

**WARNING NOTICE:** The experiments described in these materials are potentially hazardous and require a high level of safety training, special facilities and equipment, and supervision by appropriate individuals. You bear the sole responsibility, liability, and risk for the implementation of such safety procedures and measures. MIT shall have no responsibility, liability, or risk for the content or implementation of any material presented. [Legal Notice](#)



3.034 FALL 2005  
ORGANIC AND BIOMATERIALS CHEMISTRY

# LABORATORY EXPERIMENT 2

## Interfacial Polymerization

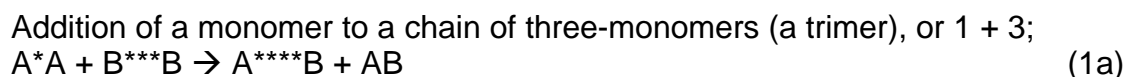
PreLab Questions:

1. In Nylon 8,6, what do the numbers 8 and 6 specifically refer to?
2. Describe step growth. How many ways can a 7 unit polymer form by step growth using only two monomers in only one step?

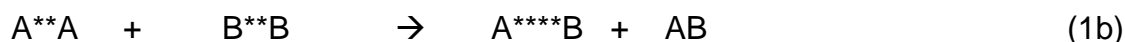
## I. Introduction

Step growth polymerization is one of the main types of polymerization reactions in synthetic polymer chemistry. Initially, monomers combine to form oligomers and polymer chains are formed by the stepwise combination of monomers, oligomers or other polymer chains. During this reaction, a byproduct may be formed. If the byproduct of the step growth reaction is a small molecule such as water or HCl, the step growth reaction is termed polycondensation.

An illustration of stepwise growth is given here for a four-unit polymer, where each \* is a monomer and A and B are the functional groups at the end of the monomer \*. This polymer \*\*\*\* could be formed in one of two ways:



Addition of two chains of two-monomers (dimers) to each other, or 2 + 2.



Similarly, there are two ways to directly form a five-unit polymer from only two monomers and three ways to form a six-unit polymer...

Nylon is an example of a polyamide, which is a polymer where monomers are connected by amide groups (  $-C(=O)-NH-$  ). At high concentrations of the monomer, the reaction will proceed via polycondensation of diacid or diamine monomers. Diacid (or diamine) condensation creates  $(n - 1)$  moles of  $H_2O$  as a byproduct for every  $n$  moles of monomer incorporated into a chain. Such a reaction is near equilibrium at moderate temperatures ( $K_{eq} \sim 1 - 10$ ), which means there is little driving force to form the polymer at these temperatures. Thus, high temperatures and efficient removal of water byproduct are required to drive the reaction to generate the amide product.

Diacid chloride condensation is an alternative synthesis route, and is also an example of nucleophilic acyl substitution. Here, the  $(-COOH)$  acid group is replaced with a more reactive acyl derivative  $(-C(=O)-Cl)$  to combine with the amine group (nucleophile). In this case, the equilibrium constant  $K_{eq}$  is  $\sim 100 - 1000$  and results in creation of  $(n - 1)$  moles of HCl as a byproduct for every  $n$  moles of reacted monomer. The HCl byproduct can be neutralized in the presence of a weak base in the reaction solvent. This is a rapid reaction (fast, irreversible and exothermic) that is consequently difficult to control. To achieve polymerization with high molecular weight, the concentration of reactants must be low, the temperature must be controlled typically below room temperature, and the solvent must be a good solvent for both the monomers and the polymer product.

Since both of these polycondensation reactions have disadvantages in terms of efficient polymerization, an important alternative is interfacial polymerization. Here, the rapid kinetics of the reaction between diamines and diacid chlorides occurs at the interface of two immiscible phases. In unstirred interfacial polymerization, one monomer A is dissolved in an organic phase and the other monomer B is dissolved in an inorganic phase. An interface forms between the two immiscible (non-mixing) phases. The

polymer is formed as a membrane at the interface, and pulled through the topmost phase by continuous mechanical removal to produce a rope. (In stirred interfacial polymerization, A-rich phase is dispersed as tiny droplets in B-rich phase through high-speed mechanical mixing. This approach is used to create hollow microcapsules and fully dense microspheres for applications such as drug delivery.)

In this laboratory experiment, you will conduct unstirred interfacial polymerization reactions to produce nylon, and will analyze the thermal properties of your nylon products. You will form three types of nylon: Nylon 8,6 8,8 and 8,10. The first number refers to the number of carbons in the amine group-containing monomer of the nylon and the second refers to the number of carbons in the diacid chloride or acyl derivative group-containing monomer of the nylon. The nylons 8,6 8,8, and 8,10 are formed by the reaction of 1,8 diamino octane (DAO) with diacid chlorides (adipoyl chloride(C=6), suberoyl chloride(C=8), and sebacoyl dichloride(C=10)), respectively.

The polymer forms at the interface between a layer of DAO dissolved in water – the aqueous phase – and a layer of diacid chloride dissolved in dichloromethane (DCM) – the organic phase. The aqueous phase contains a weak base, sodium carbonate, to neutralize the HCl and maintain the efficiency of the reaction:



The organic phase is denser than water, and thus forms the lower phase. After pouring the aqueous phase on top, the interfacial polymerization immediately forms a thin film of nylon at the interface. This film prevents or at least slows further reaction by acting as a physical barrier to monomer mixing. By pulling the film up out of the interface, new interface is exposed and the new film forms continuously at the fresh interface. The stoichiometry of the interface is controlled by the mass transfer-controlled rate of diffusion (in the organic phase) and consumption of the monomer species. That is, the ratio of A to B is 1:1 in this diffusion-controlled reaction.

## II. Objectives

The goals of this laboratory experiment are to:

- Synthesize “ropes” of Nylon 8,6 8,8 and 8,10 through unstirred interfacial polymerization
- Measure thermal properties of the synthesized polymers through differential scanning calorimetry (DSC)
- Synthesize supported membranes of nylon 8,6, 8,8 and 8,10
- Test wettability and permeability of synthesized polymer on supported membranes