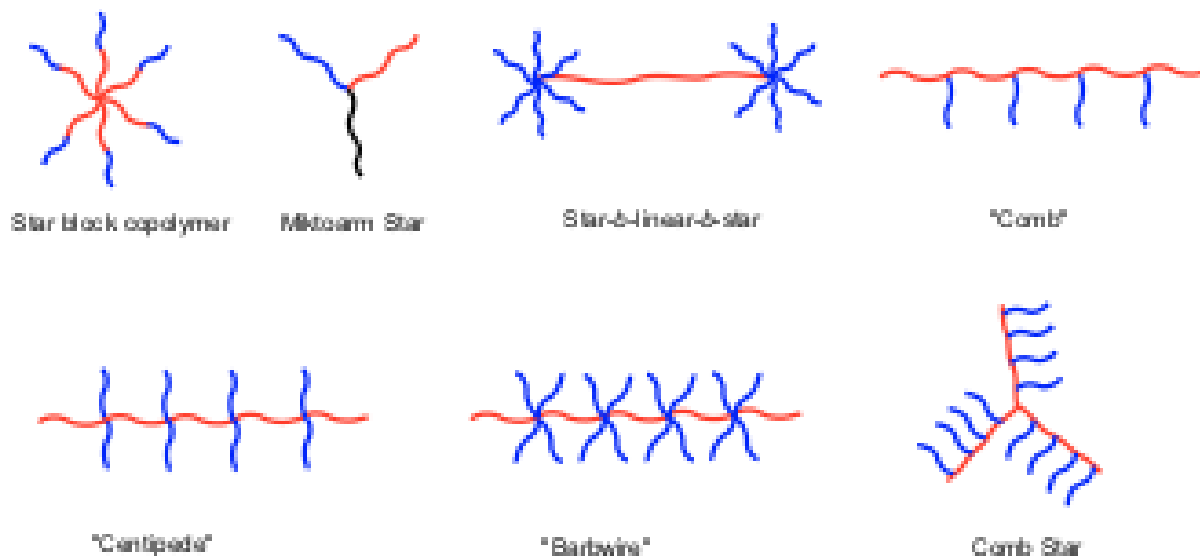"Centipede"   "Barbwire"   Comb Star

Figure 3. Illustration of complex architectures using living anionic polymerization and coupling chemistry. Adapted from Reference [55]. (Copyright (2017) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

Effects of the packing parameter
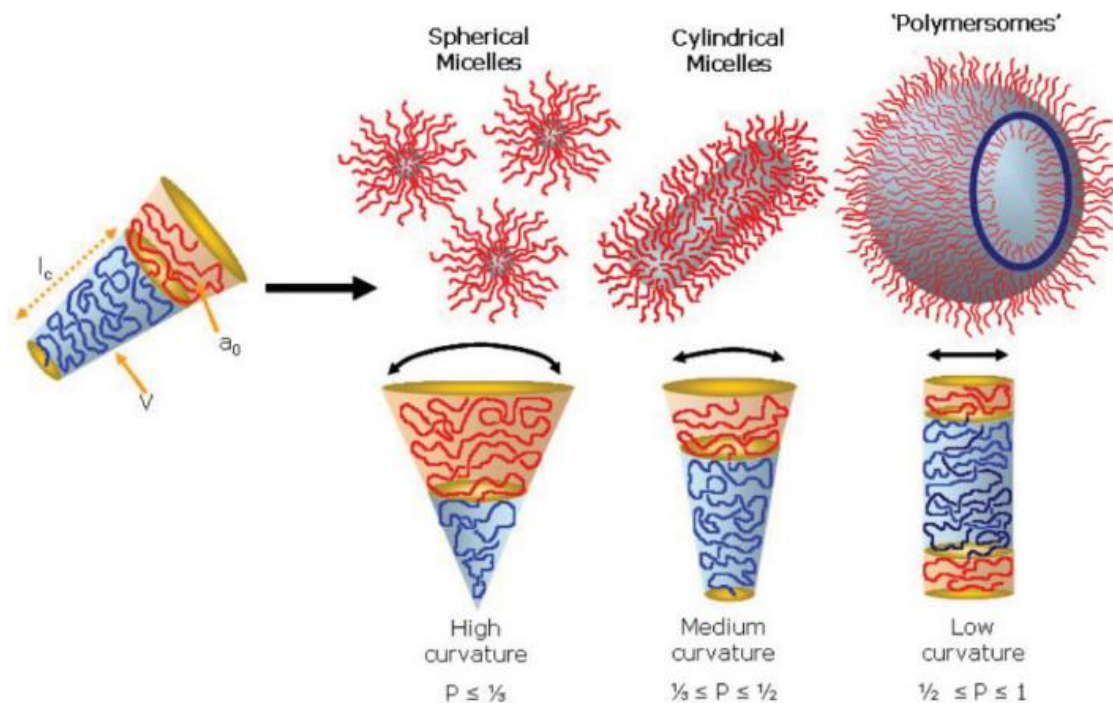$$(p = v/a_0 l_c)$$

Figure 10. The types of formed nanostructures of amphiphilic diblock copolymers due to the inherent curvature of the polymer, as estimated by chain packing parameter, p. Reprinted from Reference [80]. (Copyright (2009) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).
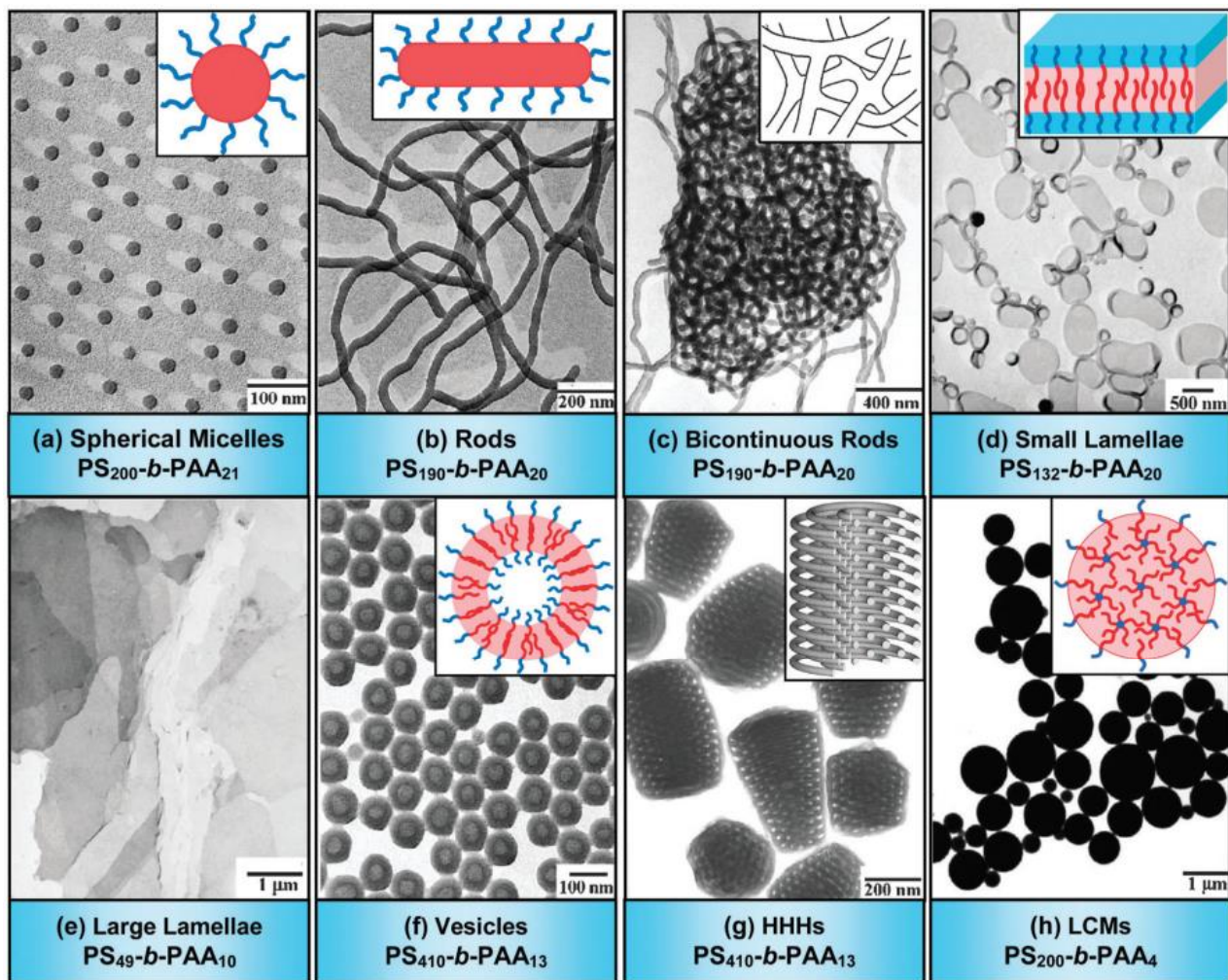
Effect of the degree of polymerization

Figure 11. TEM images and corresponding schematic diagrams of various morphologies formed by amphiphilic PS_m-b-PAA_n copolymers(m and n denote the degrees of polymerization of PS and PAA, respectively): (**a**) spherical micelles; (**b**) rods; (**c**) bicontinuous rods; (**d**) small lamellae; (**e**) large lamellae; (**f**) vesicles; (**g**) hexagonally packed hollow hoops (HHHs); (**h**) large compound micelles (LCMs). Reprinted from Reference [69]. (Copyright (2012) Royal Society of Chemistry).
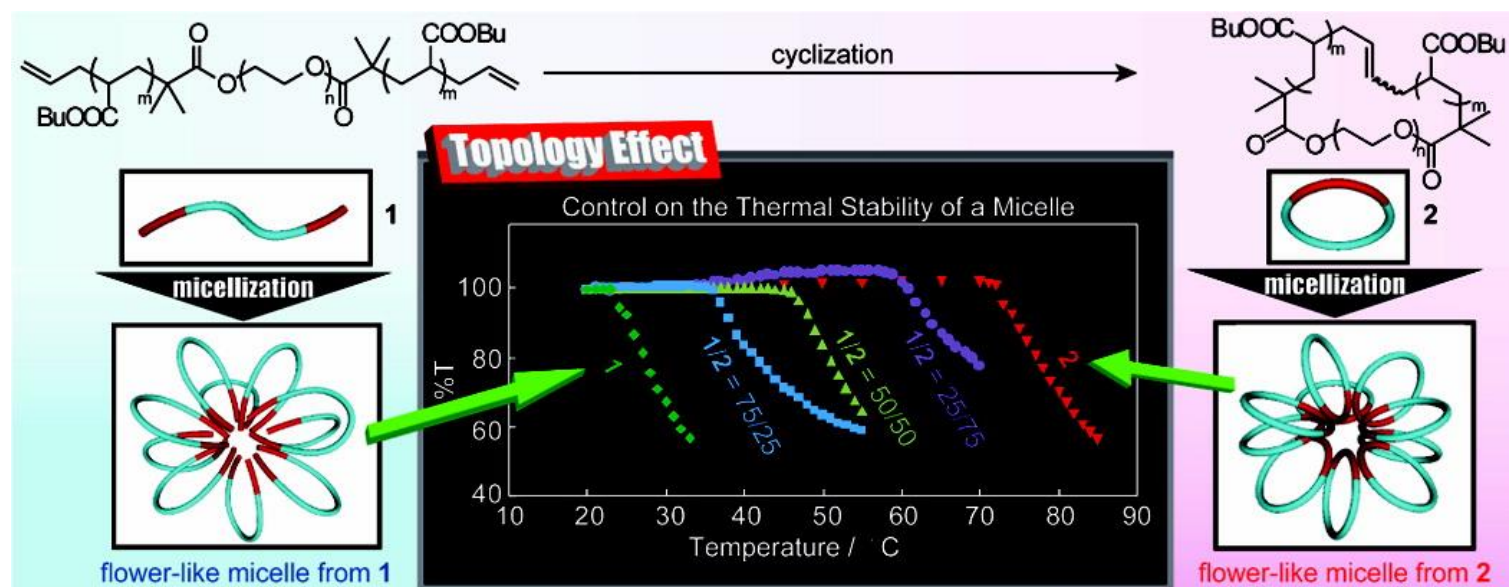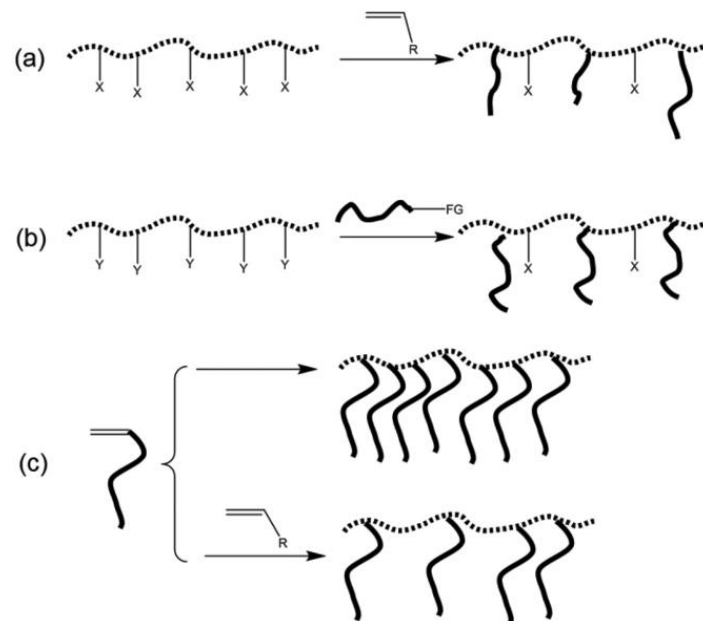
Thermal Stability and Architecture

Figure 13. The schematic illustration of linear amphiphilic PBA-*b*-PEO-*b*-PBA and cyclic PBA-*b*-PEO-*b*-PBA self-assembly in aqueous media. The cyclic BCP shows an increased T$_c$. Reprinted from Reference [83]. (Copyright (2010) American Chemical Society).

Scheme 1. Methodologies for the synthesis of graft copolymers: a) grafting from, b) grafting onto, and c) grafting through.

Design and Synthesis of Multigraft Copolymer Thermoplastic Elastomers: Superelastomers

Huiqun Wang, Wei Lu, Weiyu Wang, Priyank N. Shah, Konstantinos Misichronis, Nam-Goo Kang,* and Jimmy W. Mays*

PS-b-PMMA Copolymer
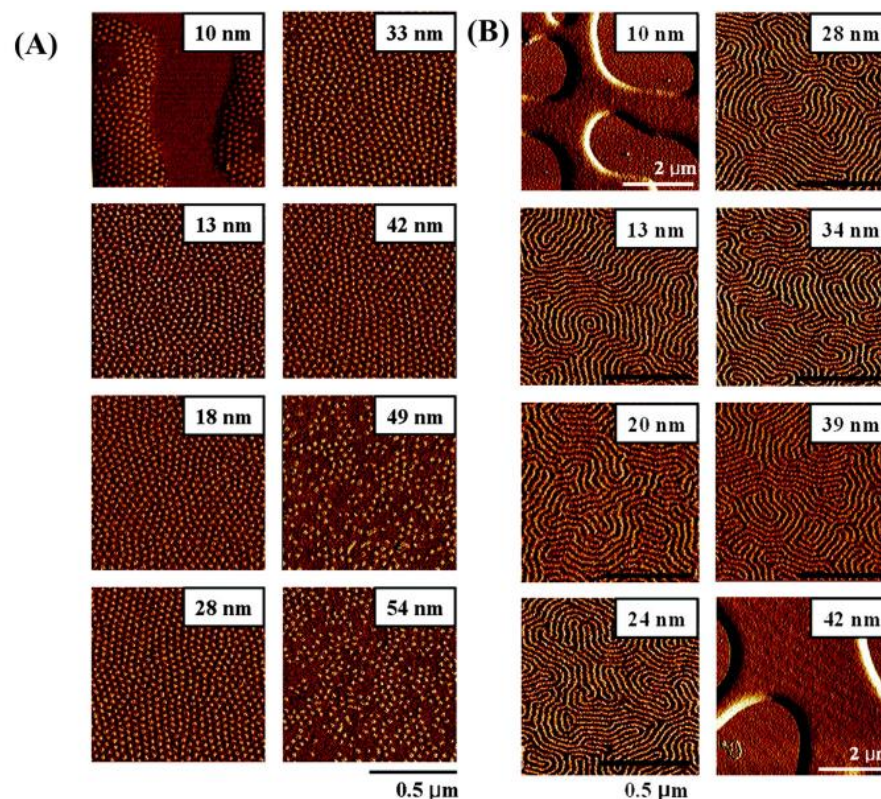## (0.64 and 0.55 of PS mole fraction)

Figure 17. Surface force microscopy (SFM) phase image of (**A**) cylinder-forming PS-*b*-PMMA and (**B**) lamella-forming PS-*b*-PMMA on the substrate modified by R64 (PS mole fraction of 0.64) and R55 (PS mole fraction of 0.55), respectively, at various film thicknesses of block copolymer after thermally annealing thin films at 170 °C for 24 h. Reprinted from Reference [119]. (Copyright (2008) American Chemical Society).
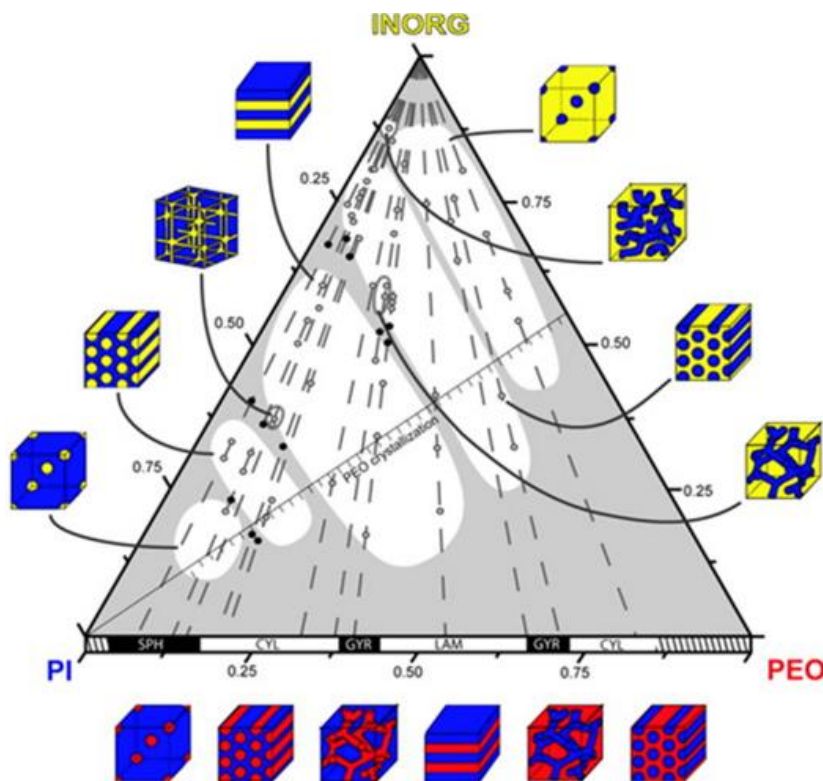
Ternary diagram

Figure 22. Ternary diagram mapping out the morphologies found for various composites directed by PI-*b*-PEO using (3-glycidyloxypropyl)trimethoxysilane (GLYMO) and aluminum sec-butoxide as inorganic precursors. At the bottom of the diagram, schematics of the morphologies found for the pure PI-*b*-PEO are shown. Hatched areas along the PI-*b*-PEO axis indicate areas where no data was available from the diblock copolymer diagram. Each white region within the diagram is labeled with a schematic representing the morphology of the composites formed. The yellow (light) regions in these schematic morphologies on the right and left are a representation of the PEO/inorganic domains. Closed dark points on a gray background indicate areas where biphasic behavior is observed. Reprinted from Reference [161]. (Copyright (2009) American Chemical Society).

Conventional and Selective Directed Self Assembly

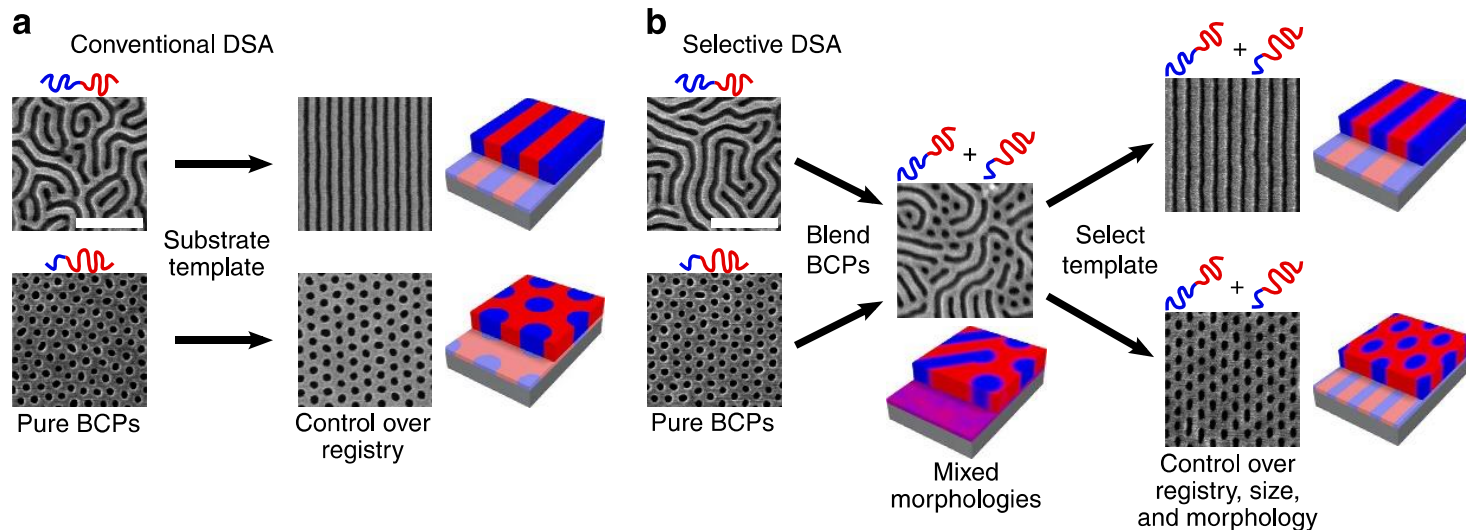$$(M_{\mathrm{W}} = 104 \, \mathrm{kg \, mol^{-1}}, \ \mathrm{PS:PMMA} \ 50:50)$$

Figure 1 | Conventional and selective directed self-assembly. (**a**) Directed self-assembly utilizes a substrate prepattern to impart long-range order to both lamellar and cylindrical self-assembled block copolymer films. (**b**) In selective directed self-assembly, the substrate prepattern also selects the local morphology formed by a block copolymer blend (either cylindrical or lamellar), in addition to imparting long-range order. White scale bar in scanning electron microscope images denotes 250 nm.

Selective directed self-assembly of coexisting morphologies using block copolymer blends

A. Stein[1], G. Wright[1], K.G. Yager[1], G.S. Doerk[1] & C.T. Black[1]
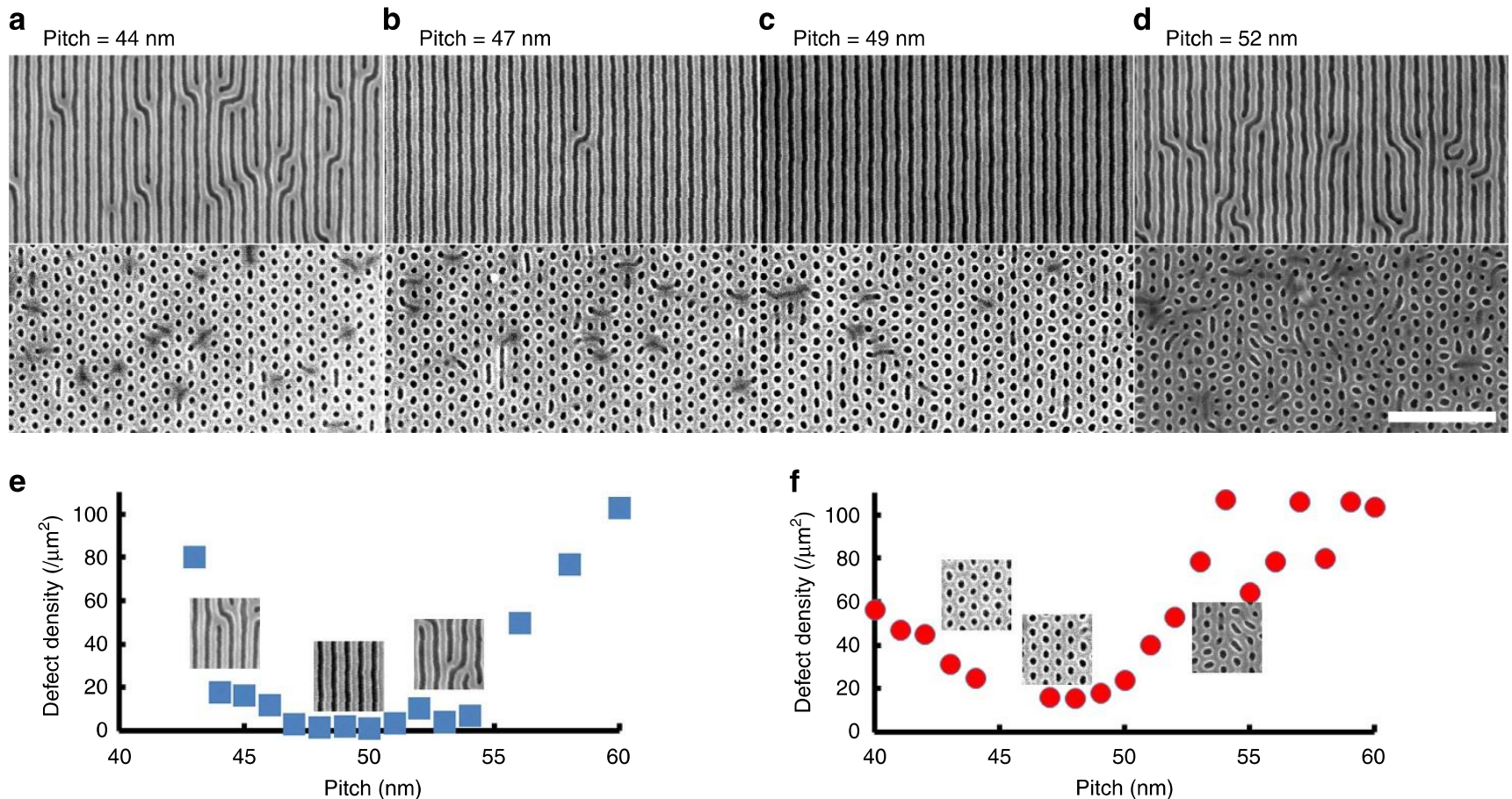
Influence of grating pitch

Figure 2 | DSA of lamella and cylinders on chemical line grating patterns. (**a**–**d**) Scanning electron microscope images of lamella (top row) and cylinder (bottom row) forming block copolymers self-assembled on chemical line grating patterns with (**a**) 44 nm, (**b**) 47 nm, (**c**) 49 nm and (**d**) 52 nm. The white scale bar denotes 400 nm. (**e**,**f**) Defect density versus chemical pattern pitch for (**e**) lamellar and (**f**) cylindrical phase block copolymer films with representative scanning electron microscope images.

Let us Talk about Laboratory Experiences to come

- Pluronic Surfactant three different Mw
- TEOS
- Sodium dodecyl sulfate
- Hexadecyl trimethyl ammonium