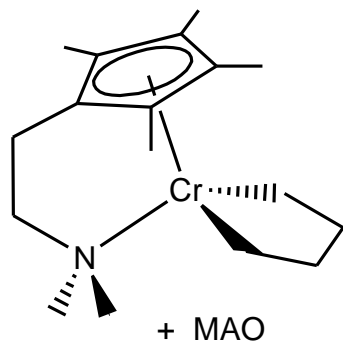


Late TM olefin polymerization Catalysts

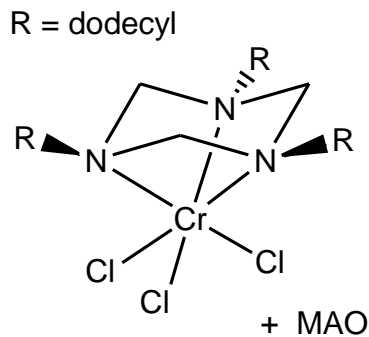
Why develop late TM polymerization catalysts?

- increased functional group tolerance (copolymerization with certain polar comonomers)
- decreased air sensitivity (easier to handle)
- may reduce costs and environmental impact by using a cheaper metal (e.g. Fe)
- unknown territory
 - could turn out to be better catalysts
 - may give polymers with different properties

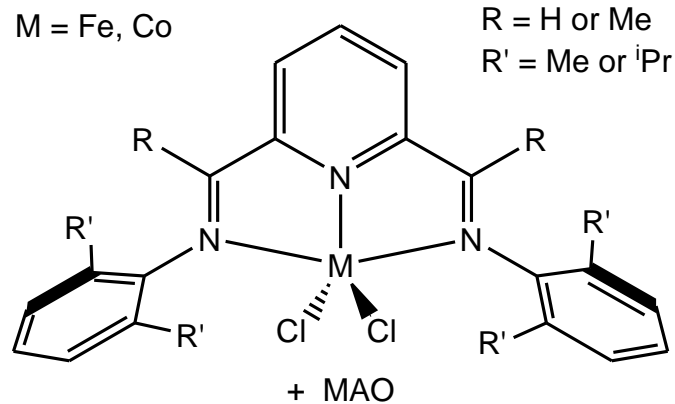
Late TM olefin polymerization Catalysts



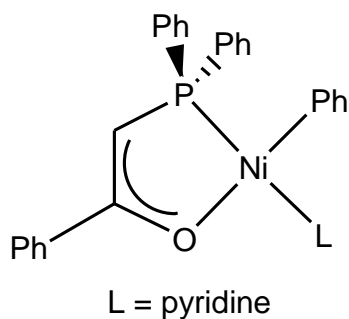
A



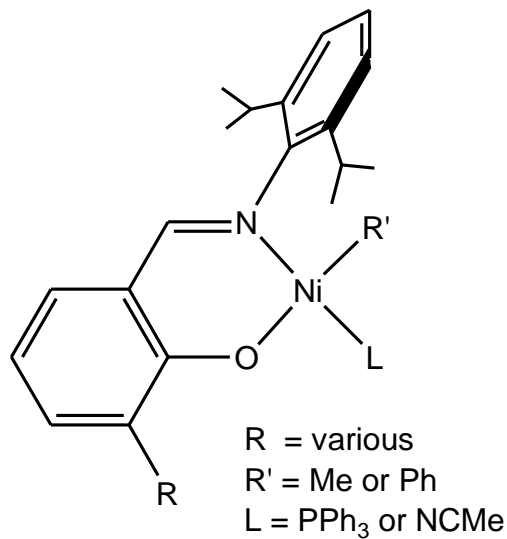
B



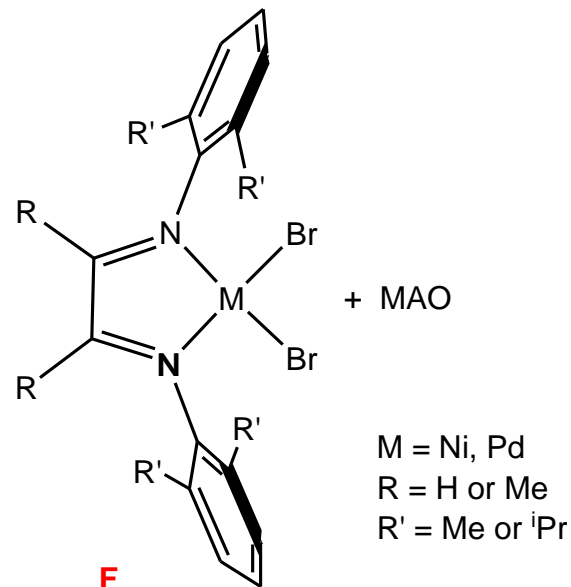
C



D



E



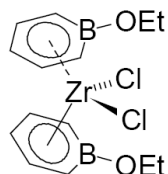
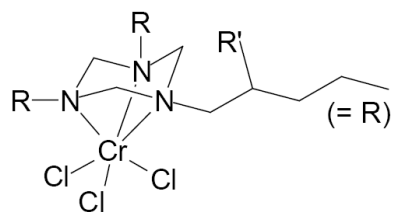
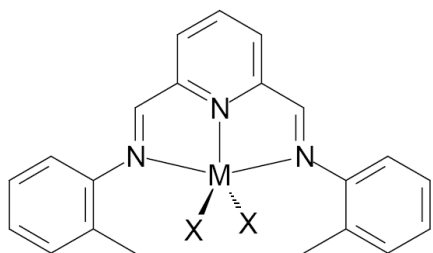
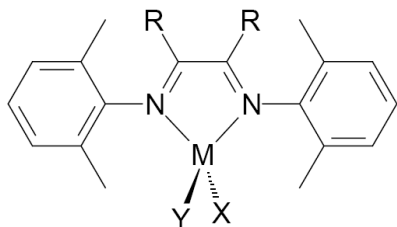
F

Late TM olefin polymerization Catalysts

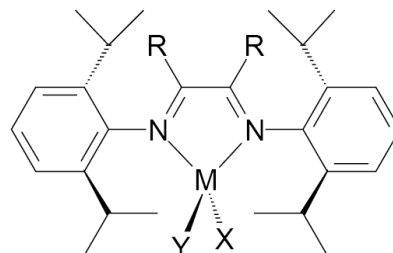
- A** - Jolly *et al.*, *Organometallics*, **1997**, 1511
- B** - Köhn *et al.*, *J. Chem. Soc., Chem. Commun.*, **2000**, 1927
- C** - Brookhart *et al.*, *J. Am. Chem. Soc.*, **1998**, 4049
 - Brookhart *et al.*, *J. Am. Chem. Soc.*, **1998**, 7143
 - Gibson *et al.*, *J. Chem. Soc., Chem. Commun.*, **1998**, 849
- D** - Ostoja *et al.*, *Angew. Chem., Int. Ed. Engl.*, **1985**, 599
 - Ostoja *et al.*, *Angew. Chem., Int. Ed. Engl.*, **1987**, 63
- E** - Grubbs *et al.*, *Science*, **2000**, 460
- F** - Brookhart *et al.*, *J. Am. Chem. Soc.*, **1995**, 6414 (DuPont Versipol Catalysts)

Oligomerization vs Polymerization Catalysts

Oligomerization catalysts

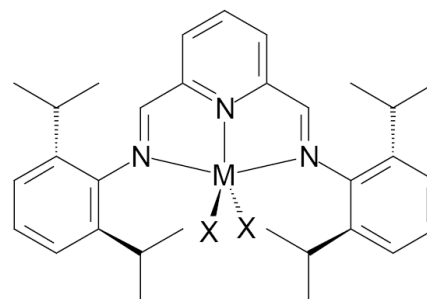


Polymerization catalysts



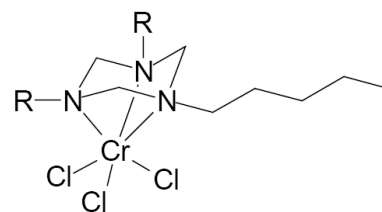
A (M = Ni, Pd)

Greater Steric Bulk



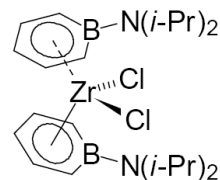
B (M = Fe, Co)

Greater Steric Bulk



C

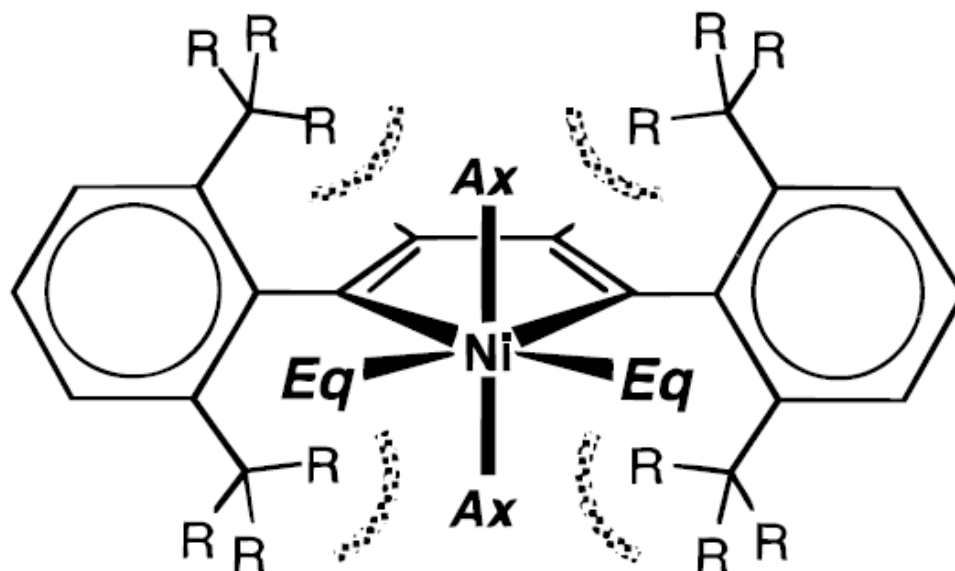
Decreased Steric Bulk



D

More Electron Rich or Steric ?

Theoretical study of the Brookhart α -diimine catalysts



Ziegler *et al.*, *J. Am. Chem. Soc.*, **1997**, 6177.

- Bulky substituents in the 2 and 6-positions of the aryl rings on nitrogen have the following effects (due to increased steric hindrance in the axial sites):
 - They destabilize the resting state of the catalyst (alkyl π -alkene complex), therefore lowering the barrier for insertion.
 - They raise the energy barrier for chain termination.

Theoretical study of the Brookhart α -diimine catalysts

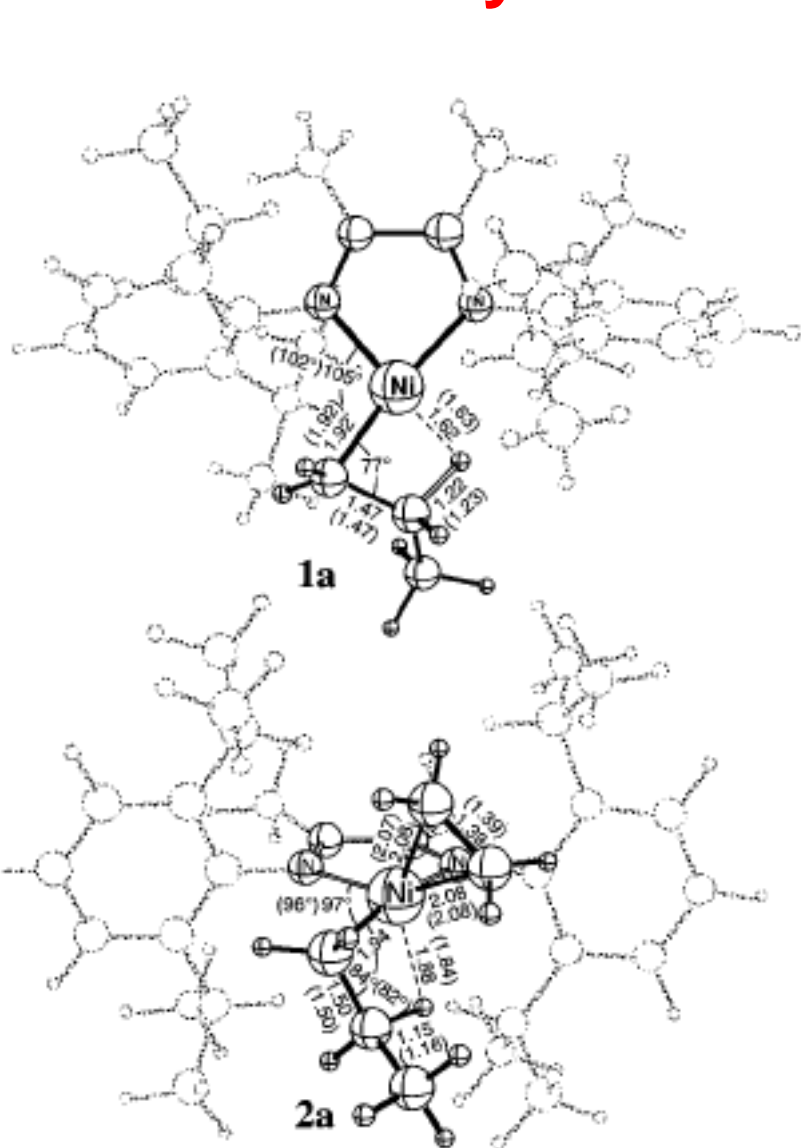


Figure 2. Optimized QM/MM metal alkyl cation and metal alkyl π -ethylene resting state structures. MM atoms (set 3 and set 4 atoms

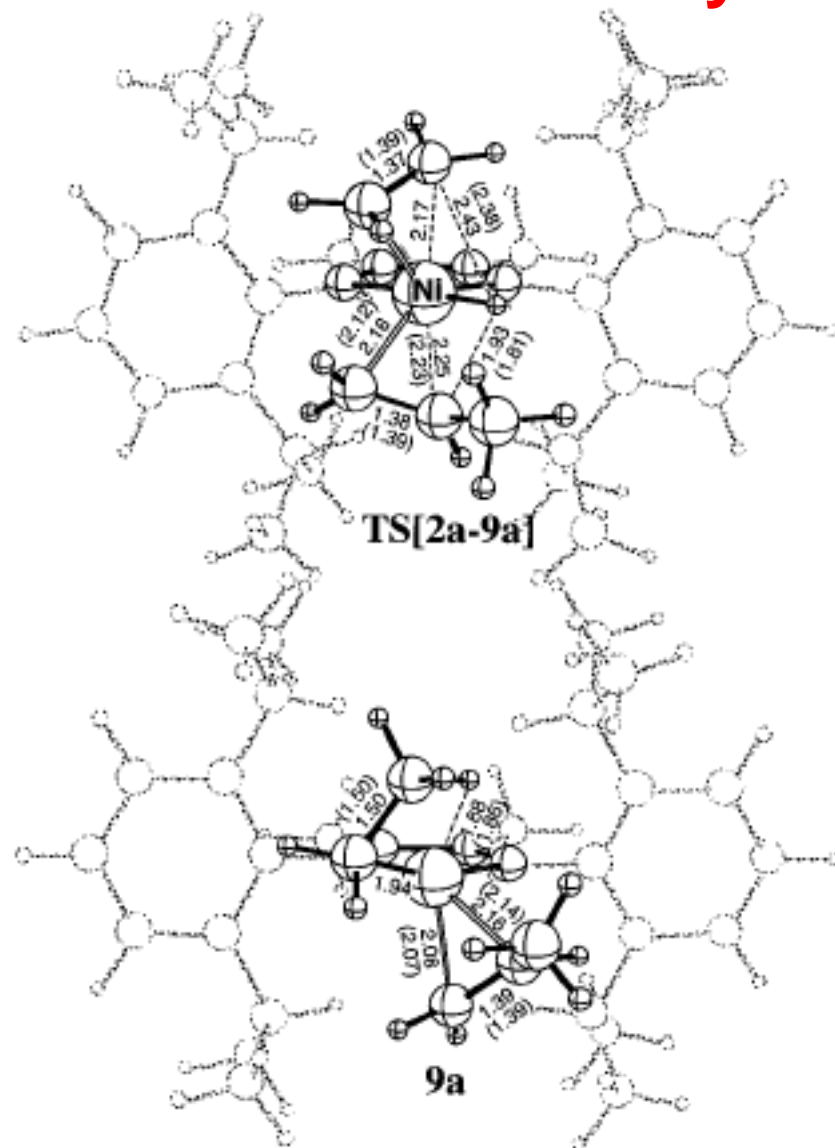
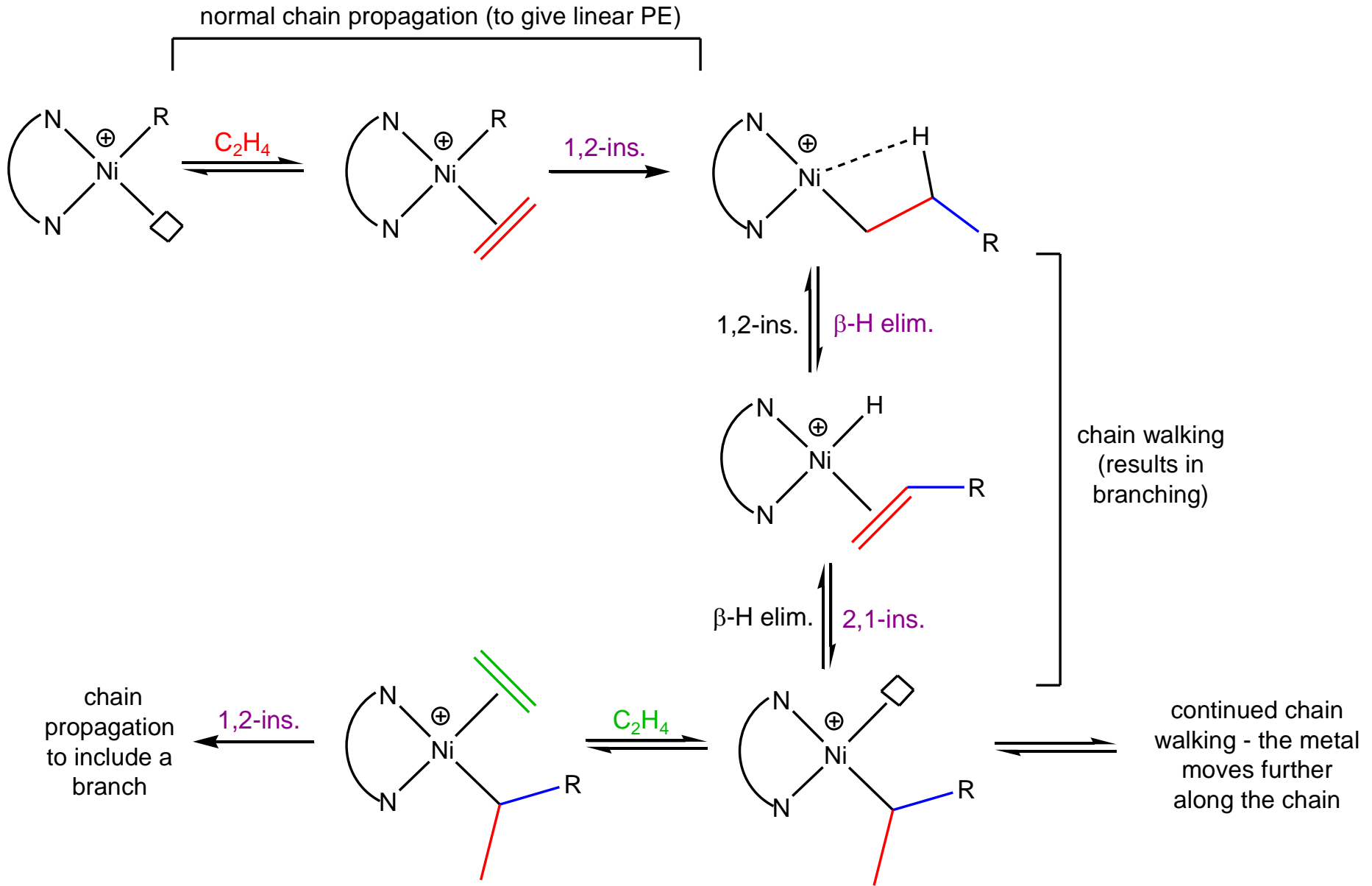


Figure 10. Transition state and product of the chain termination process. Conventions as in Figure 2.

Chain walking mechanism for Pd or Ni diimine catalysts



Chain walking mechanism for Pd or Ni diimine catalysts

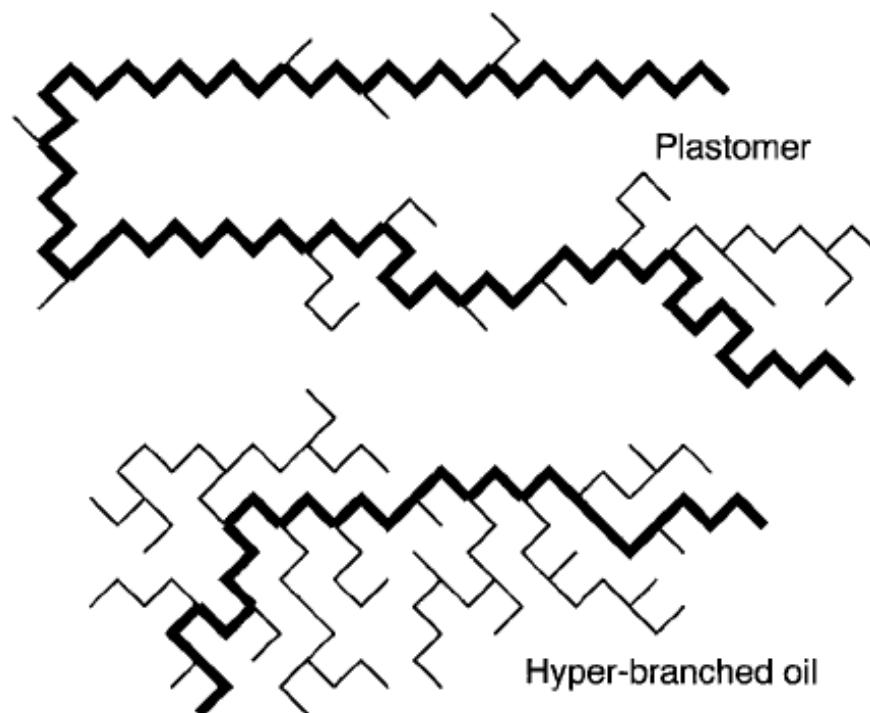


Figure 2. Computer simulations of typical 100 carbon-atom fragments of a polyethylene plastomer and a polyethylene hyperbranched oil. The simulations are calculated from probabilities of various migrations and insertions that are back-calculated from observed NMR spectra. The heavy line is the longest chain through the structure, but it does not necessarily contain either the first or last ethylene inserted. By chance, the hyperbranched structure contains three equal C_{30} "longest chains".