Homework 4
February t0, 2025
Polymer Physics

Conjugated conducting polymers generally require doping with an ionic molecule, polymer or a doping species on the same polymer chain for conduction and these are called donor/acceptor pairs. Conceptually this seems to be a simple system composed of large persistence length chains that could be made into wires or sensors (conductivity is very sensitive to some species) or light emitting devices. In application the rigid chains are weakly soluble unless engineered for solubility and they tend to aggregate due to the steric interactions of rigid rods (spaghetti in a box), the organization of solubilizing side groups some of which are polar, and formation of hierarchical structures and phase separation at different length scales. This is typical of the kind of complex structures that you can encounter in polymers and in biology so it might merit a brief look. While extended chain persistence is a characteristic feature of these polymers, they are generally used in thin films in the solid state after some type of elongation process so analytic methods that study solution properties might be distanced from commercial importance. An interesting and comprehensive paper was published in 2022 from a group at UIUC, Kwok JJ, Park KS, Batel BB, Dilmurat R, Beljonne D, Zuo X, Lee B, Diao Y, *Understanding Solution State Conformation and Aggregate Structure of Conjugated Polymers via Small Angle X-ray Scattering* Macromolecules **55** 4353-4366 (2022) and a related paper, Park KS, XueZ, Patel BB, An H, Kwok JJ, Kafle P, Chen Q, Shukla D, Diao Y *Chiral emergence in multistep hierarchical assembly of achiral conjugated polymers* Nature Com. 13:2738 (2022). Kwok (Macro) explores structural emergence in a thiophene based conductive polymer with donor and acceptor groups on the same chain (Figure 1 in Kwok (Macro) and Figure 1 in Park (Nature)). Park Figure 7 shows some of the complex hierarchy that is seen in this system that includes the emergence of chirality (handedness) from achiral (non-handed) polymers during self-assembly. Kwok's Macro paper details a structural model, Figure 4E, using mostly small-angle X-ray scattering (SAXS), Figure 2. The structure is composed of some free chains that are slightly aggregated and larger precipitated fibrous struts that form a gel structure. Within the struts "lamellar stacking" occurs that is show in the Nature Figure 7. The system displays chain persistence and strut persistence that can be seen as two regimes of power -1 scaling in Kwok Figure 2B.

a) Kwok first does a density functional theory simulation, Figure 1, which involves simulating the atomic electron cloud density in the chain to predict the rotational dihedral angles of the conjugated cyclic groups in the polymer chain. He uses these predicted angles in an algorithm to calculate chain paths and from these chain paths calculates the average tangent correlation function, equation 1. Derive equation 1 and an expression that relates the persistence length to the Kuhn length. What assumptions are necessary for each of these derivations?
b) In the context of MD simulations of semi-flexible polymers comment on changes in the persistence length along a chain. How would this impact Kwok's local calculation of the persistence length in part a? Note the following plot:

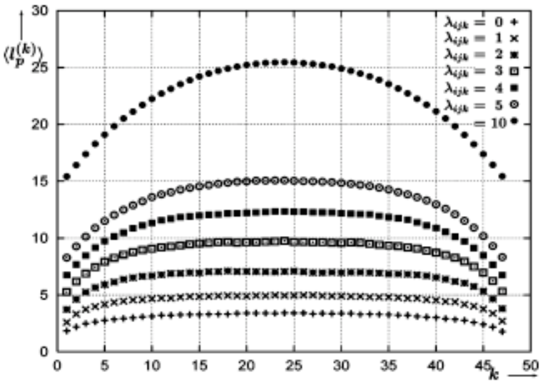
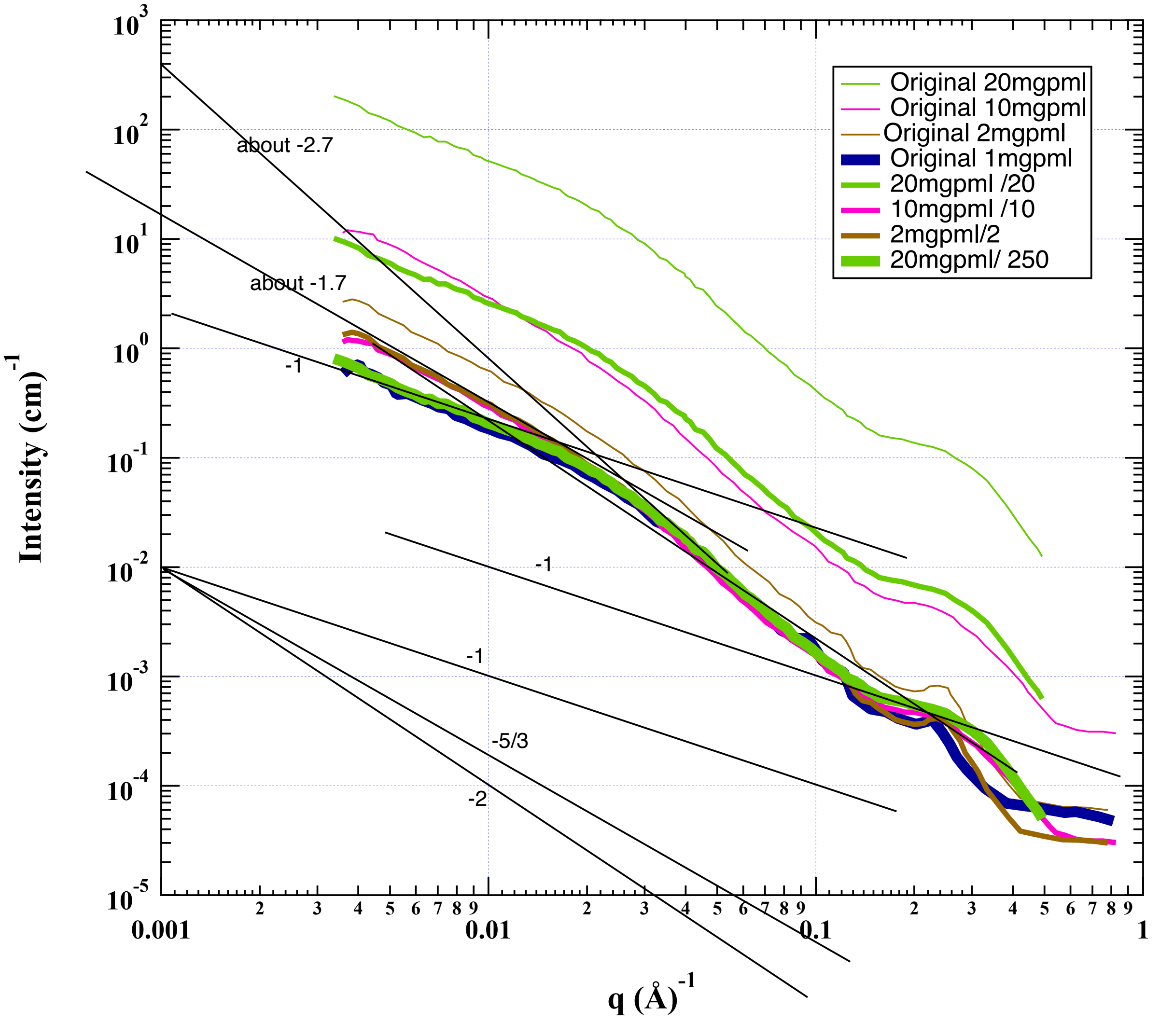


Figure 7. The persistence length plots, $\langle l_p^{(k)} \rangle$, obtained via eq 10, versus segment number, k, for various semiflexible, linear polymers, each of length 48. The strength of the intrinsic stiffness is varied between polymers by increasing the strength of the bending penalty, λ_{ijk} from 0 (bottom)...5, 10 (top).

c) Kwok's Figure 2B is SAXS for a concentration series. The scattered intensity should be proportional to the concentration, so the following digitized graph shows the original data and curves for Intensity/c and the 20mg/ml curve divided by 250.



Explain why the 20 mg/ml sample, doesn't scale with concentration but with 250 and why the 20 mg/ml sample is indistinguishable from the 1% sample except for the "lamellar stacking" hump at high-q. Why do the Intensity/c curves for 2 and 10 mg/ml mismatch the 1 mg/ml and 20 mg/ml/250 curves at low-q? Is this consistent with Kwok's description of the morphology? Kwok chose to use 10 mg/ml samples for his further studies, is this appropriate?

d) Kwok Figure 2C shows how the persistence length was determined. Do you think that the persistence length could be determined from this data given the model in Figure 4E? What is the Guinier equation, which is the basis of the Guinier plot in Figure 2D and E. What feature does it fit in a log-log plot and does that feature exist in the persistence region shown in Figure 2C? Kwok apparently equates the persistence length and the radius of gyration. Is this appropriate? What is the radius of gyration for a rod in relation to the length of the rod (Kuhn length)?

e) The radius of gyration for a random walk can be calculated from the end-to-end distance by $R_g^2 = R_{eted}^2/6$. Compare this with equation 2 using $R_{eted}^2 = n_K l_K^2$. Are there problems with this?