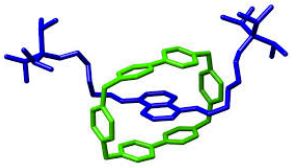
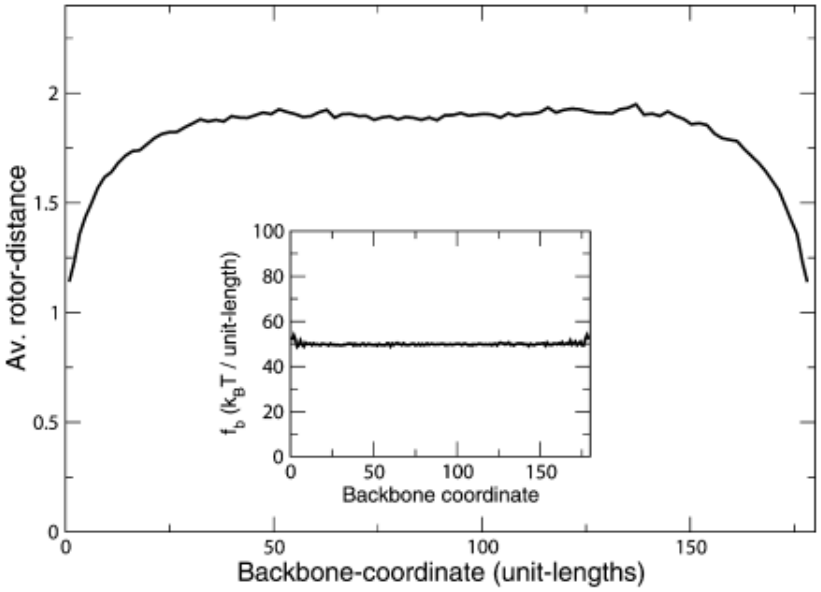
Polymer Properties
Quiz 4
September 19, 2014

A polyrotaxane is a polymer chain with freely rotating ring molecules threaded along the chain with large end-groups that retain the free cyclics along the chain. In a polyrotaxane there are many ring molecules that act like short chain branches and can stiffen the chain, increasing the chain persistence. Merlitz et al. [1] simulated polyroxtaxanes in a paper this year.





(a) *(b)*

Figure 1. a) Schematic of a single rotor threaded on a chain molecule with locking end groups (from the web). b) Average distance between rotor molecules along the chain for a chain of 180 chain units with 100 rotors threaded on the chain. The inset shows the rotor density. (from [1]).

a) Merlitz et al. [1] used the following equation for a persistent chain, that we discussed in class ($R_g^2 = \langle R^2 \rangle/6$ for a Gaussian chain),

$$R_g^{\,2} = \frac{N_b l_p}{3} - l_p^{\,2} + \frac{2l_p^{\,3}}{N_b} - \frac{2l_p^{\,4}}{N_b^{\,2}}\left(1 - \exp\left(-\frac{N_b}{l_p}\right)\right) \qquad (14)$$

to calculate the persistence length from a plot of R_g^2 versus N_b (the fit line shown below):

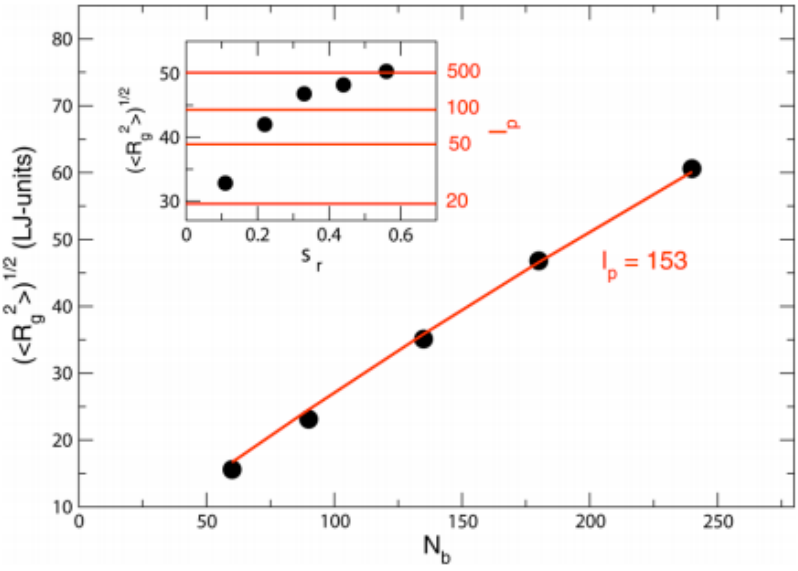


Figure 4. Root-mean-square radius of gyration of the backbone as a function of the backbone length. Here, $\sigma_r = 0.33$ and $N = 32$. In red: fit of eq 14. Inset: at different rotor densities. Here, $N_b = 180$ and $N = 32$. Red lines indicate the persistence length after eq 14.
(From [1].)

Do you think that equation 14 is appropriate for the polyrotaxane? Explain your answer.

b) From what you know about the dependence of persistence on molar mass, critique Figure 4 (assuming that equation 14 could be used for a polyrotaxane).

c) Figure 1 shows that the rotors tend to cluster near the chain ends. Explain this behavior based on what you know about changes in chain persistence with backbone coordinate (chain index). What other factors could lead to this clustering?

d) The inset to Figure 4 shows the dependence of the persistence length on the density of rotors on the chain. It is shown that the persistence exponentially increases by an order of magnitude as the rotor concentration approaches one rotor for every two chain units ($s_r = 0.5$). The final point is a persistence length of 500 chain units for a chain of 180 units. This is obtained from a plot similar to the base plot in Figure 4. Does this result make sense?

e) In class we looked at plots of chain persistence length versus backbone coordinate. Sketch this for a long linear chain, a very short linear chain, and long and very short cyclic chains of the same lengths on one plot (for a cyclic chain the two chain ends are bonded together). Write a few comments about this plot concerning the infinite molecular weight persistence length in each case.

[1] Merlitz H, Cui W, Su C-F, Wu C-X, Sommer J-U, *Macromolecules* **47** 4110 (2014).

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1) a) Equation 14 is calculated for the persistent chain model and results in a Gaussian chain with no end-group effects. One assumption in this model is that chain rigidity is constant along the chain.
The persistent chain model is not ideal for this structure since there is, apparently, variability of the rigidity along the chain. By design, the chains will have large end-group effects that could have a large effect on the persistence of the chain, especially for low and moderate chain lengths. It is unlikely that this chain is Gaussian
We have seen from papers by Connelly and others that there is a strong molecular weight dependence to the persistence length for chains of less than about 500 units. This means that each point along the curve in figure 4 has a different persistence length so equation 14 can't be used with a single persistence length to model the data in figure 4.
So equation 14 is not appropriate and the approach presented to calculate the persistence length is in error.
b) We have seen from papers by Connelly and others that there is a strong molecular weight dependence to the persistence length for chains of less than about 500 units. This means that each point along the curve in figure 4 has a different persistence length so equation 14 can't be used with a single persistence length to model the data in figure 4.
c) From the Connelly paper we found that persistence is lower at the chain ends since the chain ends have less constraints and higher mobility. It is difficult to justify a higher density of rotors for more flexible regions of the chain. It would be expected that relatively higher flexibility would drive the rotors to less flexible regions of the chain, the opposite of what is observed. (This argument is similar to the observation that gas atoms tend to cluster in colder regions due to thermophoresis.)
An alternative explanation is that the clustering at the chain ends is an artifact of the starting conditions of the simulation. In a simulation of gas atoms, if the atoms are initially evenly dispersed, a concentration buildup at the walls of the simulation box can occur because the atoms reflect from (bounce off of) the wall. With random motion there will be roughly twice the concentration of atoms one mean free path length from the wall. The rotors could be considered trapped gas atoms that reflect off the end groups of the chain in a 1-d trap leading to a higher rotor density at the chain ends. This is an artifact of the initial conditions of rotor distrigution for the chain.
d) The inset plot is an odd plot since l_p is not plotted against s_r, rather the author chooses to plot R_g^2 and show l_p values with lines. The reason for this is that R_g^2 shows a plateau at high s_r, while l_p exponentially increases, it has no plateau. This means that the behavior of persistence shows something like critical point features, something that isn't expected.
Further, it is difficult to understand what is meant beyond $l_p = N_b$ (180). For the last two points in the inset plot the persistence length is longer than the chain, so the chains are just rods. The inset plot is misleading and shows unphysical behavior for the calculated values.
e) For a long linear chain the infinite molecular weight persistence length is the plateau value in the plot at the center of the chain. For the short linear chain, the plateau is not reached so a lower value would be estimated for the infinite chain persistence length (an in correct value). For the

cyclics there is a single value for persistence length. For short chains it is longer than the linear short chain since the cyclic is more rigid than the linear chain. For the long chain it is about equal to that of the linear long chain infinite molecular weight persistence length (plateau value).