Polymer Properties
Quiz 3
September 12, 2014

Gerstl et al. compared the characteristic ratio of polyolefins $(CH_2CHR)_n$ with polyalkylene oxides $(CH_2CHR\text{-}O\text{-})_n$ and found the behavior shown in the figure below. In class we noted that C_∞ for polyethylene is 6.7 and for polyethylene oxide is 4.0 (for R = H and m_b = 1).

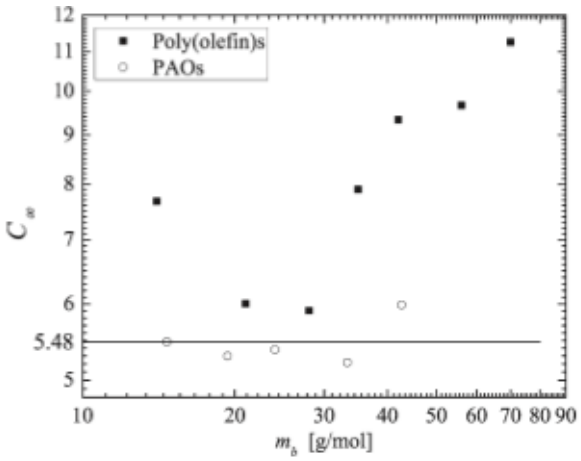

Figure 4. C_∞ vs the mass per backbone bond m_b for poly(olefin)s (filled squares; data taken from ref 10) and PAO's (empty circles). The value for PPO is calculated from ref 2. The line shows the value obtained from the BE model.

m_b is the molecular weight of branch groups (R), for example, when m_b = 15 the chain is polypropylene for a polyolefin.
Gerstl C, Schneider GJ, Pyckhout-Hintzen W, Allgaier J, Willbold S, Hofmann D, Disko U, Frielinghaus H, Richter D *Macromolecules* **44** 6077 (2011)

a) What is the characteristic ratio? What property does it reflect?
b) Gerstl calculates C_∞ using $C_\infty = \langle R^2\rangle/(N_{mono}n_b\langle l_0^2\rangle)$ where N_{mono} is the number of monomers per chain, n_b is the number of bonds in a monomer, and $\langle l_0^2\rangle$ is the average length of a bond in a monomer backbone. (The molecular weight is around 10,000 g/mole for his samples.) Critique this function.
c) For polyolefins (filled circles) C_∞ increases from 6.7 for polyethylene to almost 8 for polypropylene (m_b = 15 for CH_3). How could this be possible? (Think of structural/organizational changes that are possible for a chain).
d) After polypropylene, increases in m_b first lead to a decrease then increase C_∞. The decrease is caused by a breakup of structure described in your answer to part "c". What might cause the increase at longer branch lengths, m_b?
e) The PAO's (open circles) show a constant value for C_∞ after the initial increase from 4 for polyethylene oxide (PEO). Why do PAO's show a constant value? (What is the main difference in chain flexibility between polyolefins and PAO's?)

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2) a) $C_\infty = n_k l_k^2/(n_{bond}\, l_{bond}^2) = l_k/l_{bond}$. C_∞ is a measure of chain rigidity.
b) C_∞ is for an infinite molecular weight chain since the end groups have a lower rigidity. His function with N at around 10,000 is not a good approximation for the infinite molecular weight behavior. His values should be too low by this logic.
c) Polypropylene displays a helical structure that enhances chain rigidity. Polyethylene doesn't have an equivalent helical structure.
d) The increase at large m_b is due to steric interference of the branches that force the chain to straighten out.
e) PAO's have an oxygen in the main chain. This adds a large amount of flexibility to the structure since the O-C bond is completely freely rotating. So the steric interference of the side branches has little effect on C_∞ beyond the initial jump from 4 to 5.48.