Homework 8
March 10, 2025
Polymer Physics

Plastics waste is a major problem especially for single use plastics. One proposition to address this issue is to make polymers that have a reversible polymerization. Takahashi R, Sugawara-Narutaki A *Observing Depolymerization of a RAFT Polymer by Time-Resolved Small-Angle X ray Scattering* ACS Polymers https://doi.org/10.1021/acspolymersau.4c00095 (2025) is an in-press paper that proposes the use of reversible addition-fragmentation chain-transfer (RAFT) polymerization to produce polymers that can be "depolymerized" by raising the temperature to above 120°C in the absence of added catalysts. They demonstrate this approach using polybenzylmethacryalte (PBzMA) which is a polymer used in microelectronics manufacture known for high resolution processing of chips.

a) What is RAFT polymerization and how does it differ from atom-transfer radical polymerization (ATRP)? Compare the RAFT polymerization used by Takahashi with that used by McKenzie TJ, Brunet T, Kissell LN, Strobbia P, Ayres N *Polydimethylsiloxane Polymerized Emulsions for Acoustic Materials Prepared Using Reactive Triblock Copolymer Surfactants* ACS Appl. Mater. Interfaces **15** 58917-58930 (2023). How can RAFT polymerization be used for depolymerization? Why does high temperature cause depolymerization in RAFT polymerization?
b) Takahashi uses small angle X-ray scattering to obtain the molecular weight, M_w, and the radius of gyration for dilute PBzMA solutions in p-xylene. The M_w is obtained from the low-q plateau in Figure 1a which is proportional to $n\rho^2V^2$ where n is the number concentration of polymer, ρ is the electron density of the polymer minus that of the solvent and V is the volume of the polymer. For a polydisperse sample, why does this prefactor lead to the weight-average molecular weight, M_w? Explain what moment of the radius of gyration is obtained from a polydisperse sample, equation 8. Reference RJ Roe, *Methods of X-ray and Neutron Scattering in Polymer Science* (2000) page 170 and Takahashi's reference 29. Explain how the z-average in this case is actually $(\langle R_g^8\rangle/\langle R_g^6\rangle)^{1/2}$.
c) Takahashi resolves the depolymerization of PBzMA by RAFT as "unzipping" compared to "random scission" as shown in Figures 2 and 3 especially Figure 2c. Explain what these two models refer to and how each of these figures demonstrate "unzipping". How can M_w drop while R_g remains constant in Figure 2c? Is "unzipping" preferred over "ransom scission" in a polymer recycling scheme? Why or why not?
d) Figure 1 shows Takahashi's SAXS results plotted on three different plots. He claims that the power-law slope at high-q in Figure 1a is -2. Is this verified by Figure 1b and c? How would b and c appear for a theta, and for a good-solvent chain? What would make the curve drop below horizontal? Is that possible in this system?
e) Equations S6 and S7 include the Debye function for a Gaussian polymer chain (which is not expected in a good solvent) and a Guinier term written for a cylindrical rod, $\exp(-q^2D/16)$, where D is the rod diameter. Takahashi finds that D is 10 Å in Table S3.

What do you normally expect at high-q for a polymer chain after the Gaussian scaling ends? Comparing the Takahashi function's exponential term (which have no reference number so are presumably new but not derived) with Guinier's law what R_g does this function actually relate to? Does any of this make senses? Luckily these antics would seem to have only a small impact on the coil radius of gyration, however, the "unzipping" model for chain depolymerization becomes highly suspect if the chains are, for instance, branched. Explain this.