Polymer Physics
Quiz 7
February 26, 2021

Polycantanes are polymers composed of interlinked ring polymers (Figure 1 below left). The bond is called a *mechanical linkage* as opposed to covalent bonds. Wu Z-T, Zhou J-J *Mechanical Properties of Interlocked-ring Polymers: A Molecular Dynamics Simulation Study* Chinese J. Polym. Sci. **37** 1298-1304 (2019) simulated polycantanes in good solvent dilute solutions. Wu used molecular dynamics (Langevin) simulations and varied the size of the rings and the number of rings in a chain. They applied stretching forces to determine the mechanical properties of a single chain.

a) Wu's Figure 1 (replotted below right) is used to support their argument that the chain size scales with $N^{0.6}$, where N is m x n, m is the number of beads in a cyclic, and n is the number of cyclics in the chain (see Raicher's Figure 1 below, left). Derive an equation (*following what was done in class*) that explains this scaling behavior.

b) Wu's figure 1 actually shows deviation from the Flory-Krigbaum prediction. The digitized data is shown below (right) with fits that show a slope of 0.81 for the low N and about 2 for the large N. *A best fit to the low data using a fixed slope 0.6 is also shown.* **Would you expect to see deviations from Flory-Krigbaum behavior at large N or at small N and why? Can you explain the observed behavior?** (What would be the slope be for a rod? What about for a 3d object? Consider the simulation method.)

Figure 1. Visualization of a poly[n]catenane. For clarity, each ring is colored differently. The variable m indicates the number of beads per ring, while n denotes the number of rings per chain, as shown. For this molecule, $n = 10$ and $m = 50$. Note that this configuration was obtained during system preparation at very low density, similar to good solvent conditions, so that the interlocking structure can be more clearly observed; poly[n]catenanes in the melt are much more collapsed/globular (Figure 9b).

From Raischer et al.   *Data from Wu et al. Figure 1*

c) Wu's Figure 2 (below, left top) shows the behavior of R for the cyclics as a function of the ring size m. (Top line is for $R \sim m^1$, bottom line for $R \sim m^{3/5}$.) Comment on the behavior. Does it make sense? Is a ring of 10 to 30 beads denser than a linear chain? Could this explain the low N behavior in the replot of Wu's data above (right)? (*A chain of N = 100 has 3 to 10 rings.*)

d) Pakula T, Jeszka K *Simulation of Single Complex Macromolecules. 1. Structure and Dynamics of Catenanes* Macromolecules **32** 6821-6830 (1999) used a Metropolis Monte Carlo algorithm to obtain Figure 4 below, right top. Compare this figure with that of Wu (above right).

e) Compare the results shown in Pakula's Figure 4 (below top right) and that shown in Pakula's Figure 5 (below bottom left) where *P(q)* is the scattered intensity. Are these results consistent? The last graph (below bottom right), Figure 10, is from Rauscher PM, Schweizer KS, Rowan SJ, de Pablo JJ *Thermodynamics and Structure of Poly[n]catenane Melts* Macromolecules **53** 3390-3408 (2020) and is for polycantane's in the melt (Gaussian chains) simulated using a similar algorithm to Wu. Compare, *in terms of the chain scaling regime*, this simulated scattering pattern to that of Pakula's (below bottom left) which is made for dilute chains in a good solvent (*S(k) ~ P(q)*; *k ~q*).

Fig. 2 The radius of gyration R_g for individual rings. Here the simulation data are shown for different *m* number of beads per ring and k_θ (bending constant).

From Wu et al.

Figure 4. Mean sizes of single linear and cyclic chains as a function of chain length. The solid line shows the linear fit indicating the scaling $\langle s^2 \rangle \propto N^{2\nu}$ with $\nu = 0.6$, characteristic for polymers in a good solvent.

From Pakula et al.

From Pakula et al.

Figure 10. Single-chain structure factor for poly[*n*]catenanes of various *n* and (a) *m* = 15 or (b) *m* = 50. The dashed black curves show the single-ring structure factor for poly[*n*]catenane chain centers (cf. Figure 5a). The legend in panel b applies to both graphs.

From Raischer et al.

a) *Wu's Figure 1 (replotted below right) is used to support their argument that the chain size scales with $N^{0.6}$, where N is m x n, m is the number of beads in a cyclic, and n is the number of cyclics in the chain (see Raicher's Figure 1 below, left). Derive an equation (following what was done in class) that explains this scaling behavior.*

The 0.6 power law (3/5) is the Flory Krigbaum result. To get $<R^2> = nl^2$ we integrated R^2 times the normalized Gaussian distribution to obtain the average R^2,

$$W_0(R)dR = Z^N 4\pi R^2 \left(\frac{2\pi}{3}Nb^2\right)^{-3/2} \exp\left[-\frac{3}{2}\left(\frac{R}{b\sqrt{N}}\right)^2\right]dR$$

Alternatively, we could take the derivative of this function and set it to 0 to obtain the most probable R^2 value,
$0 = 2R(K_1)\exp(R^2 K_2)+R^2(K_1)\exp(R^2 K_2)(-3R/(nl^2))$
Dividing by like terms yields,
$R^2 = 2nl^2/3$
Which has the same scaling and mass fractal dimension as $<R^2>$ obtained by integration.
For exclusion of one monomer the probability is altered by $(1 - V_0/R^3)$ and for n binary interactions $(1 - V_0/R^3)^{n^2/2}$. To get this into the exponential we take the ln and use Sterling's approximation to obtain $\exp(-n^2 V_0/(2R^3))$ to arrive at,

$$W(R)dR = W_0(R)p(R)dR = kR^2 \exp\left(-\frac{3R^2}{2Nb^2} - \frac{N^2 V_C}{2R^3}\right)$$

Taking the derivative with respect to R and setting it to 0 we obtain,

$$-\frac{3R^{*2}}{2Nb^2} + \frac{3N^2 V_C}{4R^{*3}} + 1 = 0$$

Using $R_0^2 = nl^2$ this can be written,

$$\left(\frac{R^*}{R_0^*}\right)^5 - \left(\frac{R^*}{R_0^*}\right)^3 = \frac{9\sqrt{6}}{16}\frac{V_C}{b^3}\sqrt{N}$$

For the large size change on coil expansion the power 5 term is much larger than the power 3 term so we can approximate this as,

$$R^* \cong R_0^*\left(\frac{N^{1/2}V_C}{b^3}\right)^{1/5} = kN^{3/5}$$

b) *Wu's figure 1 actually shows deviation from the Flory-Krigbaum prediction. The digitized data is shown below (right) with fits that show a slope of 0.81 for the low N and about 2 for the large N. A best fit to the low data using a fixed slope 0.6 is also shown.* ***Would you expect to see deviations from Flory-Krigbaum behavior at large N or at small N and why? Can you explain the observed behavior?*** *(What would be the slope be for a rod? What about for a 3d object? Consider the simulation method.)*

The slope is $1/d_f$, and d_f can be between 1 and 3 in 3d space. So the slope can be between 1 and 0.33. A value of 0.81 is more extended than a self-avoiding walk. A power of 2 is not possible. Any deviations from FK theory should occur at small N where the approximation of ignoring the cubed term would have most impact. When things go bad at large N in a dynamic simulation it could be that the simulation was not run sufficiently long to reach equilibrium. The low N behavior indicates that the presence of cyclics leads to a more rigid structure than a self-avoiding walk of the FK type.

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The completely flexible rings display FK behavior, the stiffer rings are rod like. This makes sense for a linear chain but not for a ring. A small ring (10 to 30 beads) should be denser than a linear chain so it shouldn't follow the scaling shown in Figure 2, especially the rod like scaling. The low-N behavior in the right figure above shows a more rod like behavior compared to a FK chain. The unusually low dimensionality of the rings could have some impact on that.

d) *Pakula T, Jeszka K Simulation of Single Complex Macromolecules. 1. Structure and Dynamics of Catenanes Macromolecules **32** 6821-6830 (1999) used a Metropolis Monte Carlo algorithm to obtain Figure 4 below, right top. Compare this figure with that of Wu (above right).*

The results of Pakula are unusually perfect fits to the expected results. Comparing with Wu's results which show some scatter (which is normal) the Pakula results seem suspect unless it can be explained why they are in perfect agreement with the expectations. The results are too good to believe. All of the results are a perfect match to FK behavior.

e) *Compare the results shown in Pakula's Figure 4 (below top right) and that shown in Pakula's Figure 5 (below bottom left) where P(q) is the scattered intensity. Are these*

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*results consistent? The last graph (below bottom right), Figure 10, is from Rauscher PM, Schweizer KS, Rowan SJ, de Pablo JJ Thermodynamics and Structure of Poly[n]catenane Melts Macromolecules **53** 3390-3408 (2020) and is for polycantane's in the melt (Gaussian chains) simulated using a similar algorithm to Wu. Compare, in terms of the chain scaling regime, this simulated scattering pattern to that of Pakula's (below bottom left) which is made for dilute chains in a good solvent (S(k) ~ P(q); k ~q).*

Pakula's Figure 4 shows that the chains have a mass fractal dimension of 5/3 (FK self-avoiding walk), while the results in Figure 5 display a mass-fractal dimension of 2 (Gaussian). These do not agree. The d_f 2 results are what is expected in a melt, such as in Raischer's simulation. If the Pekula results can be believed, it seems that the main result of introducing long-range interactions is to remove the collapse of the rings which are observed in the data of Raischer by the -4 slope at intermediate q. -4 is surface scattering from smooth interfaces of a solid object. So Rauscher's results support collapsed globular rings in a Gaussian random walk, Pakula's results show no distinction between the rings and the chains, and both show a Gaussian random walk with no self-avoidance. Raischer's results are more believable.

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