Quiz 3 Polymer Properties September 13, 2013

 Hyperbranched polymers (hb) are polymers (left figure) with a large extent of random branching so that the structure is mostly composed of "branch-on-branch" topologies. These materials are used as viscosity enhancers, coatings, drug and chemical delivery vehicles. In the right figure from a review by Voit and Lederer the intrinsic viscosity, [η], is plotted on a log-log plot versus the total molecular weight, M, for hyperbranched polymers. Two synthetic schemes are used, one with aliphatic polyesters and the other with two monomers, aliphatic and aromatic polyesters (similar to the two cases in the left drawing).

Scheme 1. Schematic Representation of the Synthesis of hb Polymers through the AB_x and $AB_x + B_y$ Approach ($x \ge 2$; Here, 2; $y \ge 3$; Here, 3)



Figures from Voit BI; Lederer A, Chem. Rev. 109 5924 (2009)

The following relationsips between [η], c* and M exist [η] = $K_{\eta}M^{\alpha}$ and [η] ~ 1/c* ~V_{coil}/M_{coil} ~ M^(3/df-1) where α is called the Mark-Houwink parameter and M is the mass of the polymer chain.

a) Give d_f as a function of α .

b) What behavior and value of α do you expect for a linear polymer as a function of molecular weight if $d_{min} = 5/3$ (such as in a good solvent)? (That is, how would the right plot above appear for a linear polymer?)

c) What can you say about the structure of the aliphatic-aromatic hb polyester (solid circles) and the change in structure as a function of molecular weight?

d) What can you say about the structure of the aliphatic hb polyester (open circles) and the change in structure as a function of molecular weight?

e) If we can expect any polymer in a good solvent to display a minimum dimension (d_{min}) of 5/3, what is the behavior of the connectivity dimension (c) for the two cases as a function of molecular weight? Does this agree with your answers to parts c and d?

2). Gerstl et al. compared the characteristic ratio of polyolefins $(CH_2CHR)_n$ with polyalkylene oxides $(CH_2CHR-O_{-})_n$ 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 CH₃). 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?)

1) a) $\alpha = 3/d_f - 1$ so $d_f = 3/(\alpha + 1)$.

b) $d_f = cd_{min}$ and for a linear polymer c = 1 so $d_f = 5/3$, then $\alpha = 0.8$. In the plot a linear polymer would display a line of a higher slope, slope 0.8.

c) The polymer has $d_f = 3/1.73 = 1.73$ for all molecular weights. The polymers have the same branch structure regardless of the molecular weight.

d) At low molecular weight the polymer has $d_f = 3/1.7 = 1.76$ and at high molecular weight $d_f = 3/1.1 = 2.72$. If the polymer is in a good solvent then the chains are lightly branched at low molecular weight and highly branched, almost 3d at high molecular weight. There might be steric hindrance to branching at low molecular weight for instance, when the chains are longer there is more room to add branch points.

e) $d_f = c d_{min}$ so if $d_{min} = 5/3$ then c = 1.73/1.67 = 1.04 for aliphatic-aromatic hb polymers and the chains are weakly branched with the same structure across molecular weight. For the aliphatic hb polymers c changes from 1.05 to 1.63 at higher molecular weights. This is consistent with c and d.

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.