Synthesis of Laboratory Nylon: A Scale-Up Method for High Molecular Weight Polyamides

Peter M. Meyer, Michael Forrester, and Eric W. Cochran*

Department of Chemical & Biological Engineering, Iowa State University, Ames, Iowa 50011, United States

E-mail: ecochran@iastate.edu

Abstract

Here we report a benchtop scale two-stage polyamidation process for the synthesis of diacid/diamine (AA-BB) type polyamides (PAs) in quantities sufficient (30g+) to obtain ASTM dogbones, IZOD bars, and rheology specimens with molecular weights ranging from 15 to 35 kDa and minimal to no discoloration. In spite of the extensive body of research in recent years reporting biobased AA-BB type PAs, the scale and molecular weights reported by many researchers are often inadequate for meaningful comparisons with industrial resins. Commercially produced PAs often use an initially high-pressure, moderate-temperature oligomerization reaction to prevent the decarboxylation of the diacid and the evaporation of diamine. Subsequently, a second stage employs a higher temperature at reduced pressure and inert sweep gas for molecular weight enrichment without significant oxidative degradation. We have adapted this process for use with standard laboratory hardware, with several simple modifications to ensure uniform heat and mass transfer. The resulting PAs exhibit mechanical properties on par with industrially-sourced controls, demonstrating the effectiveness of our approach in bridging the gap between academic and industrial PAs. This eliminates one of the major roadblocks associated with developing new industrially relevant polyamides and should be broadly useful for researchers struggling with the challenges of polyamidation.

Introduction

The inception of polyamides was a transformative moment in history, credited to the pioneering work of Wallace Carothers and his team at DuPont in the early 20th century.[1] Initially challenged by the complex nature of polymerization reactions, Carothers' breakthrough in synthesizing the first polyamide marked a seminal moment in material science. This achievement came with significant challenges; Carothers tragically ended his own life shortly after the project.[2] This foreboding warning notwithstanding, DuPont proceeded to translate his seminal work to the industrial scale, creating a working nylon melt spinner just before the start of WWII. The commercialization was also fraught with difficulties. Indeed, visitors to the first nylon melt-spinner were told to only view the spinner sideways, as a head-on look was feared to cause the process to fail. Despite numerous technical and engineering hurdles, Carothers' success in commercializing polyamide 6,6 (PA 6,6), branded with the trade name Nylon, catalyzed the development of polyamides as a class of high-quality engineering thermoplastics and paved the way for other polycondensation polymers to be produced commercially. The properties of nylon, such as high mechanical strength, toughness, and resistance to both heat and solvents, spurred widespread adoption in countless applications,[3–6] from initial silk-replacement textiles to more complex uses in automotive, biomedical,[7,8] and textile industries. Nylon 6,6 is now found in everything from carpets to cars to toothbrushes. Its long history of successful commercial deployment belies the ongoing obstacles researchers face in mimicking Carothers' work. The same difficulties he encountered continue to frustrate researchers and stymie fruitful projects.

Contemporary PA manufacturing predominantly focuses on a select few resins, such as polyamide 6 (PA 6) and PA 6,6. These specific PAs are favored in large-scale manufacturing due to their reproducible and known synthesis protocols leading to high-volume production.[9–11] The industrial polymerization of PA 6,6 is achieved through a controlled polycondensation reaction between adipic acid and hexamethylenediamine (HMDA) initially conducted under elevated temperature and pressure to form oligomers and suppress unwanted side reactions, thus maintaining yield and stoichiometry. The oligomers are then enriched to useful molecular weights at elevated temperature with inert gas sweep, optionally at reduced pressure. Industrial settings typically use bespoke batch or continuous reactors featuring specialty designs engineered to address monomer volatility, high melt viscosity, uniform heat and mass transfer, and thermal degradation. These issues, solved in industrial settings, are prevalent in the reactors typically found in research laboratories.[12,13] The challenges of synthesizing AA-BB type polyamides have directed research towards AB type nylons like PA 6, which incorporates all functional groups within a single monomer and features lower melt temperature and viscosity, making it easier to synthesize.[14–18] AB type monomers, such as the ϵ-caprolactam used in PA 6 synthesis, enable a straightforward ring-opening polymerization (ROP) easily scalable to research-grade reactors.[16] The inherent stoichiometry of lactams eliminates the need to create a “nylon salt” for stoichiometric control, and largely removes decarboxylation and evaporation concerns. In contrast, synthesizing AA-BB type nylons from salt involves complex condensation reactions, requiring precise stoichiometric balance and water removal, posing significant engineering challenges. These factors make AB type polyamides the preferred choice for both large-scale commercial production and research-scale synthesis. Indeed, recent data on global polyamide production underscore the industrial preference for AB type polyamides, which account for a significant majority of the market. This trend is driven both by the processing advantages and the established supply chains and polymerization infrastructures favoring AB monomers.[19] Despite this, there is still a high demand for novel AA-BB type polyamides, as they are one of the highest performing engineering thermoplastics.

With perhaps the exception of well-funded research groups that focus exclusively on polyamides, the cost of laboratory scale custom reactors prohibits direct mimicry of industrial methods in the laboratory setting, creating a need for practical laboratory-scale solutions. Researchers have solved this issue in a number of ways, including interfacial polymerization (IFP),[20–22] chemical and enzymatic catalyst polymerization,[23–28] and solid state polymerization (SSP).[29–32] IFP is achieved by suspending the two monomers, including the more reactive acid halide form of the diacid, in phase-separated monomers or solutions/emulsions thereof. At the monomer-monomer interface, the monomers can readily assemble into polymer strands, *i.e.*, the famous "nylon rope trick" of many high school and undergraduate chemistry demonstrations. This technique offers some advantages over melt-state polymerization by circumventing the common issues, primarily heat control and stoichiometry. The primary disadvantage of IFP is the economic challenge of scaling the process to industrial levels and the difficulty in achieving acceptable molecular weight development. While a neat trick at laboratory scale, producing novel polyamides industrially with this inefficient method is cost prohibitive for everything but the most high-value commercially relevant polyamides such as Kevlar. The polymers often require extensive drying to remove residual solvents, which is both time-consuming and energy-intensive. Despite limited industrial use, the relative ease of use leads researchers to find IFP appealing for synthesizing complex polyamides or incorporating novel monomers that are not feasible on an industrial scale.

Solid state polymerization (SSP) is often used to address the shortcomings of low molecular weight PAs, particularly the mechanical properties. SSP involves heating to above the glass transition temperature but below the melting temperature to induce further polymerization. This step is crucial for achieving the desired mechanical strength and thermal stability in the final product. SSP remains effective at enhancing polymer properties, but adds complexity, cost, and at the lab scale, significant batch-to-batch variability, limiting its practicality in many settings. Catalyst-driven reactions are also common shortcuts used in lab settings, decreasing the thermal energy needed and subsequently leading to easier polymerization methods.[24,26–28,33] These catalysts are either enzymatic or metallic in nature. While an attractive option, they offer increased cost due to expensive and non-reusable catalyst and do not mimic industrial resins due to the differing production method. Furthermore, the inclusion of metal catalysts impact final properties, and the purification of lab-made polymers of residual catalysts can add additional time and labor costs. Laboratory-scale syntheses have also made use of tube-furnaces, which are often the cheapest method to achieve the high temperatures necessary for polymerization. However, these limit the molecular weight due to unmitigated evaporation of the HMDA or decarboxylation and cyclization of adipic acid, as they cannot easily be pressurized. As Carothers succinctly demonstrated with the equation $N_n = \frac{1+r}{1+r-2pr}$,[34] where p is the molar conversion and $r \leq 1$ is the initial AA:BB ratio, the loss of even small amounts of monomer can significantly impact the final molecular weight. Consequently, tube furnace PAs are largely relegated to the oligomeric range and are further unsuitable for SSP due to the end-chain cyclization.

While monomer volatilization issues are soluble through the use of pressure vessels, the maintenance of an inert atmosphere along with highly uniform heat and mixing are critical requirements. The polymerization rate is highly sensitive to temperature, and the melt viscosity is highly sensitive to both temperature molecular weight. “Hot spots” cause persistent inhomogeneities in the polymerization media to develop. Furthermore, in common PAs like PA6,6 temperatures as high as 300 C are needed, bringing the risk of thermal degradation.[35–37] This degradation affects molecular weight and thus alters mechanical and thermal properties, rendering the resultant PA unsuitable for research purposes. Understanding these challenges is crucial for developing new polyamides capable of meeting the stringent demands of industrial applications while retaining the innovative features explored in academic research. One option to combine both, mimic industrial reactors and limit the number of engineering challenges, is the use of small pressure reactors to overcome the significant heat and mass transfer issues, targeting 10 grams of polyamide or less. An example of such reactors include the 100 mL models available from the Parr Instrument Company, which have been previouslty demonstrated to produce small batches of high quality nylon.[38] These smaller reactors are able to remove engineering difficulties by keeping the walls of the reactors thinner than what is required for a larger reactor. Additionally, the smaller amount of material requires a less sturdy motor and agitator, meaning even small amount of mixing can overcome significant hurdles. However, the small amounts of polyamide produced in a single reaction limits the ability to perform robust mechanical testing experiments. While it is tempting to combine several batches together, or perform different experiments on different batches, batch-to-batch variability becomes a concern. If multiple trials are desired for statistically significant mechanical data, 10 grams of material is insufficient, with a single trial leading to questionable results.

Our approach to addressing these issues is summarized in Figure 1. We focus on a two-stage batch reaction similar to those used for premium industrial polyamides. This method uses a high pressure stainless steel reactor and can produce several tens of grams of both AA-BB and AB type resins, giving it greater adaptability for polyamide synthesis. We have demonstrated the ability to produce nylon copolymers, industrially common resins, and novelty polyamides all in the same system by careful engineering of the reactor to meet the specific challenges of polyamidation. By enhancing both the equipment and operational techniques, we bridge the gap between laboratory-scale synthesis and industrial polyamide production, ensuring the production of high-quality polyamides with consistent properties.

Figure 1 Traditional polyamide research is typically performed at the 10 g scale or less, using tube furnaces or glass reactors. Industrial production of polyamide happens in chemical plants the size of small cities. The significant gap between these two methods can be bridged using our 30 g reactor system.

Results and Discussion

Design Principles

Careful management of a unique set of engineering challenges must be performed to achieve the successful synthesis of high molecular weight polyamides at benchtop scale. This study focuses on the $\approx$30 g scale synthesis of AA-BB type polyamides, a process that requires precise control over several parameters, including temperature, pressure, and mixing. Each of these

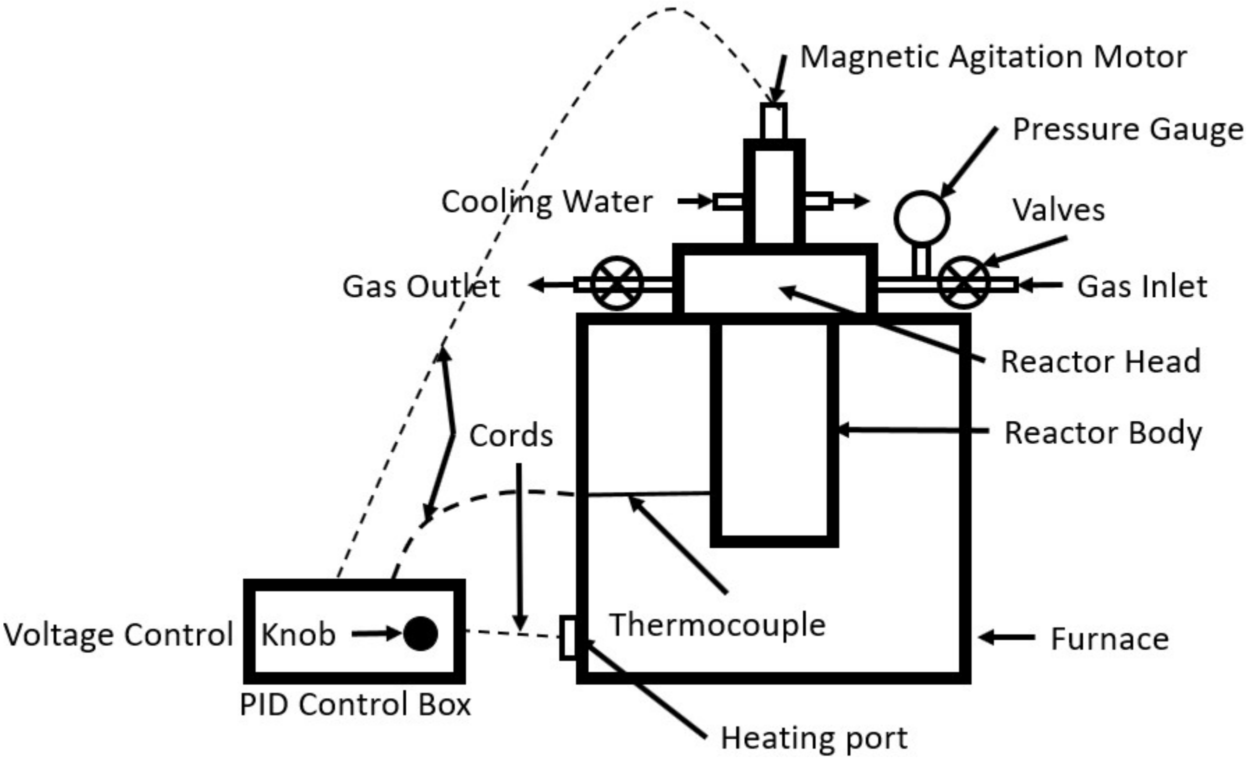

Figure 2 Detailed diagram of high-pressure reactor set up for polymerization. The reactor body is suspended in an electrical furnace. The temperature is monitored via a thermocouple touching the outside of the reactor body. The temperature and magnetically propelled agitation is controlled using a PID controller equipped with a voltage control knob. The agitator is cooled using a constant flow of water to eliminate wear on the steel. A pressure gauge is used to monitor internal pressure of the gas, and the reactor can be sealed or opened using the inlet and outlet valves.

factors plays a pivotal role in determining the quality and properties of the final polymeric product. The key challenges addressed in this research encompass the design and operation of a modified stainless steel reaction vessel, the implementation of an effective heating system, the optimal selection of available agitators for consistent mixing, and the management of pressure within the system. These components are crucial for overcoming the typical barriers associated with small-scale polyamide synthesis, such as achieving uniform heat distribution, maintaining material integrity under high-temperature conditions, and ensuring effective mass transfer in a highly viscous environment. Addressing these issues facilitates the demonstration of a scalable and replicable approach for producing polyamides that meet or exceed industrial standards in terms of molecular weight distribution and mechanical prop-

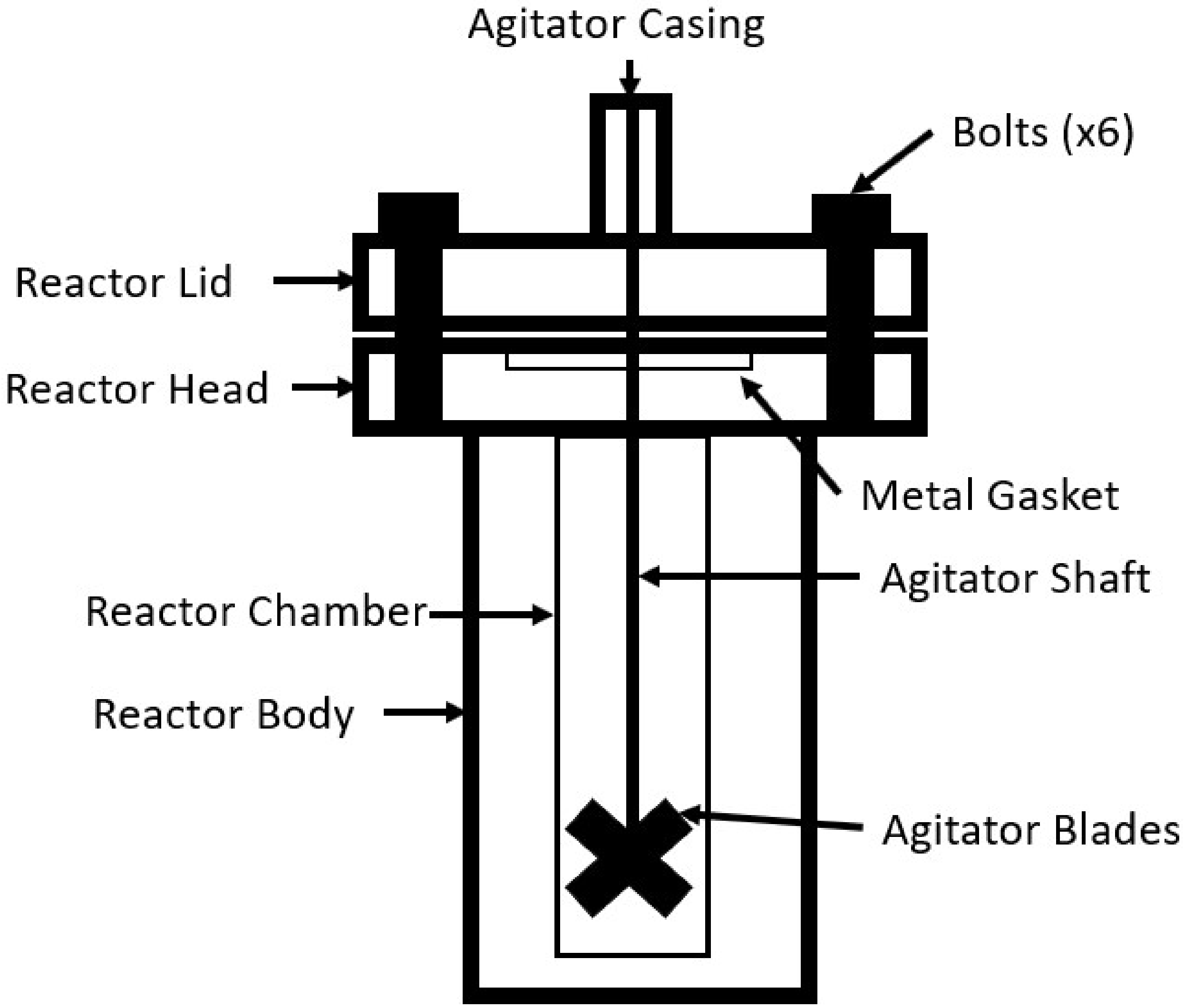

Figure 3 A close up detailed diagram of the cross-sectional slice of a 100 mL cylindrical reactor. The lid is sealed with the help of six large bolts and maintains pressure using a metal gasket. The bottom of the chamber is cone shaped.

erties. Detailed diagrams appear in Figure S10 and Figure 3.

This method, implemented in a thick-walled 100 mL high-pressure reactor, closely approximates the reaction conditions of industrial-scale production. The use of such a reactor introduces several interrelated challenges we have been able to solve. The reactor's thick walls, designed for pressure up to 3000 psig, introduces problems with precise heating. This impediment is further exacerbated by the high temperatures (as high as 300 °C) required for polymerization, which preclude the use of standard heat transfer fluids such as oil, without the use of very expensive heat transfer fluids and heating and pumping devices. Further, the use of heating fluids at such temperatures in a laboratory environment poses significant safety risks. We have experimented with several heat delivery systems, and have found that simple electrical heating provided by a well-fitting and well-insulated furnace (Figure SS9) with PID control is the most affordable heat source for this purpose, capable of providing the consistently high temperatures needed for effective polymerization.

Effective heat management does not stop at the reactor walls. The high viscosity of the polyamide melt combined with its inherently poor heat transfer characteristics poses significant challenges for heat transfer within the reactor itself. To ensure even heat distribution, crucial for uniform polymerization, we tested many agitator designs to determine the optimal design for a well-mixed melt state, considering challenges such as high-viscosity stirring, wall sweep, ease of removing cooled polymer, and mixing efficiency. Moreover, the high viscosity of the melt complicates not only heat but also mass transfer. The need for careful heat control cannot be overstated as the temperature window between melt polymerization and auto-oxidation is very narrow, especially in systems similar to PA 6,6. Achieving a homogeneously mixed state requires both a powerful motor and a well-designed agitator. This combination is critical for preventing localized overheating or incomplete reactions, which could lead to inconsistent product quality. The agitator chosen focused on a robust, simple, easy-to-source design, forgoing the more complicated, expensive, and delicate high-viscosity agitators commercially available. The resin must be cooled before it is removed, as removing while molten would open it up to oxygen, causing oxidation to occur. As a result, the necessary amount of force needed to remove the solid material from the reactor precluded a delicate and expensive agitator system such as an anchor or a ribbon agitator. Two pitch-bladed agitators, as seen in Figure S8, were attached to the shaft. The design of these blades was slightly uncommon, as most pitch blade agitators do not need to perform wall sweep. The poor heat transfer through the melt often creates an outer shell of high molecular weight polymer with an inner core of oligomer. To avoid this, the diameter of the blades was increased to within 1/8″ of the walls, allowing for good wall sweep and a more homogeneous polymer. This is unusual, as in a traditional, Newtonian fluid reactor, a pitched blade creates mixing; combined with baffles, high amounts of mixing is achieved. However, here, the fluid is highly viscous and non-Newtonian, creating a challenging system to mix. Traditional baffles would make removal of the cooled polymer impossible, so these were considered and rejected. To avoid the common vortex issue faced by pitch blade agitators, two pitch-blade agitators were installed, oriented in opposite directions.

Comparison to literature

This work followed an extensive amount of literature review. Table 1 lists numerous works in recent years that report novel polyamides. These high profile papers utilized several different polymerization methods to circumnavigate the challenges presented above.

Entries 1-3 showcase the common use of IFP used in many exotic polyamide research projects.[21,39,40] The common low molecular weight demonstrates IFP's great limiting factor. Entry 1 achieves higher molecular weight, but is synthesizing a niche material. Aromatic polyamides have excellent material properties, but their high cost limits them to specialty applications. The usefulness of IFP can be seen in Entry 3, which achieves high molecular weight of a common industrial polyamide. However, IFP polymers and melt-state polymers such as commercial resins are not identical, and comparing them can be suspect.

Entries 4-8 demonstrate the use of catalysts in polymerization is used in a wide variety of different polymerizations, but is limited to specialty polymers.[24,26,27,33] The single commercial polyamide produced using catalyst is Entry 8, which only achieved oligomeric molecular weights.[28] Additionally, catalysts add cost in materials and purification complications, leaving melt-state as the *de facto* method of production for polymers seeking to compare to industrial resins.

Entry 9-16 all relying on melt state polymerization methods.[38,40–43] Further, several offer a promising reported molecular weight. Entry 9 achieved high molecular weight in the melt

Table 1 A review of cutting-edge research focused on polyamides, showing the experimental specifications and the subsequent results. The dearth of experimental specifications demonstrates the low specificity used when developing method and materials sections.

Entry Number	Experimental Specifications[a]					Mn (kDa)		Reference
	State	Size	Batch Size	Reactor	PA X			
1	Interfacial	–	~0.5 g	Emulsion	Aromatic	24.6	–	[39]
2	Interfacial	–	~0.5 g	Emulsion	PA 2,10	7.5	–	[21]
3	Interfacial	–	–	Rope Trick	PA 6,6	3.6[b]	–	[40]
4	Catalyst	–	~0.5 g	Glass	PA 6,6	16.6	–	[33]
5	Catalyst	10 mL	~0.5 g	Glass	PA 8,12	28.4	1.75	[24]
6	Catalyst	–	~2 g	Glass	PA 8,10	3.9	1.7	[27]
7	Catalyst	25 mL	~0.9 g	Glass	PA 8F	10	–	[26]
8	Catalyst	5 mL	~0.9 g	Metal	PA 6	4.7	2.6	[28]
9	Melt	–	–	Glass	PA 6,12	38.9	2	[41]
10	Melt	25 mL	–	Metal	PA 6,6	34.3	2	[38]
11	Melt	–	~1g	Autoclave	PA 6,18	10.2	1.88	[42]
12	Melt	–	~0.82 g	Glass	PA 6,6	37.8	2	[43]
13	Melt	–	–	Glass	PA 6,6	33[b]	–	[40]
14	Melt	100 mL	~30 g	Metal	PA 5,9	31.6	1.9	This work
15	Melt	100 mL	~30 g	Metal	PA 6-co-6,20	30.7	1.9	This work
16	Melt	100 mL	~30 g	Metal	PA 6,6	29.8	1.6	This work

[a] Specifications listed where mentioned. Batch size is calculated from methods and represents an estimate.

[b] Molecular weight reported as viscosity average.

state.[41] The PA 6,12, however, is significantly easier to synthesize and offers less versatility and reproducability with a shorter chain AA-BB type polymer like PA 6,6. The longer the chain used, the easier synthesis becomes. Entry 9 uses 220 ◦C to synthesize its polyamide. These temperatures are much easier to achieve and the gap between polymerization and degradation is significantly higher. These factors eliminate many of the considerations explained above and result in a less versatile system capable of producing a limited diversity of polyamides. Entry 10 and 12 seem to fix this problem by producing the gold standard PA 6,6, at high molecular weight.[38,43] Both methods use smaller reactors and Entry 12 converts its diacids to acid chlorides in a bid to increase reactivity and circumvent the delicate engineering challenges of traditional melt-state polymerization. These papers highlight the common method of producing smaller quantities to remove the heat and mass transfer issues present in larger reactions.

In fact, all the entries listed, except our work, were performed at scales of 10 grams or less, as noted by the size column. As mentioned above, this limits the effectiveness of the material testing, as batch to batch variability is significant at laboratory scale. A single batch undergoing a complete battery of tests produces more robust sets of data and stronger conclusions.

The inclusion of our work in the table conclusively demonstrates the versatility of our method and its excellent capabilities. We were able to produce a variety of different chain lengths and keep our molecular weights equal if not higher than many other researchers. Additionally, our quantities were higher and allowed for a full suite of tests, both thermal and mechanical. An example of possibilities is seen in 4, which showcases the mechanical properties of industrial nylon as compared to some novel polyamides synthesized by the method presented here. It should be noted the conditioning for these samples was not uniform, and the monomer are not identical, leading to unique properties, but it can be seen our lab-made nylon is comparable to industrial standards.

Table 2 A cost assessment of a complete reactor system capable of producing high quality nylon at laboratory scaled batches. The machine work involves removing the internal thermocouple well and sealing it off and creating the custom threaded shaft. See Table 1 in SI for complete part list for plumbing considerations.

Item	Cost (USD)
Vivtek Reactor System[44]	$4,750.00
Custom Agitator	$400.00[a]
Machine Work	$500.00[b]
Plumbing	$913.57
Total	**$6,563.57**

[a] This includes 2 custom blades at USD$200 apiece. See SI Figure for exact quote.
[b] This is the machining for the cutting and welds required. Done at a university machine shop.

Further Scale Up

This methodology can be scaled beyond the 30 g scale illustrated, for example by implementing in a reactor similar to the one used here but having a higher capacity, such as the 1.3 L variety also offered by Col-Int. With the proper modifications adhering to the engineering

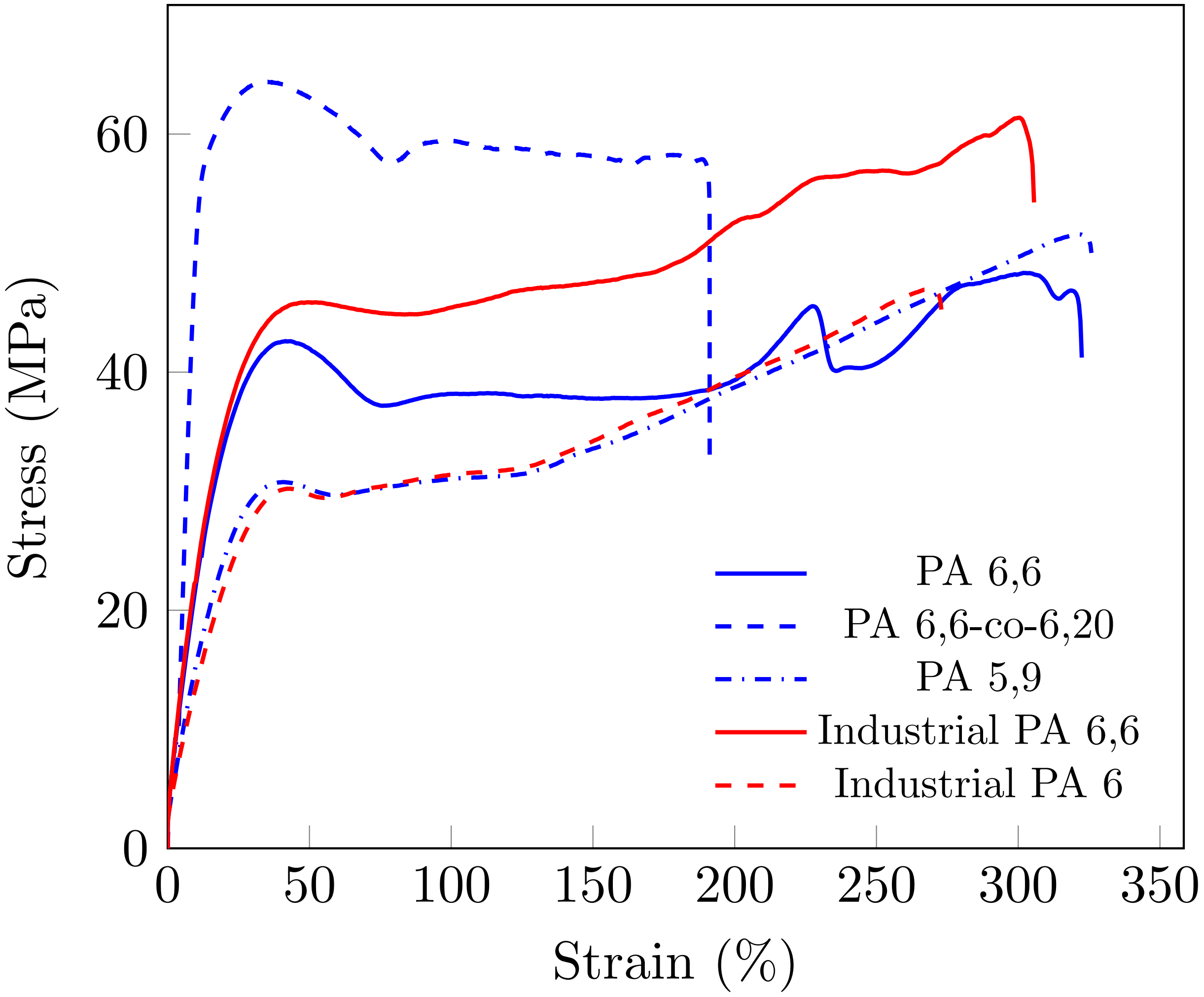

Figure 4 Instron data demonstrating the ability to obtain commercial-like material properties. Lines in blue indicate lab made nylon, while lines in red indicate commercial nylon.

principles discussed above, we believe a reactor capable of producing at least 300 g of high molecular weight polyamides is possible. The high cost of the reactor, around $10K, has prevented any testing on this scale, but it would be feasible given the information given in this work. The modifications would focus on internal space and giving the reactor proper plumbing to ensure safe and consistent use. The removal of all internal items inhibiting good mixing would be the first step. This includes removing and capping the cooling coil and the thermocouple well. If the cooling coils would be desired for other work, such as small molecule chemistry or lower viscosity polymerizations (such as solution polymerization), these could be cut to tube stubs and then compression fittings could be added on to allow for removal and reattachment of the coils as desired. The major consideration would be the agitator itself. It would need to be modified to allow for effective mixing of such an increased size. Additionally, the ability to remove it such as the system in the smaller reactor is needed. This would require specialized agitator blades adding to the cost and complexity, but following the design presented here and scaling appropriately, the mixing could be solved. The addition of proper plumbing would be the second task. The similarity of the designs between the 100 mL and 1.3 L reactors indicates the plumbing necessary would be almost identical. The major safety consideration is the greater risk operating at the same pressures. Failure of a 100 psi in a 100 mL reactor has significantly less power than failure of 100 psi in a 1.3 L reactor. Regular testing, maintenance, and replacement of the rupture disk would be absolutely required. Additionally, moving the rupture disk to point down and away from the user would be necessary. Finally, bleeding the reactor with the increase in volume becomes a more dangerous task. The use of a blast shield and excellent ventilation is the most basic engineering controls needed. The ability to open and close the outlet valve without posing a risk to hands would also need to be considered. We would propose a 2 day reaction. The electrical heating, if handled correctly, is consistent, reliable, and safe, but the significant thermal mass of the reactor and salt slurry would need a longer reaction time to achieve the extent of reaction needed. Using these considerations, we propose it would be possible to produce at least 300 grams of laboratory grade polymer. Admittedly, removal of the polymer becomes a much larger challenge. A researcher attempting this process should carefully consider whether cooling the reactor, allowing the polymer to solidify, and then removing it, is the appropriate solution given the much larger and heavier body. Many, if not all of the 1L+ pressure reactors use a hydraulic lift for the lids, and if this gets stuck, removal of the nylon becomes a challenge. Pressure transfer in the melt state through a dip tube, may be a solution; however, there are significant risks associated with this: the line can cause issue for mixing, it will have to be heated to molten state after it leaves the reactor, any clogs can ruin equipment, and the handling of molten polymer represents a serious safety risk. The authors disagree on the best practice to safely and efficiently remove such a large amount of molten polymer. One suggestion is to build or buy a metal sleeve, thin enough to not weight too much and inhibit heating, but one which would easily slide. After polymerization, the polymer would cool, and the hydraulic lift would lift the entire mass out, with the same removal principles discussed previously applying here. Another suggestion is to mimic what is common in industry, which is to have a bottom drain. This would require some modification of the heating unit along with drilling and tapping the bottom of the reactor. Caution should be done when going this route, as it will reduce the maximum pressure capacity of the reactor. While it is doubtful that this would cause failure at the modest pressures used in AA-BB-type polyamide polymerizations, it is imperative that the researcher consult with machinists to ensure that the reactor is safe to operate and at all times. Certainly, if this type of modification is done, this reactor should never be pushed toward the original pressure limits.

Alternatively, instead of driving the reaction through the to polymer, stopping the reaction at the oligomer then using SSP in a different reactor to convert to polymer would reduce difficulty of removal, and would decrease the requirements for stirring and heating. Larger scale solid state polymerization setups for polyamides are well known in the literature, and typically involve flowing a heated inert gas over the resin.

Larger quantities of material opens the possibility to industrially common tests and form factors. Sheeting and fiber spinning take large quantities of material and would open pathways into interesting research such as textiles and food packaging. Flame-retardance tests, such as the limiting oxygen index (LOI) or the UL-94 flammability test, require large quantities of material. Industry relies on ASTM D638[45,46] as the gold standard of tensile testing, but these dogbones are far too large for even our 30 g system. The scale up into this reactor would allow researchers to provide industry grade technical advice and research and eliminate the need of delicate instruments such as a video extensometer. The larger system would, therefore, create the pathway for many fruitful and high impact collaborations between industry and academia and help advance the adoption of new polyamides.

Conclusion

This study successfully demonstrated a scalable, two-stage polymerization process to synthesize high molecular weight AA-BB type polyamides at a bench top scale, bridging the gap between traditional academic research and industrial applications. Polyamides with excellent color and sheen with molecular weights ranging from 15 to 35 kDa were achieved by utilizing a high-pressure, high-temperature stainless steel reactor equipped with a robust agitator. The resulting polyamides exhibited mechanical properties comparable to those of industrial standards, affirming the efficacy of the approach. Careful engineering of the reactor system to address the inherent challenges of polyamide synthesis, such as high melt viscosity, narrow temperature ranges, and unfavorable side reactions ensured a successful approach, allowing for uniform heat distribution, effective mass transfer, and suppression of side reactions, crucial for producing high-quality polyamides. While this work focused on traditional polyamides like PA 6,6 and PA 6, the simplicity of the machine would allow for any novel polyamide to be produced at useful scales, increasing its versatility and contributing to better scientific research.

Methods

Polymer salt

Polymer salt was synthesized by dissolving 1.8 kg adipic acid and 1.5 kg (1.02 molar equivalents) of hexamethylenediamine (HMDA) separately in methanol, using a 3.15 mL of methanol for every gram of HMDA or adipic acid used. The two solutions were then combined under vigorous agitation and cooled to 50 °C for 16 hours. The salt was filtered and washed with warm methanol then dried in a heated vacuum oven until all methanol was removed.

Polymerization

The polymerization was conducted in a stainless steel Columbia-International High Pressure Stirring 100 mL Reactor. It could be done with prepared polyamide salt for AA-BB type resins, pure industrial ϵ-caprolactam for AB type resins, or a mixture of the two for copolymers.

First stage (oligomerization): The reactor was loaded with the monomer and DI water. The amount of DI water should be 60 wt % of the monomer, or a 1:0.6 ratio.The first stage starts by a deoxygenating step, with the vessel pressurized to 70-80 PSI of argon then slowly bled, then repeated an additional four times. The reactor is charged with argon to 80 PSI, then the gas inlet valve is closed. The temperature was set to 350 ◦C and controlled via an external thermocouple touching the reactor body. The voltage is kept at 65% throughout the duration of the reaction. The internal pressure was continuously monitored with a digital pressure gauge to monitor, by proxy, the internal temperature and ensure consistency throughout the oligomerization process.

Second stage (polymerization): The reactor is bled and a 1-2 psi sweep is established. For AA-BB type polyamides, the temperature is increased to 400 °C and held for 6 hours. The reactor is then bled and an argon sweep is established at 1 psig. The external temperature is increased to 400 °C and held for 4 hours. The reactor is then sealed with argon and allowed to cool. The removal from the reactor uses liquid nitrogen and a chisel, being exceptionally careful around the blades of the agitator to avoid bending the blades.

Conflicts of Interest

No conflicts to declare.

Supporting Information Available

Instrument specifications, images, detailed installation instructions, instructional video.

Acknowledgement

The authors acknowledge the National Science Foundation supported Center for Bioplastics and Biocomposites (NSF-2113695) and Genomatica in the support of this work.

References

(1) Fisher, H. L. Collected Papers of Wallace Hume Carothers on High Polymeric Substances (Mark, H.; Whitby, G. S.; eds.). *Journal of Chemical Education* **1941**, *18*, 99, Publisher: American Chemical Society.

(2) Wallace Carothers and the Development of Nylon - Landmark. https://www.acs.org/education/whatischemistry/landmarks/carotherspolymers.html.

(3) Kondo, M. Y.; Montagna, L. S.; Morgado, G. F. d. M.; Castilho, A. L. G. d.; Batista, L. A. P. d. S.; Botelho, E. C.; Costa, M. L.; Passador, F. R.; Rezende, M. C.; Ribeiro, M. V. Recent advances in the use of Polyamide-based materials for the automotive industry. *Polímeros* **2022**, *32*, e2022023, Publisher: Associação Brasileira de Polímeros.

(4) Polyamides – Still Strong After Seventy Years - Marchildon - 2011 - Macromolecular Reaction Engineering - Wiley Online Library. https://onlinelibrary.wiley.com/doi/10.1002/mren.201000017.

(5) Matthies, P.; Seydl, W. F. In *High Performance Polymers: Their Origin and Development*; Seymour, R. B., Kirshenbaum, G. S., Eds.; Springer Netherlands: Dordrecht, 1986; pp 39–53.

(6) Kohan, M. I. In *High Performance Polymers: Their Origin and Development*; Seymour, R. B., Kirshenbaum, G. S., Eds.; Springer Netherlands: Dordrecht, 1986; pp 19–37.

(7) Tomasini, A.; León-Santiesteban, H. H. In *Biocomposites*; Misra, M., Pandey, J. K., Mohanty, A. K., Eds.; Woodhead Publishing Series in Composites Science and Engineering; Woodhead Publishing, 2015; pp 319–346.

(8) Shakiba, M.; Rezvani Ghomi, E.; Khosravi, F.; Jouybar, S.; Bigham, A.; Zare, M.; Abdouss, M.; Moaref, R.; Ramakrishna, S. Nylon—A material introduction and overview for biomedical applications. *Polymers for Advanced Technologies* **2021**, *32*, 3368–3383, _eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/pat.5372.

(9) Adams, S. R. Method for the preparation of poly amides. 1958.

(10) Tsujii, Y.; Maruyama, G.; Ogawa, K.; Takada, Y.; Koishi, K.; Susuki, K. Method for continuous production of polyamide. 2006.

(11) Jahnke, T. S. Nylon Plastics Handbook Edited by Melvin I. Kohan (MIK Associates). Hanser: Cincinnati, OH. 1995. xii + 631 pp. $198.00. ISBN 1-56990-189-9. *Journal of the American Chemical Society* **1996**, *118*, 8186–8186, Publisher: American Chemical Society.

(12) How Nylon Is Made | INVISTA. `https://www.invista.com`.

(13) Ali, M. A.; Kaneko, T. In *Encyclopedia of Polymeric Nanomaterials*; Kobayashi, S., Müllen, K., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2015; pp 1–14.

(14) Su, K.-H.; Lin, J.-H.; Lin, C.-C. Influence of reprocessing on the mechanical properties and structure of polyamide 6. *Journal of Materials Processing Technology* **2007**, *192-193*, 532–538.

(15) Touris, A.; Turcios, A.; Mintz, E.; Pulugurtha, S. R.; Thor, P.; Jolly, M.; Jalgaonkar, U. Effect of molecular weight and hydration on the tensile properties of polyamide 12. *Results in Materials* **2020**, *8*, 100149.

(16) Schlack, P. Polymerizable lactams. *Pure and Applied Chemistry* **1967**, *15*, 507–524, Publisher: De Gruyter.

(17) Griehl, W.; Ruestem, D. Nylon-12-Preparation, Properties, and Applications. *Industrial & Engineering Chemistry* **1970**, *62*, 16–22.

(18) Bansal, S.; Raichurkar, P. Review on the Manufacturing Processes of Polyester-PET and Nylon-6 Filament Yarn. **2016**, *2*.

(19) Wesołowski, J.; Płachta, K. The Polyamide Market. *Fibres and Textiles in Eastern Europe* **2016**, *24*, 12–18.

(20) Li, X.; Wang, Z.; Han, X.; Liu, Y.; Wang, C.; Yan, F.; Wang, J. Regulating the interfacial polymerization process toward high-performance polyamide thin-film composite reverse osmosis and nanofiltration membranes: A review. *Journal of Membrane Science* **2021**, *640*, 119765.

(21) Mytara, A. D.; Chronaki, K.; Nikitakos, V.; Papaspyrides, C. D.; Beltsios, K.; Vouyiouka, S. Synthesis of Polyamide-Based Microcapsules via Interfacial Polymerization: Effect of Key Process Parameters. *Materials* **2021**, *14*, 5895, Number: 19 Publisher: Multidisciplinary Digital Publishing Institute.

(22) Raaijmakers, M. J. T.; Benes, N. E. Current trends in interfacial polymerization chemistry. *Progress in Polymer Science* **2016**, *63*, 86–142.

(23) Douka, A.; Vouyiouka, S.; Papaspyridi, L.-M.; Papaspyrides, C. D. A review on enzymatic polymerization to produce polycondensation polymers: The case of aliphatic polyesters, polyamides and polyesteramides. *Progress in Polymer Science* **2018**, *79*, 1–25.

(24) Zeng, H.; Guan, Z. Direct Synthesis of Polyamides via Catalytic Dehydrogenation of Diols and Diamines. *Journal of the American Chemical Society* **2011**, *133*, 1159–1161, Publisher: American Chemical Society.

(25) Jiang, Y.; Maniar, D.; Woortman, A. J. J.; Alberda van Ekenstein, G. O. R.; Loos, K. Enzymatic Polymerization of Furan-2,5-Dicarboxylic Acid-Based Furanic-Aliphatic Polyamides as Sustainable Alternatives to Polyphthalamides. *Biomacromolecules* **2015**, *16*, 3674–3685, Publisher: American Chemical Society.

(26) Jiang, Y.; Loos, K. Enzymatic Synthesis of Biobased Polyesters and Polyamides. *Polymers* **2016**, *8*, 243, Number: 7 Publisher: Multidisciplinary Digital Publishing Institute.

(27) Ragupathy, L.; Ziener, U.; Dyllick-Brenzinger, R.; von Vacano, B.; Landfester, K. Enzyme-catalyzed polymerizations at higher temperatures: Synthetic methods to produce polyamides and new poly(amide-co-ester)s. *Journal of Molecular Catalysis B: Enzymatic* **2012**, *76*, 94–105.

(28) van Dijk, A. J. M.; Duchateau, R.; Hensen, E. J. M.; Meuldijk, J.; Koning, C. E. Polyamide Synthesis from 6-Aminocapronitrile, Part 2: Heterogeneously Catalyzed Nitrile Hydrolysis with Consecutive Amine Amidation. *Chemistry – A European Journal* **2007**, *13*, 7673–7681, _eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/chem.200601898.

(29) Vouyiouka, S. N.; Karakatsani, E. K.; Papaspyrides, C. D. Solid state polymerization. *Progress in Polymer Science* **2005**, *30*, 10–37.

(30) Cakir, S.; Nieuwenhuizen, M.; Janssen, P. G. A.; Rulkens, R.; Koning, C. E. Incorporation of a semi-aromatic nylon salt into polyamide 6 by solid-state or melt polymerization. *Polymer* **2012**, *53*, 5242–5250.

(31) Journal of Applied Polymer Science | Wiley Online Library. `https://onlinelibrary.wiley.com/doi/full/10.1002/app.21811`.

(32) Journal of Applied Polymer Science | Wiley Online Library. `https://onlinelibrary.wiley.com/doi/full/10.1002/app.51017`.

(33) Gnanaprakasam, B.; Balaraman, E.; Gunanathan, C.; Milstein, D. Synthesis of polyamides from diols and diamines with liberation of H2. *Journal of Polymer Science Part A: Polymer Chemistry* **2012**, *50*, 1755–1765, _eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/pola.25943.

(34) Carothers, W. H. Polymers and polyfunctionality. *Transactions of the Faraday Society* **1936**, *32*, 39–49, Publisher: The Royal Society of Chemistry.

(35) Herrera, M.; Matuschek, G.; Kettrup, A. Main products and kinetics of the thermal degradation of polyamides. *Chemosphere* **2001**, *42*, 601–607.

(36) Ballistreri, A.; Garozzo, D.; Giuffrida, M.; Impallomeni, G.; Montaudo, G. Primary thermal decomposition processes in aliphatic polyamides. *Polymer Degradation and Stability* **1989**, *23*, 25–41.

(37) Levchik, S. V.; Weil, E. D.; Lewin, M. Thermal decomposition of aliphatic nylons. *Polymer International* **1999**, *48*, 532–557, _eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/%28SICI%291097-0126%28199907%2948%3A7%3C532%3A%3AAID-PI214%3E3.0.CO%3B2-R.

(38) Carter, P.; Trettin, J. L.; Lee, T.-H.; Chalgren, N. L.; Forrester, M. J.; Shanks, B. H.; Tessonnier, J.-P.; Cochran, E. W. Bioenabled Platform to Access Polyamides with Built-In Target Properties. *Journal of the American Chemical Society* **2022**, *144*, 9548–9553, Publisher: American Chemical Society.

(39) Thiem, J.; Bachmann, F. Synthesis and properties of polyamides derived from anhydro- and dianhydroalditols. *Die Makromolekulare Chemie* **1991**, *192*, 2163–2182, _eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/macp.1991.021920922.

(40) R. Vardon, D.; A. Rorrer, N.; Salvachúa, D.; E. Settle, A.; W. Johnson, C.; J. Menart, M.; S. Cleveland, N.; N. Ciesielski, P.; Xerxes Steirer, K.; R. Dorgan, J.; T. Beckham, G. cis ,

cis -Muconic acid: separation and catalysis to bio-adipic acid for nylon-6,6 polymerization. *Green Chemistry* **2016**, *18*, 3397–3413, Publisher: Royal Society of Chemistry.

(41) Rejaibi, M.; Bigot, S.; Kébir, N.; Burel, F.; Desilles, N.; Barrère, C.; Hubert-Roux, M.; Loutelier-Bourhis, C.; Lecamp, L. Elaboration of novel biosourced AA–BB polyamides with dangling chains from methyl ricinoleate. *European Journal of Lipid Science and Technology* **2014**, *116*, 918–927, _eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/ejlt.201400096.

(42) Cui, X.; Li, W.; Yan, D.; Yuan, C.; Di Silvestro, G. Synthesis and characterization of polyamides X 18. *Journal of Applied Polymer Science* **2005**, *98*, 1565–1571, _eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/app.22160.

(43) Rorrer, N. A.; Notonier, S. F.; Knott, B. C.; Black, B. A.; Singh, A.; Nicholson, S. R.; Kinchin, C. P.; Schmidt, G. P.; Carpenter, A. C.; Ramirez, K. J.; Johnson, C. W.; Salvachúa, D.; Crowley, M. F.; Beckham, G. T. Production of beta-ketoadipic acid from glucose in Pseudomonas putida KT2440 for use in performance-advantaged nylons. *Cell Reports Physical Science* **2022**, *3*, 100840.

(44) Stirred High-P Reactor 50-500mL. `https://www.col-int.com/products/high-pressure-chemical-reactor-100-500ml`.

(45) compass. `https://compass.astm.org/document/?contentCode=ASTM%7CD0638-22%7Cen-US&proxycl=https%3A%2F%2Fsecure.astm.org&fromLogin=true`.

(46) Instron. `https://www.instron.com/en-us/testing-solutions/astm-standards/astm-d638`.

(47) Swagelok How to Properly Install a Swagelok Tube Fitting. 2010; `https://www.youtube.com/watch?v=FdthSQDH8qk`.

(48) Swagelok How to Assemble Tube Fittings (1 and Under) | Tech Tips | Swagelok [2020]. 2012; https://www.youtube.com/watch?v=jB_Nyje_HNE.

(49) Brennan Industries Fittings 101 NPT & NPTF. 2019; https://www.youtube.com/watch?v=o7qui1QzDS0.

Supporting Information:

Synthesis of Laboratory Nylon: A Scale-Up Method for High Molecular Weight Polyamides

Peter M. Meyer, Michael Forrester, and Eric W. Cochran*

Department of Chemical & Biological Engineering, Iowa State University, Ames, Iowa 50011, United States

E-mail: ecochran@iastate.edu

Electronic Supplementary Information

Table S1 All items purchased from McMaster-Carr, with appropriate part numbers provided. Additionally, the authors suggest a 9/16" steel wrench and a adaptable wrench. The authors have also found a vice-grip wrench to be useful in many cases.

Part	Number	**Cost (USD)**	**Part #**
Three Way Valve	1	177.05	45165K42
Valve	2	157.69	2363N11
Digital Pressure Gauge	1	171.89	3834K111
NPT to Yor-Lok Adaptor	4	20.26	5182K251
Tubing (1/4") - 3 ft	1	26.16	89895K719
Yor-Lok Nuts (1/4")	10	1.87	5929K263
Yor-Lok Sleeves (1/4")	10	0.85	5929K304
NPT 1/4" Tee	1	38.35	4443K642
	Total	913.57	

Figure S1 Bolts used to hold hold reactor head in place to the reactor body. For size reference, a pen is included.

Plumbing Instructions

The researcher should first use the following resources to understand NPT, compression fitting such as Swagelok and Yor-Lok, and other good plumbing practices.[S47–S49] Plumbing, or connecting the reactor to an inert gas source, is critical to the success of this design. A detailed parts list and diagram can be found in Table S1 and Figure S1. This paper will not cover how to connect the reactor to a gas tank, as each user will have different requirements and placements of the gas tank.

For the inlet pipe, three main design considerations were implemented. The first is a three way valve leading to the inlet. The three way valve was crucial to allow for a place to let gas in and as a secondary place to bleed the reactor should the outlet become plugged, as is possible. The second consideration was the placement of the digital pressure gauge. From experience, it was determined the placement needed to be between the two different valves. The inlet plumbing, from three way valve to reactor, is the most likely place to leak. As covered previously, leaking is a major concern and should be eliminated completely. By placing the gauge between the two valves, users can effectively isolate the piping and tubing leading to

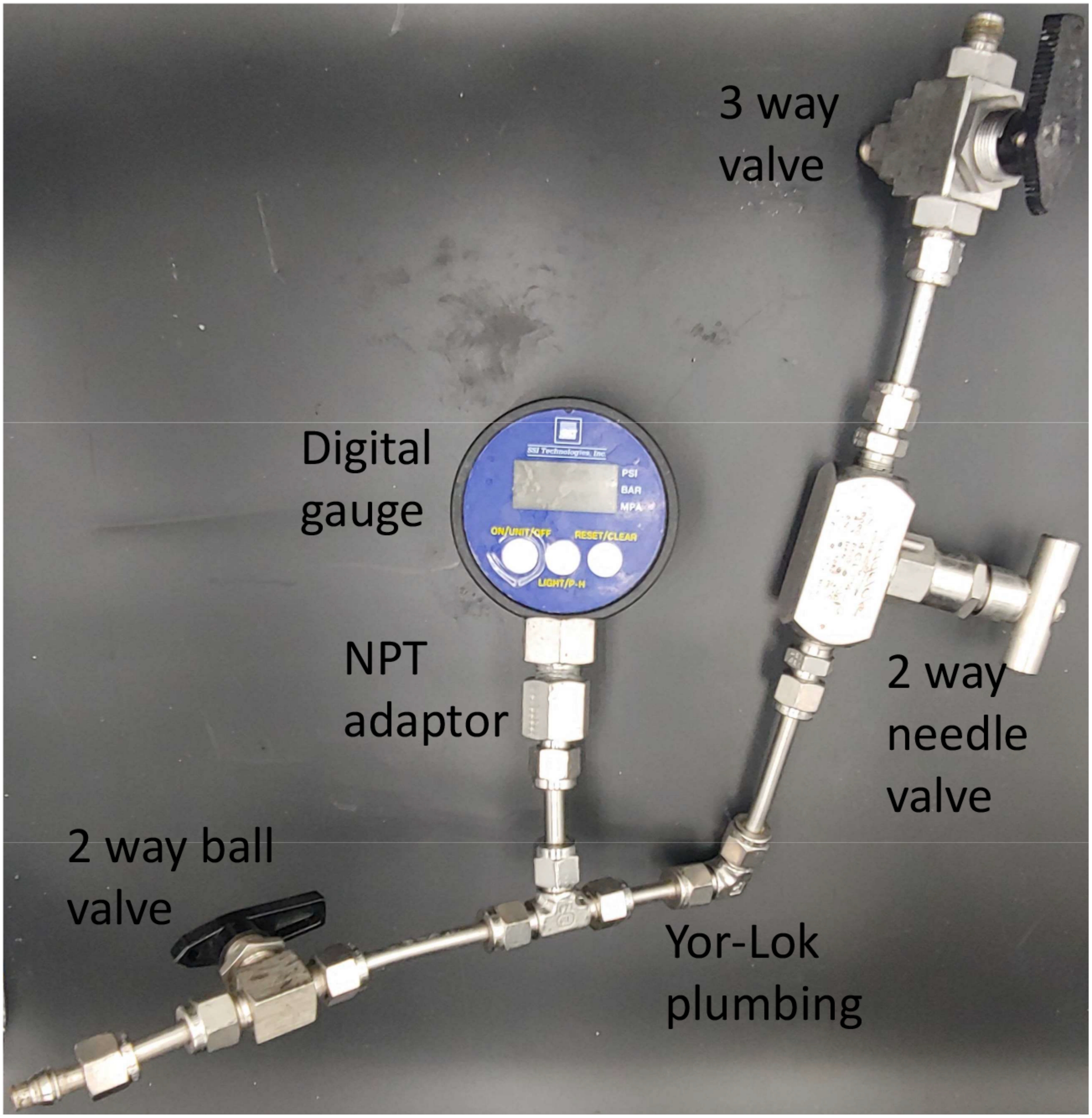

Figure S2 The inlet valve for our reactor. The top right is the 3-way valve inlet, where the gas tank connects, with the bottom left being where it connects to the reactor. Due to space constraints, an elbow was added to the line. This is not necessary and is not reflected in the parts list or Figure S10. Regardless, this is the real-life version of the model presented in Figure S10.

the reactor and determine the source of the leak. The last consideration is the inlet valve. This is necessary to control the flow of gas into the reactor. To join all this together, it is necessary to change from NPT to Yor-Lok threading. Several adaptors were included in the parts list

Figure S3 Photo of the magnetic drive which screws into the top of the reactor head. This mag drive spins the agitator while keeping a tight seal, forming excellent polymer. The tines in the top receive the power from the control box.

to allow for this need. The basic design is three way valve leading to the pressure gauge which leads to the valve. This last valve would lead into the reactor. As a note, the 2 way valve can either be a ball valve or a needle valve. It is our experience the needle valves offer finer control of the gas flow but are more expensive and delicate. Ball valves are excellent for quickly closing and opening and are also cheaper.

The outlet is much simpler but equally important. During the bleed cycle, when high pressure argon and super heated steam are being removed, it is common for solids, either unreacted salt or oligomer, to bump, clogging the outlet. A clogged outlet ruins the outlet

Figure S4 Photo of the 100 mL reactor body, with placement for 6 bolts. The inner ring is the metal gasket, crucial for a good, high temperature seal.

valve and makes the entire reaction fail, as the inability to remove water keeps molecular weights low. Therefore, the outlet tube should have two key features: short and straight. The shorter the length of tubing the less likely it will clog. And any elbows or bends will create an immediate clog point.

The use of Yor-Lock and NPT as a tubing and piping system is very intentional and reflects significant trial and error on the authors part. NPT piping is industry standard and has many excellent characteristics, including high pressure, good chemical resistance, and low cost. However, this system often needs to be disassembled for cleaning and maintenance, making piping inconvenient. As a result, Yor-Lok was chosen for its high pressure capabilities and its ease of use. It is elementary to detach Yor-Lok connections and simply needs a wrench, a common tool often laying around. Piping needs a pipe wrench, which is a more specialized tool and might not be as widely available.

With these considerations in mind, the step by step instructions for assembling the piping are below. In Figure S6, each part has been given a number. Those numbers will be referred too in the following list.

1. Take the three-way valve (#1) and determine the inlet. This is located on the T side. Connect argon or nitrogen tank here. On one side, attach a short length of Yor-Lok tubing.
2. Connect a 1/4″ Yor-Lok to 1/4″ NPC adapter(#4.1)to the 3-way valve.
3. Connect the 1/4″ NPT tee (#2) to the adapter. Then screw in the bottom of the digital gauge (#5) to the top of the tee.
4. On the opposite side of the three-way tee, connect the second adaptor (#4.2) and a short length of Yor-Lok tubing.
5. Connect the Yor-Lok tubing to the first (#3.1) valve.
6. Check the integrity of the seals by pressurizing this length of tubing. Close the end valve and pressurize it. Leave it for 10 minutes and check the pressure. If it has not decreased more than 3 psi, continue. If it has decreased 4 or more psi in 10 minutes, tighten all connections and try again.
7. Connect the valve (#3.1) to the reactor. Most reactors come with female NPT joints. If this is the case, then attach the valve to a length of tubing capped by the third adapter (#4.3). The adapter will then go into the female NPT holes on the side of the reactor.
8. Connect the fourth and last adapter (#4.4) to the other side of the reactor. Place a short length of Yor-Lok tubing then cap it with a valve (#3.2).
9. Seal the reactor and check pressure. If it holds for 10 minutes, continue with experiments. Otherwise, double check reactor seal and joints with soapy water.

Machining Instructions

The machining necessary to carry out this reaction is simple, but a few items should be considered beforehand. First, the removal and sealing of the thermocouple well is important. The amount of pressure the reactor can hold will be limited by the quality of the weld. After a successful weld, check the pressure capacity several times before use. Secondly, the creation of the proper agitator is simple in principle, but mistakes by the authors highlight even small mistakes can be detrimental. Be sure the rotation of the tap matches the rotation of the agitator; if it does not, the agitator will simply spin off the threads the first time it is turned on. Additionally, the closer the threading is to the motor, the less chance of unwanted clogging. If the connection between the agitator shaft and the blade shaft is too low, monomer can enter the threads then polymerize, making removal exceptionally difficult. Our thread is placed 1/2" from the bottom of the reactor lid.

Removal and Clean Up

Upon successful polymerization and subsequent cooling, a homogeneous mass of polymer now surrounds the blades. The removal of the reactor head should be trivial, as long as the agitator is properly set up as discussed in the Machining Instructions in the SI. The removal of the polymer from the blades is simple, but requires time and patience. Even with the thicker, stronger impeller blades, they are not immune to damage and appropriate care should be taken to maximize life cycle. Removal focuses on maximizing the difference in the coefficient of thermal expansion between polymer and metal by super-cooling the entire block using LN2. Once suitably cooled, the block of nylon can be clamped, and very carefully chipped away using a hammer and chisel. The gaps created by the difference in thermal expansion between the metal and the polymer, combined with an overall embrittlement, allows the prudent the ability to remove large chunks of polymer without damaging the blades. This is a delicate process and should be taken slowly, with as many LN2 baths as needed.

Upon the removal of the polymer, small amounts will remain. It is up to the user to determine how much time and how much yield they are willing to spend. It is critical to clean the reactor after each use. Formic acid is an excellent cleaning agent for polyamides, being among the few solvents capable of dissolving polyamides. A 12 hour formic acid soak of both the reactor and the agitator is necessary for repeat polymerization's. Due to its expense, formic acid was kept and reused until it was mostly solid, then new formic acid was used. It should be noted, any residual formic acid remaining in the reactor during polymerization will participate in complex reactions leading to charring, coloring the polymer. Three washes of ethanol is required to achieve a white nylon.

Troubleshooting

Below are common issues and our recommendations for fixing problems. In general, major issues lead to failed experiment. In this case, it is best for the researcher to abort the test, open up the reactor, and begin again. However, some common issues can be fixed during the reaction. They are compiled below.

|p0.3|p0.3|p0.3|

Issue Immediate fix Future prevention

Table S1 Continued from previous page

Issue Immediate fix Future prevention

| Continued on next page|

Outlet valve clogs during bleed If most of the bleed was completed before the clog, open valve all the way and set gas tank pressure to 10 psi. Complete reaction. If most of water is not removed, cool reaction, open, heat to 100 ° C to remove water, close reactor, and drive reaction forward. Too many clogs can ruin valve seats. Replace valve if necessary. Opening valve too slowly increases chances of clogging. Open quickly to allow full air flow. Shorten outlet pipe length and ensure straight path. Soak valve in formic acid to clean.

Leaking reactor During reactor seal check, reactor should lose no more than 3 psi per 10 minutes. If leaking, close inlet valve leading into reactor. Check pressure of inlet valve (Figure S2). If leaking, use soapy water on all connections. Leak will produce bubbles, and can be very small. Check carefully. If not leaking, open valve and fill reactor. Check outlet valve connections with soapy water. If no leak is discovered, the leak is where the reactor head meets the reactor. Bleed reactor, remove head, and reattach. Check all connections regularly for leaks, especially ones commonly adjusted. For gasket leaks, make sure the reactor bolts are tightened in a star pattern with even force to ensure a good seal.

Insufficient heating or PID controller is not turning on. Check the emergency knob is not accidentally bumped. If working, check fuses. The Col-Int PID controller has three fuses. If still not heating, check cable connection. Increase set temperature and voltage. If nothing works, and the PID is turning on, contact customer support. Check fuses regularly. To check heating capability, open reactor, fill with water, insert thermometer, and set heating to 120 $circ$C. Measure time vs. actual temperature to determine heating capabilities.

Stuck reactor head If the reactor head is stuck, and the agitator is not dethreading, polymer likely formed in the threads or in the gasket. To break gasket polymer, insert increasingly larger wedges of wood and gently tap into place until polymer releases. If gasket is releasing but agitator is not dethreading, pipe LN2 into the reactor several times, let cool, and gently apply torsional force. Too much force could lead to broken threads, so be careful. Polymer was likely pushed to the top of the reactor during bleed. Work to ensure a smooth bleed by opening valve completely quickly.

[t]0.45

Figure S5 The top of the head of the reactor

[t]0.45

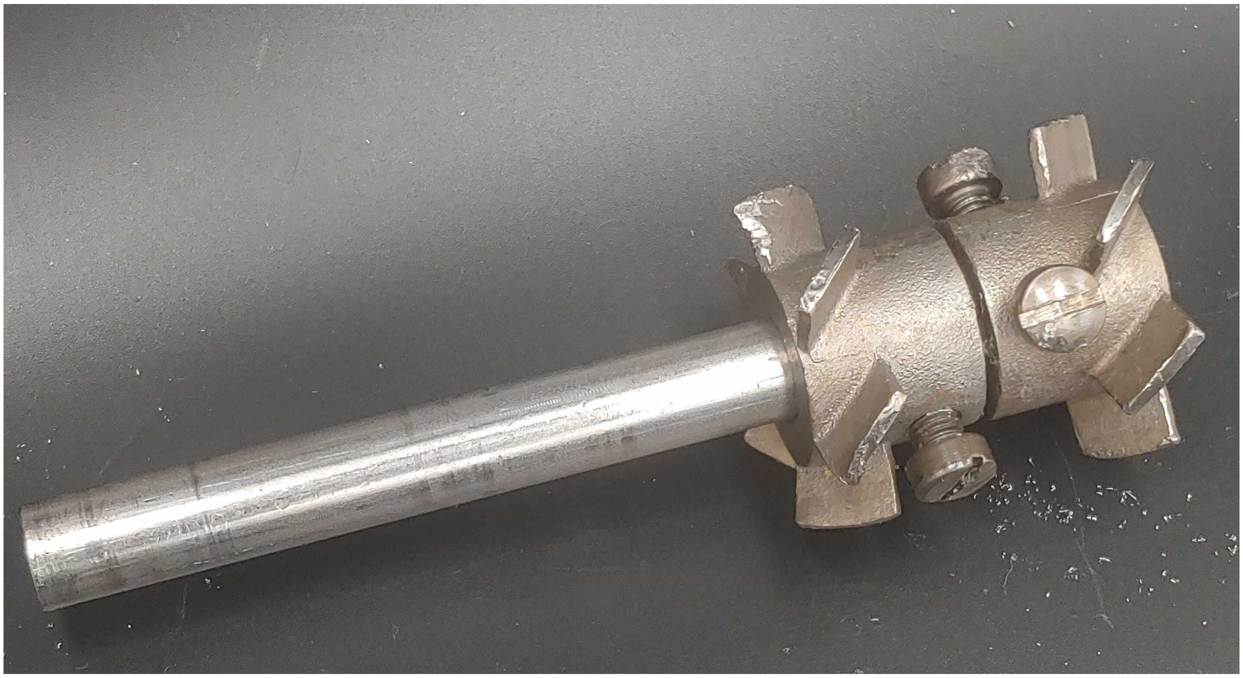

Figure S8 Photo of the agitator. The top is tapped, allowing the agitator to be screwed on and off. The blades are angled in opposite directions, allowing for thorough mixing.

Figure S9 Photo of the furnace purchased from Vivtek. The arrow points to the location of the small hole drilled in the side threading between the heating coils. It is here the thermocouple is threaded into the chamber and placed on the outside of the reactor vessel.

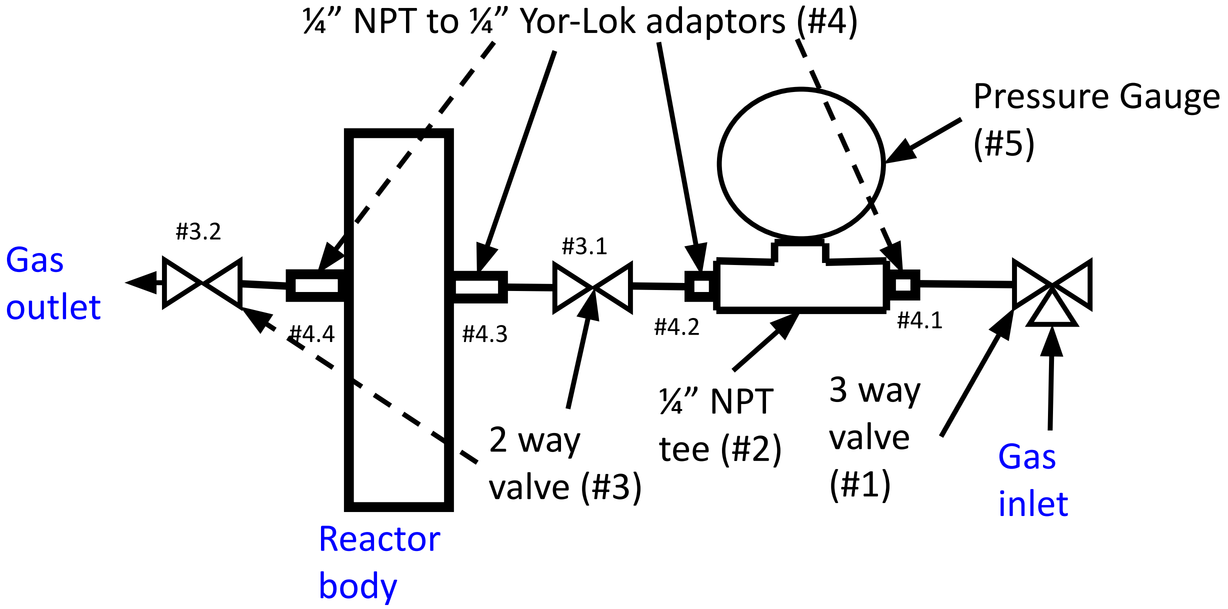

Figure S10 Detailed diagram of plumbing line. A parts list has been provided in Table S1. The blue text represents important parts which do not need to be built but need to be included for clarity.

TOC Graphic