

Nylon 6—A Simple, Safe Synthesis of a Tough Commercial Polymer

A Demonstration Experiment for High School and College Chemistry Students

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The study of polymers is increasingly a part of chemistry curricula at all education levels because of their pervasive use in industry and the consumer economy. Textiles and fibers provide some of the most obvious, everyday examples of synthetic polymers. Among commercial fiber-forming polymers, the polyamides or nylons are probably the most widely recognized because of their strength, durability, and diversity of application. Nylons are found in lingerie and windbreakers, fishing line and barge rope, and, increasingly, in high-performance items such as automobile panels and self-lubricating bearings.

The two most common polyamides (comprising over 90% of the total production of nylons) are Nylon 6 and Nylon 66. While the commercial synthesis of Nylon 66 involves the thermal dehydration of a salt made from adipic acid and 1,6-hexanediamine, the commonly used laboratory procedure employs the interfacial reaction between the diamine and adipoyl chloride. This reaction has been exceedingly popular as an effective visual demonstration of polymerization and is usually referred to as the nylon rope trick (1). Despite a recent procedure for *in situ* generation of the acid chloride (2), both the diamine and the adipoyl chloride are corrosive, irritating to the eyes and skin, and very difficult to handle and store. The low strength of the polymer obtained with the rope trick is a further drawback.

We have developed an improved procedure for the synthesis of Nylon 6 which provides an alternative that is easier, safer, and gives a product with impressive strength. Our method is based on the ring-opening polymerization of caprolactam (3). This monomer can be synthesized from cyclohexanone as an extension of the experiment (4) or purchased inexpensively and in high purity.¹ The more expensive co-initiators employed are N-acetylcaprolactam and a 60% dispersion of sodium hydride (NaH) in oil which can be handled like a solid.² These compounds are used in very small amounts. The additional reagent which allows such rapid, simple conversion in air and without special precautions is polyoxyethylene (POE), also called polyethylene oxide or polyethylene glycol. This simple polymer consists of $-\text{CH}_2\text{CH}_2\text{O}-$ repeat units and is able to form strong complexes with metal ions such as Na^+ . The only real danger in the procedure is splashing or bumping of molten monomer or polymer, and this can be readily avoided with instructor supervision and demonstration of good heating technique.

Experimental

Caprolactam (8–10 g), polyoxyethylene of molecular weight 2000–7500 daltons (0.5 g or one small spatula full), and N-acetylcaprolactam (2–5 drops) are mixed in an 18 × 150 or larger disposable test tube. Using a test tube holder and a Bunsen burner with a 1-in. flame, the mixture is melted by passing the lower middle of the test tube in and out of the flame. To the just-melted mixture is added a small amount of the gray sodium hydride (0.05 g or a 5 × 5 mm flat portion on a spatula). It is important that all of the NaH contact the mixture to ensure uniform initiation. The clear solution is now heated rapidly but *carefully* with the Bunsen burner until reflux is just starting, as evidenced by continuous but not violent bubbling. While it is very difficult to heat too rapidly unless one is deliberately careless, the students should be shown the correct procedure for heating a liquid in a test tube and cautioned that the mixture (at 200–230 °C) can cause severe burns.

After NaH addition, heating to the polymerization temperature should only take 2–4 min. Polymerization will be apparent by a rapid increase in the solution viscosity until it becomes difficult to cause flow on tilting. If polymerization occurs too soon or has not occurred after several minutes, cool to just above the melting point and reinitiate with NaH. Too much NaH will give brittle fibers and heating too slowly will allow reaction of the active species with moisture in the air. Sodium hydride itself reacts rapidly with atmospheric moisture, turning from gray to white (NaOH formation). The instructor should put out only a small amount in a resealable vial for student use and keep the main container carefully sealed.

Results and Discussion

We have supervised this polymerization with hundreds of undergraduates, high school teachers, and college instructors who had 60–70% success on their first attempt. Almost all succeeded after two tries. With a little experience in judging weights or a good demonstration of the experiment, students do not even need to weigh their reagents. The reaction is very forgiving of imbalances and has a higher chance of success the more quickly it is carried out (up to a point).

The most exciting part of the experiment involves pulling fibers from the molten polymer. Timing is important in that polymerization should be essentially complete (very slow bubbling and flow) and the molten polymer allowed to cool a little. Fibers are drawn by dipping a glass or wooden stirring rod into the melt and rapidly drawing out the solidifying material. With two students working together and one of them walking rapidly down the hallway trailing barely-visible fiber, thin strands 75–100 ft long can be obtained. These fibers will

New lectures and laboratory experiments and directions in teaching chemistry through the use of the laboratory are provided in this feature. Experiments will be fully detailed and will be field tested before they are published. Contributions should be sent to the feature editor.

¹ Aldrich Chemical Company.

² Alfa Products, Thiokol-Ventron Division.

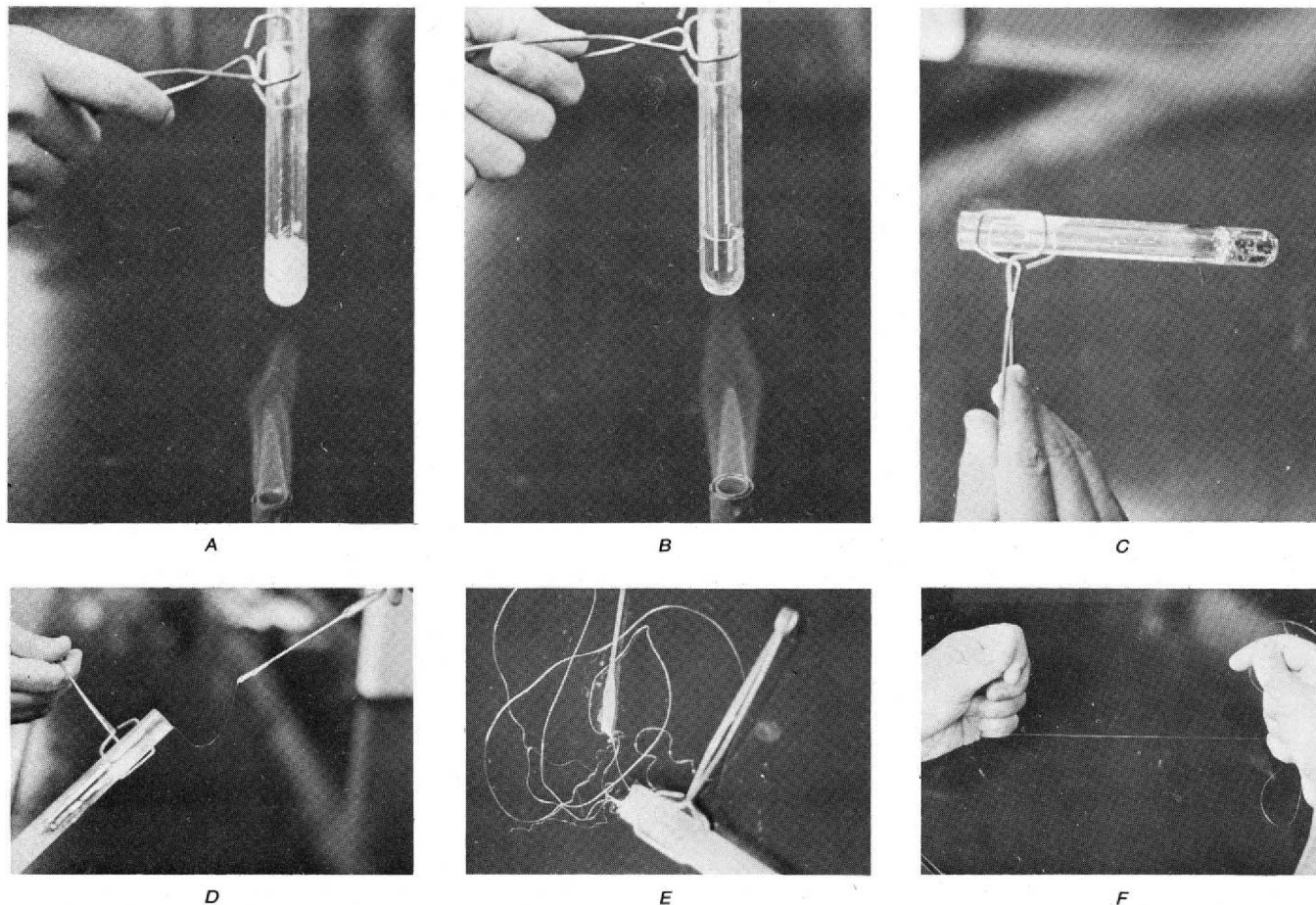


Figure 1. Steps in the polymerization process and fiber formation.

stretch under tension to complete polymer orientation and are then very tough. Thicker samples can be made by slower fiber formation and by using a cooler polymer melt. Figure 1 illustrates the polymerization process and fiber formation. Students are surprised by the similarity between their fibers and commercial nylon thread or fishing line.

The detailed mechanism involved in this polymerization has been well established (3) and is given in Figure 2. Ring-strain in the 7-membered ring provides the overall driving force for the polymerization. The normal initiation process involves the initial slow attack and ring-opening shown in Step 1. Formation of the very unstable amine anion resists the opening of the ring. Once the acylcaprolactam intermediate is formed, however, attack at the ring carbonyl and ring-opening is facile since an amide anion is now formed by this process (Step 2). Proton exchange then regenerates the caprolactam anion and the propagation step repeats. The addition of *N*-acetylcaprolactam eliminates the initial slow step and allows rapid initiation of polymerization.

Even greater rate enhancement is realized by addition of a cation complexing agent. Step 3 illustrates how the macrocyclic crown ether, 18-crown-6, complexes with the sodium cation and increases ion separation. Such behavior has been employed extensively in what is called phase-transfer catalysis (5). We have found that in Nylon 6 formation, use of the open-chain polyether POE is almost as effective and much less expensive. In fact, with the combination of reagents and coinitiators employed here, rapid polymerization occurs even in air whereas previous methods required an inert atmosphere and longer reaction times (4).

This procedure is inexpensive and requires a minimum of equipment and instructor expertise with polymers. It is reasonably safe (no student has suffered burns yet in our labs)

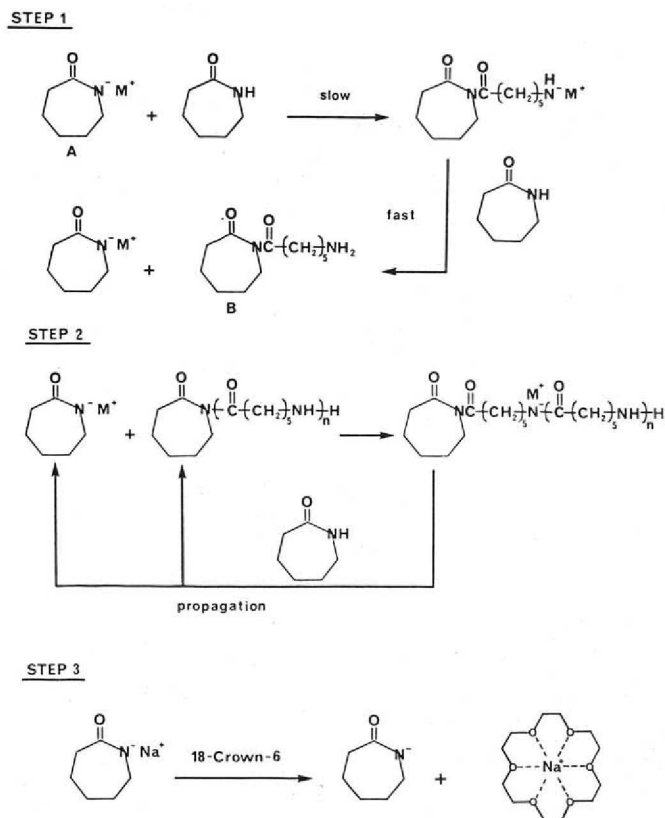


Figure 2. Mechanism of the polymerization reaction.

and simple, yet gives a fiber which is surprisingly strong. Finally, it is an effective demonstration and hands-on student experiment illustrating the enormous change in properties involved in converting a crystalline monomer to a commercially valuable polymer. Most importantly, students have fun with this experiment while learning about polymers.

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