

# Optimised polymerization conditions for inkjetting of caprolactam to produce polyamide parts

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## Abstract

Rapid Manufacturing (RM) techniques have been developed to shorten the processing cycle, and lead to efficient production of ready-to-use complex items. This project aims to manufacture three dimensional parts, directly from monomer, using a 3D Printing process based on ink-jet printing technology. A fast polymerisation and high monomer conversion are essential. This work describes conditions for the rapid anionic polymerization of caprolactam after inkjetting to produce polyamide (nylon 6) parts. The effect of polymerization temperature and different catalyst/initiator types and concentrations on the rate of reaction were studied. Results show that, although increasing polymerization temperature results in quicker polymerization, the highest polymerization rate is achievable with 0.38g of sodium hydride and 320 $\mu$ l of N-acetylcaprolactam.

**Keywords:** anionic polymerization, caprolactam, polyamide 6, inkjetting.

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## Introduction

The objective of this project is to synthesis polyamide 6 via anionic ring opening polymerization of caprolactam [1-3]. This material will be used in manufacturing of three dimensional parts using the multi-layer printing technique using standard jetting heads. This process leads to production of ready to use items, without the need for expensive procedures such as moulding and machining.

Polyamide 6 has a wide range of industrial applications (e.g. injection moulding and cast nylon components). Its monomer, caprolactam, has a low melting point at around 70 °C and a low viscosity in its molten form, which makes it appropriate for jetting using the available jetting heads. However, the main concern is to have a solid part in a very short time. The current solidification time for cast nylon, which is made by a similar process as in this work, is about 10-15 minutes, however, desirable solidification time should be reduced to about 1 minute to make this process viable.

The present work is aiming to optimise the polymerization conditions in order to minimize the solidification time of the liquid mixture and, at the same time, produce desirable mechanical properties of manufactured parts. Catalyst/activator concentration [4,5] has a major influence on the speed of polymerization as well as initial polymerization temperature. It is important to notice that moisture and oxygen behave as inhibitors in this polymerization method; therefore this process is preferably carried out in a dry, oxygen free environment.

## Experimental

### *Materials*

Caprolactam (purity: 99%), sodium hydride (NaH, Dry, purity: 95%) and N-acetylcaprolactam (purity: 99%) as monomer, catalyst, and activator respectively were supplied by Sigma-Aldrich.

Phosphorus pentoxide (purity: 98%), purchased from Fisher Scientific, was used as a drying agent.

### *Experimental rig*

Caprolactam was melted in a tall 150 ml glass beaker which was fitted inside a cylindrical controllable heater to provide a steady and reasonably uniform temperature. A lid sat on top of the heater to simulate the adiabatic conditions and also prevent contact of molten reactants with air. Inert atmosphere was also maintained inside the reaction area. A port fitted with a stopper was provided in the lid to allow the injection of catalyst and activator during reaction.

The progress of polymerization was monitored by measuring the torque required to rotate a glass paddle immersed in the molten reacting mixture. The current which was required for the small DC motor to rotate the glass paddle was measured and recorded using a computer. It was obvious, as the polymerization progressed, the viscosity of the mixture increased and therefore the required current for rotating the DC motor increased as well.

### *Polymer synthesis*

30g caprolactam was mixed with the desired amount of sodium hydride (catalyst) and melted at 70 °C in a nitrogen environment. Then, temperature was raised to the initial polymerization temperature (140-170 °C). At this stage activator, N-acetylcaprolactam, was added to the above mixture and the computer started recording the data. It took a few minutes for the mixture to solidify depending on the amount of catalyst, activator, and initial polymerization temperature.

### *Inert Atmosphere*

Nitrogen was used in this work as the inert atmosphere of reaction. For selected experiments, in order to investigate influence of environment on the polymerization (figure 1), further treatment was performed to reduce the moisture content of nitrogen as follows: nitrogen was passed through a finger type glass tube immersed in liquid nitrogen and then led to a U shaped glass tube containing phosphorus pentoxide.

As drying nitrogen is not a commercial process, the rest of the experiments (the optimization experiments in table 1) in this work have been performed in an untreated nitrogen environment.

### *Optimizing the conditions*

The optimisation was performed with the aid of a randomized standard quadratic design using ECHIP 7 software with three design variables including: catalyst concentration, activator concentration, and initial polymerization temperature. The response variables is Polymerization half time\* (see Table 1).

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\* Polymerization half-time, ( $t_{1/2}$ ), here is the time taken for a polymerization solidification process to be half completed. The method to obtain the polymerization half-time point has been indicated in figure 1(c).

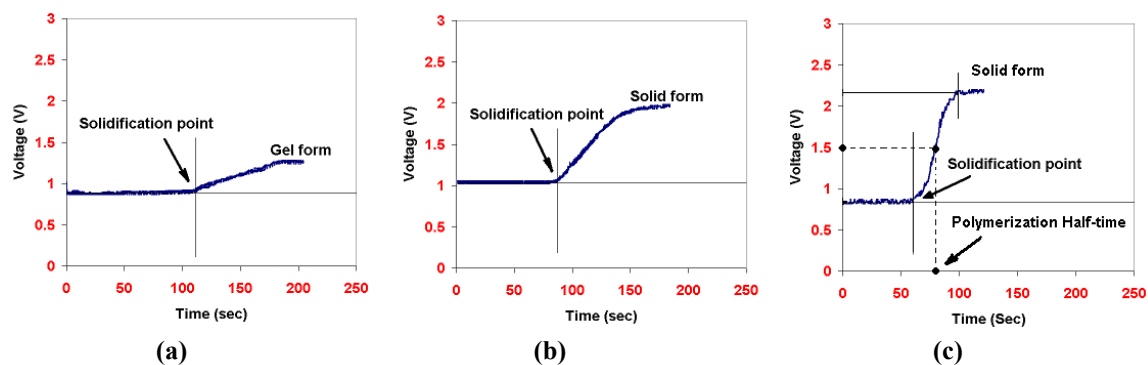
**Table 1:** Trials in the Randomized Standards Quadratic Design

<b>Trials</b>	<b>Catalyst Conc. (g)</b>	<b>Activator Conc. (Micro litre)</b>	<b>Initial Temperature (°C)</b>	<b>Polymerization half time <math>t_{1/2}</math> (sec)</b>
5	0.39	320	180	38
2	0.52	160	180	No polymer
10	0.52	160	160	No polymer
19	0.52	266.667	166.667	99
9	0.26	320	140	141
5	0.39	320	180	39
12	0.39	160	140	No polymer
4	0.26	240	180	55
7	0.39	160	180	135
18	0.43333	213.333	153.333	138
4	0.26	240	180	65
16	0.39	320	160	70
13	0.26	160	180	96
1	0.52	320	140	108
15	0.26	160	140	322
3	0.26	320	160	83
2	0.52	160	180	No polymer
3	0.26	320	160	85
1	0.52	320	140	136
21	0.43333	266.667	140	170
8	0.52	240	140	No polymer
6	0.26	240	140	209
17	0.34667	213.333	153.333	179
14	0.52	320	180	87
20	0.26	213.333	166.667	102
11	0.26	160	160	256
22	0.39	380	180	44

## Results and discussion

### *Influence of environmental on the polymerization*

Different polymerization conditions were investigated in this work. Figure 1 shows the speed of polymerization in the different environments.



**Figure 1:** Polymerization behaviour under three different atmosphere: (a) air, (b) nitrogen, (c) Dry nitrogen.

The results, which are shown in Figure 1, have been obtained at the same polymerization conditions, however, in different atmospheres. Figure 1 (a) indicates that no solid polymer was obtained in air, while solid polymer was produced after about 140 seconds when nitrogen was in use (b). It is also important to notice that the solidification point occurred about 30 seconds quicker when the moisture was removed from nitrogen (c).

These results confirm that anionic ring opening polymerization of caprolactam is sensitive to moisture and oxygen as reported in literature [6,7]. Oxygen and moisture deactivate the anions and active sites, which polymer chains should start growing from; thus, the components in air can behave as inhibitors.

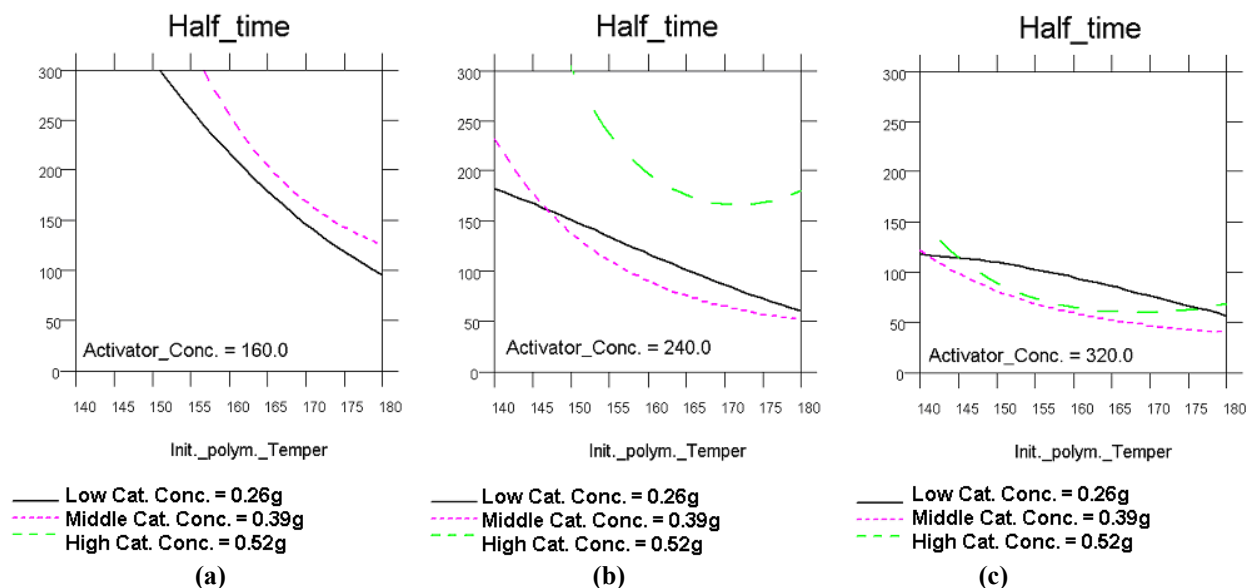
#### *Influence of initial temperature on the polymerization*

Initial polymerization temperature has a strong influence on polymerization rate and most of the synthesised polymer properties such as: crystallinity [13], molecular weight [12], and final degree of monomer conversion [8].

Generally, as seen in figure 2, an increase in polymerization temperature results in a quicker polymerization time; because, at higher temperatures, the activation energy which is needed for initiation stage of polymerization is achieved more quickly [9-11].

The influence of initial polymerization temperature was investigated in this work. The temperature range between 140 to 180°C was chosen because temperatures higher than 180°C results in a very low crystallinity in the synthesised polymer. Temperatures below 140°C were found to be inefficient for fast polymerization. The influence of initial polymerization temperatures at three concentrations of activator is indicated in figure 2. Each figure also shows the effect of different catalyst concentrations on the trend of temperature-half\_time curves.

Polymerization and crystallization are two simultaneous processes that occur during anionic polymerization of caprolactam. However, the competitive nature of these processes [12] do not permit a fast polymerization with a high percentage of crystallinity. The reason is that, at higher polymerization temperature, the thermal motion of the polymer chains is too high to let them crystallise [13].

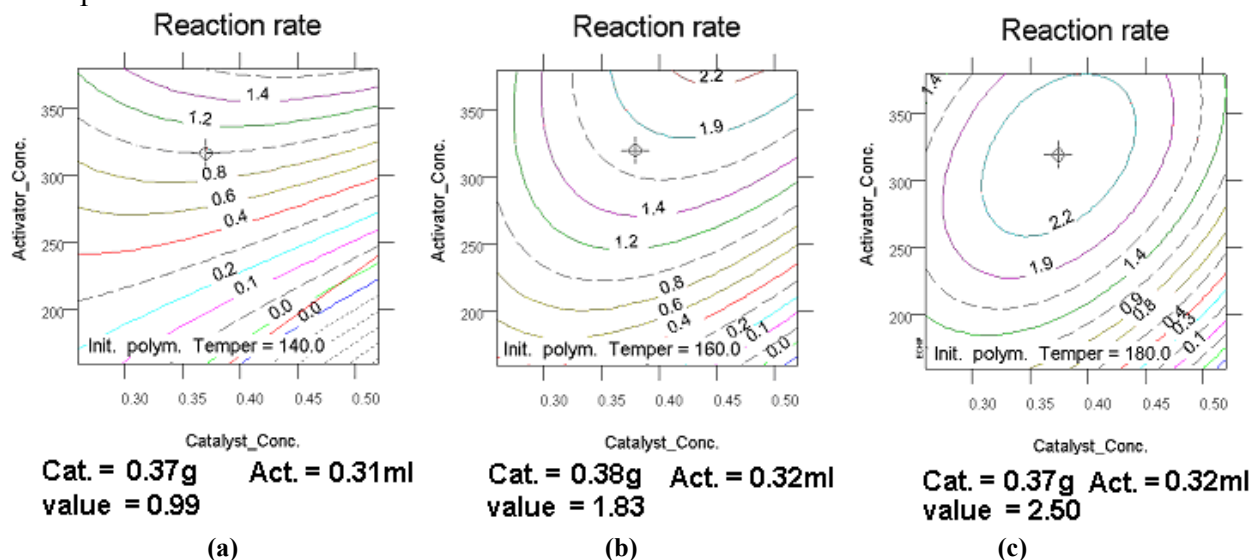


**Figure 2:** Initial polymerization effect against polymerization Half\_time at various activator concentrations (a) 160  $\mu$ l (b) 240  $\mu$ l (c) 320  $\mu$ l.

### *Influence of Activator and catalyst concentration*

A number of experiments were performed using various concentrations of catalyst and activators to find out the optimum amount and ratio of these components in order to maximize the polymerization rate ( $1/t_{1/2}$ ).

To minimize the polymerization time, having the optimum catalyst/activator concentration seems to be essential. Further analysis was performed to find the optimum point at which the polymerization time is minimized at various initial polymerization temperatures. Figure 3 shows the 2 dimensional graphs of activator and catalyst concentration against rate of polymerization ( $1/t_{1/2}$ ). It is obvious that lines which are marked with zero means there is no polymerization at these points.

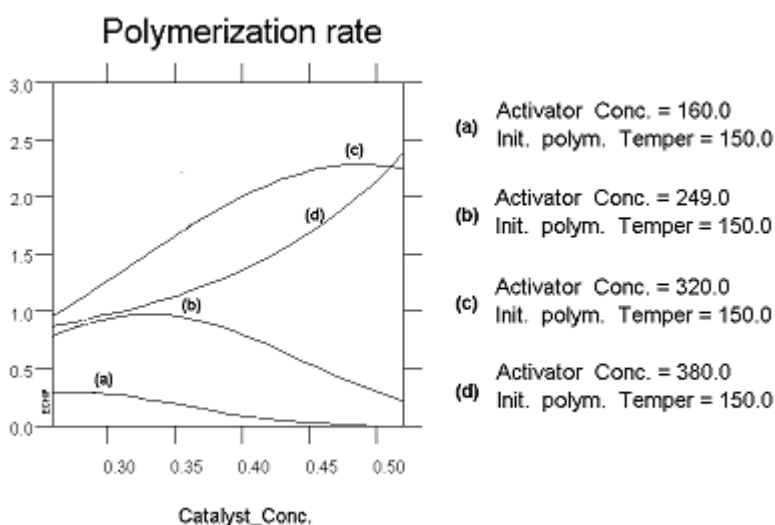


**Figure 3:** Maximizing polymerization rate at different polymerization temperature (a) 140°C (b) 160°C (c) 180°C.

The rate of polymerization at different concentrations of catalyst and activator at three initial polymerization temperature is shown in figure 3. As expected, the fastest polymerization occurs at the highest polymerization temperature (180°C). It can be seen that at all temperatures, the amount of catalyst and activator is 0.38 g and 320 µl respectively. These values are in weight concentration units (After converting to molar units giving, Catalyst: 6% molmol<sup>-1</sup>, Activator: 0.7% molmol<sup>-1</sup>).

It can be seen that, there is a large difference between the molar concentration of catalyst and activator. Two reasons can account for this difference, first, moisture reacts with a proportion of catalyst and deactivates the free anions as the nitrogen which is used in this work contains moisture (about 0.002 %). The second reason is that, not all of the catalyst molecules are successful in reacting with caprolactam to form active anions (sodium caprolactam). This will lead to no further reaction with activator.

Figure 4 shows the relationship between catalyst concentration and polymerization rate at different activator concentrations. This graph helps to find out how far increasing catalyst concentration can increase the rate of polymerization.



**Figure 4:** Polymerization rate (speed) vs. catalyst concentration at four different activator concentration.

Increasing catalyst concentration results in higher polymerization rate due to more anions which are set free. On the other hand, increasing the activator concentration results in creation of more initiation points for chain growth and consequently the polymerization rate rises [14]. This has been confirmed as shown in figure 4.

However, using higher concentrations of activator, due to the higher amount of initiating points, causes more polymer chains to start growing simultaneously and therefore the final molecular weight of the polymer drops and results in a poor final mechanical properties [15].

### Processing window

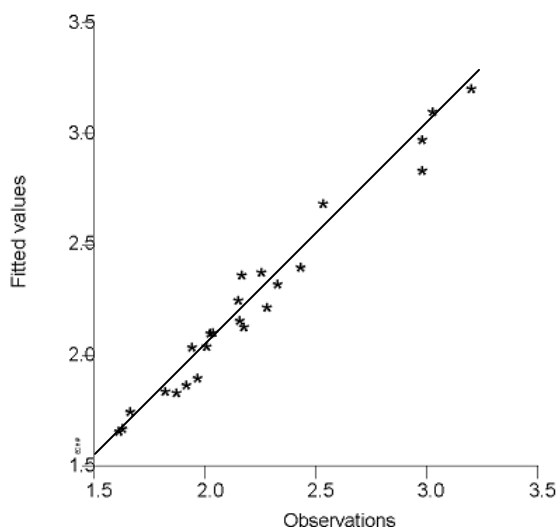
Figures 1,3, and 4 indicate the conditions which are necessary for polymerization. Graph 1-(a) shows that the final polymer will have a gel form if normal air is used as the reaction atmosphere, while using nitrogen and treated nitrogen lead to production of a solid polymer (see 1-(b) and (c)).

Figure 2-(a) indicates that there will be no polymerization at any temperature when the concentration of activator and catalyst is 160 ( $\mu\text{l}$  / 30 g caprolactam) and 0.52 (g / 30 g caprolactam) respectively. If the concentration of activator increases to 240 ( $\mu\text{l}$  / 30 g caprolactam) polymerization half\_time will be less than 300 seconds after the initial polymerization temperature reaches 150 °C.

Figure 4 shows the same thing and confirms these conclusions (no polymerization occurs in fig 4 (a) after the catalyst concentrations exceed 0.45 when 160  $\mu\text{l}$  activator at 150 °C is used). In addition, It can be seen that there is no increase in polymerization rate when the amount of activator exceeds 320  $\mu\text{l}$ . The small difference between (c) and (d) is due to the enhancement of depolymerisation and side reactions when the concentration of activator is too high.

### Accuracy of modelling

The accuracy of the modelling which is used in this work was shown in Figure 5 by comparing observed data against fitted data.



**Figures 5:** Fitted values against Observations

The nearer these points lie to a straight line at 45° to the axes, the higher the accuracy of the model.

### Conclusion

The optimisation of polymerization conditions for converting caprolactam to polyamide 6 was performed in this work. It has been shown that the concentration of catalyst and activator have significant influence on the rate of reaction. Also, influence of initial polymerization temperature was studied.

Results show that, although increasing polymerization temperature results in quicker polymerization, the highest polymerization rate is achievable with 0.38 g of sodium hydride and 320  $\mu$ l of N-acetylcaprolactam regardless of initial polymerization temperature.

Also, it was discussed that using a higher amount of catalyst may prevent polymerization reaction regardless of activator concentration and initial polymerization temperature.

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