

Exp 11B: Multistep Synthesis of Nylon-6,6 from Cyclohexene**Introduction**

This experiment involves a three-step synthesis of Nylon-6,6, which is a widely used polyamide known for its mechanical durabilities and thermal resistance. Starting with cyclohexene, the synthesis pathway leverages phase transfer catalysis and interfacial polymerization to efficiently produce Nylon-6,6, the target polymer. Day 1 of the experiment focused on the oxidation of cyclohexene to adipic acid, using sodium tungstate and Aliquat 336 to mediate the oxidation reaction. On Day 2, adipic acid formed from the previous steps was converted to adipoyl chloride using the dimethylformamide (DMF) catalyst and oxalyl chloride, then polymerized by slowly adding hexamethylenediamine under unstirred interfacial conditions to form the eventual Nylon-6,6 product. 1.255g of Nylon-6,6 in the clump form was converted, thus a 129.12% yield was attained. The longest strand of Nylon-6,6 obtained was 153.0 inches long. During a stretch test, a 9-inch long Nylon strand underwent a 22.2% elongation until it broke at a length of 11 inches.

Methods and Discussion

Step 1 - Oxidation of Cyclohexene to Adipic Acid

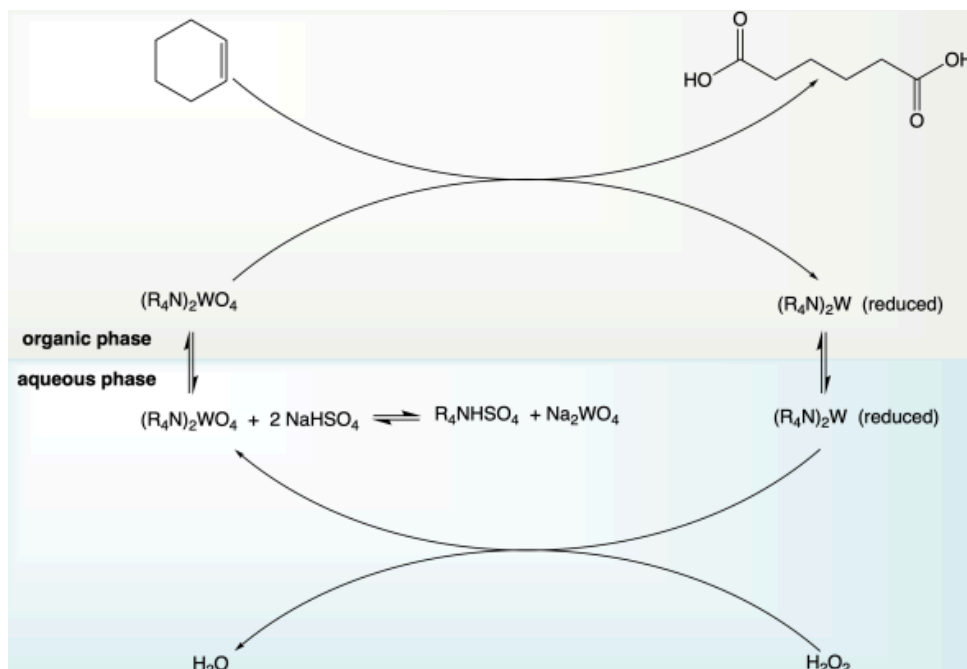


Fig 1. Mechanism of the Phase Transfer Catalyzed Oxidation of Cyclohexene

The oxidation of cyclohexene employed sodium tungstate Na_2WO_4 as the active oxidant and H_2O_2 as the terminal oxidant. However, due to that cyclohexene is only soluble in organic solvents and that tungstate is not very soluble in organic solvents, Aliquat 336 was used as a phase transfer catalyst to shuttle tungstate ions into the organic phase through complexation. Because Aliquat 336 has a dual organic-inorganic nature, the catalyst was carried and moved between the layers, improving contact between reagents and therefore increasing the rate of reaction. As a result, during this step, the tungstate first reacted with H_2O_2 and Aliquat 336 to become more soluble in the organic cyclohexene phase. In addition to this design, vigorous stirring was performed to increase the interaction between reagents. The reaction mixture was

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Chem 6BL

April 20th, 2025

heated to reflux and stirred at reflux for 60 minutes. Throughout the reflux, a total of 1-2 mL of water was used to rinse off the condensed vapors on the inside of the air condenser. Following oxidation, adipic acid was isolated by cooling the aqueous layer and inducing crystallization. The total mass of adipic acid obtained was 0.51g, and the melting point was measured to be 140-145°C, indicating a relatively high purity of the recovered product as the reported value is 152.10°C^[2]. Theoretically, with 2.00g of cyclohexene as the starting chemical reagent, 3.47g of adipic acid was to be obtained. Thus, a 1.47% yield was attained. An IR spectrum was also taken for the recovered product, as shown in Figure 2.

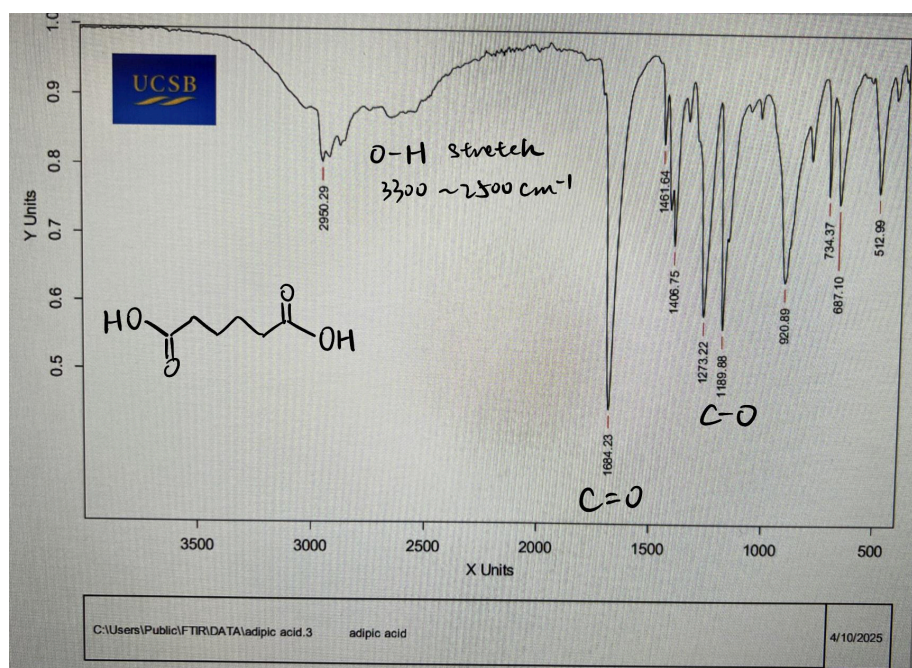


Fig 2. IR Spectrum of the Adipic Acid Product from Day 1

In Fig 2., it is shown that the O-H stretch is present from approximately 2500-3300 cm⁻¹ and a signature C=O bond is present at around 1700 cm⁻¹. With these being observed from the spectra and a melting point between 140-145°C measured for the product. A high purity of

April 20th, 2025

acidic acid was confirmed. However, since the adipic acid obtained was not sufficient in volume for the following synthesis, stock supplies of adipic acid were used to step 2 and 3.

Step 2 - Conversion to Adipoyl Chloride

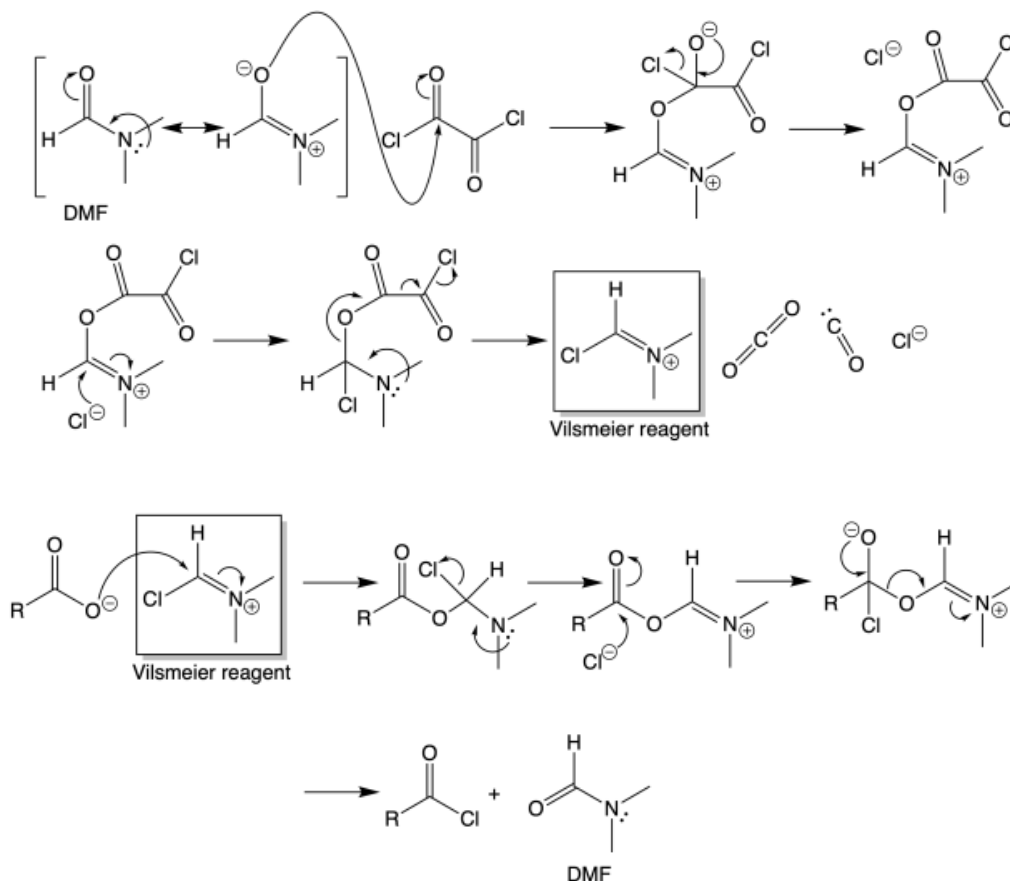


Fig 3. Arrow-pushing Mechanism of the Formation of Vilsmeier Reagent and Adipoyl Chloride

In the following step, oxalyl chloride and a catalytic amount of DMF were utilized to convert the adipic acid formed in the previous step to adipoyl chloride. As shown in Fig 3., the reacting mechanism starts with DMF reacting with oxalyl chloride to form the Vilsmeier reagent, which activates the carboxylic acid and nucleophilic acyl substitution. The reaction releases CO_2 as a byproduct, and this is validated by the CO_2 evolution observed. Then, through a series of

Kaitlyn Freiberg

Chem 6BL

April 20th, 2025

electron rearrangements after the adipic acid attacks the Vilsmeier reagent, adipoyl chloride is formed. A flamed-dried round-bottom flask, drying tube filled with CaCl_2 and 55-65°C water bath were employed to avoid hydrolysis and HCl gas evolution. The drying tube was utilized to exclude atmospheric moisture, which would hydrolyze oxalyl chloride and thus lower the yield of adipoyl chloride. No further purification was needed due to the high reactivity of adipoyl chloride in the next step. At this point, purification risks degradation, so crude product is directly used towards the next steps.

Step 3 - Interfacial Polymerization to Nylon 6,6

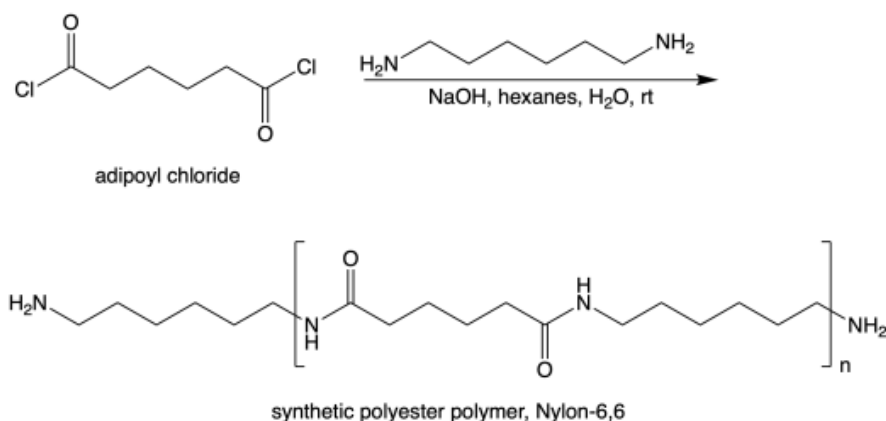


Fig 4. Production of Nylon-6,6 from Adipoyl Chloride and Hexamethylenediamine

In this final step, interfacial polymerization between hexane-dissolved adipoyl chloride and hexamethylenediamine ($\text{pH} > 7$). A basic environment must have been ensured so that amine could be deprotonated during polymerization. Notably, the adipoyl chloride was dissolved and diluted in hexane to ensure thorough and rapid polymerization. The unstirred condition, together with the way of carefully pipetting the adipoyl chloride reagent dropwise, served to preserve the interface at which the reaction takes place, and therefore minimizing phase mixings, unwanted emulsions, and incomplete polymerization. The Nylon-6,6 product was collected by pulling from the interface using a clean copper wire. After thoroughly drying the Nylon product using paper

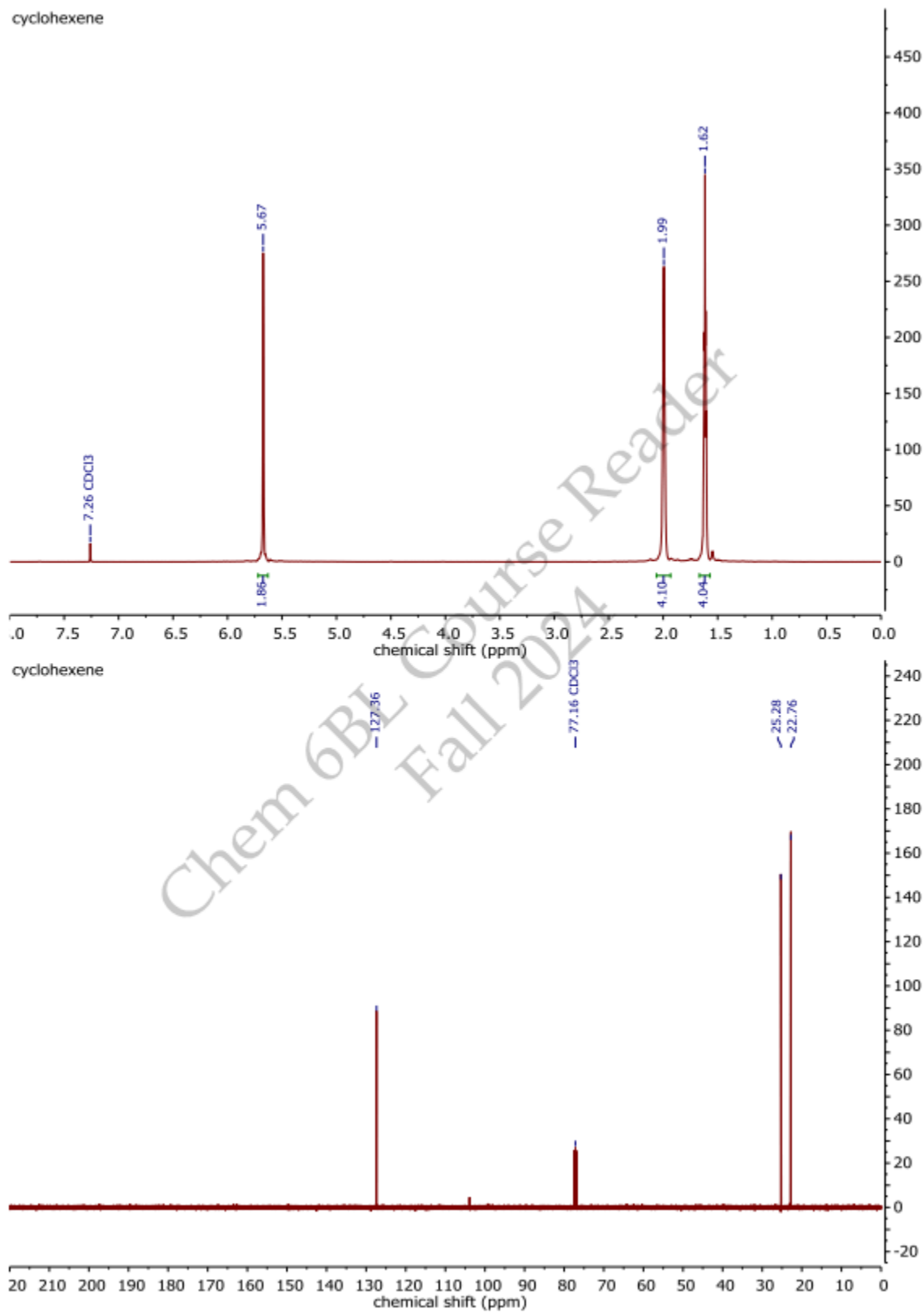
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Chem 6BL

April 20th, 2025

towels, the total mass of the Nylon-6,6 polymer obtained was measured as 1.255g, among which the longest Nylon strand pulled was 153 inches in length. A stretch test was performed on a 9-inch strand. The strand stretched to 11 inches before breaking, which is about 122.2 % of its original length. Since hexamethylenediamine is the limiting reagent and was weighted to be 4.31 mmol before the reactions, the theoretical yield of Nylon-6,6 is 0.972g. However, the actual yield is 1.255g, which leaves us with a percent yield of 129.12%. This is most likely due to the insufficient drying of the Nylon product before weighting its mass. Also, the mass was measured after performing the stretch test, so dirt and powders on the bench top would have attached to the polymer, which would cause an overestimate of the total product recovered.

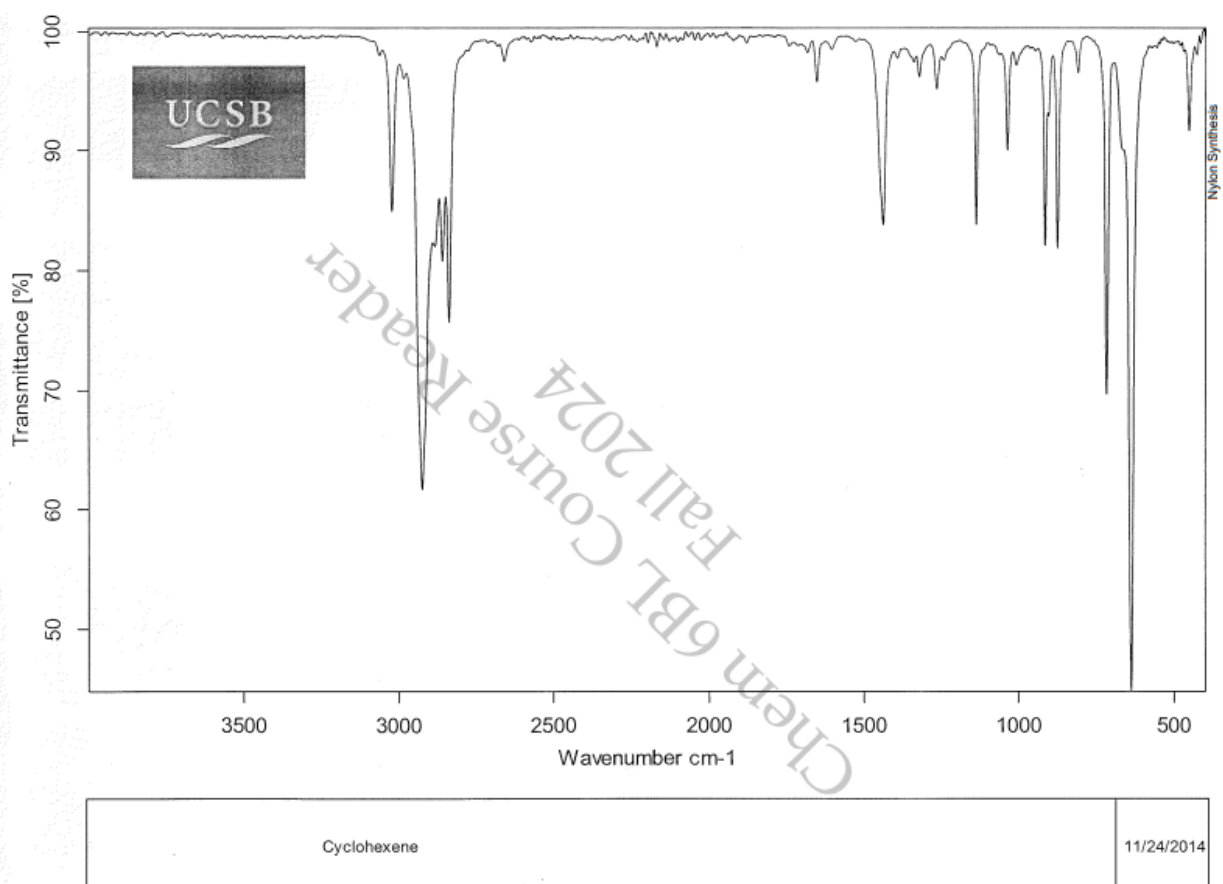
The annotated IR and NMR spectra are shown as follows.



Kaitlyn Freiberg

Chem 6BL

April 20th, 2025

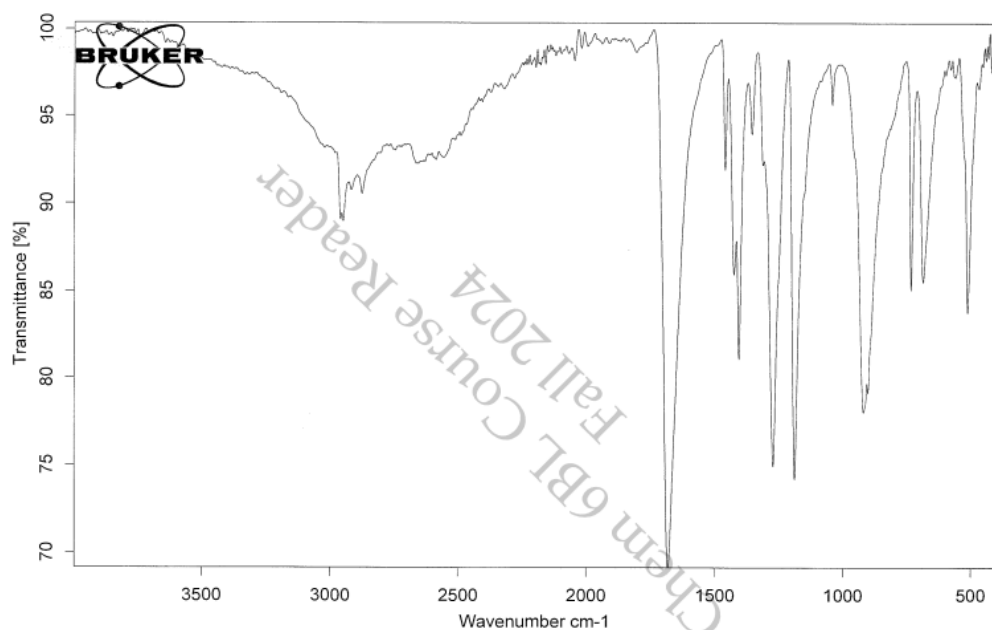
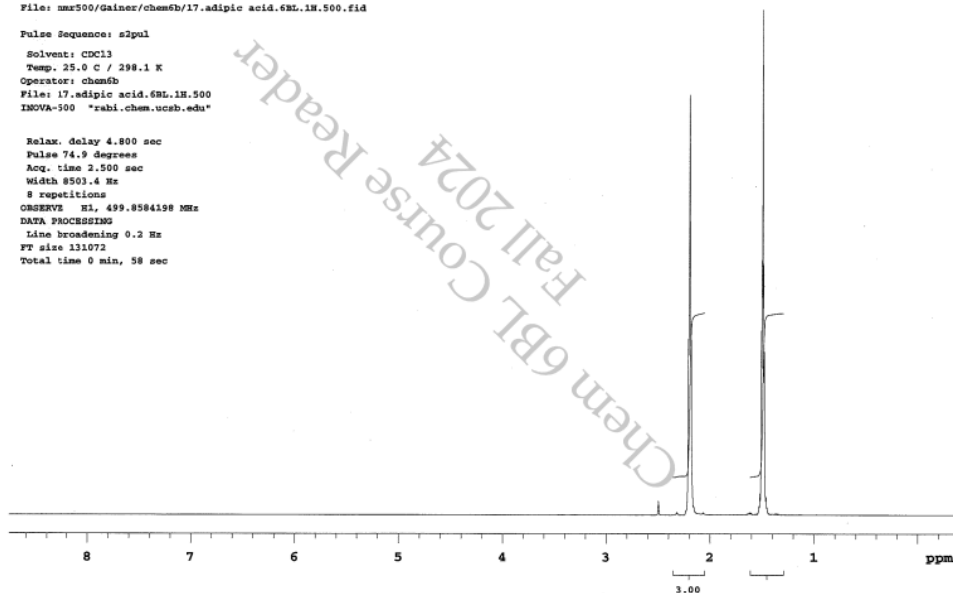


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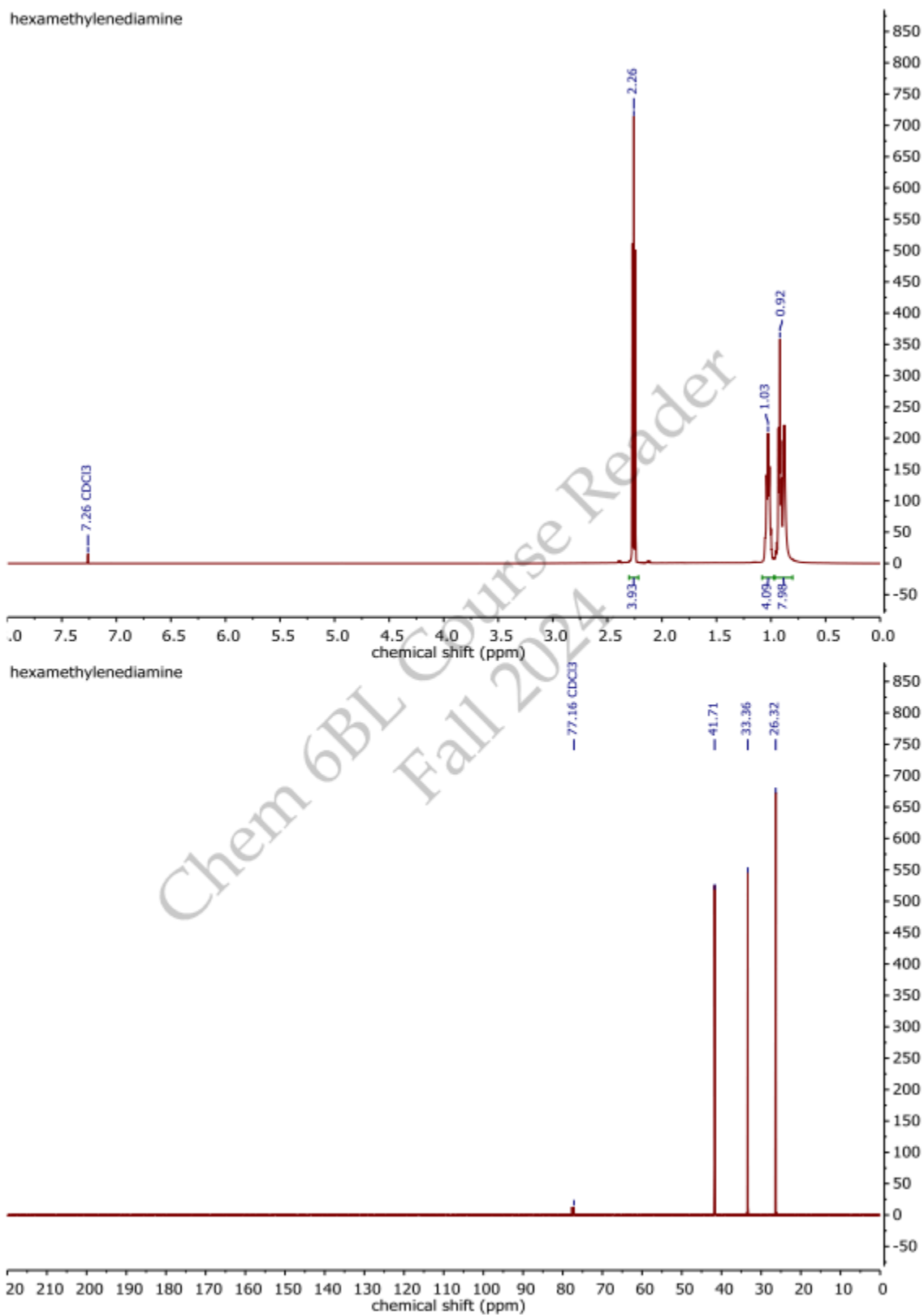
April 20th, 2025

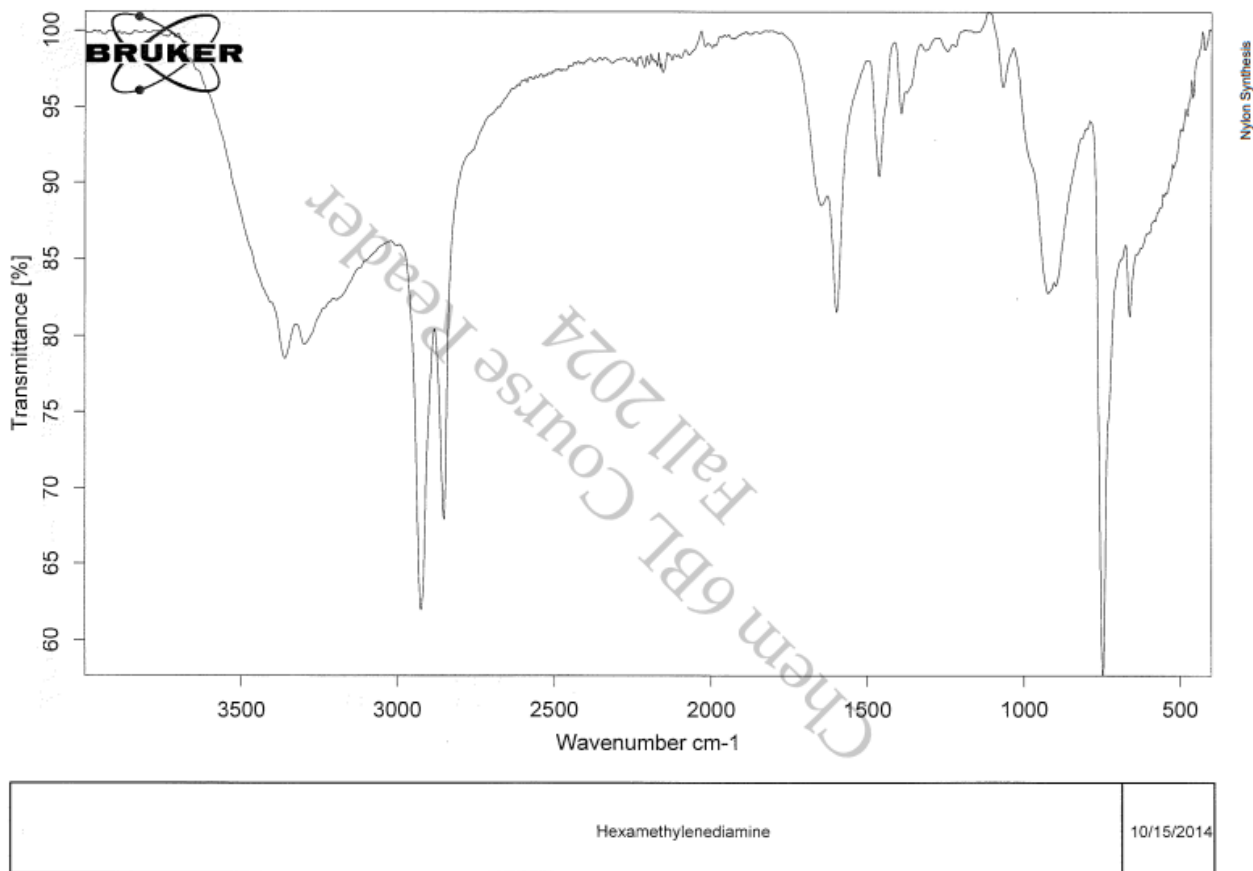
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Adipic Acid

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Conclusion

The experiment successfully demonstrated the way of synthesizing Nylon-6,6 using a three-step pathway starting with cyclohexene. Potential sources of error include ineffective cooling during the crystallization causing a lower yield of adipic acid, ineffective polymer pulling technique causing the loss of products, and insufficient drying which might cause an overestimate of the total mass of the Nylon product obtained.

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Chem 6BL

April 20th, 2025

Reference

1. Catalyst Education, LLC. *Multistep Synthesis of Nylon-6,6 from Cyclohexene*; Laboratory Manual prepared for the Department of Chemistry, University of California at Santa Barbara, 2025.
2. National Center for Biotechnology Information. PubChem Compound Summary for CID 196, Adipic Acid. *PubChem*. <https://pubchem.ncbi.nlm.nih.gov/compound/Adipic-Acid> (accessed April 20, 2025).
3. Sigma-Aldrich. IR Spectrum Table & Chart. *Sigma-Aldrich Technical Article*. <https://www.sigmaaldrich.com/US/en/technical-documents/technical-article/analytical-chemistry/photometry-and-reflectometry/ir-spectrum-table> (accessed April 20, 2025).