10.569 Synthesis of Polymers
Prof. Paula Hammond
Lecture 18: Radical copolymerization: Alternating to block copolymers

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Recap from last lecture

Low Density Polyethylene (LDPE)

- Formed using traditional free radical polymerization
- It has 40-60% crystallinity
- Its density (ρ) is 0.91 g/cm^3
- Melting temperature: T_m = 105-115°C
- Glass transition temperature: T_g = -120°C

High Density Polyethylene (HDPE)

- Formed using a Ziegler-Natta (Z-N) catalyst
- Crystallinity is much higher: 70-90%
- Its density (ρ) is 0.94-0.96 g/cm^3

Additionally, the Z-N catalyst can be used to control branching easily to form:
Linear Low Density Polyethylene (LLDPE)

Metallocene Catalyst

- The metallocene catalyst is similar to the Z-N catalyst.
- It's composed of a group IV-B transition metal (e.g. Hf, Ti, Zr)
- It's used to obtain a narrow MW distribution (narrower than the Z-N catalyst), but because Z-N catalyst is much easier to use, it is often the preferred method of polymerization
- In addition, usage of metallocene catalyst can result in random distributions in copolymer. In contrast, Z-N catalyst results in clusters.
- Finally, the metallocene catalyst is less sensitive to functional groups in monomers.

Terminal Functionalization

- End capping only good for living system
- Functional initiation not good for Ziegler-Natta catalyst
- Chain transfer: β-hydrogen transfer to monomer

Handouts about metallocene catalysts:

Hlatky, G. G. Page 246 in "Metallocene Catalysts for Olefin Polymerization: Annual Review for 1996." *Coordination Chemistry Reviews* 181, no. 1 (1999): 243-296.

Yanjarappa, M. J. and S. Sivaram. Pages 1350-1353, 1356, and 1364 in "Recent Developments in the Synthesis of Functional Poly(olefin)s." *Prog. Polym. Sci.* 27, no. 7 (2002): 1347-1398.