

Experiment 6: Interfacial polymerization of Nylon 6,10

Aim: (a) To synthesize unsupported membranes of Nylon 6,10 by unstirred interfacial step polymerization of hexamethylene diamine (HMDA) and sebacoyl chloride. To observe the quality of the nylon film produced as a function of the rate of removal and of the concentrations of diamine and diacid chloride in their respective phases.

(b) To study the tensile properties of the synthesized collapsed film and compare it to the tensile properties of Nylon tire cord.

(c) To synthesize supported membranes of Nylon 6,10 on hydrophilic Millipore membranes.

Materials and Apparatus:

Sebacoyl chloride (tested for degradation)

Dichloromethane

Hexamethylene diamine

Na_2CO_3 in water

Methanol/Ethanol

Yellow food dye

Nylon undrawn tire cord

Spatula

Forceps

Vessel (1-2 l)

String

Beakers 250 ml (narrow diameter preferred)

25 mm 0.45 microns Millipore membrane

Petri dishes

Variable speed lab mixer (check for stability of rotation rate at slow speeds before using. Use Variacs if necessary)

Stopwatch

Dial micrometer (0.001 ")

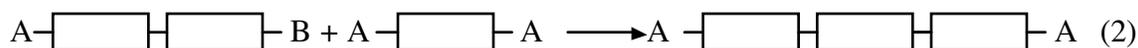
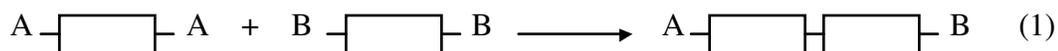
Weighing machine

Hand held force gauge (max. load of 1000g or 2.5 lbs)

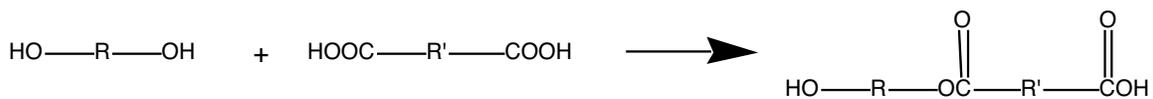
Brief Background:

Step polymerization: (see handouts from Rempp & Merrill, *Polymer Synthesis*, pp35-40 and 50-57.)

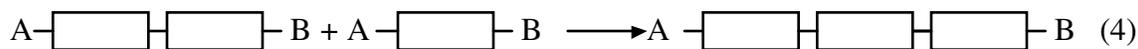
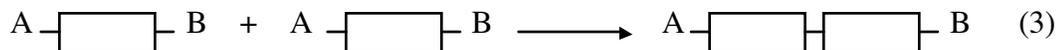
As we noted before, the two main types of polymerization are chain and step polymerization. In chain polymerization, only the monomer can attach to the growing chain. However, in step polymerization the chain can grow by addition of monomers, oligomers and other polymer chains. For example, a chain consisting of four units could be formed by two routes - a) the addition of a monomer to a trimer (chain with three units) or b) the reaction of two dimers (chain with two units). Note that in chain polymerization only the first route would occur. Step polymerization involves the reaction of bifunctional monomers (i.e., the two ends of the monomer each have a reactive functional group). Often in notes and texts, the functional groups are generically written as -A and -B; these two groups react to form a new group, -C-. Some steps of the reaction are illustrated below for the case where two different monomers are involved:



For polyesters, this reaction might be:



Step polymerization can take place even if there is only one monomer but then the two functional groups on the monomer have to be different and reactive. Schematically:



For example

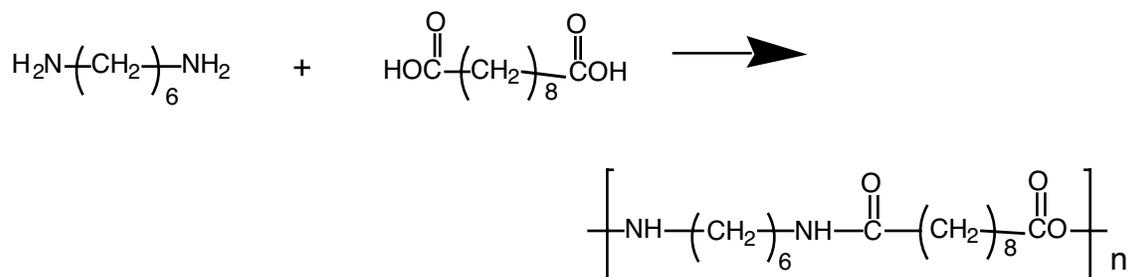


Note that a water molecule is produced as a by-product in each step. Step polymerizations where a small molecule (like water or HCl) is produced during reaction is called polycondensation.

Step Growth Polymerization – Polyamides (Nylons):

Polyamides are polymers where the monomer units are connected together by amide groups ($-\text{C}(=\text{O})-\text{NH}-$). Two generic schemes for polyamide synthesis include condensation of diacid and diamine monomers in the bulk state or at high concentrations. The first illustrated in Equation 8.

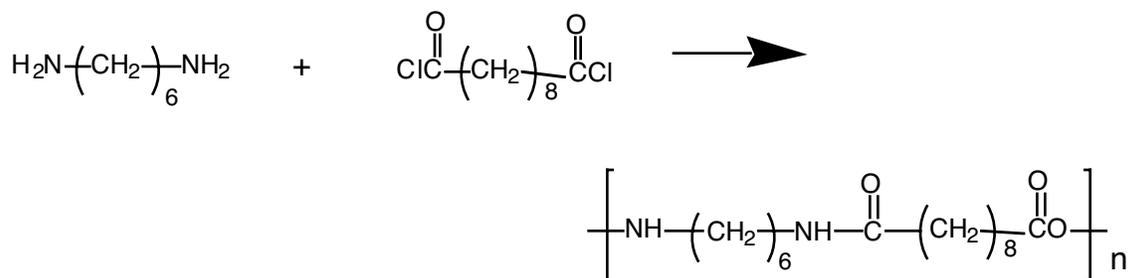
Equation (8)



The above reaction creates H_2O as a byproduct, producing $(n-1)$ moles of water for n moles of repeat units. It turns out that the reaction above is at or near equilibrium at low to moderate temperatures (K_{eq} is around one to ten in value). To drive toward the product, high temperature and very effective water byproduct removal must be achieved for high polymer conversion.

A second approach is to use the much more reactive acid chloride group in place of the acid. The reaction of diamines with diacid chlorides have equilibrium constants that are about two orders of magnitude higher than those of diamines with diacids. The reaction greatly favors the production of amide product, and the reaction kinetics is extremely fast:

Equation (9)



Here (n-1) moles of HCl is created as a byproduct. HCl can be neutralized by the presence of weak base in the reaction solvent.

This second reaction is extremely rapid, and rather difficult to control in moderate to high monomer concentrations. It is possible to accomplish a polymerization of diamine and diacid chloride in a good solvent for both monomers. On the other hand, the reaction is very fast, irreversible, and highly exothermic. The concentrations must be kept low, and the temperature must also be controlled, often below room temperature, to prevent overheating and side reactions. The solvent must be a good one not only for the monomers, but for the resulting polymer, to achieve high molecular weight.

Interfacial polymerization: (see handout from Rempp & Merrill, *Polymer Synthesis*, pp280-287).

A rapid, but more controlled approach is to take advantage of the fast kinetics of the polymerization of diamines and diacid chlorides at the interface between two immiscible phases. Interfacial polymerization involves the reaction of monomer A dissolved in an organic phase with a monomer B dissolved in an inorganic phase at the interface between the two non-miscible phases. Interfacial polymerization can be of two types. In one case, there are two separate macroscopic layers in contact with each other. This is called unstirred interfacial polymerization. This is what we are going to study in this experiment. Unstirred interfacial polymerization is used to produce membranes and to create polymer by continuous removal in a single rope. The other case is one where one phase is dispersed as tiny droplets in the other (continuous) phase by using high speed stirring. This is called stirred interfacial polymerization. Stirred interfacial polymerization is used to produce tiny

microcapsules (hollow inside) and microspheres (not hollow) for various applications like controlled release of drugs and pesticides.

Unstirred interfacial polymerization of Nylon 6,10: We shall study the reaction of 1,6 diamino hexane (HMDA) with diacid chloride (sebacoyl dichloride-SC) to form Nylon 6,10 as shown in reaction (9). The polymer will form at the interface between a layer of diamino hexane dissolved in water (aqueous phase) and a layer of diacid chloride dissolved in dichloromethane-DCM (organic phase). The aqueous phase also contains sodium bicarbonate as a getter for HCl (see reaction 10).



The denser organic phase forms the lower phase (chlorinated solvents are used, which are denser than water) while the aqueous phase will be carefully poured on top of the organic phase. Interfacial polymerization occurs instantly forming a thin film of solid nylon 6,10 at the interface. The film at the interface stops further reaction by preventing the monomers from meeting each other (actually some monomers do reach other by diffusion through the film but this is so slow that the film appears to have stopped growing). The hydrochloric acid is rapidly neutralized by the carbonate in the aqueous phase. If the nylon film is pulled up, out of the interface, new film is formed continuously. In contrast to reaction in the bulk (discussed before while discussing reaction 8), there is no need to control of the stoichiometric ratio in this experiment. The stoichiometry at the interface is controlled perfectly by the mass transfer controlled rate of diffusion and consumption of each monomer species. In other words, in this diffusion controlled situation, the monomer a to b ratio is essentially one to one. Notice that interfacial polymerization is a very nice problem to observe the interplay of core chemical engineering concepts like diffusion and reaction. Can you identify all the diffusion and reaction processes? If these processes are important, then what experimental variables are important? (

(handout in class)

Figure: A polyamide film forming at and being withdrawn from a liquid interface.

(Ref. Encyclopedia of Polym. Sci., vol 8, Wiley-Interscience, p. 223)

Fibers: Natural (eg., cotton, silk etc.) and synthetic fibers (Nylon, Rayon, Polyester etc.) are all polymers. They are visibly different in being "thread-like" -- elongated in one direction and small in cross-section. Further, they distinguish themselves from other polymers in being anisotropic in their properties, i.e., their properties along their long axis are different from that in the perpendicular direction. Fibers are usually very strong in direction of the long axis but are weaker in the perpendicular directions. Synthetic fibers are typically drawn from undrawn polymers by stretching them with a specific force.

Membranes: Membranes are films that are used to separate out a mixture of species into its constituents. Often, a membrane will contain nano to micro-scale pores, and may thus have some void space within its structure. This void space is useful for separations operations. It also has a large effect on the final mechanical properties of the material.

Tensile testing: Tensile testing is perhaps the most commonly used form of mechanical testing of polymeric materials. As shown in the figure below, a polymer sample of initial area of cross-section A_0 and length L_0 is subjected to a variable tensile (as opposed to say, compression or shear) force F such that the sample is elongated at a constant rate of dL/dt where L is the length of the sample at time t .

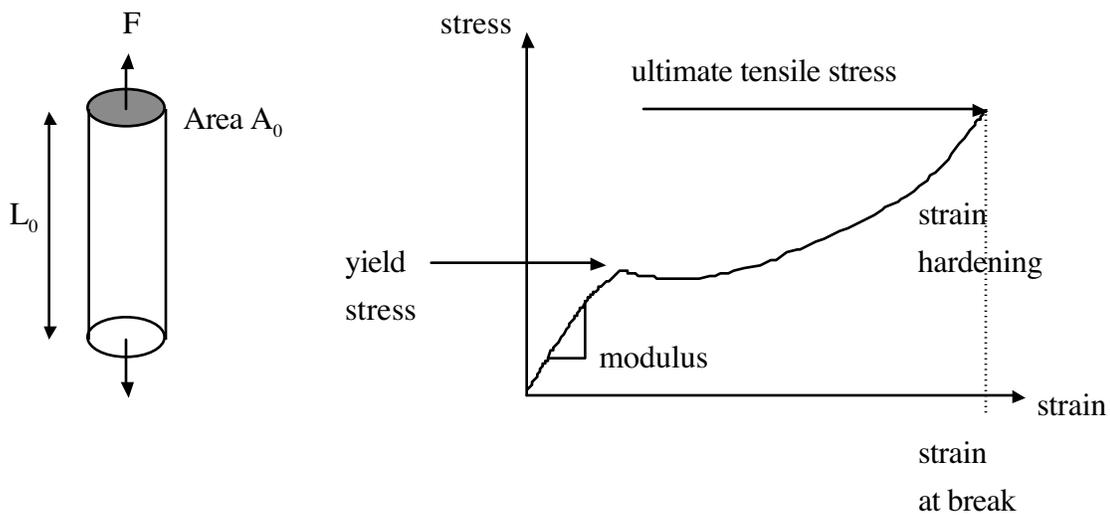


Figure: Schematic illustrating the tensile test and features on a stress-strain plot.

The force F and the length L is noted at periodic intervals. Following this the following quantities are calculated:

$$\text{Draw ratio, } \lambda = \frac{L}{L_0} \quad (11)$$

$$\text{Engineering strain, } e = \frac{L-L_0}{L_0} \quad (12)$$

$$\text{Engineering stress, } s = \frac{F}{A_0} \quad (13)$$

The plot of σ vs. ϵ is called the stress-strain plot. The stress-strain plot gives properties of the material like the elastic modulus and the yield stress which are independent of the shape and size of the test sample but depends on the rate of strain (or elongation rate). The elastic modulus is the slope of the stress-strain plot at very low strains.

Precautions:

Use vinyl gloves. Prepare the two phases and introduce the aqueous phase on top of the organic phase in the hood.

Procedure:

Recipes

Recipe Organic Phase	Aqueous phase	Groups doing it
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α	1.5ml SC + 50 ml DCM	2.20g HMDA +50 ml water +4 g Na ₂ CO ₃	A, B, C, D, E, F
β	0.75ml SC + 50 ml DCM	1.10g HMDA +50 ml water +4 g Na ₂ CO ₃	A, C, E
γ	3.0ml SC + 50 ml DCM	4.40g HMDA +50 ml water +4 g Na ₂ CO ₃	B, D, F

A. Synthesis of unsupported membranes of Nylon 6,10:

1. First, set the variable speed shaft (a lab mixer shaft) to its lowest STABLE rotating speed. Estimate this RPM by measuring how much string is wound up in, say, 60 seconds, or by counting revolutions. Record this value. What you really want is the linear rate of withdrawal, cm/s, so the string test will give it directly. Otherwise it will be (RPM/60) (πD) where D = shaft diameter, cm.
2. For each of the recipes you are to do, follow the procedure below: Using a 250 ml beaker in a hood, introduce 50 ml of the organic phase. Then tip the beaker and slowly let the 50 ml of aqueous solutions slide down the glass wall over the organic phase. Restore the beaker upright.
3. Remove from hood and set under the lab-mixer shaft (the shaft held horizontally). With spatula or forceps, "catch" the membrane that has formed at the interface, draw it up and out, and attached the top end to the shaft of your variable speed set. Now run the set until you have produced 3 to 4 meters of collapsed membrane (which will be wound around the shaft).
4. Unwind the collapsed membrane into a large (1 to 2 liter) vessel of water, so as to rinse away the soluble salt.
5. Separate into two portions. Leave one portion wet for tensile testing. Dry other portion in the 70°C air oven for weight measurement
6. Using the dial micrometer (calibrated in 0.001 inches), estimate the wet thickness of the film. Determine the approximate weight per meter of length of dry film.

B. Tensile test properties of the collapsed film:

1. Take a length of about 50 cm of your wet film. Make two lines 10 cm apart. Fasten one end of the length to a post, the other end to the force gauge. If the gauge reaches its limit, disconnect and pull manually until the film breaks.
2. Record the final length L_f as a ratio to the original length L_0 . This is the draw ratio. You will plot tensile force (read from the gauge) as a function of L/L_0 . Do this for two or three 50 cm lengths from each run α and β or α and γ , to establish how closely the data agree.
3. Repeat the same experiment with Nylon undrawn tire cord furnished to you from a spool. You will probably be able to take a single filament of this material and measure its tensile load vs. L/L_0 relation all the way to break. Measure the weight of a known length of the nylon cord. Using this and the literature value for the density of commercial nylon, you can determine the cross-sectional area of the cord.
4. Determine what happens when you do similar measurements on a dried film. Postulate as to the differences between the wet and dry film.

C. Synthesis of supported membranes:

1. Use the solutions of recipe α only. Use a hydrophilic Millipore 25 mm 0.45 micron membrane to absorb from a petri dish the aqueous solution. Then float this on a layer of the organic phase in another petri dish, for 10 minutes. Remove and wash by submersion in water.
2. Using a second 25 mm 0.45 micron hydrophilic membrane, let it absorb from a petri dish the organic solution. Then float this on a thin layer of the aqueous solution. After 120 minutes, remove and wash.
3. For each of the supported membranes, test for wettability: Will a water drop spread on the nylon film or not? Test the supported membranes for permeability to yellow food dye. Will the dye pass through the membranes?

Observations and Calculations:

1. Record all the experimental conditions /variables and the measurements mentioned in the lab note book.
2. Unsupported membranes:
 - a) Compare the weight per meter of length of the two recipes. Choose your method of presentation --- table or bar chart etc.?

b) Plot the stress-strain plots for the different recipes. The plot should illustrate the difference, if any, between the two recipes. Be sure to indicate the recipe used as a legend. You can estimate the elastic moduli of each recipe from the slopes of the stress-strain plots.

c) Plot stress-strain plots of Nylon tire cord and determine its elastic modulus

d) Explain the differences in b and c results. What is different between the cord filament and the nylon rope that you made?

3. Supported membranes: Tabulate the required observations. Comment on whether your nylon films supported on Millipore membranes are porous and permeable to dye, or impermeable. Considering that the membrane is hydrophilic, what do you think happened in each case.