Chemistry/MatSci 5223W Wednesday, March 8

Assignment 15

Due: *In Lab*, Thursday, March 9/Friday, March 10

1. In Lab 5, you will be synthesizing polymers via atom-transfer radical polymerization (ATRP), 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 early 1990's, ATRP is a popular controlled radical technique, but it is not the only one. Nitroxide-mediated polymerization (NMP) and reversible addition fragmentation chain transfer (RAFT), for example, are also used to synthesize polymers with controlled molecular weights and polymer structures. The mechanistic schemes for these methods are extremely similar to that of ATRP. A recent review article compares and contrasts controlled radical polymerization techniques:

   Davis, K. A.; Matyjaszewski, K. "Statistical, Gradient, Block, and Graft Copolymers by Controlled/Living Radical Polymerizations," *Adv. Polym. Sci.* **2002**, *159*, 1-157. (Available on the web through MNCAT.)

   Show the radical activation/deactivation mechanism for an example NMP or RAFT polymerization, using chemical structures. How is this mechanism similar to that of ATRP?

2. The ATRP lab is a relatively new addition to the course, and it works well, but you will be participating in an effort to work out some of the kinks. In particular, the synthetic conditions of this lab succeed for some P(*n*BA) molecular weights, and for some P(*n*BA-*co*-S) copolymer ratios, but not for others.

   Calculate the amounts, in mL, of methyl 2-bromopropionate initiator, *n*-butyl acrylate, and styrene you will need to synthesize 10 g each of the homopolymer and copolymer listed for your pair below. You will be running your polymerizations to 100% completion. So, in the case of P(*n*BA), you will need 10 g of monomer to make 10 g of homopolymer. In the case of P(*n*BA-*co*-S) copolymer, you will need to do some calculations; remember that, for 100% completion, $F_{styrene} = f_{styrene}$.

Pair #	**MW, P(*n*BA), g/mol**	**MW, P(*n*BA-*co*-S), g/mol**	**$F_{styrene}$ in P(*n*BA-*co*-S)**
1	5,000	5,000	0.05
2	7,500	7,500	0.05
3	10,000	10,000	0.05
4	5,000	5,000	0.10
5	7,500	7,500	0.10
6	10,000	10,000	0.10
7	5,000	5,000	0.15
8	7,500	7,500	0.15
9	10,000	10,000	0.15
10	5,000	5,000	0.20
11	7,500	7,500	0.20