Quiz 10
Polymer Physics
April 3, 2020

G. Polymeropoulos, P. Bilalis, X. Feng, E. L. Thomas, Y. Gnanou, and N. Hadjichristidis *Synthesis and Self-Assembly of Well-Defined Star and Tadpole Homo-/Co-/Terpolymers* Macromolecules **52**, 5583−5589 (2019) discuss the synthesis of "Tadpole" polymers which consist of a cyclic polymer (head) and a linear polymer (tail).

a) They present the following GPC curves with blue polyisoprene (elastomeric) blocks, red polystyrene (glassy) blocks and green poly(2-vinylpyridine) blocks (hydrophilic elastomeric). Explain the meaning of the GPC curves shown in Figure 1 below from bottom to top in terms of the hydrodynamic radius of the molecules.

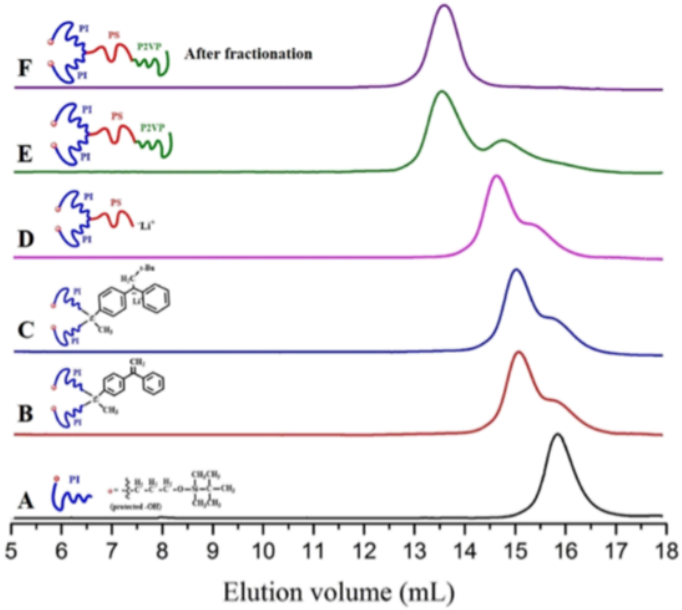


Figure 1. Monitoring the synthesis of the 3-miktoarm star terpolymer by SEC.

b) In the same paper Polymeropoulos et al. show the formation of the tadpole structure in two GPC curves, Figure 2. Explain Figure 2 in terms of the hydrodynamic radius and the molecular weight.

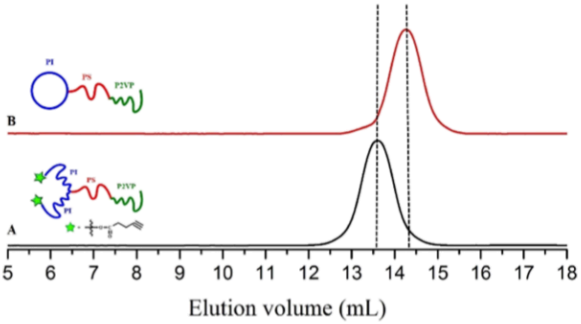
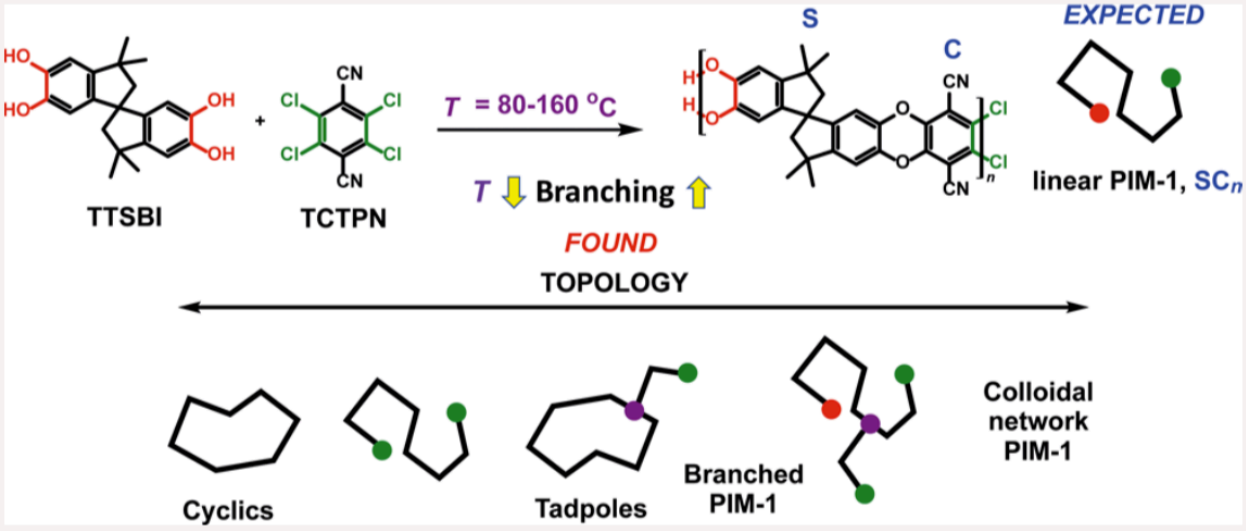


Figure 2. SEC traces of the (A) 3-miktoarm star terpolymer and (B) tadpole terpolymer.

c) A. B. Foster, M. Tamaddondar, J. M. Luque-Alled, W. J. Harrison, Z. Li, P. Gorgojo, and P. M. Budd *Understanding the Topology of the Polymer of Intrinsic Microporosity PIM-1: Cyclics, Tadpoles, and Network Structures and Their Impact on Membrane Performance* Macromolecules **53** 569−583 (2020) also studied tadpole polymers that were produced in a mixture of reaction products from a somewhat complex condensation polymerization that leads to a di-ether ring linkage (leading to linear chains, scheme shown) or mono-ether linkages (resulting in trifunctional branch points). Cyclics are possible as are networks and tadpoles. The resulting polymers can be used as membranes for separation of CO_2 from air (atmospheric CO_2 reduction); or CO_2 from methane (natural gas purification).



Foster et al. studied their synthetic product using MALDI mass spec and a multi detector GPC. Figure 3 shows a plot of the log of the intrinsic viscosity (viscosity detector) versus the molar mass (light scattering detector) for low molecular weight samples. First, **explain how the reaction scheme above could lead to a tadpole** molecule. Second, in the Mark-Houwink plot, Fig. 3, the linear part of the curves has a slope of 0.66 (dashed line). **What type of structure** do you expect for this slope?

d) Foster et al. indicate that a negative deviation in the Mark-Houwink plots (Figures 3 and 4) away from the power-law behavior indicates the presence of cyclic species. **Explain why this might be the case**. **Use the *g*-ratio in your answer**. Under your model **what would a strong positive deviation from the power-law indicate**?

e) A. Borodavka, S. W. Singaram, P. G. Stockley, W. M. Gelbart, A. Ben-Shaul, and R. Tuma *Sizes of Long RNA Molecules Are Determined by the Branching Patterns of Their Secondary Structures* Biophysical Journal **111** 2077–2085 (2016) studied the hydrodynamic radius of RNA which can form a kind of branched structure composed of ladder associations of a linear strand (similar to DNA) as shown in Figure below. The bottom plot shows the behavior of the hydrodynamic radius with the mass of the RNA. The red line $R_H \sim M^1$; green line $R_H \sim M^{0.5}$; blue line $R_H \sim M^{0.6}$. Why did Borodavka choose these three dependencies and what can you say about the structure from this data?

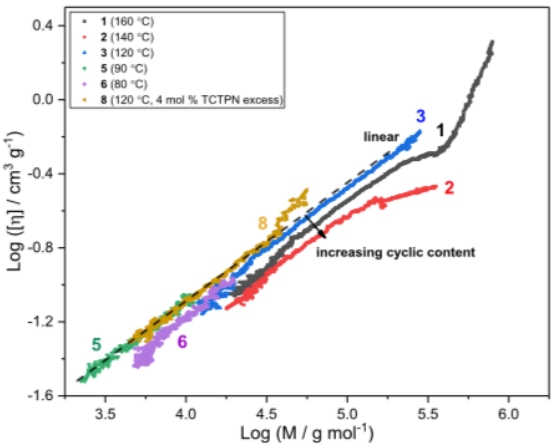


Figure 3. Mark–Houwink plots obtained in multiple detector SEC analysis of PIM-1 polymers produced in stoichiometric reactions (1–3, 5, and 6) compared against 4 mol % TCTPN excess reaction "linear" polymer (8).

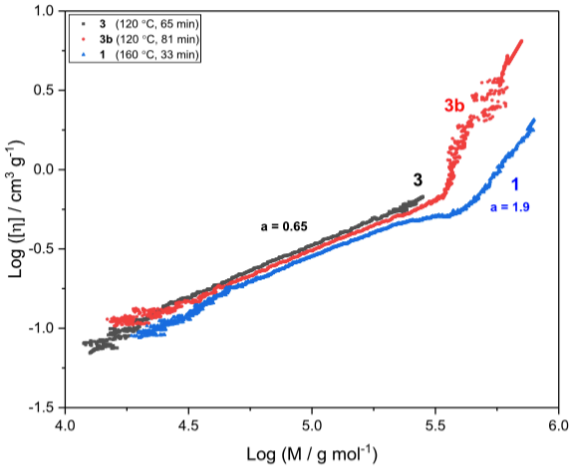
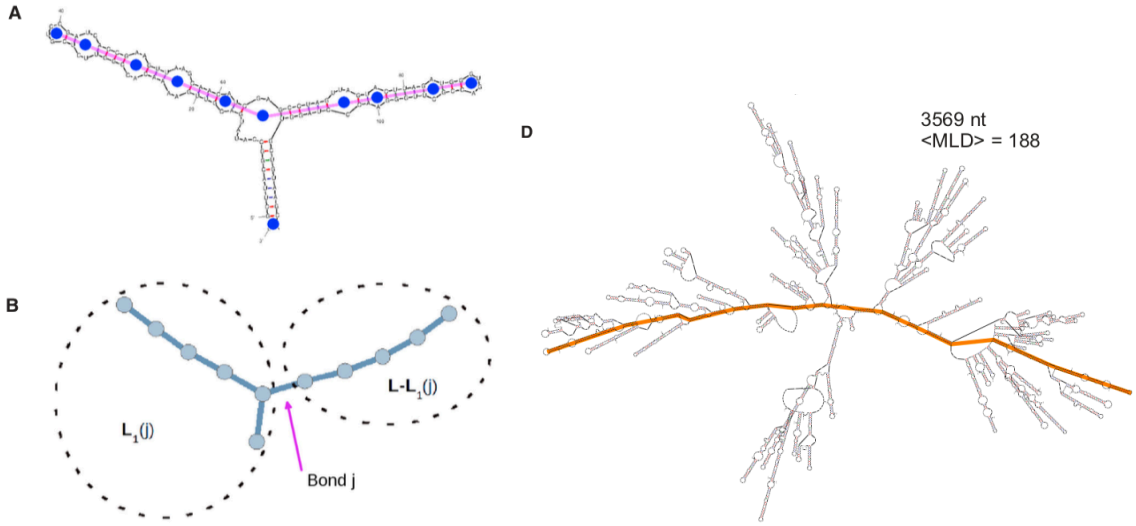
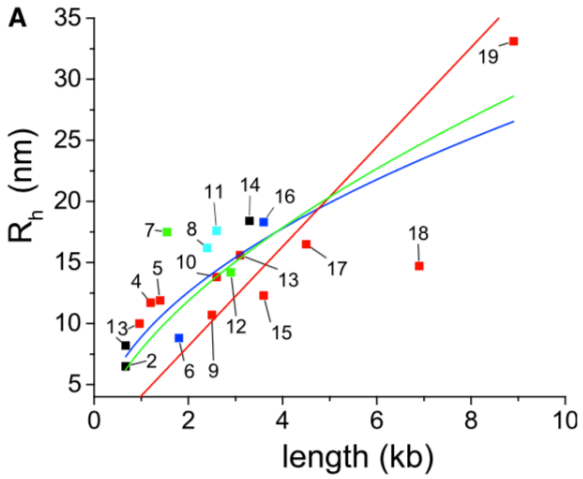


Figure 4. Mark–Houwink plots obtained in multiple detector SEC analysis of high molecular weight PIM-1 polymers produced in 120 °C reactions (3, 3b) compared against the 160 °C reaction (1).



RNA Branched Structure Formed From Ladder Bonding of a Linear Chain.



Answers Quiz 10
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a)

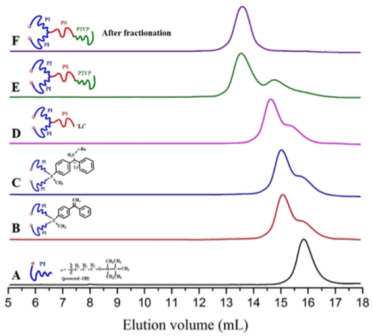

Figure 1. Monitoring the synthesis of the 3-miktoarm star terpolymer by SEC.

The A is the polyisoprene block with a functional end-group; B shows some of the unreacted poyisoprene plut the polyisoprene with the trifunctional group; in C a small linker group is added so that polystyrene block can be added, no change in the GPC; D the PS chain is added and both the polyisoprene block and the deblock shift to the left by the same amount; E the P2VP block is added to both linear chains and three arm polymers; F the linear chains are removed. Molecular weight increases to the left since the larger the hydrodynamic volume the shorter the elution time.

b)

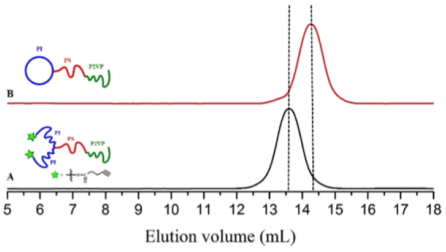

Figure 2. SEC traces of the (A) 3-miktoarm star terpolymer and (B) tadpole terpolymer.

The molecular weight remains unchanged but the hydrodynamic volume decreases on formation of a tadpole since the molecule with a cyclic is about half as large as the molecule with three arms. This leads to an increase in the elution volume (retention time).

c) The tetrachloride molecue could react with both chlorides (on one side) to make a linear chain. If only one chloride reacts the other partner hydroxyl in the tetra hydroxyl molecule can react with a different tetrachloride molecule leading to a trifunctional branch point. So you have, at a minimum, linear and trifunctional reactions. A sequence of linears followed by a trifunctional could lead to a loop and if the open dichloride site reacts with a dihydroxyl this will lead to a tadpole. It is a specific sequence of reactions that lead to tadpoles. The probability would seem to be low with many other options and much polydispersity in the tadpole structures.

The slope of the log-log plot is the Mark Houwink coefficient, a. $[\eta] \sim V/M$ for the coil, and $V \sim R_H^3 \sim M^{3/df}$, so
$[\eta] \sim M^{3/df-1}$ and $a = 3/d_f - 1$. For a rod M^2; for a theta coil $M^{0.5}$; for a good solvent coil $M^{0.8}$. $M^{0.66}$ could be for a branched chain or for a cyclic chain in a good solvent. The dimension goes up with more topological complexity, so the power, a, goes down. The observed slope could indicate a good solvent chain with some branching or a cyclic chain or a tadpole.

d) The g-ratio is the ratio between R_H^2 for a branched or cyclic or tadpole molecule to R_H^2 for a linear molecule of the same molecular weight. g drops with increasing topological complexity. g is monotonic with the intrinsic viscosity since $[\eta] \sim V/M$ and M is related to the linear size, while V is related to the hydrodynamic size of the branched chain. g is expected to drop with the presence of cyclics so $[\eta]$ should also drop. The amount that g and $[\eta]$ drop could be calculated.

The large upturn at high molecular weights is probably due to breakdown of the assumptions in the measurement technique. For highly branched chains of high molecular weight, significant interaction between chains is possible, i.e. entanglements or clustering. This can lead to a dramatic rise in the viscosity. In the context of the gel separation, high molecular weight, viscous samples at short retention times can lead to breakdown of the gel.

e) Borodavka et al. are using the definition of the end-to-end distance for different fractal objects with $R \sim M^{1/df}$. For a rod $1/d_f = 1$; for a Gaussian coil $1/d_f = 0.5$; and for a self-avoiding walk $1/d_f = 3/5 = 0.6$. R_H is a measure of the drag of an object not a measure of the end-to-end distance. The assumption that the end-to-end distance is proportional to R_H isn't good. For instance, for a rod R_H might be the diameter of the rod not the length. Their assumption that R_H is the end-to-end distance is not accurate.

The data does not show a trend except that the hydrodynamic radius might increase with molecular weight, it is, for the most part, a scatter plot with no trends. *Biophysical Journal* is the most famous journal for the physics of biological materials. It is surprising that this paper was published given the glaring problems. It is not mentioned how R_H was measured. One must assume that these are measurements made with dynamic light scattering, which is the simplest measurement. DLS isn't necessarily accurate for all systems. Probably the paper was published because the authors are from well-known research institutes and universities. Otherwise the paper contributes nothing except a nice graphic in Figure 1. No conclusions can be made from the data except that the data has no real trend. This would be a good paper for a critical review since the main conclusions are not supported by what is presented.