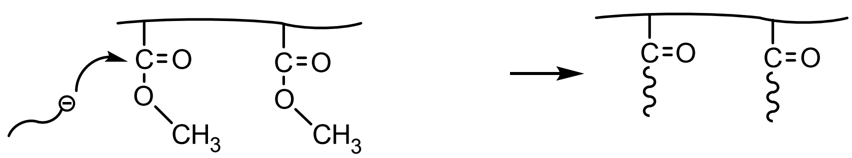
Lecture 24: Introduction to Cationic Polymerization. Monomers, Kinetics.

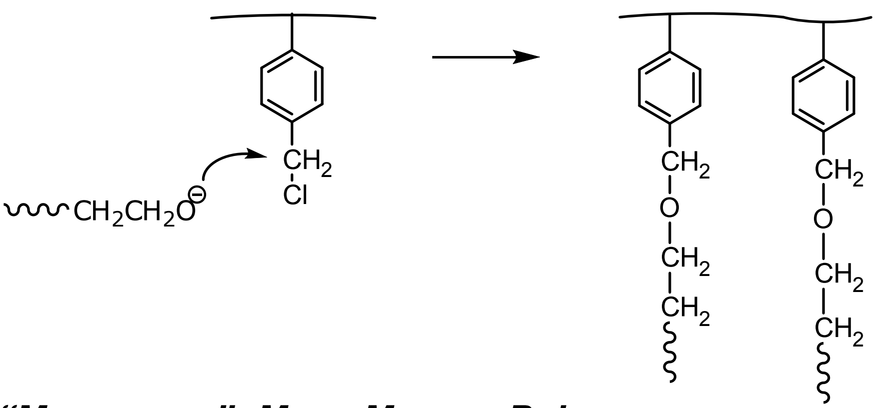
From Last Time

comb/graft copolymers

e.g. $PS^{\ominus}$ onto PMMA backbone

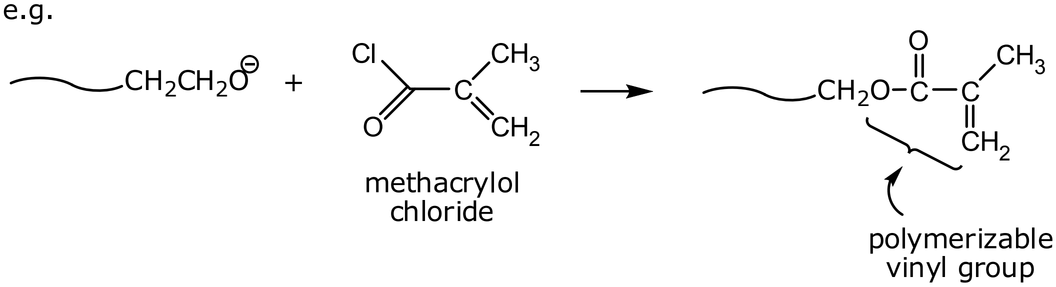


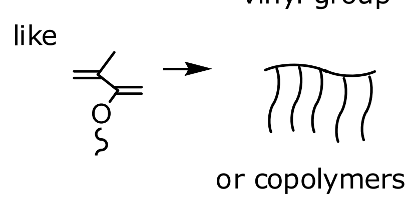
e.g. $PEO^{\ominus}$ onto chloromethylated PS backbone



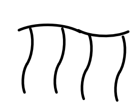
"Macromers": Many Mers → Polymer

e.g.





free radical
r_1 and r_2 are similar
$r_1 \cdot r_2 \leq 1$
→ alternating polymer



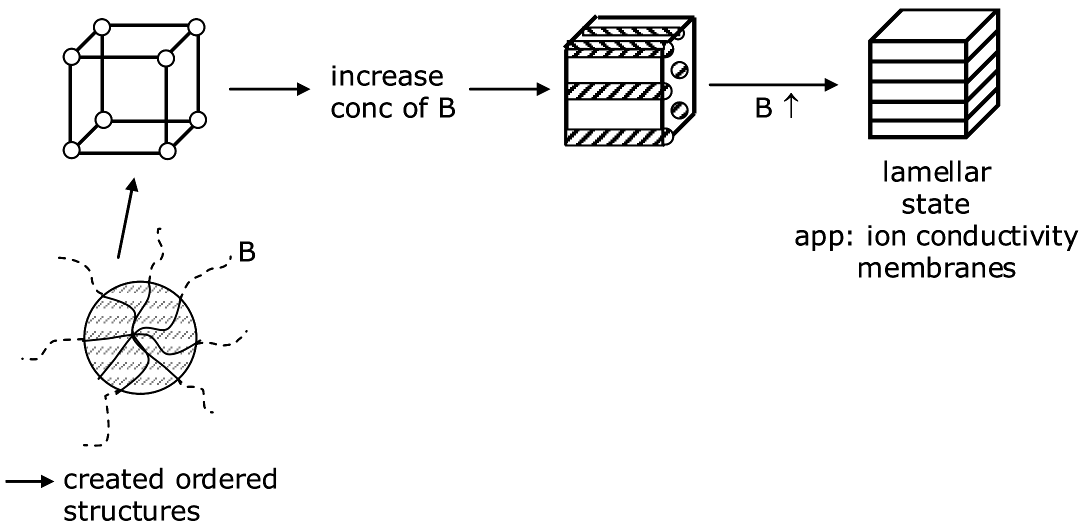
dispersed on backbone

General fact: ionic propagation is more monomer selective than free rad: large diff between r_1 & r_2

- hard to get random copolymer
  thus if you see a random copolymer, assume made by free radical
  NOT ionic polymerization
  → consumes monomer very quickly,
  then the other monomer

Slide: structure and properties of polymers
- polymer and block copolymer morphology
- physical properties/deformation behavior
- diffusion & flow
- case studies: product design

→ mix 2 polymers (immiscible)
  → different arrangements w/different degrees of phase separation



Presentation: Examples of Block Copolymers

Bates, Frank S., and Glenn H. Fredrickson. "Block Copolymers—Designer Soft Materials: Advances in synthetic chemistry and statistical theory provide unparalleled control over molecular-scale morphology in this class of macromolecules." *Physics Today* (February 1999): 33, 34, and 36.

From Bates and Fredrickson, Phys Today (1999)

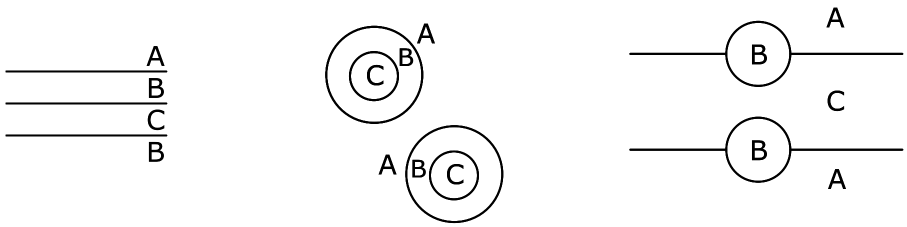
$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$ $\qquad$ $\Delta S_{mix} \approx \frac{1}{N}$ $\qquad$ as chain length ↑

solubility ↓

Degree of microphase separation controlled by χN
  As (χN) ↑ get stronger separation

Hamley, I. W. Pages 1707 and 1705 in "Nanotechnology With Soft Materials."*Angew. Chem. Int. Ed.* 42, no. 15 (April 17, 2003): 1692-1712.

Triblock Copolymers



Cheng, J. Y., C. A. Ross, E. L. Thomas, H. I. Smith, and G. J. Vansco. "Fabrication of Nanostructures With Long-Range Order Using Block Copolymer Lithography." *Appl. Phys. Letter* 81, no. 19 (November 4, 2002): page 3658 Figures 1 and 2. Full paper runs 3657-3659.

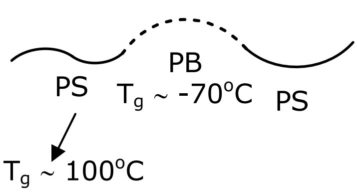
Lazzari, Massimo, and M. Arturo López-Quintela. "Block Copolymers as a Tool for Nanomaterial Fabrication." *Advanced Materials* 15, no. 19 (October 2, 2003): pages 1583 and 1587. Actual paper is from 1583 to 1594.

Examples and Applications of Block Copolymers

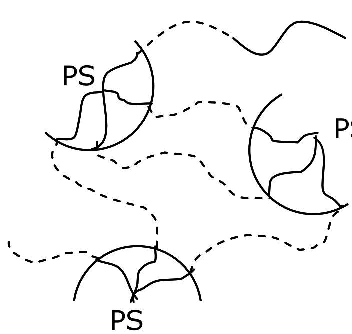
- nanostructures for magnetic storage
- membranes
- nanopatterns
- vehicles in solutions
- networks

Properties of copolymer

random copolymer → avg of properties: T_g
time mixing
- block copolymer

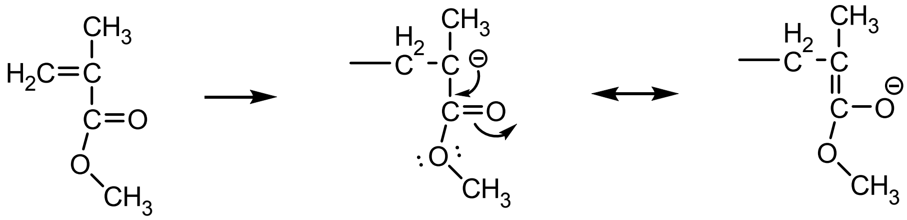


⇒ see both Tg phase transitions in thermogram
2 independent blocks



→ rubbery property
SBR
styrene butadiene rubber

Anionic Polymerization

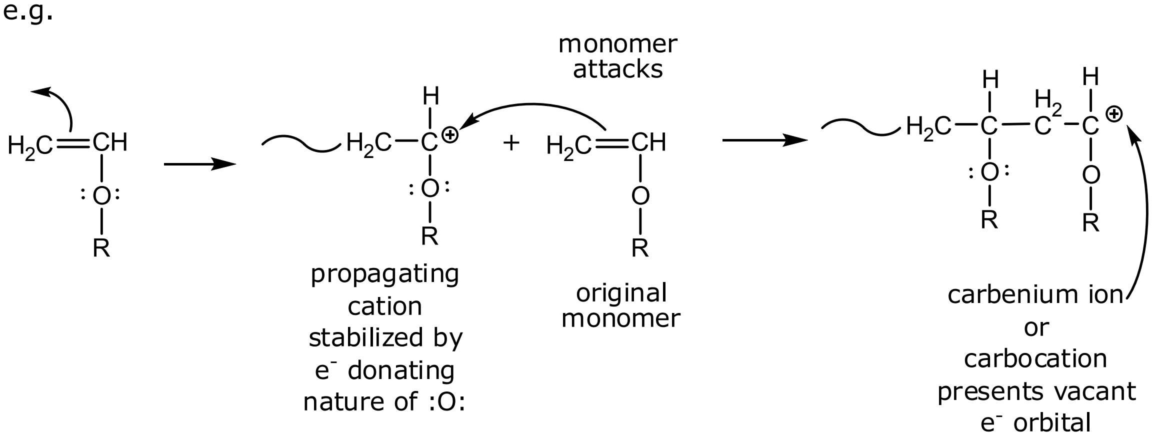


methyl methacrylate
e^--drawing group

Cationic Polymerization

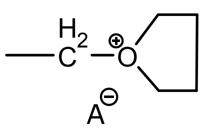
- need substituent that is e^- donating

e.g.



Can also have propagating oxonium ions

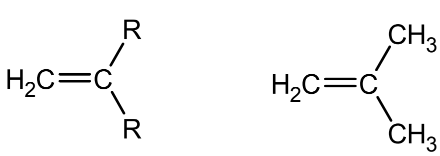
e.g.



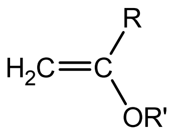
also ammonium ions
NOT limited to carbon chemistry

Typical Cationic Monomers

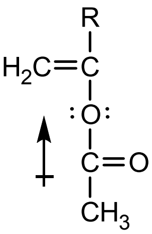
alkenes, isobutenes



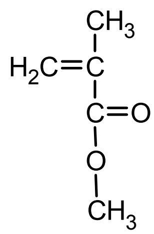
vinyl ethers



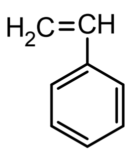
vinyl acetates



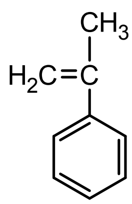
contrast with methyl methacrylate



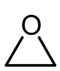
styrene*
* = also by anionic



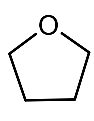
α-methyl* styrene



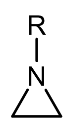
some cyclics

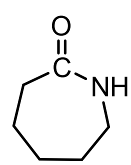


epoxides*



tetrahydrofuran (THF)





lactanes

etc