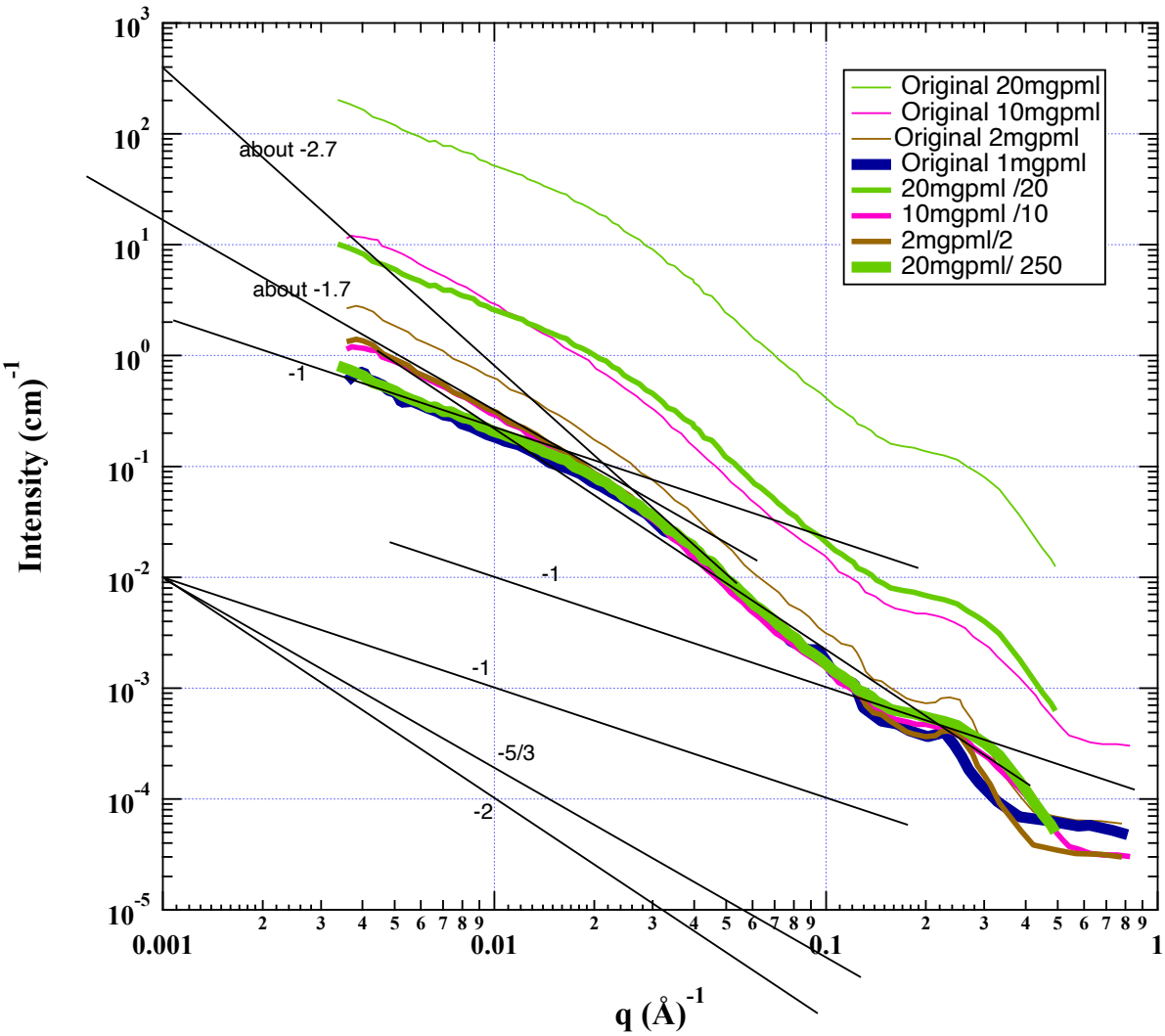
Homework 4
February t0, 2025
Polymer Physics

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 a 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) Wonk 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) 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 I/c and the 20% divided by 250.



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

c) Kwok Figure 2B 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)?

d) 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?

e) On page 4359 first column top Kwok states that he can ignore the large sizes observed in microscopy because SAXS is a “number average method”. Why would a number-average method ignore large sizes. Generally scattering is considered a weight average method since the intensity is proportional to the structural volume squared. Explain why this would yield a weight average. The radius of gyration squared is considered a ratio of the eight moment to the sixth moment. Show that this is true. For this measure of size do you expect the large sizes from a distribution of sizes observed in microscopy to significantly impact the radius of gyration?