

Homework 12
April 16, 2025 (***Due Wednesday not Monday***)
Polymer Physics

Comb and bottle brush polymers are composed of a linear main chain with polymeric or oligomeric side chains. Parameters of interest are the side chain graft density which can be quantified by $1/N_g$, the number of chemical mer units between side chains, the length of the side chains N_{sc} , the number of side chains, n_{sc} . Cai L-H *Molecular Structure of Foldable Bottlebrush Polymers in Melts* **In press** *Macromolecules* <https://doi.org/10.1021/acs.macromol.4c02981> (2025) discusses bottle brush polymers where the backbone chain is highly incompatible with the side chains. Cai's paper is a long, single-author paper, 20 printed journal pages so about 60 double spaced pages, about 1/5 of an issue of *Macromolecules*. The paper is too long to take a careful look at everything that is presented, but it is worth taking a glance at since it deals with tensile blobs. Cai proposes that when the side chains and backbone of a BBP are incompatible it is possible to uniquely tune the modulus and extensibility of the material independently. For all materials, except for this type of "foldable" bottle brush polymer, the extensibility and modulus are inversely related. This is true for conventional bottle brush polymers which are brittle but have high modulus, Figure 8 bottom left. Uniquely for "foldable" bottle-brush polymers of Cai's invention, the extensibility can increase with modulus allowing materials that can be tuned particularly for biomedical applications (he is supported by an NSF Career grant, by the National Institute of Health, and by a University of Va Diabetes grant). Cai has patented foldable BBPs (U.S. provisional patent application (No. 63/395,430) for the synthesis and applications of foldable bottlebrush polymers described in Reference 51).

- a) Describe the four regimes for conventional bottle brush/comb polymers. Include a description of the events that occur at the transition between these regimes. (You can also look at Reference 50 by Rubenstein which is the basis of Cai's discussion, however, this is an equally long paper.)
- b) In which regimes of conventional BBPs are tensile blobs involved? Explain the dependence of tensile blob behavior on N_g , Figure 2b.
- c) Describe the three regimes and the transition points for Cai's foldable bottle-brush polymers. What is the main difference between conventional and foldable bottle-brush polymers?
- d) In which regimes of foldable BBPs are tensile blobs involved? Explain the dependence of tensile blob behavior on N_g , Figure 3d.
- e) Explain Cai's experimental verification of his model for foldable BBPs in Figures 6c, 7b and c, and Figure 8. Is his verification convincing in your opinion?