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.

1. 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?
2. Takahashi uses small angle X-ray scattering to obtain the molecular weight, Mw, and the radius of gyration for dilute PBzMA solutions in p-xylene. The Mw is obtained from the low-q plateau in Figure 1a which is proportional to nr2V2 where n is the number concentration of polymer, r 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, Mw? 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 (<Rg8>/<Rg6>)1/2.
3. 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 Mw drop while Rg remains constant in Figure 2c? Is “unzipping” preferred over “ransom scission” in a polymer recycling scheme? Why or why not?
4. 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?
5. 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(-q2D/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 Rg 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.