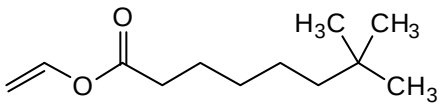
Chem/MatS/ChEn 4223W Tuesday, March 26/Thursday, March 28-
Tuesday, April 16/Thursday, April 18

Lab 5
Controlled Radical Polymerization: Reversible Addition–Fragmentation Transfer (RAFT) Polymerization of Vinyl Neodecanoate

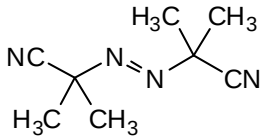
Introduction

In Lab 4, you were exposed to living polymerization—polymer synthesis in which there were no termination or transfer reactions and in which initiation was much faster than polymerization. Recently, researchers have developed a number of alternative radical polymerizations which, while not strictly living, suppress termination and transfer enough that they can be termed "controlled" radical polymerizations. Controlled free-radical polymerizations offer good control over molecular weight and polydispersity. (This is in obvious contrast to normal radical polymerizations, which are characterized by poor control over molecular weight.) In addition, controlled free-radical polymerizations retain the principal advantage of all radical polymerizations: that they are relatively insensitive to monomer functionality or reaction impurities such as water.

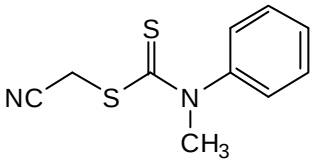
Controlled radical polymerizations (CRPs) are characterized by reversible activation and deactivation of the propagating radical site. A number of CRP methods have been developed over the last 20 years, including nitroxide-mediated polymerization (NMP), atom-transfer radical polymerization (ATRP), and reversible addition-fragmentation chain-transfer (RAFT) polymerization. All of these techniques are similar in that generate monodisperse polymers and are capable of producing block copolymers. They differ, however, in the reaction mechanism of activation and deactivation of the propagating radical species. In the case of RAFT, this is accomplished by reversible chain transfer. In this lab, you will be preparing a homopolymer and extending the chain using the RAFT polymerization technique.[1,2] The monomer (VND), free-radical initiator (AIBN), and chain transfer agent (CMCD) that you will be using are shown on the right.



vinyl neodecanoate (VND)



azobisisobutyronitrile (AIBN)



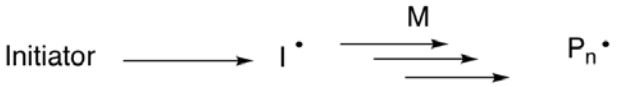
2-cyanomethyl-*N*-methyl-*N*-phenyldithiocarbamate (CMCD)

The mechanism of RAFT polymerization is essentially a modification of conventional free-radical polymerization. In RAFT, the chain transfer agent lowers the concentration of propagating free radicals (M•) and thus suppresses

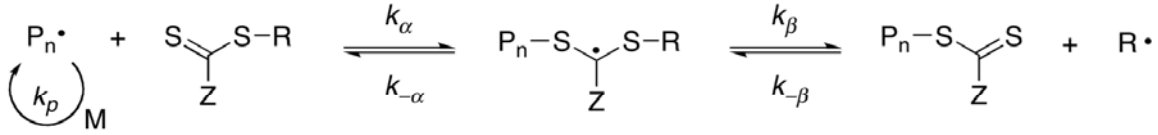
[1] Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2006**, *59*, 669
[2] Lowe, A. B.; McCormick, C. L. *Prog. Polym. Sci.* **2007**, *32*, 283

undesired, biomolecular termination reactions. This also reduces the rate of propagation (R_p), but because the rate of termination (R_t) is proportional to $[M\bullet]^2$, while R_p is only proportional to $[M\bullet]$, the effect of termination on the polymerization is decreased dramatically. Some of the most effective chain transfer agents for this task are thiocarbonyl thiols. The scheme below depicts the chemical reactions involved in a generic free-radical polymerization using a RAFT agent:

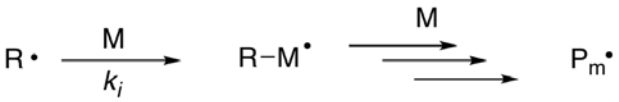
Initiation



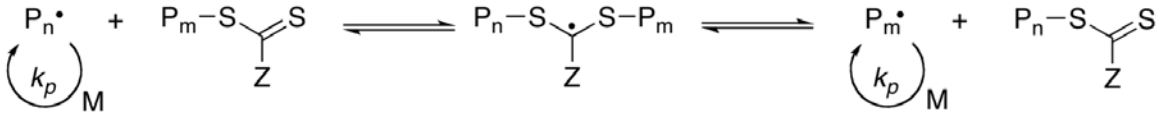
Reversible chain transfer



Reinitiation



Chain Equilibration



Termination

In this scheme, the generic R and Z groups dictate the ability of the chain transfer agent to function properly. R must be a good leaving group. Z can be chosen to activate or deactivate the thiocarbonyl double bond and thus modify the stability of the intermediate radical species.

In this experiment, we will be investigating the ability of CMCD in exhibiting efficient chain transfer and producing polymers with controlled molecular weights. If the chain transfer agent participates effectively in the process, and the concentration of chain transfer agent is significantly larger than the initiator concentration, then the molecular weight can be predicted by equation 1,

(1) $$M_{n,th} = \frac{M_{MW}[M]_0 p}{[CTA]_0 + 2f[I]_0\left(1-e^{-k_d t}\right)} + CTA_{MW}$$

where M_{MW} is the molecular weight of the monomer, p is the degree of conversion, and CTA_{MW} is the molecular weight of the chain transfer agent. The right hand side of the denominator arises from the influence of the free radical initiator on the molecular weight based on the number of chains that are initiated by this species, where f is the initiating efficiency and k_d is the decomposition rate constant (both introduced in Lab 1). The contribution from the initiator will be considered negligible compared to the chain transfer agent, and so equation 1 can be simplified. (What is the simplified equation?).

A living polymerization, as we have seen before, is one in which termination and irreversible chain transfer reactions are absent. Although CRPs are not technically living (because termination reactions are suppressed, but not eliminated), they often exhibit trends that are typical of traditional living polymerization mechanisms like anionic polymerization. One criterion that is shared between living and controlled radical polymerizations is that the rate of the reaction should be first order in monomer concentration. In this lab, we will test this criterion experimentally. You will experimentally determine the extent of reaction at various times to determine if the polymerization is first order in monomer concentration, according to the polymerization rate equation:

(2) $$[M] = [M]_0 e^{-k_p [I]_0 t}$$

You will be measuring the extent of reaction at various time intervals, and construct a plot that will allow you to extract an apparent rate constant for polymerization, k_p.[3] The extent of reaction will be measured using size-exclusion chromatography (SEC). In the case of RAFT polymerization, we are assuming the "initiator" concentration is equal to the concentration of CTA (CMCD) in equations 1 and 2.

Experimental

Polymerization of VND using CMCD chain transfer agent (Mar 26/28)

The goal of this experiment is to prepare PVND with varying amounts of chain transfer agent, and to analyze the living nature of the polymerization by sampling the polymerization mixture at various times.

- Get a 20 mL scintillation vial from the drying oven. Add a small stirbar, and the amount of vinyl neodecanoate assigned to your group in Assignment 14. Then add the amount of

[3] For a more detailed discussion, including examples of methods for implementing the fit, see (a) Odian, G. *Principles of Polymerization*, pp. 313–322 and (b) Hiemenz, P. C. and Lodge, T. P., *Polymer Chemistry*, pp. 118–126.

CMCD you were assigned, and 3.5 mg AIBN. Stir the mixture until the initiator dissolves.

- Purge the reaction mixture with a N_2 balloon for 10 min. Make sure that the needle is submerged in the solution throughout the purging process, in order to sparge away dissolved gases. Place a rubber septum on top of the vial, and seal it by stretching the septum over the vial. Purge the air inside the vial by inserting another N_2 balloon and an exhaust needle into the septum. After a few minutes, remove the exhaust needle, such that the vial is under a slight positive pressure of N_2.

- Place your vial in one of the heat blocks, pre-set to 70 °C. Check to make sure that your reaction solution is homogeneous. This will be time zero for the polymerization.

- Allow the polymerization to proceed for 15 min. At this time, use a clean syringe and provided needle, or a clean disposable pipette (whichever the TA says to use), to remove 1 mL of the reaction mixture Add this solution to a **pre-weighed**, marked aluminum pan that is sitting on ice. Record the mass of the pan and solution. Repeat this procedure every 15 minutes until you have 4 aliquots.

- Carefully place your uncovered pans in the hood to allow the unreacted monomer to evaporate. The TAs will place them in the vacuum oven later.

Percent conversion calculation and SEC analysis of PVND (Apr 2/4)

- Weigh your dried pans, which should now contain only polymer. Calculate the percent conversion for each pan.

Percent conversion calculation and SEC analysis of PVND (Apr 2/4 - Apr 16/18)

- From each of the aliquots that you isolated from the polymerization of VND at different times, place 3-5 mg of polymer material in a scintillation vial. Follow the instructions from Lab 3 for performing GPC on your aliquotted polymer product. As in Lab 4, your materials should be relatively monodisperse, and you can get away with a more dilute sample than in Lab 3. Use the spreadsheet/software you developed in Lab 3 to analyze your data.

There is no Lab Report due for this Lab. Instead, you will analyze your results in Assignment 16 (due *By Lecture*, Monday, April 22).