COMMERCIAL APPLICATIONS OF BLOCK COPOLYMERS

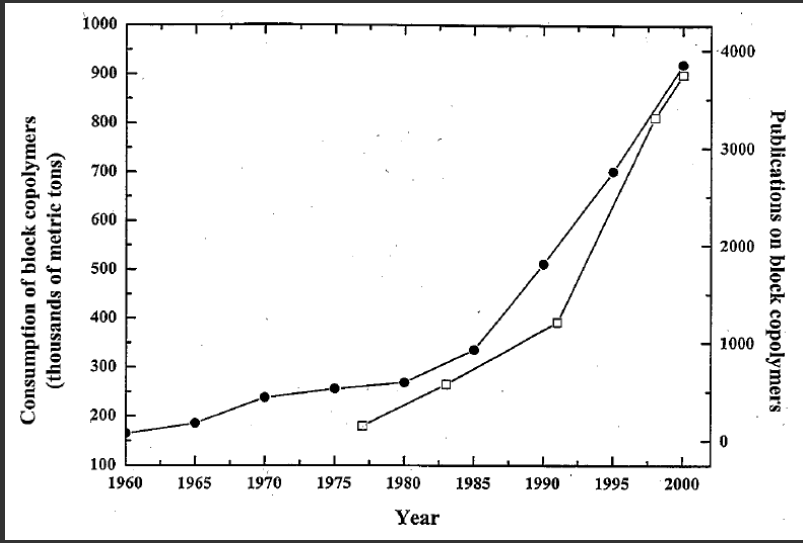
Outline

- History
- Usage
- Early products
- Thermoplastic elastomers
- Current research

History

- Anionic polymerization discovered in mid 1950s
- First commercial block copolymers soon followed
- First hard-soft block materials in late 1950s
- Thermoplastic elastomers (TPEs) comprise vast majority of production
- More recently, adhesives, surfactants, membranes, cosmetics

Block Copolymer Usage



- SBS 2005 consumption: 1.15 million tons

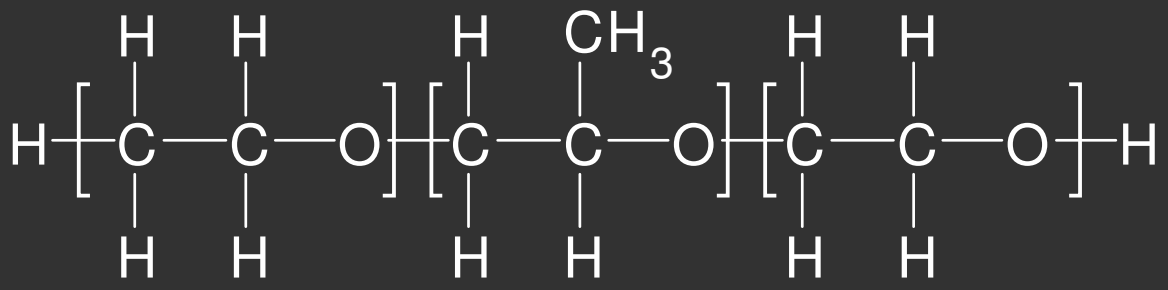
Source: China Chemical Reporter, Nov. 16, 2006

- Total references: 110,099
- References from last 5 years: 28,537
- 2008 references: 6,863
- 2009 references to date: 1,704

Source: SciFinder Scholar

First Commerical Block Copolymer

- Surfactant, trade name “Pluronic”
- Addition of propylene oxide to ethylene oxide carbanions, i.e. ring opening polymerization

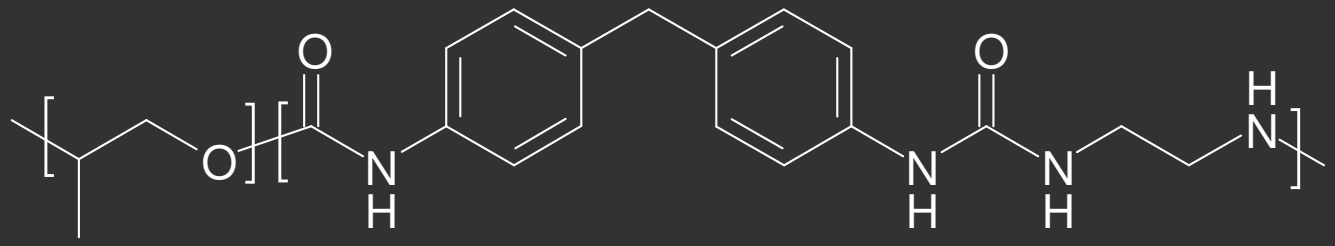


ABA block copolymer

- Ethylene oxide is hydrophilic, propylene oxide is hydrophobic
- Blocks typically 20+ monomer units

Spandex

- Invented in 1959 by Joseph Shivers of DuPont
- Originally “Fiber K”
- Step polymerization of polyether or polyester and diisocyanate to form a polyurethane



- Not well defined, i.e. high polydispersities
- Urethane/urea linkages form stiff segments, poly(ethylene oxide) forms flexible segments

Spandex

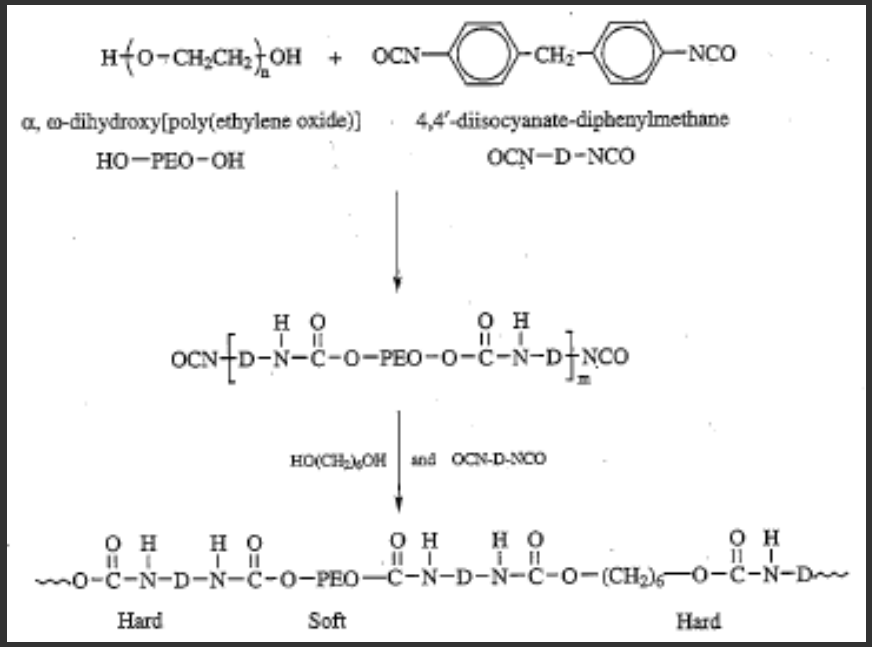
- Fibers typically 85% segmented polyurethane
- Can stretch up to 600% and retain shape
- Blended with cotton, wool, other synthetic fibers before use
- Does not break down with exposure to perspiration, oils, detergents

Thermoplastic Elastomers (TPEs)

- Most common block copolymer products
- Both thermoplastic and elastormeric properties
  - Can be remelted and remolded
  - Crosslinked bond network imparts elasticity
    - Thermosets have covalent crosslinking
    - TPEs have dipole or hydrogen bond crosslinks
- Classes include styrenics, polyurethanes, segmented polyesters, and segmented polyamides

Polyurethane TPEs

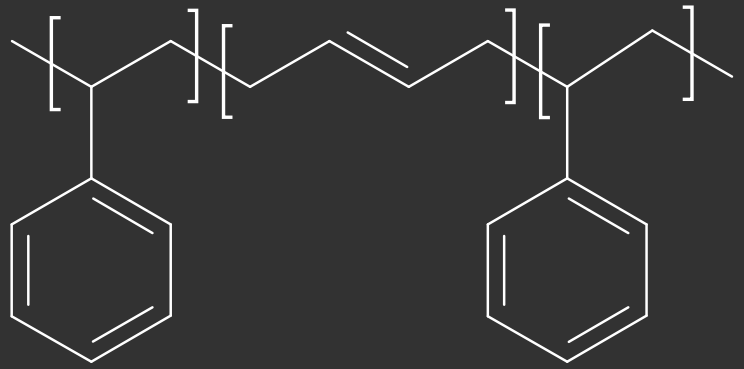
- First commercially available TPEs
- B. F. Goodrich Co. in late 1950s
- Two step condensation polymerization



- Similar structure to spandex, urethane hydrogen bonding imparts strength and wear
- Used in automobile bumpers, snowmobile treads, etc.

Styrenic TPEs: Kraton

- Introduced by Shell in 1965
- Polystyrene-b-polybutadiene(or polyisoprene)-b-polystyrene (SBS or SIS)
- Anionic polymerization



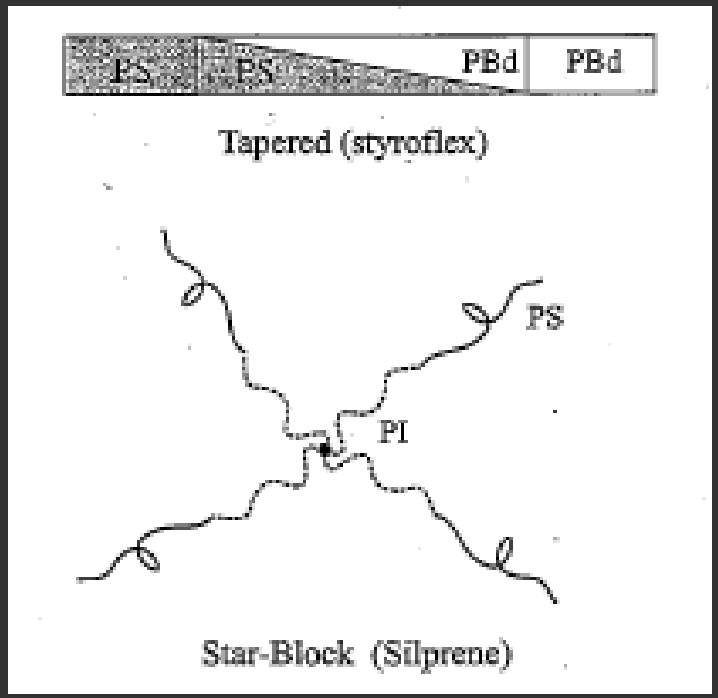
PS T_g = 100℃

PB T_g = -70℃

- Linear molecules with homopolymer blocks
- Low molecular weights and polydispersities

Styrenic TPEs: Others

- Tapered blocks: Styroflex
- Star blocks: Solprene
- Typical styrene content 25 to 40 wt%
- Uses include footwear, bitumen modification, molding products, adhesives, insulation

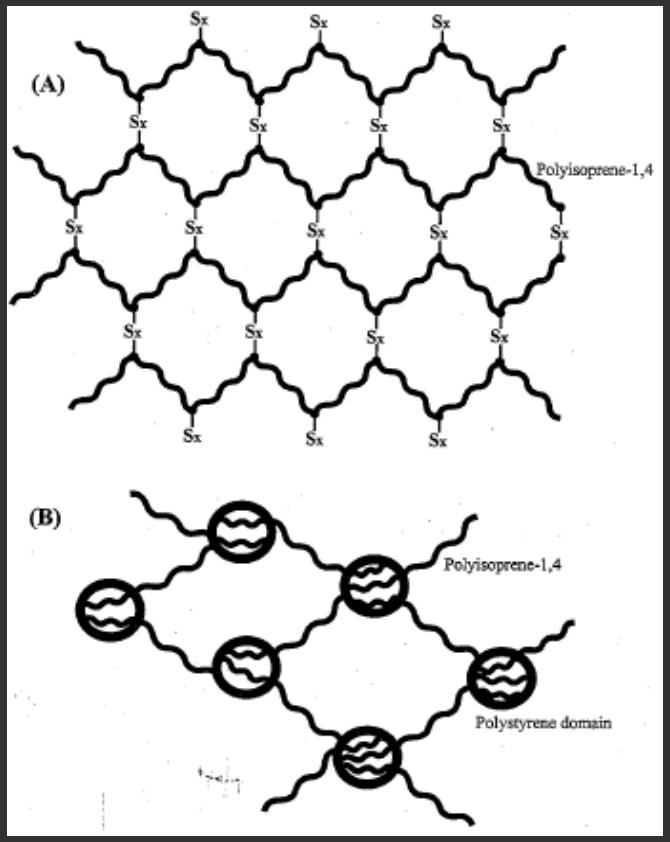


Polyester and Polyamide TPEs

- TPES produced by DuPont
- TPA produced by Huls and Ato Chimie (now part of Arkema)
- Step polymerization process similar to polyurethanes
- Ester (-CO-O-) or amide (-CO-NH-) linkages
- Applications in hose tubing, sporting goods, automotive components

TPE Characteristics

- Microphase separation caused by
  - Crystallinity for TPES and TPA
  - Hydrogen bonding for TPU and TPA
  - van der Waals interactions for styrenics
- TPEs not good for high temperature or solvent resistive service
- Exhibit mechanical hysteresis

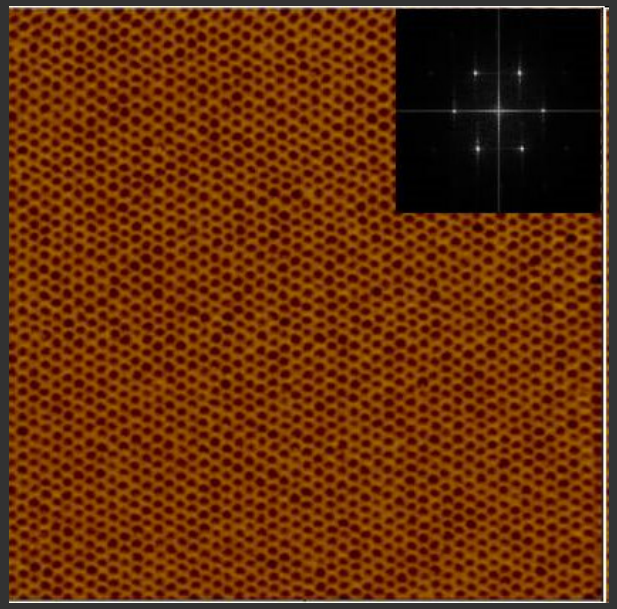


TPE Characteristics

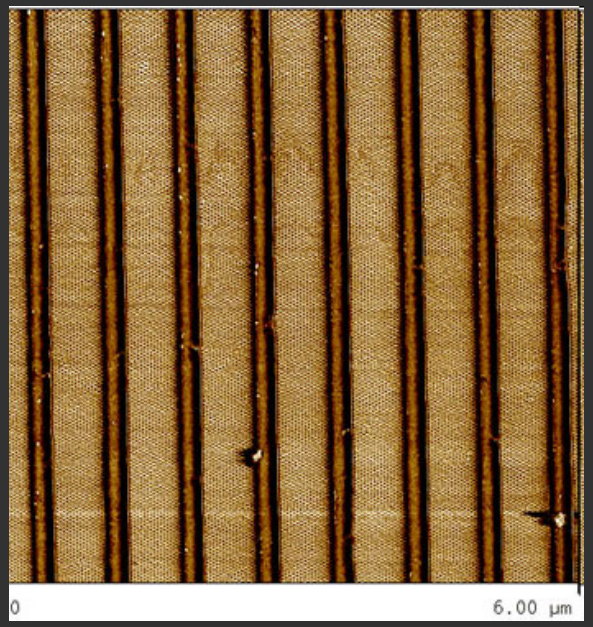
- Glassy, hard chains must anchor flexible chains
  - Triblock copolymers with polydiene end blocks
  - Diblock copolymers
- Diene-containing TPEs reactive towards oxygen
  - Polybutadiene typically hydrogenized to poly(ethylene-co-butylene)
  - Kraton family includes SIS, SBS, SEBS
- Kraton family represents 50% of TPE market
- Polycondesation TPEs represent 20%
- Polyolefin TPEs make up other 30%

Current Research

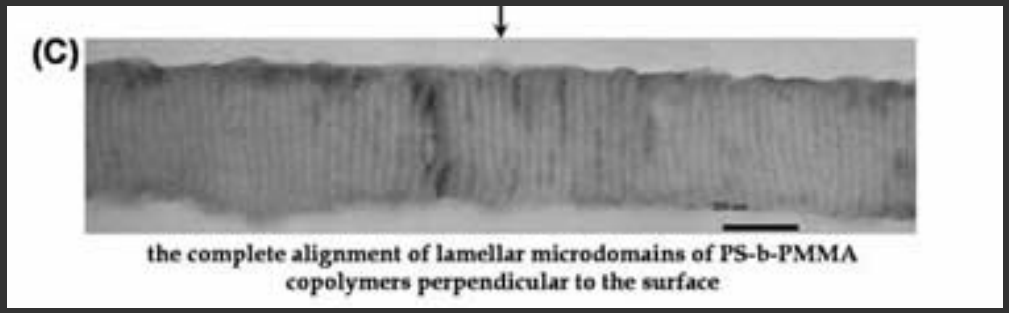
- Templating materials



PE-PEO thin films



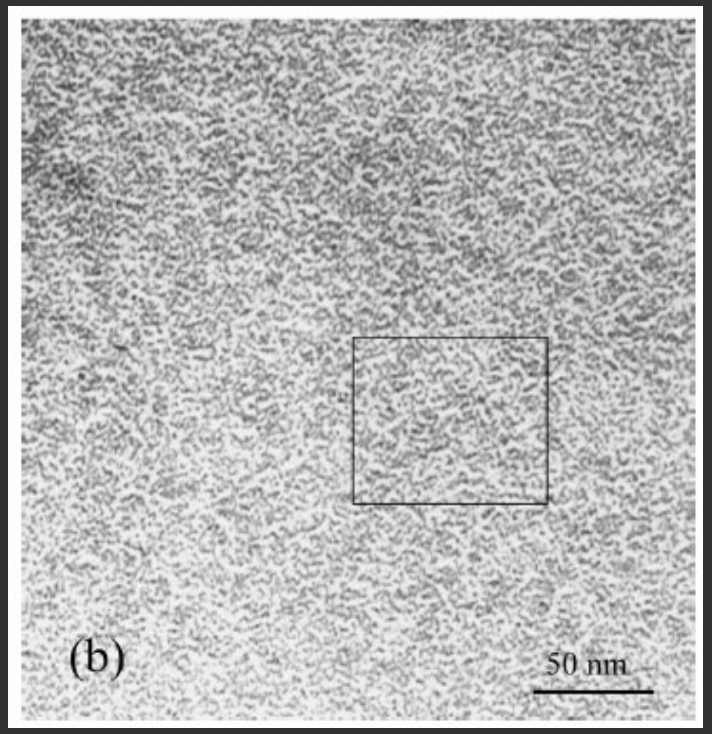
PS-PEO surface



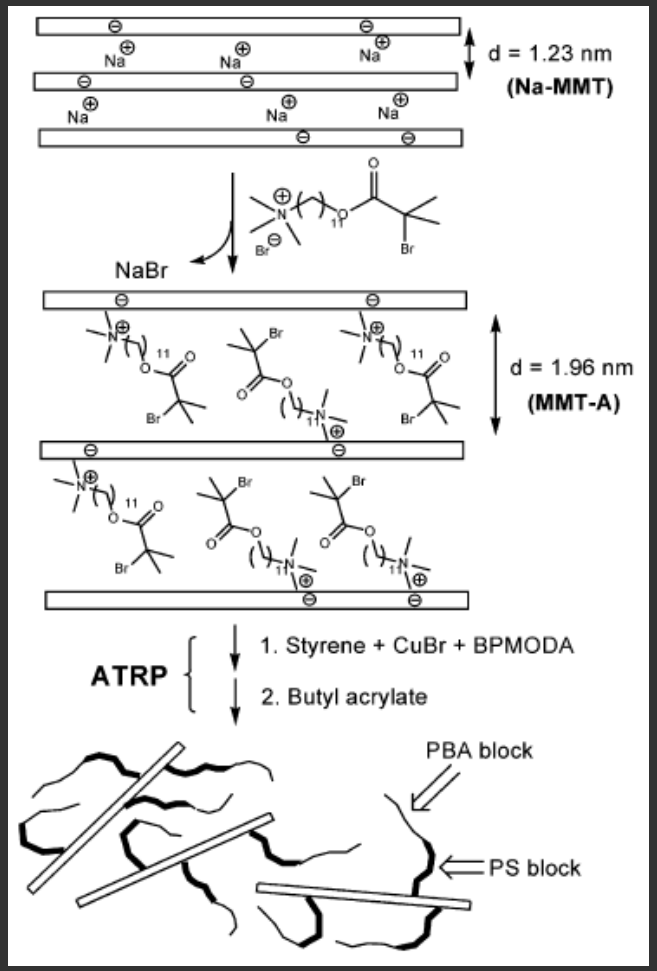
Russel Research Group, UMass

Current Research

- Nanocomposites



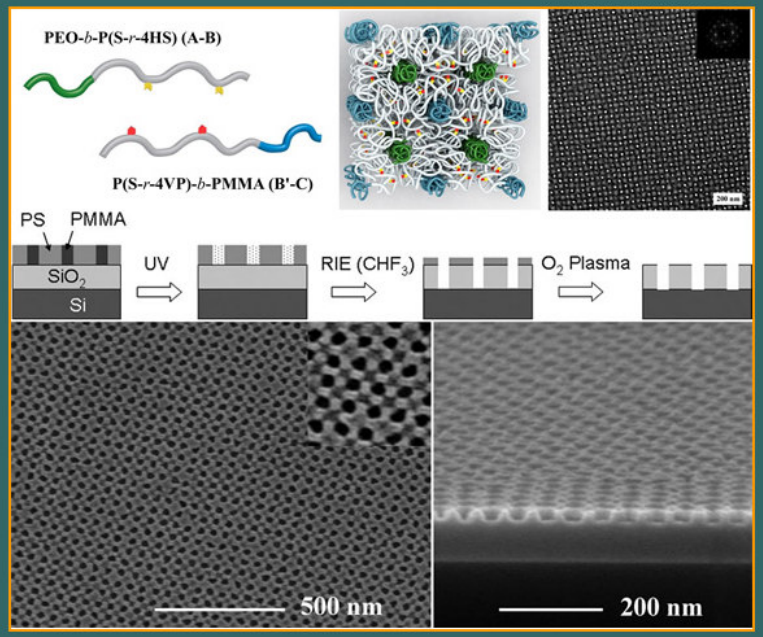
PSBA-MMT



Current Research

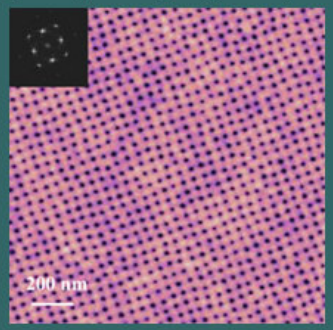
- Lithography

Supramolecular Diblock Copolymer Lithography

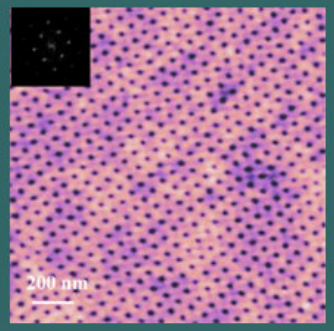


Triblock Copolymer Lithography

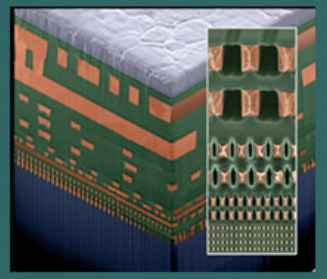
The self-assembly of triblock copolymers of poly(ethylene oxide-b-methyl methacrylate-b-styrene) [PEO-b-PMMA-b-PS), synthesized by controlled living radical polymerization, provides a robust route to highly ordered, nanoporous arrays with cylindrical pores of 10-15 nm. The key strategy is the use of PMMA as a photodegradable mid-block which leads to nanoporous structures with a high degree of lateral order. The power of using a triblock copolymer is evidenced by the ability to exploit the advantages of two separate diblock copolymer systems while negating the corresponding disadvantages; the high degree lateral ordering inherent in PS-PEO diblocks (poor degradability) and the facile degradability of PS-PMMA diblock copolymer systems (poor long range order).



Square Packed



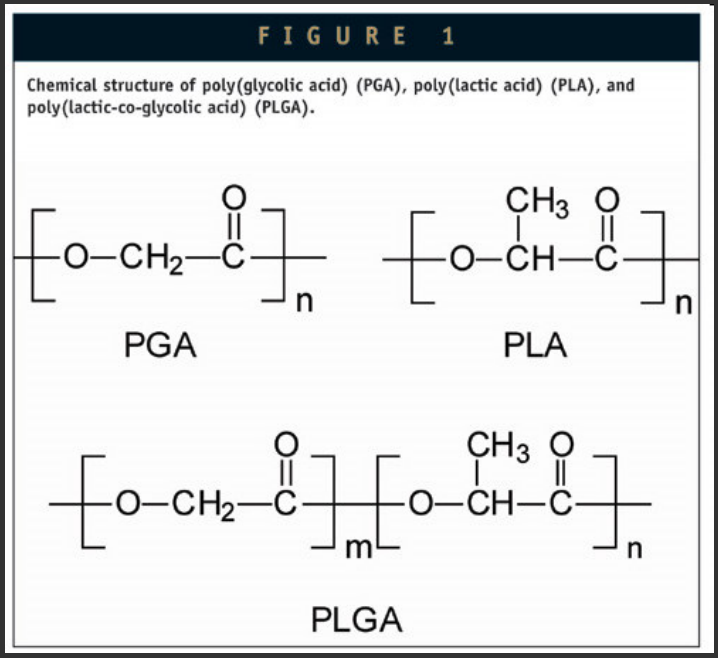
Hexagonal Packed

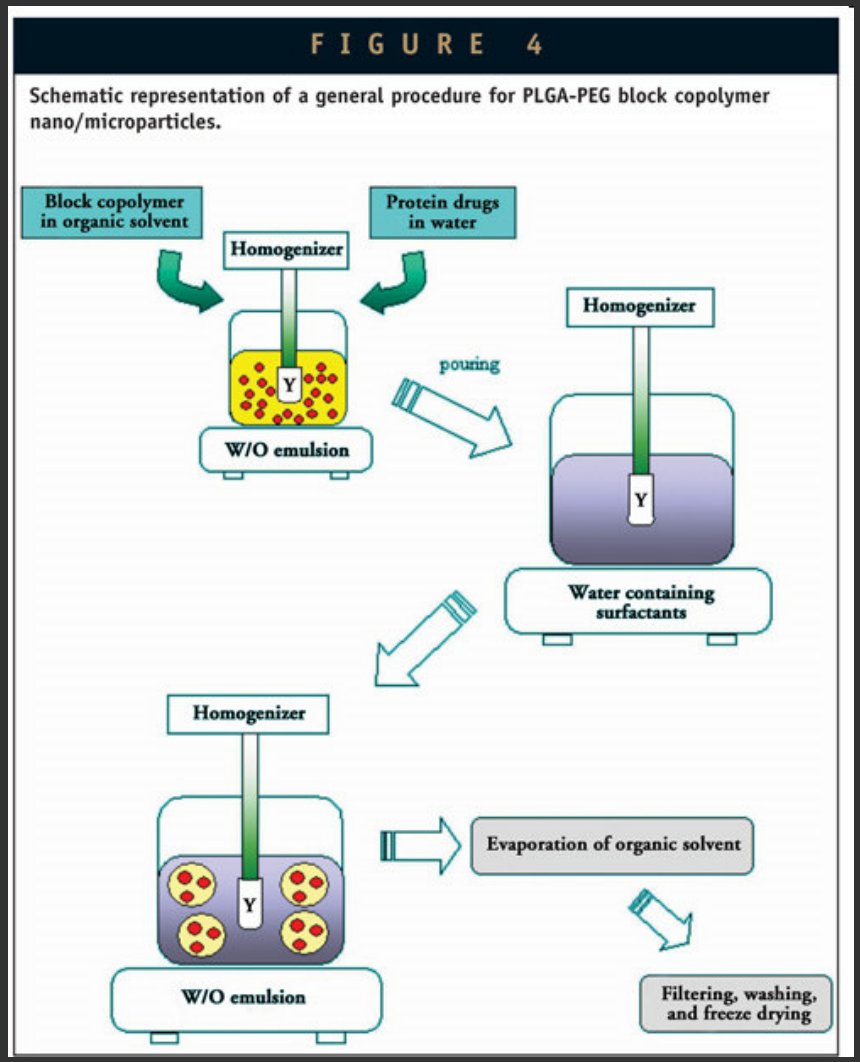


Hawker Research Group, UCSB

Current Research

- Drug Delivery
- PLGA-PEG





Akina, Inc.

Questions?

References

Carraher, C. E. (2003). *Seymour/Carraher's Polymer Chemistry*. New York: Marcel Dekker.

Hadjichristidis, N., Pispas. S., Floudas, G. A. *Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*. Hoboken, New Jersey: John Wiley & Sons, Inc.