

Polymer Physics
Homework 6
Due February 21

Poly(2,6-diphenyl-p-phenylene oxide) (PPPO) is a glycol polymer (like PEO) with a para phenylene group replacing the ethylene group in PEO (Figure 1). This substitution makes polyphenyleneoxide, PPO, which is used to blend with polystyrene, PS, (a Sabic (formerly GE Plastics) product Noryl). With di-substituted phenyl groups at the 2 and 6 phenylene ring positions you have PPPO which is used to reversibly adsorb chemicals such as ethanol in a breathalyzer test (of “*blow into the tube*” fame). This reversible adsorptive ability could be used in biomedical devices, chemical warfare agent tests and simple environmental testing devices if nanoparticle PPPO could be mass produced. O’Connell RA, Sharratt WN, Aelmans NJJ, Higgins JS (Lady), Cabral JT *SANS Study of PPPO in Mixed Solvents and Impact on Polymer Nanoprecipitation* *Macromolecules* **55** 1050-1059 (2022) investigated a method to make such nano PPPO using non-solvent induced phase separation, NIPS, using a rapid quench device shown in the supplemental information (Figure S1). The process involves shooting a jet of a dichloromethane (solvent) solution of PPPO at a jet of heptane (non-solvent) and after turbulent and rapid mixing collecting nano to micro particles in a heptane bath, Figure 8. It seems that some single molecule particles of 176 kg/mole linear PPPO could be produced by this method. (Mostly particles contain many polymers, Figure 8e and 8h.) O’Connell recently did an in-depth study of the single chain structure for this process using blob models to understand how these single molecule nanoparticles can be formed and how the process might be improved.

- a) Figure 1 shows a ternary phase diagram with the top corner 50% PPPO, the bottom left pure deuterated di-chloromethane, bottom right 50% deuterated heptane. Region I is dilute, semi-dilute and concentrated PPPO solutions in the good solvent d-DCM. Region II is dilute PPPO in mixed solvents up to the poor solvent (like a temperature drop in a UCST system with the phase separated region in brown (or “red”). Region III semi-dilute solvent quality change and IV concentrated solvent quality change. Explain what you expect to see in the regions I, II, and III of this phase diagram in terms of a cartoon of the polymer structure as it goes through these transitions in concentration and solvent quality.
- b) Figure 2b is a log-log plot of I/ϕ versus q for a neutron scattering measurement for region I. Why is I/ϕ plotted rather than just I ? The data reaches a knee at low- q which tails over at some value of q to a power-law of $-5/3$ slope. What does $1/q$ at this knee reflect for these curves? What kind of blob is involved here?
- c) Figure 3b shows the behavior of the blob size with concentration with a power-law slope of $-3/4$. Derive this power-law dependence.
- d) Figure 4a shows Region II, dilute PPPO as a function of reducing solvent quality (like dropping the temperature for a UCST system). The curves have a significant background which might be associated with the solvent mixture or could be experimental. In the attached Igor experiment a flat background has been subtracted from digitized data to bring out the power-law dependence at high- q . What power laws do you expect at low and high- q ? What does the transition size ($1/q$ at the power-law transition) reflect? Comment on Figure 3c where O’Connell proposes a discrete transition from a good solvent to a theta solvent with increasing concentration in Regime I.

- e) Regime IV reflects the final stage of the O'Connell process shown in Figure S1 of the supplemental. This is partly shown in Figures 5 and 6. Compare figure 6b with the micrographs shown in Figure 8. Is there a connection between the two sizes seen in Figure 6b and the micrographs? A single chain particle will be about 10 nm in size. In Figure 8 O'Connell plots number of molecules per particle as a function of heptane concentration. Try to use the information in this paper to make a coherent description of the particles that are produced in the process of Figure S1. Try to show that O'Connell's analysis is of use in understanding the production of nano PPPO.