Chem/MatS/ChEn 4223W

Assignment 14
Due: *In Lab*, Tuesday, March 26/Thursday, March 28

1. In Lab 5, you will be synthesizing polymers via reversible addition-fragmentation chain-transfer (RAFT), a controlled radical polymerization technique. There has been a great deal of recent research on methods for mediating the kinetics of radical polymerization. Demonstrated for the first time in the late 1990's, RAFT is a popular controlled radical technique, but it is not the only one. Atom-transfer radical polymerization (ATRP) and nitroxide-mediated radical polymerization (NMRP), for example, are also used to synthesize polymers with controlled molecular weights and polymer structures. The mechanistic schemes for these methods are somewhat similar to that of RAFT. A recent review article compares and contrasts controlled radical polymerization techniques:

   Braunecker, W.; Matyjaszewski, K. "Controlled/living radical polymerization: Features, developments, and perspectives," *Prog. Polym. Sci.* **2007**, *32*, 93-146. (http://dx.doi.org/10.1016/j.progpolymsci.2006.11.002)

   Draw a mechanism for an ATRP or NMRP polymerization, using "electron pushing" and complete chemical structures. DO NOT abbreviate any chemical structures.

2. How is the mechanism you drew similar to that of the RAFT polymerization we are doing in class?

3. The RAFT lab is a relatively new addition to the course, and you will be participating in an effort to work out some of the kinks. In particular, we are trying to determine whether the polymerization exhibits first-order kinetics, whether there is an incubation time to the polymerization (unfortunately common for controlled radical polymerizations), and whether final molecular weight depends on the ratio of monomer to chain transfer agent (CTA) in the polymerization mixture.

   Find the amount of CTA (CMCD) and monomer (VND) you need to use in the chart below:

Pair #	CTA (CMCD)	Monomer (VND)
1,5,9,13	10 mg	6 mL
2,6,10,14	13 mg	6 mL
3,7,11,15	16 mg	6 mL
4,8,12,16	19 mg	6 mL

   The efficiency of your AIBN initiator is fairly low (f = 0.2-0.4, depending on reaction conditions). Based on these values, what would you predict for the final molecular weight of your group's polymer?