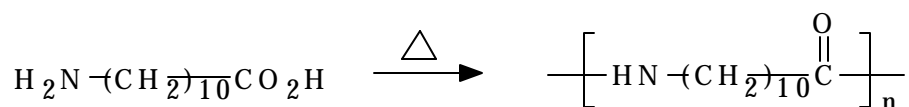


BULK STEP-GROWTH POLYMERIZATION, END-GROUP ANALYSIS, AND KINETICS

INTRODUCTION: In this experiment, Nylon 11 will be prepared by bulk polymerization, i.e., by thermal polymerization of the neat monomer, ω -aminoundecanoic acid. This is an A-B monomer, thus, exact stoichiometry of the reactants in this step-growth polymerization is assured.



Four polymerizations will be run for various times affording polymer samples with differing molecular weights. Since the DP of these samples is relatively low and each polymer molecule contains a suitable terminal end-group, the average molecular weight of the samples can be determined by end-group analysis.

A convenient method for end-group analysis is titration, but this technique is not widely applicable. The main problem is finding a solvent for the polymer that is also suitable for the titration. However, an appropriate solvent system is available for Nylon: Titration can be performed with HCl using phenol as the solvent and thymol blue as indicator. Since the sample weight and moles of end-groups is known for each titrated sample, the molecular weight can be calculated as follows:

$$M_n = \frac{\text{weight of sample titrated}}{\text{moles of acid needed to reach end-point}} \\ \text{(= number of chains)}$$

The DP for each of the polymer samples can be obtained from M_n . An A-B polymerization follows second-order kinetics and, if perfect stoichiometry is assumed, the following relation holds:

$$\text{DP} = k C_0 t + 1 \quad \text{where } C_0 = \text{the initial concentration of the monomer and } t = \text{time}$$

The second-order rate constant for the polymerization, k , can be determined from the slope of a plot of DP vs $C_0 t$. NOTE: C_0 , the initial concentration, is obtained by dividing the density of the monomer (assume that the density is 1.0 g/mL) by the monomer molecular weight.

FIRST LAB PERIOD: Four polymer samples will be prepared. All of the polymerization vessels must be introduced into a 220°C bath simultaneously and maintained under a flowing nitrogen atmosphere to help remove the by-product, water. The initial time is taken as the time at which the monomer in all of the vessels has melted. The polymerizations are stopped at 15 min intervals affording four samples with different molecular weights.

1. Set-up a high-temperature silicone-oil bath. Be sure to handle the bath with two hands since the walls are quite weak and can break easily. The bath is equipped with a nichrome heating wire connected to a variable transformer. The bath should be magnetically stirred to ensure uniform heating. The Variac is adjusted so that the temperature of the bath is 220°C. Rapid heating to a temperature near 200°C is advised with small adjustments then made to attain a constant temperature of 220°C. This can be time-consuming so it should be started as early in the lab period as possible.

2. Place approximately three grams of ω -aminoundecanoic acid in each of four large (200 cm) test tubes. Cap each test tube with a 24/40 serum stopper. Insert a 10 inch copper tube (3/8 inch OD) that is connected to a nitrogen gas supply (gas not flowing!) into the serum stopper so that it will fit about halfway into the tube ("Y's" may be necessary so that two long tubes can be connected from each nitrogen source). A short needle also should be inserted into the stopper. Slowly turn on the nitrogen gas supply and purge the test tubes for about two minutes - use care to avoid blowing the monomer about.

3. Lower the four test tubes into the 220°C bath at the same time. Once the monomer has melted in each tube, note the time and then slide the long copper tube through the serum stopper so that it is just below the level of the molten monomer. This is important since the nitrogen slowly bubbling through the monomer will provide mixing.

4. At times of 15, 30, 45, and 60 min, remove one of the tubes from the bath. Disconnect the nitrogen supply from the reaction tube by removing the serum stopper (if a "Y" has been used on the gas line, be sure to pinch off this side of the tubing so that flow on the other side is not diminished). Cool the test tube under running tap water while rotating it so that the polymer forms a thin film on the sides of the tube (the high viscosity of the later samples may make this difficult). Be sure to cool all tubes under tap water for at least five minutes so that the plug of polymer is completely cool.

5. Wrap the tube in cloth or paper towels and carefully break it with a hammer. Isolate the polymer from the glass fragments and break the polymer into the smallest pieces possible. A hammer and/or mortar and pestle are helpful for breaking the polymer plug into pieces. Label each sample and save it for the next lab period.

SECOND LAB PERIOD: In order to titrate the samples that were prepared in the previous lab period, they first must be dissolved in an appropriate solvent. The solvent for these Nylon samples will be phenol. This is a good solvent for the polymer but phenol readily oxidizes in air and discolors making it virtually impossible to detect the endpoint during the titration. To avoid this problem, use a fresh, unopened bottle of phenol or distill the phenol prior to use. Also, since the phenol must be heated to dissolve the polymer samples, be sure to do this under a nitrogen atmosphere. The titration does not have to be performed under nitrogen since the phenol is then at room temperature. However, it is necessary to dissolve the samples and do the titration during the same lab period.

1. Place 35 g of phenol and 15 g (19 mL) of methanol into each of five 19/22 100 mL round bottom flasks.
2. Equip one of the flasks with a stir bar, condenser, and nitrogen inlet. It may be necessary to gently warm the flask in order to melt the phenol. Add 1.5-2 g (accurately weighed) of the first polymer sample (ground-up) to the solution in the flask. Purge the flask with nitrogen and then maintain it under a positive pressure of nitrogen. Heat the mixture at the reflux temperature until the polymer is completely dissolved. Remove the heat and allow the flask to cool to room temperature. It may be helpful to have a second condenser available so that the second sample can be prepared while the first is cooling.
3. While the first sample is dissolving, fill a 10 mL microburet (0.01 mL graduations) with standardized 0.1 N HCl. Preparing a standard for detecting the end-point: Dissolve about 100 mg (accurately weighed) of the monomer in one of the flasks containing phenol and methanol. Add 4 drops of thymol blue indicator to the flask. Knowing the molecular weight of the monomer, the milligrams of monomer that were added to the flask, and the normality of the acid, calculate the expected amount of titrant that will be needed to reach the end-point (assume a 1:1 stoichiometry, that is, one molecule of monomer or polymer for each molecule of HCl). Then titrate to a pink end-point. Use this end-point for comparison when the polymer samples are analyzed.
4. To titrate the polymer samples, add 4 drops of thymol blue indicator to the flask and titrate with 0.1 N HCl to a pink end-point. Add the HCl slowly to the polymer samples, since the concentration of end-groups may be quite low and the end-point can be easily missed.
5. Repeat step 4 for each of the polymer samples.
6. Calculate M_n (g/mole) and DP for each of the polymer samples. Obtain the second-order rate constant from the slope of a plot of DP vs C_0t .