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ANIONIC POLYMERISATION OF CAPROLACTAM: AN APPROACH TO OPTIMISING THE POLYMERISATION CONDITIONS TO BE USED IN A JETTING PROCES
ACKNOWLEDGEMENTS

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ABSTRACT

The main aim of this project was to investigate the possibility of manufacturing 3D parts of polyamide (nylon or PA) 6 by inkjetting its monomer caprolactam (CL). The principle of this process was similar to the other rapid prototype (RP) and rapid manufacturing (RM) processes in which a 3D part is manufactured by layer on layer deposition of material. PA6 was used as the thermoplastic polymer in this work because of its good properties and also because PA6 can be produced by heating its monomer (i.e. plus catalyst and activator) in a short time. Two polymerisation mixtures of CL-catalyst (mixture A) and CL-activator (mixture B) are intended to be jetted separately using conventional jetting heads and polymerise shortly after heating.

Anionic polymerisation of CL (APCL) was investigated in the bulk and on a smaller scale. Sodium caprolactamate (CLNa and C10) and caprolactam magnesium bromide (CLMgBr) were used as catalysts and N-acetylcaprolactam (ACL) and a di-functional activator (C20) were used as activators. The influence of polymerisation conditions was investigated and optimised. These were catalyst-activator concentration, polymerisation temperature and the influence of the polymerisation atmosphere. The physical properties (monomer conversion, crystallinity, and viscosity average molecular weight) of PA6 samples produced using each catalyst-activator combinations were measured and compared. Small scale polymerisation was carried out using a hotplate, by hot stage microscopy and using differential scanning calorimetry (DSC). The influence of heating strategy on small scale polymerisation was studied using DSC. The polymerisation mixture compositions were characterised using rheometry, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and optical microscopy to investigate their suitability in jetting for using the available jetting heads.

It was shown that the combination of CLMgBr-ACL resulted in fast polymerisation which was not sensitive to moisture. The C10-C20 combination resulted in fast polymerisation with the best properties in a protected environment (nitrogen); however, the polymerisation was affected by moisture in air and the properties of polymer produced and rate of polymerisation decreased in air. Polymers produced using CLNa-ACL had the poorest properties and polymerisation did not occur in air. Material characterisation showed that micro-crystals of CLMgBr existed in CLMgBr-CL mixture at the jetting temperature (80°C) which were too large to be jetted. However, the mixture of C10 in CL could be partially jetted. The activator mixtures had similar properties to CL and were easily jetted. Drop on drop polymerisation
was carried out by dripping droplets of mixtures A and B (at 80°C) on top of each other on a hotplate at the polymerisation temperature. Small scale polymerisation in a DSC showed that the monomer conversion increased with increase in polymerisation temperature from 140°C to 180°C and decreased from 180°C to 200°C. The crystallinity of the polymer produced in the DSC decreased with increase in polymerisation temperature. Hot stage microscopy produced evidence for simultaneous polymerisation and crystallisation processes on heating. Small scale polymerisation in an oven and analysed by DSC showed that increasing catalyst-activator concentration resulted in increasing monomer conversion and decrease in crystallinity. Monomer conversion also increased with increase in polymerisation temperature and polymerisation time. Comparison between small scale and bulk polymerisations shows a good agreement between the two polymerisation rates. This shows that the polymerisation mechanism did not change significantly when the quantity of materials was reduced to less than 20mg. Finally, the polymerisation was carried out in a DSC after jetting C10-CL and C20-CL mixtures into a DSC pan using a jetting system, which was made in another work.

**Keywords:** Polyamide 6, Anionic polymerisation, Caprolactam, Jetting of polymerisation mixtures, Optimising polymerisation conditions, Small scale polymerisation.
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CHAPTER ONE: INTRODUCTION

1.1 Description of this work

This project aimed to invent a new way of manufacturing plastic parts in polyamide 6 (PA6, or nylon 6), which is one of the main engineering thermoplastic materials in use today. The proposed work was entirely novel with no known similar activity. The long term aim was to produce three dimensional objects or components using the technique of multi-layer printing from a standard jetting head. This process was intended to lead to the direct mass production of ready-to-use items, which avoids the need for existing expensive procedures such as injection moulding or CNC machining. The process has already been demonstrated using materials that can be used in rapid prototyping, such as nylon 12 and poly(methylmethacrylate) (PMMA) powders, epoxy and acrylate-epoxy hybride UV-curable resins, but generally these materials or processes do not provide product with sufficient mechanical properties to make the rapid manufacturing of mass produced components feasible.

PA6 has had a long history of being a robust material for the production of a wide range of engineering components by injection moulding and standard manufacturing methods but its melting point and the viscosity of the melt are far too high to allow it to be printed using currently available jetting heads. However, its monomer, caprolactam (CL), has a relatively low melting point at about 70°C and, in its molten form, a low viscosity which make it feasible to be jetted using available jetting heads.

1.2 PA6 polymerisation

PA6 can be synthesised using anionic polymerisation of caprolactam (APCL). This is the fastest polymerisation method to produce PA6 from its monomer. Suitable catalyst and activator components are required in APCL to reduce the polymerisation time and improve the mechanical properties of the polymer produced. Polymerisation temperature is another significant parameter which influences APCL.

The polymerisation process used in this work is similar to the casting PA6 process which is shown in Fig. 1.1.

In the process of casting PA6, two mixtures of CL and catalyst, and CL and activator in measured ratios are produced and kept in separate containers. The content of these containers are mixed together and poured in a hot mould. A solid PA6 part is expected to be produced
after about 15 minutes of moulding (i.e. this time depends on the size of the mould, concentration of catalyst-activator and mould temperature).

\[
\begin{align*}
(1) \text{ Caprolactam + activator (72 ± 5°C)} & & (2) \text{ Caprolactam + catalyst (72 ± 5°C)} \\
\text{Mixed (1) + (2) and cast into mould (150°C)} & & \\
\text{Solid part (15 mins)}
\end{align*}
\]

**Figure 1.1**: the process casting PA6.

The PA6 synthesised in this process usually has a melting point (Tm) of 215 to 225°C, glass transition temperature (Tg) of 50 to 75°C, molar mass range of \((1.8-5.2 \times 10^4) \sim (1 \times 10^5)\), and crystallinity of 30 to 50%. PA6 has an excellent combination of physical properties, which leads to a variety of applications.

The relationship between application and properties plays the most important role in choosing plastics. For example, in some applications that require great toughness (e.g. hammer handles, American football face guards) PA6 is used. Additional applications of PA6 requiring resistance to fatigue or repeated impact are a backing of a PA6/66/610 terpolymer for metal printing plates. PA6 is used as a thin extruded jacket over PVC insulated building wire. The superior abrasion resistance of PA6 permits a reduction in the thickness of the PVC. However, the most common application of PA6 is in the fibre industry. PA6 gasoline tanks of irregular shapes processed by rotational moulding are another application. It is also used for packaging of non-food products, including greased machinery parts, because of the grease resistance and the puncture resistance of its films.

**1.3 Inkjetting**

Generally, inkjet printing comes from the printer and plotter industry where the technique involves depositing tiny droplets of ink on paper to produce graphic images. Rapid
prototyping (RP) inkjet techniques utilise inkjet technology to deposit droplets of liquid to solid compound and form a layer of an RP model\(^1\).

In this work the monomer (CL) of PA6 in a mixture with catalyst (mixture A), and with activator (mixture B) is to be jetted through the jetting heads onto a moving substrate. These droplets should solidify by polymerisation quickly after jetting to be able to carry the next layer of droplets. In this way layers of material will be manufactured on top of each other. Fig. 1.2 is a schematic of a jetting system. It is obvious that in this work at least two jetting heads are required, as there are two different mixtures to be jetted.

![Figure 1.2: Schematic of jetting system.](image)

1.4 Objectives and main tasks

The overall aim of the project is to investigate the feasibility of jetting CL monomer to form a thermoplastic material. The deposited monomer is required to polymerise (solidify) quickly after jetting. It was intended that this work would explore the task of material formulation and processing to enable a proof of concept, that shows it is possible to jet CL to form PA6 and then to understand any issues that might arise from the use of a support material.

This project included the following tasks:

1.4.1 Exploring processing parameters of raw materials

The eventual material delivery system needed to be taken into consideration so that it was as simple and reproducible as possible. It would be possible to supply a future jetting process with three materials-liquid CL, catalyst and activator. However, these three materials would make an eventual system more complicated so the plan was to eventually have two solid

\(^1\) [http://www.efunda.com/processes/rapid_prototyping/inkjet.cfm](http://www.efunda.com/processes/rapid_prototyping/inkjet.cfm) updated 21Aug.08.
materials entering the process. Therefore, in material preparation, the A mixture would be prepared by melting CL and adding the catalyst. It would then be cooled to a solid. The B mixture would be prepared in a similar way with CL and activator. At the machine, the blocks of A and B would be melted in separate reservoirs to feed their dedicated jets. Therefore, there was significant work required to explore the processing conditions for these mixtures such as melting temperature, concentrations and other processing conditions such as oxygen and humidity level, as these are known to inhibit the polymerisation process. Therefore, a comprehensive investigation is required to optimise the polymerisation conditions to achieve the shortest polymerisation time and the best final properties of the polymer produced at the same time. This part of the polymerisation studies was carried out in bulk.

1.4.2 Droplet optimisation

Once the material has been formulated, as a second research program the jets were optimised to form uniform droplets. This involved the use of a jetting rig with and determining basic jetting parameters such as the relationship between mass of droplet and impulse frequency and nozzle voltage, droplet velocity and voltage, impulse shapes and droplet mass.

1.4.3 Drop on drop polymerisation

When the droplets were optimised it was necessary to deposit a droplet of mixture A onto mixture B or vice versa and study the polymerisation process. Since tiny droplets of polymerisation mixtures are supposed to react after jetting, the polymerisation process must be investigated in detail on a smaller scale. Conventional techniques such as differential scanning calorimetry (DSC) and hot stage microscopy can be employed to study small scale polymerisation. Results from bulk and small scale polymerisation were compared to investigate the influence of polymerisation scale.

There would also be some work required to characterise the polymerisation mixtures because jetting heads have some limitations in materials which can be jetted.
1.4.4 Effect of support material within the process

A material needs to be identified as a possible support material. The work involved in this task was to identify a suitable material, determine the jetting parameters and then investigate any issues of inhibiting and mixing with the CL.

The whole project was divided into three individual PhD programs which were carried out in close collaboration. Among the tasks above, 1.4.1 and 1.4.3 were of the main concern of this PhD work and the other two tasks were studied by the other researchers.
CHAPTER TWO: LITERATURE REVIEW

2.1 Jetting of 3D PA6 parts
This section deals briefly with the rapid manufacturing part of the current project. This applies deposition of different mixture compositions made of caprolactam to achieve PA6 on a surface at appropriate polymerisation conditions (e.g. temperature and nitrogen flux) in a layer wise technique.

2.1.1 Rapid manufacturing
There is considerable interest in the use of additive manufacturing (AM) processes to produce end-use parts. In Europe, this is often referred to as "rapid manufacturing" (RM), whereas in the USA it is often known as solid freeform fabrication (SFF). This relatively new method of manufacturing end-use products is now widely recognised as a future manufacturing technique and has been described as “An Industrial Revolution for the Digital Age” [1]. Using AM processes to manufacture end-use parts has considerable benefits over conventional manufacturing (e.g. injection moulding, casting, machining, etc), especially where design for manufacture restrictions encountered in conventional manufacturing can be removed. These processes are attracting significant industrial interest. The main processes currently used for layer manufacturing of end use plastic parts are:

- Stereolithography (SL) where a UV laser selectively cures a photosensitive resin.
- Selective laser sintering (SLS) where a CO$_2$ laser selectively sinters a powder.
- Jetting, where a liquid photopolymer droplet is deposited onto a substrate and is subsequently solidified by exposure to UV light.

2.1.2 Ink-jet technology
In an ink-jet head, the periodic change of volume by the actuation system induces an acoustic pressure wave inside the ink chamber by either deformation of a piezoelement or growth of a bubble (in thermal systems) [2]. The pressure wave propagates towards the nozzle and interacts with the surface of the ink in the nozzle. Ink-jet technology has been classified into two main techniques based on the jetting head used, continuous mode and drop-on-demand (DoD) mode.
2.1.3 Jetting technology in rapid manufacturing
Since the introduction of ink-jet printers in the 1970s, ink-jet technology has made considerable progress thanks to its high commercial potential in the printing industry [2]. Many companies have made large investments in research to develop their ink-jet technology for faster and cheaper printers. This has led to the development of jetting heads with high deposition speed as well as printing resolution by increasing the number of nozzles and decreasing the nozzle diameter. The diameter of generated droplets has been reduced to a few micrometres while jetting frequency has increased considerably.

The range of jetting materials, high throughput CAD-based processes, and multi-material jetting have enabled the ink-jet technology to be applied in a wide range of applications namely electronics, medical, optics, and rapid prototyping RP/RM. In the RP/RM world, ink-jet technology was first applied by MIT in early 1990s [3] and three-dimensional printing process entered the RP market.

2.2 Polymerisation of caprolactam

2.2.1 PA6 background
Synthetic polymers started to develop from the 1920s, and their annual production has grown rapidly in subsequent years. Among many people that contributed to this achievement, Wallace Hume Carothers who worked for the Du Pont Company carried out pioneering studies on condensation polymerisation in 1928. His work led to the production of a high molecular weight Polyamide (PA) 6.6 from hexamethylenediamine and adipic acid in 1935. The name “Nylon” was invented by Du Pont for the polymers that contain the carbonamide group –CONH- as the repeating unit in their main chain. PA was a new concept in plastics because of its superior properties. For instance, PA has a sharp transition from solid to melt at its melting point. PA also provides a combination of rigidity and toughness which is important for mechanical usage such as bearings and gears. Unlike metals, plastics can be tough and at the same time stiff; so can be more useful in many engineering applications [4].

Schlect in 1938 showed that by careful selection of catalysts including amino carboxylic acids, 6.6 salts and water, the caprolactam (CL) ring could be opened and straight chain polymerisation effected. The stability and ease of purification of CL brought success in the early experiments and high polymers were produced with properties very similar to PA66. The high polymers from CL were designated ‘Perlon’. In 1939 the first production form of
PA6 was produced in I.G. Farben’s Berlin-Lichtenberg factory and became commercially available. Technical work continued during the Second World War, and injection moulded parts in PA6 were produced and tested in service. In 1954, the number of United States manufacturers gradually grew. Other countries, e.g. UK, France, and Holland, quickly followed the two leading nations in the production of PA6 and set up plants for both fibre and plastics production [6].

Du Pont produced six polymer grades for PA moulding and extrusion in 1948, increasing its number of formulations and number of service colours over the next twenty years. After this time sales of all PAs in United States had an annual growth rate of 12.2%. Performance, versatility, and decreasing cost, have made PAs engineering plastics with broad ranges of applications today.

2.2.2 Anionic polymerisation

Among all the polymerisation methods, anionic polymerisation is the one which provides the most versatile methodologies for the synthesis of polymers with well defined structures, remarkable uniformity of chain length, desired chain-end functionality, molecular weight (MW) and also molecular weight distribution (MWD). This is because of the stable nature of the growing chain, which can be prevented from undergoing any termination or transfer reactions. This section of the report is a discussion of the anionic polymerisation principles, benefits, and anionic ring opening polymerisation of CL.

2.2.2.1 Definitions

An “anionic” or “living” polymerisation is a polymerisation that proceeds without any termination step or chain transfer [6,7]. The term “living polymers” is often used to describe a system in which active centres remain after complete polymerisation, so that a new batch of monomer subsequently added will add to the existing chain and increase its degree of polymerisation [8]. Therefore, unless an inhibitor is added to the system, polymerisation has two main steps:

\[
\begin{align*}
\text{Initiation} & \quad \text{eq. 2.1} \\
I & \rightarrow I^* \\
I^* + M & \rightarrow I-M^*
\end{align*}
\]
where I is initiator, I* is the initiating species, M is monomer, and star “*” represents a free radical centre.

\begin{align*}
\text{Propagation} \\
\text{eq. 2.2} \\
P_i^* + M \rightarrow P_i^-M^* \equiv P_{i+1}^*
\end{align*}

where i indicates the degree of polymerisation, and P* is growing polymer chain.

2.2.2.2 Molecular weight and molecular weight distribution

The MW of a polymer is one of the most important variables that control the final properties of the product. The MW in an anionic polymerisation is determined by the degree of conversion. For a monofunctional activator (initiator) one polymer chain is formed for each initiating species and the MW can be calculated after complete monomer conversion as follows:

\[
\text{Mn} = \frac{\text{g of monomer}}{\text{moles of monofunctional initiator}}
\]

In the case of difunctional activator species, the MW is twice as high per mole of initiator:

\[
\text{Mn} = \frac{\text{g of monomer}}{(1/2) \text{ moles of initiator}}
\]

At intermediate degrees of conversion:

\[
\text{Mn} = \frac{\text{g of monomer consumed}}{\text{moles of initiator}}
\]

In general, it is possible to prepare a polymer with a narrow MWD using a living polymerisation when the rate of initiation is competitive with the rate of propagation [9]. This condition ensures that all chains grow for essentially the same period of time. It is easier to make higher MW polymers with narrow MWD [10].

2.2.2.3 Anionic polymerisation of caprolactam

This polymerisation method was first described by Joyce et al. in 1939 [11]. It is an autocatalyst reaction which leads to a high monomer conversion after a short polymerisation time. The mechanism has been described by many authors, such as Ney and Crowther [12], Mottus et al. [13], Sebenda and Kralicek [14]. Further references also relate to this polymerisation [15-23].

The polymerisation consists of three steps:

I. \textit{Catalyst formation}: The catalyst attacks monomer (CL) and caprolactamate forms. This step is usually a fast reaction.
II. *Initiation:* Caprolactamate attacks the monomer with the help of activator. This stage is also called the complex formation stage.

III. *Propagation:* Polymer chains start growing.

\[
\text{catalyst formation} \quad \text{eq. 2.3}
\]
\[
(CH_2)_5-CO \xrightarrow{\text{NaH}} (CH_2)_5-CO + H_2 \uparrow
\]
\[
\text{NH} \xrightarrow{\text{N}^- \text{Na}^+}
\]

\[
\text{normal initiation (without activator)} \quad \text{eq. 2.4}
\]
\[
(CH_2)_5-CO + (CH_2)_5-CO \rightarrow (CH_2)_5-CO
\]
\[
\text{NH} \xrightarrow{\text{N}^-} (CH_2)_5-CO \text{NH} \xrightarrow{\text{N}^-}
\]
\[
\text{activated initiation (with activator)} \quad \text{eq. 2.5}
\]
\[
(CH_2)_5-CO + (CH_2)_5-CO \xrightarrow{\text{Fast}} CH_3CO
\]
\[
\text{NCH}_3\text{CO} \xrightarrow{\text{N}^-} \xrightarrow{\text{N}^--(CH_2)_5\text{CON}-(CH_2)_5}
\]
\[
\text{Acetyl lactam} \quad \text{+monomer (Proton exchange)}
\]
\[
\text{propagation} \quad \text{eq. 2.6}
\]
\[
\text{CH}_3\text{CO}-[\text{NH}-(CH_2)_5\text{CO}]_1-N^-(CH_2)_5 \xrightarrow{\text{CO}} \text{N}^--(CH_2)_5\text{CO}-N^-(CH_2)_5
\]
\[
\text{CH}_3\text{CO}-[\text{NH}-(CH_2)_5\text{CO}]_1-N^-(CH_2)_5\text{CO}-N\text{N}-(CH_2)_5
\]
Lactams, as weak bases, may act either as H-bond acceptors in interactions with other weak protic acids or as proton acceptors when interacting with strong dissociated acids, or generally as Lewis acid acceptors. The lactam carbonyl oxygen acts as a basic site \[24\].

It is shown that when CL is heated in presence of a base, for example sodium caprolactamate (CLNa), polymerisation proceeds with increasing velocity after a certain induction period. It has been proposed that active amino and imide groups are formed in the initial stage, but since amine groups have been shown to inhibit rather than initiate polymerisation, the active initiating group is identified as the imide. The mechanism of the polymerisation can be described by a nucleophilic attack of CL anion on the carboxyl of the imide group. Equations 2.3-2.6 represent the mechanism of reactions that occur in this polymerisation method.

Two types of active species are also involved in this polymerisation. Several names can be found in the literature for these active species: catalyst, activator, initiator, promoter, cocatalyst, co-initiator, and accelerator. Generally in this work the term catalyst is used for the caprolactamate anion, (anionically activated monomer e.g. sodium caprolactamate (CLNa)), and activator to the substances that produce N-substituted caprolactams (e.g. isocyanates) or substances containing N-acyllactams (e.g. N-acetylcapro lactam) which are the species producing caprolactams with increased electrophilicity.

Polymerisation occurs within a few minutes after caprolactam is heated in the presence of a base. The speed of polymerisation depends on both initial polymerisation temperature (i.e. 100 to 200°C) and catalyst concentration. Below 150°C, activated anionic polymerisation is slow and no useful polymers are formed, but above this temperature the reaction proceeds exothermally [5]. The anionic polymerisation of caprolactam (APCL) is significantly affected by chemical additives due to the high reactivity of growing chain ends [25].

PA6 usually contains a low MW portion which may be more or less completely removed by extraction. This portion is often called “the extractables” and contains the residual CL, cyclic oligomers, low MW chain molecules starting with the corresponding ω-aminocarboxylic acid (linear monomer), and the residues of the catalyst and activator, which are not incorporated.
into macromolecules. The amount of residual CL and other cyclics depends on the ring-chain equilibrium which is characteristic for the CL at different temperatures [26]. Contamination in CL directly influences the polymerisation and the properties of the synthesised polymer. Therefore, the monomer CL must have a high level of purity (> 99.9%) [27]. The impurities may be derived from raw materials used in the process, from side and secondary reactions, and from decomposition combined with oxidation of the CL at elevated temperatures [28].

2.2.3 Kinetics

The anionic polymerisation of caprolactam (APCL) consists of exothermic reactions (polymerisation) and processes (crystallisation). This polymerisation method has a complex chemistry [29-31] and consists of many reversible and irreversible reactions. Many side reactions are reported to happen during polymerisation especially at higher temperatures [29].

![Figure 2.1: Temperature rise versus time (from reference [33])]
Generally, the kinetics of polymerisation via free ions can be described by the following equation:

$$-\frac{d[M]}{dt} = k_p[M][I] - k_d[P'][I]$$

*eq. 2.7*

where $M^-$ and $P^-$ are anions of monomer and polymer, and $k_p$ and $k_d$ are the rate constants of polymerisation and depolymerisation.

Crystallisation can occur either during polymerisation or after polymerisation, depending on catalyst-activator combination and initial polymerisation temperature. Therefore, the temperature rise may occur in two stages. The first stage is attributed to the polymerisation exotherm and the second rise is due to the crystallisation exotherm (see Fig. 2.1). Kinetics of polymerisation and crystallisation are separately discussed in this chapter.

### 2.2.3.1 Kinetics of polymerisation

The detailed mechanism and kinetics of this polymerisation are not absolutely clear. However, two types of models have been used in past work to describe the kinetics: mechanistic models [34], and overall models [35]. The mechanistic models, which are not very accurate because of the unknown mechanism in the propagation step, individually account for each possible reaction. Mechanistic models are not completely successful in predicting the APCL. On the other hand, the overall models combine all the possible reactions into one reaction and account for that [33]. In this case, the deviation between experimental and calculated data is minimised.

In 1971, Sebenda and Kouril [36] used the following equation to determine the rate of anionic polymerisation:

$$\nu_p = -\frac{d[M]}{dt} = k_p[L^-][I] = k_pK^{0.5}[LNa]^{0.5}[I]$$

*eq. 2.8*

where $[L^-]$ is the concentration of lactam anions and $[I]$ is the concentration of acyllactam growth centres. $K$ is dissociation constant of lactamate. It should be mentioned that it is not correct to insert the initial concentrations of both catalytic species in this equation as their concentrations decrease during polymerisation. Therefore, no absolute $k_p$ (polymerisation constant) value may be calculated.
Fifteen years later, in 1986, Stehlicek and Sebenda [37] found that the initial rate of consumption of the acyllactam \( \nu_o \) was proportional to initial concentration of the lactam salt as shown by the following equation:

\[
v_0 = -\frac{d[I]}{dt} = 0.002[I]_0[KL]_0^{0.87}
\]  

eq 2.9

Malkin et al. [35] proposed an autocatalytic model which was modified by Bolgov et al. [33] to be used in the APCL with unequal concentrations of initiator and catalyst. The equation below represents an autocatalytic equation of this type [33]. The terms in this equation are described in Table 2.1.

\[
dX/dT = k \exp \left( \frac{U}{RT} \left[ \frac{AC}{M_0} \right] (1-X) \right) \times \left[ 1 + \frac{b}{([A][C])^{1/2}} X \right]
\]  

eq 2.10

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X )</td>
<td>Fractional conversion</td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature, K</td>
</tr>
<tr>
<td>( K )</td>
<td>Pre-exponential or front factor, l mol(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>( U )</td>
<td>Activation energy, J mol(^{-1})</td>
</tr>
<tr>
<td>( R )</td>
<td>Universal gas constant, J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>([A])</td>
<td>Activator concentration, mol(^{-1})</td>
</tr>
<tr>
<td>([C])</td>
<td>Catalyst concentration, mol(^{-1})</td>
</tr>
<tr>
<td>(M_0)</td>
<td>Initial monomer concentration, mol(^{-1})</td>
</tr>
<tr>
<td>( b )</td>
<td>Autocatalytic term, l mol(^{-1})</td>
</tr>
</tbody>
</table>

It should be mentioned that in eq. 2.10, the concentration of activator, \([A]\), is equal to the real concentration of the substance multiplied by its functionality. For example, in the same concentrations of a mono-functional activator and di-functional activator, \([A]_d\) is twice the \([A]_m\). The value of the pre-exponential factor \( k \) allows a comparison of the efficiency of various activators in the initial polymerisation of CL and the value of \( b \) describes the intensity
of the self-acceleration effect during chain growth [33]. The optimum values of $b$, $k$, and $U$ vary for different catalyst-activator systems and can be determined by regression analysis$^2$.

Another similar equation proposed by Macosco et al. [38] is:

$$\frac{d\beta}{dt} = A_0 \exp\left(-\frac{E}{RT}\right)(1-\beta)^n(1+B_0\beta)$$  \hspace{1cm} \text{eq. 2.11}$$

where $A_0$ is the pre-exponential factor, $E$ is apparent activation energy, $n$ is the order of the reaction, $B_0$ is the autocatalytic factor, and $\beta$ is the degree of conversion.

Generally, the rate of reaction is determined by measuring any convenient parameter that changes in the system with time. This parameter should be easy to measure and should change sufficiently in the course of reaction to permit an accurate distinction to be made as time passes [40]. One of these parameters that can be measured during polymerisation is monomer conversion which will be discussed in the next chapter.

2.2.3.2 Kinetics of crystallisation

As the APCL is carried out below the melting point of PA6, non-isothermal crystallisation occurs as the reaction proceeds. The crystallisation behaviour during polymerisation depends on the process variables such as temperature of the melt and cooling conditions.

Before 1988, most of the crystallisation studies were based on the Avrami equation [41], which was not appropriate for studying non-isothermal crystallisation. Lee and Kim [42] proposed a new equation in 1988 to describe the non-isothermal crystallisation behaviour during the adiabatic polymerisation of CL. The modified form of their equation is:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_o}{RT}\right) \times \exp\left(-\frac{\psi T_o^\alpha}{T(T_m^\alpha-T)}\right) \alpha^{2/3}(\alpha_{eq} - \alpha)$$  \hspace{1cm} \text{eq. 2.12}$$

$^2$"Regression analysis is a technique used for the modelling and analysis of numerical data consisting of values of a dependent variable (response variable) and of one or more independent variables (explanatory variables). The dependent variable in the regression equation is modelled as a function of the independent variables, corresponding parameters ("constants"), and an error term. The error term is treated as a random variable. It represents unexplained variation in the dependent variable. The parameters are estimated so as to give a "best fit" of the data. Most commonly the best fit is evaluated by using the least squares method, but other criteria have also been used" [39].
where \( A = C \times (36\pi\rho_c \cdot N\nu_o^3)^{\frac{1}{2}} \)

The other terms in above equation are described in Table 2.2.

**Table 2.2: Description of terms in eq. 2.12**

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>The degree of crystallinity</td>
</tr>
<tr>
<td>( E_D )</td>
<td>Activation energy for diffusion</td>
</tr>
<tr>
<td>( \Psi )</td>
<td>Constant</td>
</tr>
<tr>
<td>( T_m^p )</td>
<td>Equilibrium melting temperature</td>
</tr>
<tr>
<td>( C )</td>
<td>Arbitrary constant</td>
</tr>
<tr>
<td>( \rho_c )</td>
<td>The density of spherulite</td>
</tr>
<tr>
<td>( N )</td>
<td>The number of nuclei per unit mass</td>
</tr>
<tr>
<td>( \nu_o )</td>
<td>Universal constant for semi-crystalline polymers: ( \nu_o = 7.5 \times 10^8 \mu m/s )</td>
</tr>
</tbody>
</table>

As indicated in Fig. 2.1, the temperature rise during APCL is due to polymerisation and crystallisation. Davtyan and his co-workers [43] suggested that at temperatures below 150°C both polymerisation and crystallisation occur simultaneously, whereas at temperatures of about 150°C polymerisation is followed by the crystallisation process. So they believed that the total generated heat during the polymerisation process was sum of the enthalpy of crystallisation and polymerisation.

\[
cp \frac{dT}{dt} = q_\alpha \cdot M_0 \frac{d\alpha}{dt} + q_\beta \cdot M_0 \frac{d\beta}{dt}
\]

\[
\text{eq. 2.13}
\]

where \( c \) and \( \rho \) are the heat capacity and specific density of reacting media, \( q_\alpha \) and \( q_\beta \) are heat effects of polymerisation and crystallisation, and \( M_0 \) is the initial concentration of monomer.

### 2.2.3.3 Degree of polymerisation and monomer conversion

Fig. 2.2 indicates that the degree of polymerisation, \( \bar{P}_r \), increases with increase in conversion of CL.
Figure 2.2: Dependence of degree of polymerisation on monomer conversion catalysed by CLNa, in the presence of different activators, (symbols represent different activators) [44].

2.2.4 Branching and side reactions

Deactivation, branching, and a series of reversible transacylation reactions occurring during the APCL [33], produce side reaction products, heterogeneities in the resultant polymer structure, and a broad MWD [29]. Side reactions are responsible for the presence of structural irregularities in polymer chains.

Branching may occur via side reactions in anionically polymerised PAs [45]. After some time, which depends on the concentration of activator and the temperature of polymerisation, viscosity average molecular weight ($\bar{M}_v$) starts decreasing more or less quickly. This phenomenon has been explained by the branching of the polymer chain [46]. Petit et al. [47] have observed a rapid change in the imide and lactam ion concentrations during the initial stages of polymerisation, and attributed this phenomenon to a Claisen-type condensation between low MW growing chains and/or initiating species which results in branching reactions [40].

Van Rijswijk et al. [48] reported that branching reactions initiated at temperatures exceeding 160°C. Although these types of reactions occur for both mono- and di-functional carbamoylcaprolactam activators, branching is enhanced by difunctional activators [49]. Due to the fact that all chain ends remain active after branching, continued growth of all branches
occurs and even the formation of a second branch is possible, ultimately forming a 3D network structure.

Ricco et al. [50] reported that for hexamethylene-1,6-dicarbamoylcaprolactam, the rate of branching is only significant at polymerisation temperatures exceeding 180°C. It must be kept in mind that the efficiency and concentration of the catalyst-activator combination in polymerisation, has an important effect on the rate of branching and branching temperature. Van Rijswijk et al. [48] suggested that with higher activator concentration (i.e. a higher chance of branching reaction taking place) and using a slower catalyst-activator combination (i.e. a longer time during which branching can take place), a significant degree of branching even at lower temperatures can be produced. The dependence of the degree of branching on the activator concentration and the reaction rate has also been reported by Mateva et al. [49]. The higher basicity of, for instance, a sodium caprolactamate catalyst, commonly used in combination with acyllactam activators, causes alternative branching mechanisms to occur such as Claisen condensation and trans-amidation [33,49-51].

![Branching reactions in APCL](image)

**Figure 2.3:** Branching reactions in APCL [52].
Branching reactions can lead to some very high MW species. At high conversion, coupling and/or condensation (Claisen type) reactions take place resulting in branching and high molar mass. It is believed that with high levels of activator, due to fast polymerisation kinetics, the monomer concentration depletes rather rapidly and active amide anions are likely to attack neighbouring polymer chains to cause branching, when they cannot find monomer units to regenerate the catalyst species [52]. Fig. 2.3 shows the possible reaction type for branching in APCL.

The reduced reptation times of branched polymers decrease the melting point and increase the crystallisation rate, which may result in reducing the final degree of conversion of PA6, because of the competitive nature of crystallisation and polymerisation [53]. Branching can even cause a transition in the crystal structure [50,51], which is a reason for decreasing melting point as is explained as follows [48]: two types of crystals appear in anionic PA6: those with the α-structure (melting point (Tm): 220°C) and those with the γ-structure (Tm: 214°C). For anionic PA6 it is reported that due to excessive branching the γ content can increase [50,54], hence reducing the melting point.

Many side reactions have been reported to participate in the polymerisation process, especially at elevated temperatures [33]. At higher temperatures side reactions leading to the decay of the active components is likely. Therefore, it is quite possible that a significant amount of active components disappear immediately at the beginning of polymerisation [37].

The side reactions in APCL are not only linked to the strong basicity of the reaction medium but also highly favoured by its high temperature increase (i.e. up to 52°C), due to the heat of polymerisation and the very poor heat exchange with surroundings. Ricco et al. [50] suggested five requisites in order to reduce side reactions in APCL: (1) sufficiently low polymerisation temperature, (2) reaction under strictly isothermal conditions, able to efficiently prevent any local temperature increase of the reacting mixture; (3) very fast polymerisation reactions allowing the viscosity of the medium to grow very rapidly; correspondingly, both chain mobility and susceptibility to side reactions decrease; (4) polymerisation temperatures lower than the PA6 melting point, with further reduction of side reactions due to crystallisation immediately after polymerisation; (5) fast cooling which entirely stops side reactions.
2.2.5 Polymerisation in DSC

Activated APCL can be studied by differential scanning calorimetry (DSC). The superimposed polymerisation and crystallisation kinetics can be separated and studied in DSC thermograms.

In 1977, Karger-Kocsis and Szafner [55] used DSC to investigate the effect of crown compounds on the APCL. They calculated the heat of polymerisation by subtracting the heat of crystalline melting characteristic of crystalline PA6, from the area of the overall exothermic peak. Two years later, in 1979, Karger-Kocsis and Kiss [56] attempted to separate the polymerisation and crystallisation processes in APCL on the basis of DSC analysis. The outcome of this work was to promote a closer control of the heat generation during polymerisation and thereby, the quality of the polymer formed. They carried on similar investigations over the next two years, mainly studying the effect of crown compounds on activated APCL [57,58]. Another group in Italy [59] used DSC to study the APCL in the presence of lithium chloride (LiCl). They evaluated the variation of polymerisation enthalpy, $\Delta H_P$, as a function of LiCl content.

Several years later, in 1991, Wilfong and co-workers [60] attempted to separate polymerisation kinetics from crystallisation using DSC. The non-isothermal polymerisation of CL was carried out in sealed pans. They filled large pans with the pre-mixed polymerisation mixture (40g) and sealed them inside a nitrogen glovebox. They used the combination of CLNa and adipoyl-bis-caprolactam (ABC) as catalyst and activator respectively, which resulted in a slow reaction, therefore the separation of polymerisation and crystallisation could be achieved. Fig. 2.4, obtained from their work, shows the endothermic and exothermic peaks due to the reactions and processes during the heating of reactants. Curve A was followed by the nearly simultaneous polymerisation and crystallisation processes and then at about 217°C by melting of crystalline PA6. In curve B, the exothermic polymerisation and crystallisation processes can be identified as separate events. At higher temperatures, melting of crystallised PA6 was observed as previously shown for the slower heating rate. At the fastest heating rate, curve C, melting of CL was followed by its polymerisation to form PA6. The absence of the PA6 melting endotherm at high temperatures indicates that the exotherm solely comprised heat from the reaction. So process kinetics influenced not only formation of the PA6, but also its subsequent crystallinity. A newer investigation was carried out in 2001 by Luisier and co-workers [61]. They used DSC to measure the reaction heat flow versus time at different constant temperatures (see Fig. 2.5).
Figure 2.4: DSC Thermograms of polymerisation mixtures at the heating rate of (a) 1, (b) 5, and (c) 10°C/min [60].

Figure 2.5: The reaction rate \((d\beta/dt)\) versus time at different polymerisation temperature (isothermal conditions) [61].

The reaction rate \((d\beta/dt)\) can be calculated in the following equation using the heat flow rate \((dH/dt)\):

\[
\frac{d\beta}{dt} = \frac{dH}{dt} \frac{1}{\Delta H_0}
\]

\textit{eq. 2.14}
It should be mentioned that this equation is only correct if we can assume a direct proportionality between the heat flow and reaction rate.

2.2.6 Thermal stability of PA6

At higher temperatures, some reactions proceed at measurable rate in polyamides. Reactions in the temperature range up to 300°C are important as possible secondary reactions occurring during polymerisation and polymer processing. Pyrolytic reactions proceeding at 350 to 500°C are utilised in polymer analysis [45]; thermogravimetry to 500 to 600°C is applied as a method for characterisation of polymer thermal stability [62]. Thermally initiated breaking of the C-N and C-C backbone bonds in linear polyamides only occurs at temperatures above 350°C. At lower temperatures, polyamides undergo depolymerisation, condensation and hydrolytic reaction, as well as reactions of the end groups. Depolymerisation mainly occurs by reaction of the –NH₂ end groups, and it is catalysed by –COOH groups [63]. In PA6, generation of CO₂, H₂O and NH₃, i.e. of substances indicating end group reactions may be observed at temperatures as low as 250°C. At this temperature, the overall MW of the polymer increases, with condensation reactions (i.e. branching) dominating breakdown. Chain splitting is significant at temperatures over 260°C [64].

The main products of high temperature oxidation or burning are CL, CO₂, and unsaturated and aromatic hydrocarbons [62].

Czernik et al. [65] reported that three main reaction types occur during thermal decomposition of PA6 in the temperature range of 200 to 300°C; hydrolysis, acidolysis, and aminolysis.

2.2.7 Other methods for polymerisation of caprolactam

Ring opening polymerisation of CL to PA6 is possible by either hydrolytic or non-hydrolytic processes. The latter processes include cationic and anionic mechanisms. Since APCL has already been discussed, the other two methods for polymerisation of CL are briefly described here.
2.2.7.1 Hydrolytic polymerisation

Hydrolytic polymerisation of CL is performed at elevated temperatures between 215 to 260°C and in the presence of water or water releasing material. This technique is usually used for the large scale production of PA6 in industry.

The first step in the sequence of reactions consists of a hydrolytic ring opening reaction leading to an amino acid. Three principal reactions play the most important role in this polymerisation. Mechanisms and the chemical reactions of polymerisation can be illustrated by the following equations [29]:

\[
\begin{align*}
(CH_2)_5-NH + H_2O & \leftrightarrow (CH_2)_5-NH_2 \\
& \text{polycondensation (PC)} \\
\end{align*}
\]

\[
\begin{align*}
~~~COOH + H_2N~~~ & \leftrightarrow ~~~CO-NH~~~ + H_2O \\
& \text{eq. 2.16}
\end{align*}
\]

\[
\begin{align*}
~~~NH_2 + (CH_2)_5-NH & \leftrightarrow (CH_2)_5-NH_2 \\
& \text{and polyaddition of caprolactam to end groups (PA)} \\
~~~COOH + (CH_2)_5-NH & \leftrightarrow (CH_2)_5-NH-CO~~~ \\
& \text{eq. 2.17}
\end{align*}
\]

The first reaction is an autocatalytic process. The majority of CL converts to polymer by polyaddition and only a small fraction of CL is polymerised by polycondensation [66].

2.2.7.2 Cationic polymerisation

The term “cationic polymerisation” defines a polymerisation process that is initiated under anhydrous conditions by protonic acids with anions, Lewis acids, and salts of strong acids [67] at temperatures between 220 to 260 °C [68]. Because of the complicated mechanism of cationic polymerisation and existence of several kinds of active species that determine the type conversion reactions, its mechanism is not elucidated in this report.
2.3 Parameters influencing the anionic polymerisation of caprolactam and their effects on the final properties of synthesised polymer

The anionic ring opening polymerisation of CL into high MW PA6, with final conversions of up to 99%, can be obtained in a short time depending on the type and amount of reactants and polymerisation temperature [69].

This chapter will provide general information about the work that has been done in the literature to investigate the influence of polymerisation parameters such as polymerisation temperature, and reactant concentrations and type on the polymerisation. This chapter will provide a discussion of the variety of catalysts and activators that can be used.

2.3.1 Catalysts

Generally, catalysts in APCL can be divided into three types.

1. Strong bases that produce caprolactamates in reaction with CL (e.g. NaH).
2. Caprolactamates (e.g. alkali metal cations).
3. Substances with low basicity which decompose under reaction conditions into strong bases (e.g. C₆H₅CH₂COOK).

Group 2 are usually obtained from reaction of CL dimer and group 1 substances during the first step of polymerisation (catalyst formation). Group 3 is more advantageous just for specific requirements. Despite this division, a variety of catalysts can be found in literature [71].

A literature review has shown that the first choice of catalyst is CLNa, except in the studies at the Monsanto Company by Gabbert and Hedrick [70] and Greenley et al. [34], where caprolactam magnesium bromide (CLMgBr) was used as catalyst. The main advantage of using CLMgBr (a Grignard salt) as the catalyst, is ease of handling and a less acidic MgBr⁺ cation compared to the Na⁺ in CLNa [52]. In addition the formation of cyclic oligomers is
markedly suppressed in polymerisations initiated with magnesium compounds compared with the polymerisation initiated with the sodium salt of caprolactam (CLNa) [72,73]. The structure of CLNa and CLMgBr are shown in Fig. 2.6.

Two other catalysts that have been mentioned in the literature are complexes derived from CLMgBr and aluminium alkyls, and the quaternary salts of lactams often referred to as onium salts [74].

Increasing catalyst concentration results in higher polymerisation rates as more anions are produced [75]. On the other hand, adding more catalyst causes the final degree of conversion to decrease. The reason for this is because for each catalyst molecule added a cation is introduced which needs to be compensated for by a CL anion; thus 100% monomer conversion is not achievable [76].

The other reason for the reduction in the final monomer conversion by adding more catalyst is due to the exothermic nature of this polymerisation. As the rate of reaction increases by adding more catalyst, the temperature build up increases and the ring-chain equilibrium shifts to the monomer side [77,78]. It is reported that this equilibrium can shift back towards the polymer at low cooling rates as long as the anions are not deactivated [53].

2.3.2 Activators

As described in Reference 6, activators are “substances like N-acyllactams, precursors from which the latter are generated in situ under polymerisation conditions (esters, acyl halides), or substances producing N-substituted lactams with electronegative substituents of increased electrophilicity of the cyclic carbonyl group (isocyanates)”. Although activators can be either mono-functional (f = 1) or multi-functional (f ≥ 2), most of the literature is based on mono-functional activators. Activators with functionality more than two are expected to produce branched polymers [29].

A large number of activators are reported in the literature. However, different groups have used different activators due to the variation of properties which can be achieved. For instance, Wilfong and his co-workers used adipoyl-bis-caprolactam in their work [60]. This activator resulted in a slow reaction enabling separation of the polymerisation and crystallisation processes in their studies. In another paper, Lombardi and Calvert chose activators which are stable at 70°C (i.e. caprolactam jetting temperature) and have the ability to polymerise quickly after the temperature is raised to 165 °C. They used 3-isopropenyl dimethylbenzylisocyanate (TMI) and tetramethyl-1,3-xylylene diisocyanate (TMXDI) (see
Shleifman and his co-workers [80] used polyacryloylcaprolactam and N,N’,N”-trimesinoyltercaprolactam (f = 3) as multi-functional activators. Polymer chains start growing from three points on the activator molecule when a three functional activator is used. Among all of the activators, N-acetylcaprolactam has proved to be the most efficient among those investigated [52].

Udipi and his co-workers used isophthaloyl-bis-caprolactam as a di-functional activator and N-acetylcaprolactam as a mono-functional activator (see Fig. 2.8) [52].

Some groups tried to synthesise new activators for their own researches. In research in Kyung Hee University (Korea), tolylene dicarbamoyl dicaprolactam (TDC), hexamethylene dicarbamoyl dicaprolactam (HDC), and cyclohexyl carbamoyl caprolactam (CCC) were synthesised and used as activators [40]. In other research, (HDC), (CCC) and isophorone dicarbamoyl caprolactam (IDC) were produced in laboratory [50].

Many other activators are reported in the literature such as: 2,6-toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), cyclohexyl isocyanate (CHI), cycloaliphatic esters, acylcaprolactam, N,N’-diphenylurea (DPU), N-butyl, N’-phenylurea (BPU), N,N’-
dibuthylurea (DBU), 4,4-diphenylmethane-bis-carbamoyl caprolactam, chlorophenylcarbamoyl caprolactam, N,N'-isophthaloyl-bis-caprolactam, and N-benzoyl caprolactam (see Fig. 2.9) [81].

![Chemical structures](image)

**Figure 2.9:** (a) N-benzoyl caprolactam, (b) N,N'-isophthaloyl-bis-caprolactam [81].

Increasing the activator concentration results in creation of more initiation points for chain growth and consequently the polymerisation rate rises [52]. However, due to the higher amount of initiating points, more polymer chains start growing simultaneously and therefore the final MW of the polymer drops [30,52], which results in a decrease in toughness [82], Tm, and glass transition temperature (Tg) [83].

Udipi *et al.* [52] reported that the amount of final monomer conversion varies with the activator concentration and increases from 84% at 0.2% molmol\(^{-1}\) of CL to 93% at 0.5% molmol\(^{-1}\) of CL. He believes that the reason was due to a very slow polymerisation rate at lower concentrations of activator. Therefore, as the polymer chains were formed and started to crystallise, the active sites would have been encapsulated inside the crystals.

The mono- and di-functional activators usually lead to linear polymer chains, whereas, higher functional ones result in star-branched polymers [84,85].

### 2.3.3 Catalyst-activator combination and ratio

In the literature the most commonly used combination is CLNa as catalyst and N-acetylcaprolactam as activator. Gabbert and Hedrick [70] preferred to use CLMgBr as the catalyst and N-acetylcaprolactam as the activator because of ease of handling and fewer side reactions compared to the other combinations. Udipi and Dave [52] used a CLMgBr and isophthaloyl-bis-caprolactam combination in their study. The reason for choosing this system was the “stability of CLMgBr compared to sodium and the proven efficiency of isophthaloyl-bis-caprolactam in their earlier studies at Monsanto Company”.

CLNa / N-acetylcaprolactam, CLNa / hexamethylene-1,6- dicarbamoylcaprolactam, CLMgBr / N-acetylcaprolactam, and CLMgBr / hexamethylene-1,6-dicarbamoylcaprolactam
combinations were used to investigate the influence of catalyst-activator combination on the rate of the reaction. Results are shown in Fig. 2.10 [53].

![Graph showing reaction rate for four catalyst-activator combinations](image)

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Activator</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium caprolactam</td>
<td>'C10'</td>
<td>No complex</td>
</tr>
<tr>
<td>Caprolactam</td>
<td>'C1'</td>
<td>Complex</td>
</tr>
<tr>
<td>Magnesium bromide</td>
<td></td>
<td>Initially no complex</td>
</tr>
</tbody>
</table>

*Figure 2.10: Reaction rate for four catalyst-activator combinations [53].*

The combination of catalyst-activator has a direct influence on the rate of reaction. This influence can be explained by the fact that the rate of dissociation and therefore the activity of the catalyst decreases with increasing size of the cation due to a decreasing ionisation potential and restricted mobility. An alternative way to generate anions is through complex formation between the activator and the cation of the catalyst [30,34,75]. However, not all combinations of activator and catalyst are able to form a complex. If no complex is formed, anions would only be generated in small quantities due to dissociation, so the rate of reaction would be low [53].

In most reported research, an equivalent molar concentration of catalyst and activator has been used [37], as each active site can attack one catalyst anion, when as Malkin et al. [35]
suggested, the concentration of activator [A] is equal to \([A] = [C]/N\), where [C] is catalyst concentration, and N is the functionality of activator.

Wilfong et al [60] observed a reduction in polymerisation temperature as the ratio of catalyst-activator increased from 1:1 to 2:1 or more.

Greenley et al. [34] suggested that in the case of using di-functional activators, if an activator to catalyst ratio of two is employed, there may be simultaneous growth of two molecules from one catalyst site. Otherwise, if ratios less than two are employed, because of the excess of activator, degradative and branching processes should be enhanced (i.e. active sites react with polymer chain instead of monomer).

### 2.3.4 Initial polymerisation temperature

Initial polymerisation temperature has a strong influence on the polymerisation and crystallisation processes that make it one of the most important processing parameters. Polymerisation temperature has effects on both microscopic and macroscopic properties such as monomer conversion, molar mass, crystallinity, tensile properties and density of synthesised polymer. Rijswijk and co workers [48] investigated the influence of polymerisation temperature on most of these properties.

#### 2.3.4.1 Influence of polymerisation temperature on the reaction rate

Other authors have investigated the influence of polymerisation temperature on the reaction rate [43,52,75]. Almost all agree that increasing polymerisation temperature results in a higher reaction rate.

#### 2.3.4.2 Influence of polymerisation temperature on the molar mass

Fig. 2.11 [48] shows that with increasing polymerisation temperature \(\overline{M_v}\) increases rapidly. On the other hand, a higher polymerisation temperature (>160°C) causes more branching reactions and as a result, broader MWD.

#### 2.3.4.3 Influence of polymerisation temperature on the monomer conversion

Kohan [4] suggested that monomer conversion decreases with increasing polymerisation temperature for two reasons. The first reason is due to the shift in the ring-chain equilibrium
of the anionic ring opening polymerisation towards the monomer side. The second reason is because of the degree of crystallinity, which decreases with increasing polymerisation temperature. If the rate of crystallisation is low enough for the monomer to be expelled from the crystals, the crystalline region will have 100% conversion. Therefore the overall conversion of synthesised PA6 increases at higher crystallinity. However, this trend would not be true at lower temperatures (around 140°C) when the rate of crystallisation is very high. It should be mentioned that, at higher crystallisation rates, monomers can be trapped inside the growing crystals reducing the monomer conversion and causing a white colour on the surface of PA6 samples [48]. This theory has been confirmed, as a decrease in monomer conversion from 97% at 155°C to 94% at 195°C was reported by Ricco and Russo [50].

Unlike Kohan and Ricco-Russo, Dave et. al. [33] reported that the monomer conversion was increased from 64.4% at 110°C to 93% at 160°C and decreased a little to 92% at an initial polymerisation temperature of 210°C.

![Figure 2.11: Viscosity average molar mass for different polymerisation temperature [48].](image)

### 2.3.4.4 Influence of polymerisation temperature on the crystallinity

It is believed that the degree of crystallinity is gradually decreased by increasing the polymerisation temperature. There are two reasons for this. The first reason is a thermodynamic explanation, and the second one is due to the structure and symmetry of the synthesising polymer. The thermodynamic explanation is that at higher polymerisation temperatures, the thermal motion of the polymer chains is too high for them to crystallise.
The second reason is that the rate of branching increases by increasing the polymerisation temperature; the branch points disturb the formation of crystals and reduce the degree of crystallinity [54]. At temperatures below 130°C, the crystallisation rate is very high and reactive groups can become trapped inside growing crystals before they can polymerise. Consequently, the conversions obtained are low and mechanical properties poor. At temperatures above 180°C, due to the reaction exotherm, the reacting mixture will heat up to temperatures exceeding the melting temperature of PA6 (220°C). As a result, the morphology (bigger crystal size) and the properties of the polymer after cooling will be different and will more resemble hydrolytic PA6. Rijswijk et al. [53] suggested that polymerisation at approximately 145 to 150°C results in the highest crystalline fraction.

2.3.4.5 Influence of polymerisation temperature on the tensile properties

It is believed that for most of semi-crystalline polymers, the mechanical properties of manufactured parts are predominantly determined by the degree of crystallinity and the conversion, and not so much by the degree of branching or the MWD. Therefore a decrease in Young’s modulus and tensile strength is expected with increasing the polymerisation temperature which correlates with decreasing degree of crystallinity [52]. However, further reduction of polymerisation temperature results in a very high crystallisation rate which causes entrapment of monomer in the crystals. This phenomenon reduces the structural integrity of the material and also the final monomer conversion of synthesised polymer, resulting in poorer mechanical properties. The higher density of PA6 synthesised at lower temperatures due to higher crystallinity and higher packing is another reason for increasing mechanical properties [86].

2.3.4.6 Influence of polymerisation temperature on the void content

There are two causes of void creation during the PA6 polymerisation process: (i) nitrogen dissolved in CL [87] and (ii) CL boiling. The amount of dissolved nitrogen increases very slowly with increasing polymerisation temperature. It is highly unlikely that the processing conditions used in the APCL induce boiling of CL. However, if boiling occurs, the effect will be greater with increasing polymerisation temperature.
2.3.5 Influence of polymerisation environment

The above concerns any effects of environment on the polymerisation process irrespective of polymerisation temperature and component concentrations. Unfortunately as the kinetics of APCL have not been fully described, there is no specific report on the influence of these parameters. However, it is known that any anionic polymerisation is sensitive to moisture, oxygen, and carbon dioxide [88,89], as these components can react with the free anions and deactivate the catalyst system during polymerisation.

It has been reported without giving any explanation that the APCL should be carried out under anhydrous and oxygen free conditions [53]. Water present in the polymerisation mixture decreases the concentration of lactam anions and also takes part in the hydrolysis of N-acyllactam growing centres [21].

In polymerisation catalysed by CLNa the rate constant decreases with increasing amount of water. The values of apparent activation energies increase with water concentration and the final degree of monomer conversion decreases with increasing water content. The retardation effect of water could be explained by partial decomposition of the catalyst (eq. 2.18) and decrease of its active concentration. NaOH formed can influence dissociation [90] of the catalyst and consequently the rate of polymerisation. Also hydrolysis in the CL cycle results in the formation of its sodium salt (eq. 2.19) which influences the basicity of the system by formation of the sodium salt of a weak acid and as a primary amine influences the course of polymerisation. It was confirmed [91] that primary amines are responsible for the aminolysis of growth centres [21].

\[
CL^-Na^+ + H_2O \leftrightarrow NaOH + HCL \quad eq.2.18
\]

\[
CL + NaOH \rightarrow H_2N\text{COO}^-Na^+ \quad eq. 2.19
\]

Decrease in the rate of polymerisation could be explained by the decrease in concentration of active growth centres in the polymerisation mixture.

Water may also hydrolyse formed growth centres resulting in formation of terminal carboxyl groups (eq. 2.20). Decrease in polymerisation rate is connected with the decrease in the concentration of the sodium salt of CL.

It is reported that magnesium catalysts are capable of eliminating the retardation effect of water on polymerisation [21].
2.4 Polymer characterisation and properties

The final properties of the synthesised polymer are one of the most important issues for the part manufacturer. For specific applications, manufacturers have to change processing variables to meet the customer’s demands. This can be achieved using the proper polymerisation conditions as discussed in previous sections.

The most important parameters that control the final properties of a PA6 product are MW of the synthesised polymer, percentage of crystallinity (i.e. regularity of the polymer structure), and the final degree of monomer conversion.

Later in this section, the properties that are important for a synthesised polymer such as Tm, Tg, mechanical and thermal properties are discussed.

2.4.1 Properties of PA6

The purpose of this section is to provide a brief general survey of the properties of PA6 such as mechanical and physical properties and their dependence on processing conditions.

Values for some of the properties of cast PA6 are listed in Table 2.3. It should be mentioned that the test conditions (room temperature and humidity) will affect some of these values.

Table 2.3: Cast PA6 properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Test Method</th>
<th>Units</th>
<th>Cast PA 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>ISO 527</td>
<td>MPa</td>
<td>75 – 85</td>
</tr>
<tr>
<td>E-modulus</td>
<td>ISO 527</td>
<td>MPa</td>
<td>3900</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>ISO 527</td>
<td>%</td>
<td>&gt;25</td>
</tr>
<tr>
<td>Maximum compressive strength</td>
<td>ISO 604</td>
<td>MPa</td>
<td>90 – 100</td>
</tr>
<tr>
<td>Compressive modulus</td>
<td>ISO 604</td>
<td>MPa</td>
<td>2700</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>ISO 178</td>
<td>MPa</td>
<td>100 - 110</td>
</tr>
<tr>
<td>Flexural modulus of elasticity</td>
<td>ISO 178</td>
<td>MPa</td>
<td>3300</td>
</tr>
<tr>
<td>Impact strength</td>
<td>ISO 180</td>
<td>kJ/m²</td>
<td>5.6</td>
</tr>
<tr>
<td>Hardness</td>
<td>ISO 7619</td>
<td>Shore D</td>
<td>83 – 85</td>
</tr>
<tr>
<td>Melting point</td>
<td>ISO 1218</td>
<td>°C</td>
<td>220</td>
</tr>
</tbody>
</table>

*Reference: www.nylacast.com
An important guide to the effect of temperature and moisture on the properties of polyamides is Tg. Moisture has a plasticising effect in polyamides and causes decreasing Tg and tensile properties. For example, the tensile modulus of PA6 increased from 1,500 to 3,000MPa after drying. Moisture and temperature have similar effects on the tensile properties. The equilibrium moisture absorption of PA6 at 50% RH and 23°C is 2.8% [92]. Increasing polyamide crystallinity decreases moisture absorption [93].

The melt processing of PA6 may be divided into three broad categories: melt spinning, extrusion, and injection moulding. Reaction injection moulding (RIM) or reactive extrusion, which may be used to cast very large structural elements of PA6 from the monomer or pre-polymer [94] are not yet as popular as their potential suggests, but efforts directed at broader acceptance of these techniques are continuing [95].

2.4.1.1 Mechanical properties

Tensile, compression, flexural, and shear strength are basic mechanical properties. Many factors affect the behaviour of materials. These factors are divided into three groups: (i) material factors e.g. MW, moisture content, crystallinity, and orientation; (ii) environmental factors e.g. temperature, and relative humidity; (iii) stress factors (e.g. nature of stress, rate of loading, and duration of stress [96]. Some of the commonly employed mechanical properties are as follows:

Tensile properties: one of the most important types of mechanical test is the tensile strength test. Results are usually derived from stress-strain curves.

Flexural properties: the elastic modulus of PAs can be determined in tension, compression, and flexure, but the modulus in flexure is the most commonly encountered value. However, tensile modulus is often provided as well [96].

Shear properties: shear strength, like flexural and compressive strength, is of more significance in low elongation and reinforced compositions. Shear modulus data can be obtained by dynamic mechanical testing [96].

Impact properties: in general, PA6 is known as a “tough” plastic, however, it is also notch sensitive. Increasing MW, moisture content and plasticiser increase impact strength [96]. Moisture can be absorbed by PA6 and behave like a plasticiser in the polymer, so the level of humidity during the test has a significant influence on the results.
Creep: creep measurement is a time-dependent test. It is concerned with the long term deformation due to a constant, continuous, or cyclic stress. The information from creep is used in design for applications involving long term loads [96,97].

Fatigue resistance: PAs have excellent fatigue resistance. A common method of obtaining fatigue data is by means of a Sonntag Universal machine. This device can be used to test the sample in tension, compression, and flexure and is characterised by provision of a constant maximum stress [96].

Abrasion resistance: PAs have a good abrasion resistance so are capable of being used as unlubricated bearings. The abrasion resistance of PA can be reported as milligrams lost in 1000 cycles of a brush [96,98].

Dimensional stability: PA parts may have dimensional changes due to water absorption, crystallisation, stress relief, and thermal expansion or contraction. The moisture absorption of PA6 depends on crystallinity, relative humidity, and temperature [96]. Fig. 2.12 shows a typical relationship between moisture absorption and deformation for PA6.

![Figure 2.12: Linear increase versus water absorption for injection moulded PA6 (120mm \times 10mm \times 4mm at 20^\circ C immersion temperature) [99].](image)

The following equation has been found valid for calculation of the moisture absorption of plates of PA [5]:

\[
C_r = C_r \frac{2.256}{s} \sqrt{(Dt)}
\]

\textit{eq. 2.21}
\[
\frac{q}{Q} = 1.128\omega Dt
\]

where \(c_t\) is concentration of moisture in part after \(t\) seconds (g/cm\(^3\)), \(c_s\) is saturation concentration of moisture (g/cm\(^3\)), \(s\) is Plate thickness (cm), \(D\) is diffusion coefficient (cm\(^2\)/s), \(q\) is moisture absorbed in \(t\) seconds (g), \(Q\) is total moisture absorbed at saturation (g), and \(\omega\) is ratio of surface (cm\(^2\)) to volume (cm\(^3\)).

### 2.4.1.2 Thermal properties

The coefficient of thermal expansion of unmodified PA6 (5 to 8 \(1/k.10^{-5}\)) depends on its moisture content, as it increases with moisture absorption [96]. The specific heat of PA6 increases with increasing temperature [96], and the thermal conductivity of a melt of PA6 also increases from 0.11 to 0.12 kcal hr\(^{-1}\)m\(^{-2}\)\((^\circ\text{C}/\text{m})\(^{-1}\), when the temperature is raised from 220 to 280\(^\circ\text{C}\) [100].

### 2.4.1.3 Chemical resistance

PAs have a good chemical resistance, except to acids and alcohols which can cause hydrolysis. The effect of chemicals on PAs increases with temperature. This effect can be either due to the reaction of chemicals with polymer functional groups or diffusion of fluid into the polymer, or both.

The crystallinity of the PAs has a strong influence on the rate of diffusion or interaction between chemicals and PAs. In general, increasing the crystallinity of PAs results in less chemical action and a lower diffusion rate. However, the permeability of PAs increases with moisture content of polymer, due to increased chain mobility in the amorphous portion of the polymer [5].

### 2.4.2 Glass transition temperature (Tg)

It is well known that Tm and Tg of semi-crystalline polymers are correlated with their molecular structures. This correlation is dominated by three main factors [101]: (i) chain geometry and regularity, (ii) chain stiffness, and (iii) intermolecular forces such as hydrogen bonds in the case of PAs. The first factor, chain geometry and regularity, is associated with the ability of the polymer chains to form crystals. When a polymer chain does not have
regularity, it is not able to lie in a parallel array with its neighbour chains to form crystals [102].

The second and third factors, chain stiffness and H-bonds, also have significant influences on the ability of PAs to crystallise. The existence of very stiff groups in the main chains such as isocyanate groups facilitates the parallel packing of chains and consequently crystallisation [102]. H-bonds, obviously, have a major role in crystallisation of PAs. Essentially all amide groups participate in H-bonding intermolecular links. It is suggested [103] that the Tm increases with number of H-bonds and chain stiffness. It is also reported that Tm is reduced by methyl branches [104].

Tan $\delta$ is given by the ratio of “loss modulus ($E''$) / storage modulus ($E'$)” and is proportional to the ratio of energy dissipated / energy stored. This is called the loss tangent or damping factor [105] and can be measured using dynamic mechanical analysis (DMA). The peak temperature for Tan $\delta$ in a DMA graph can be used to measure the Tg. Tg shifts to lower temperatures with increasing amount of residual monomer [106]. Both Tg and modulus enhancement decreased together with increasing flexibility (flexibility decreases with H-bonds) of the segments and the branched points of the polymer [102].

In considering how a molecular or experimental parameter might change the value of Tg, it is useful to think in terms of flexibility of the chain concerned, about the intermolecular forces involved and of the likely changes in free volume. Increasing chain flexibility leads to a decrease in Tg. An increase in intermolecular forces causes Tg to rise and any factor increasing the free volume occasions a decrease in Tg. Polar interactions such as H-bonds and dipole-dipole interactions raise the Tg because they have to be overcome before the segments are free to rotate to new conformation. As side chain flexibility increases, ease of rotation due to side groups, the Tg decreases [107]. In general the factors affecting Tg are as follow:

a) Molecular weight: in the polymer range, Tg is more dependent on MW than is Tm. Since chain end segments are restricted only at one end, they have relatively higher mobility than the internal segments, which are constrained at both ends. At a given temperature, therefore, chain ends provide a higher free volume for molecular motion. As the number of chain ends increases (which means a decrease in Mn), the available free volume increases, and consequently there is a depression of Tg [108]. This relationship is:
\[ T_g = T_{g}^{\infty} - \frac{k}{M_n} \quad eq. 2.23 \]

Where \( T_g^{\infty} \) is the glass transition temperature at infinite MW, and k is a constant [109].

b) Chemical structure [110]: The effects of the nature of the chain repeat units on \( T_g \) are closely related to intermolecular forces, chain stiffness, and symmetry.

c) Geometric factors: geometric factors such as the symmetry of the backbone and the presence of double bonds on the main chain affect \( T_g \). Polymer that have a symmetrical structure have lower \( T_g \) than those with asymmetric structures [108].

d) Inter-chain attractive forces: it is to be expected that the presence of strong intermolecular bonds (e.g. polarity or H-bonds) in a polymer chain will significantly increase \( T_g \).

e) Branching: the effect of branching on \( T_g \) can be explained in term of free volume. The higher concentration of chain ends in a branched polymer increases the free volume and lower \( T_g \) [109].

### 2.4.3 Influence of monomer conversion on properties

As the concentration of residual monomers increases, large reductions in the viscosities of the melt ensue. In a similar fashion, the concentration of extractables, that is, monomers and cyclic oligomers, and the concentration of water have a strong effect on the melting point of PA6. It becomes apparent that monomer molecules and water serve as sufficient plasticisers for the amorphous phase of PA6, reducing \( T_g \) and in the melting temperature range greatly increasing the chain mobility, helping to disrupt the crystalline lattice and melt the polymer at lower temperature than when only the higher MW, less mobile extractable organic molecules are present [102].

### 2.4.4 Influence of molecular weight on properties

Generally, the properties of polymers depend mainly on their MW. MW is therefore of fundamental importance in a polymer, also understanding its detailed molecular structure, and correlating this with its physical and mechanical properties [111].

48
Practical properties such as melting point, toughness, and resistance to stress cracking are dependent not only on the MW but also very strongly on the MWD [93]. Therefore, a uniform polymer structure is very important. The polydispersity can be reduced or prevented by higher melt temperature, better stirring of the melt, longer residence time [112], and by addition of a small amount of catalyst/activator. MW has influence on mechanical damping (tan δ) and the capacity of material to absorb energy [5]. In the low MW range of flexible range polymers, Tg shows a strong dependence on MW. At higher MWs the dependence asymptotically vanishes [102]. Bulk mechanical properties such as strength show a dependence on MW but this dependence is strongly affected by a dependence on interchain entanglements. To impart strength to a solid bulk polymer, each chain must be involved in no less than two entanglements on average [113]. The modulus and breaking stress are expected to be insensitive to MW. The breaking elongation is slightly sensitive to MW in tensile studies.

Although the importance of MW and MWD on mechanical performance has long been recognised, quantitative correlation between these parameters has always been a difficult endeavour. In addition to MW and MWD, mechanical properties are controlled by a large number of structural and external factors. Some of these variables, such as chain orientation, crystalline structure and morphology, are not independent so a change in MW or MWD can affect the other parameters [114]. After chemical structure, the polymer chain length and its distribution are the next most important molecular parameters controlling the physical, mechanical and processing properties of plastic materials.

Flory [115] reported that there is clear relation between MW and MWD with mechanical properties. The equation originally proposed by Flory could be reformulated as:

\[
P = A_P - \frac{B_P}{\bar{M}_P}
\]

\textit{eq. 2.24}

Where P is the property, \(A_P\) and \(B_P\) are positive constants and \(\bar{M}_P\) some average MW which has to be defined with respect to the property.

Brittle failure occurs if the polymer breaks at low elongation before reaching the yield point. Unlike the yield strength, which seems not to depend directly on MW, the brittle strength decreases substantially with a reduction in MW. For many polymers, a good correlation in the form of eq. 2.24 has been obtained between the brittle strength and number average
molecular weight ($\overline{Mn}$). Lowering MW of the sample will cause a ductile test specimen to fail in a brittle mode.

The ultimate elongation ($\varepsilon_b$) indicates the maximum strain that a material can withstand before rupture. For most of semi-crystalline polymers $\varepsilon_b$ improves with the increase in $\overline{Mn}$ and with narrowing in MWD but decreases with density as result of change in crystallinity [114].

2.4.5 Influence of crystallinity on properties

Some properties of polymers depend strongly on crystalline structure or morphology. For example the elongation at break may depend on the conformation of tie molecules linking crystalline lamellae. To obtain polymers with a high elastic modulus it may be desirable to prepare highly crystalline materials [116]. Along with increase in modulus and yield stress there is reduction of extension at break with increasing crystallinity. The yield stress can be approximately related to density (and hence crystallinity) by an expression of the form:

$$\log \sigma_y = \log \sigma_A + a(\rho - \rho_A)$$  

Where $\sigma_y$ is the sample yield stress, $\sigma_A$ the amorphous yield stress, $\rho$ the density, $\rho_A$ the amorphous density and $a$ a constant [116].

The mechanical properties of PA6 are predominantly determined by the degree of crystallinity and the conversion, and not so much by the degree of branching or the MW [48]. When decreasing the polymerisation temperature from 150 to 140°C, a higher degree of crystallinity did not lead to the expected increase in strength and stiffness. As mentioned earlier, the high crystallisation rate at 140°C causes entrapment of CL in the crystals, which reduces the structural integrity of the material. Consequently, a brittle polymer was obtained. The amount of trapped CL was high enough to fully account for the reduction in mechanical properties because the conversion at 140°C was much lower than 150°C and because the degree of branching is similar at 140°C and 150°C, one would expect the entrapped CL to cause a drop in melting point according to equation below [48]:

$$\frac{1}{T_m} = \frac{1}{T_m^0} - \frac{R}{\Delta H_m} \ln(1 - X_B)^{[117]}$$  

$eq. 2.26$
where $R$ is universal gas constant and $X_B$ the mole fraction of imperfections such as chain ends, branch-points and trapped monomer. $T_m^0$ is the melting point of perfect crystalline PA6 (221°C [48]).

It is well known that the physical, chemical and mechanical properties of crystalline polymers depend on the morphology, the crystalline structure and degree of crystallisation [118]. Tuzum suggested that tensile strength, hardness and elongation at break decrease regularly with increasing the catalyst/activator ratio due to the effect of variation in MW, but density increases [119].

Semicrystalline polyamide is often annealed at temperatures between the Tg and Tm. This leads to an increase in crystallinity, a reduction in residual stress, and property changes in the direction of higher strength and modulus but lower elongation at break. Three key temperatures determine annealing temperature boundaries: the rigid phase preceding onset of glass transition (Tg-50°C) at which no relaxation occurs, the Tm, and rapid crystallisation point (T_k). Annealing is often done at temperatures at or above T_k leading to increased crystallinity and reduced toughness [112]. In general the properties related to crystalline morphology are as follows:

a) Mechanical properties: the modulus of polymers increases significantly by increasing the crystallinity of the sample [120]. For other aspects of mechanical behaviour, however, the results available in the literature present no such simple picture and one obvious reason for this probably arises from the fact that order can exist at various levels in polymer morphology. Consequently, when attempts are made to correlate a given property with, say, crystallinity, it may also happen that spherulite-size is changing, and that this may be a more dominant parameter [120]. It has been observed, however, that a certain minimum MW is necessary before polymeric properties develop at all, and in this low MW region, MW can be considered as a determining factor in its own right [121].

b) Optical properties: transmission of light through polymer samples decreases drastically when crystallisation occurs. Scattering arises from the fact that the ordering arising from crystallisation produces variations in refractive index.

c) Permeability: although other aspects of morphology need to be considered in order to account completely for the permeation behaviour, this property usually decreases with increasing crystallinity [120].

Harkin-Jones and co-workers [122] have shown that spherulite size increases rapidly with increasing initial polymerisation temperature but crystallinity decreases. It has been found
that as spherulite size increases, impact strength, elongation at break, and yield point stress all decrease [120]. It is reported elsewhere that the flexural modulus increases with increasing spherulite size [123]. To summarise, higher crystallisation results in better chemical resistance, lower water absorption, higher modulus and lower toughness [122,124].

2.5 Crystallinity and morphology

Crystallography grew up as a branch of mineralogy, and involved mainly the recognition, description, and classification of naturally occurring crystal species. Crystallography is a relatively old discipline, dating from the discovery in 1912 of the diffraction of X-rays by crystals [125].

2.5.1 Introduction

Typically polyamides begin to crystallise on cooling 20 to 30°C below their Tm. At temperatures close to Tm the crystallisation rate is slow and large spherulite sizes can be obtained. At temperatures far below Tm the crystallisation rate is faster but smaller spherulites are formed. In polyamides with a higher density of amide groups, the memory effect (the heating history of the polymer) has more effect on the crystallisation rate on cooling as some H-bonds remain fixed even in the melt and result in effective nucleation sites. The influence of residence time in the melt on crystallisation kinetics has been studied for PA6, and it was found that heating the melt above the equilibrium Tm for a sufficient time can irreversibly eliminate all nuclei [126]. It was shown that the crystallisation data for PA6 are difficult to compare as even the same sample nucleates differently and has a different mechanism. This is due to the difficulty of separating nucleation from growth especially for fast crystallisation.

After initial crystallisation a typical polyamide undergoes a secondary crystallisation. This is a reorganisation process which occurs in the solid state and improves the already formed spherulites with no effect on morphology. So, DSC crystallisation exothermic peaks usually consist of a primary (sharp exotherm) and secondary crystallisation (a broad exotherm).

As mentioned before, it has been reported that polyamide samples with small spherulites show higher flexural modulus, higher upper yield stress, and lower ultimate elongation than do samples with large spherulites, both having similar crystallinities [127].
2.5.2 Factors affecting the crystallisation process

Factors affecting the crystallisation process:

a) Polymer composition:
   i. Chain constitution: an indication of the overwhelming effect of the nature of the chain on crystallinity can be obtained by considering the following factors; chain mobility and the free energy change on crystallisation, the one kinetic and the other thermodynamic. The more closely the chains can pack in this state, the more will it be possible for strong and co-operative forces of a Van der Waals nature to come into play between the segments; and it is this factor which contributes largely to the free energy change, or driving force for the process [120].
   ii. Branch points: one direct effect of branching is to reduce the amount of crystallinity present in the final product. As a consequence of this effect, the melting point is decreased [128].

b) Temperature: the effect of temperature on nucleation and growth rate is significant.

c) Molecular weight: increase in the rate of crystallisation with decreasing MW is also paralleled by a corresponding increase in the overall amount of crystalline material produced, although at very low MWs there is a subsequent fall. This effect is believed to be due influence of MW on growth rate not on the nucleation rate (density) [120]. MWD is also important, in that for a given average value, the rate of crystallisation decreases, as the distribution broadens [120]. Generation of low MW chains (degradation or chain scission) increases the chain mobility and leads to faster crystallisation and also increases the crystallisation temperature and sharpens the crystallisation peak [129].

2.5.3 Morphology

Crystal structure refers to the specific dimensions of a single, three dimensional lattice represented by the unit cell. Morphology deals with structure on a larger level. The molecules fold to form thin ribbon or layer shaped crystals termed lamella which aggregate into spherical stacks or clusters called spherulites (Fig. 2.13) [127]. Morphology is concerned with the nature of the final state after the crystallisation process is complete [120].
Figure 2.13: Proposed overall picture of polymer structure, for melt crystallised sample, showing interaction of various morphological units within a developing spherulite. Amorphous regions are also formed at the inter-spherulitic boundaries [120].

Crystallisation consists of nucleation and growth. Spherulites grow from a nucleation site and terminate by impingement on other spherulites [130]. The highest spherulitic growth rate for PA6 is reported at 405°K (132°C) [131]. As discussed, MW affects crystallisation through the increase in viscosity that it causes [132]. Spherulitic structure is characteristic of crystallisation in an environment free from mechanical and thermal stresses.

In polyamides crystallinity is favoured by such features of the molecule as a high degree of regularity in space (stereo-regularity) of the functional groups, the small molecular volume of these groups, and the ability of the secondary valence forces to develop a regularly packed array of atoms. On cooling the polymer from the melt, in which this is complete molecular disorder, the functional groups of one molecule during random motion of the segments become favourably aligned with those of a neighbouring molecule and a crystalline ordered region is formed. Other segments of the same molecule chain may lie outside the ordered region and show no crystalline characteristic. Thus single chains may pass through an ordered crystalline and a disordered amorphous region [5]. The secondary valence forces operative in crystallisation of polyamides can be largely identified with the hydrogen bonds. Stereo-regularity and the hydrogen bonds are generally recognised to be the main structural features of polyamides that result in high Tm of PA6. The number and size of the spherulites formed on cooling from the melt depend on the rate of cooling and on the number of nuclei present or formed during the cooling. A small number of large spherulites are formed on slow cooling and crystallisation from a small number of nuclei, while with rapid cooling and growth from
a large number of nuclei the reverse is the case [5]. Optical and x-ray studies have shown that (a) the entire structure of a given spherulite originated from a single primary nucleus and (b) crystallisation proceeds continuously from the nucleus outwards [133].

The crystalline thickness, $l$, is usually determined by the crystallisation temperature, processing conditions, and thermal history of the sample. When PA6 crystallises isothermally and is allowed the time to reach thermodynamic equilibrium, the fold surface of lamellae become increasingly smoother with time and the distribution of chain stems in the lamellae increasingly narrow. When it crystallises non-isothermally, the evolving crystals do not have the time to improve their regularity and perfection, their fold surfaces are more rough, and the distribution of chain stems in crystals remains broader than in isothermal crystallisation [102]. PA6 has been reported to exhibit two dominant monoclinic crystalline forms, termed $\alpha$ and $\gamma$. The $\alpha$ form consists of all trans chain conformation, and the hydrogen bonds are formed between adjacent antiparallel chains (resulting in the $ac$-plane sheets). In the $\gamma$ form, the chains are instead twisted to allow H-bond formation between parallel chains. The existence of these two forms depends mainly on the crystallisation conditions or the addition of specific fillers. The $\alpha$ form is recognised as the most thermodynamically stable. The characteristic X-ray diffraction (XRD) peaks of the $\alpha$ form at room temperature are located around $2\theta=21^\circ$ and $24^\circ$, and indexed as (200) and (002)/(202) diffractions, respectively. For the $\gamma$ form, the peaks are at around 11, 22 and $23^\circ$. They are diffractions from (020), (001) and (200)/(201) planes, respectively [50,134-140]. It is well known that upon rapid cooling from the melt (i.e. $> 20^\circ$C/min), PA6 prefers to crystallise first in the $\gamma$-form [135,136]. It may or may not convert partially or totally to the $\alpha$-form. The fraction of conversion and the degree of crystal perfection in both forms depend on many experimental conditions. Among them, cooling rate, isothermal annealing, moisture, and physical strain have been reported in literature [135,136] as having significant effects on the $\gamma$-to-$\alpha$ transition and on the levels of perfection in each coexisting crystal form. In general, $\alpha$-form is more stable and conversion of $\alpha$-to-$\gamma$ form is harder than $\gamma$-to-$\alpha$ form [102].

### 2.6 Methods of characterisation

#### 2.6.1 Fourier transform infrared spectroscopy (FTIR)

Infrared (IR) spectroscopy is one of the most established methods for characterisation of polymers [141] including polyamides. The strong IR bands at $3300\text{cm}^{-1}$, $1640\text{cm}^{-1}$, and
1545cm\(^{-1}\), correspond with hydrogen bonded N-H stretch, amide I C=O stretch, and amide II, C-N stretch plus CONH bend respectively and they are characteristic of the \textit{trans} planar conformation of the amide group [142]. Variations in position and intensity of the (usually sharp) crystalline bands and broader bands from the amorphous phase, permit identification of the type of PA and determination of sample crystallinity and orientation. Of the amide I and II and N-H stretch bands, the amide II band is especially sensitive to crystalline structure and appears at about 1540cm\(^{-1}\) (\(\alpha\)-phase) and 1560cm\(^{-1}\) (\(\gamma\)-phase). The latter band in the amorphous phase also appears near 1560cm\(^{-1}\) which is important in samples of low crystallinity. The IR bands for out-of-plane bends of the N-H (amide V) and C=O (amideVI) groups are also polymorph sensitive. They appear as relatively sharp bands at 690 and 580cm\(^{-1}\) for the \(\alpha\)-phase but are shifted to 712 and 625cm\(^{-1}\) for the \(\gamma\)-phase. Highly amorphous samples show much broader bands near each of these frequencies, indicating that the amorphous phase consists of a wider distribution of structures \(\alpha\)-like and \(\gamma\)-like associated with the amide group. The relatively sharp bands in IR spectra indicate the form of the crystalline phase [143].

Although there are other bands associated with the amide group in the fingerprint region (1500 to 4000cm\(^{-1}\)), most of the bands arise from vibrations of the methylene backbone. The sharp IR bands for CH\(_2\) groups adjacent to NH and CO in the \(\alpha\)-phase are easily detected at 1475 and 1415cm\(^{-1}\) respectively. The amorphous and \(\gamma\)-phases both show bands at 1465 and 1440cm\(^{-1}\), the former being relatively sharper in the \(\gamma\)-phase. The doublet between 1200 and 1170cm\(^{-1}\) is especially diagnostic. The higher cm\(^{-1}\) band (1200 to 1190cm\(^{-1}\)) is present only in the \(\alpha\)-phase whereas the lower cm\(^{-1}\) band (1189 to 1170cm\(^{-1}\)) indicates amorphous components. The broad band at 1140 to 1120 cm\(^{-1}\) is useful for monitoring the amorphous content. The sharp bands between 980 and 920cm\(^{-1}\) can identify the \(\alpha\)- and \(\gamma\)- crystalline phases respectively [143].

The amide I band is usually the most intense in the IR spectrum of polyamides. In the solid state it falls at 1640cm\(^{-1}\). The band is attributed to the stretching mode of the C=O double bond. It is sensitive to both intermolecular interaction, such as participating in H-bond formation, and intermolecular configuration and order changes such as changes in crystal form or difference between the crystal and amorphous phases. The amide II band contains contributions from the in-plane N-H bending mode and the stretching mode of the central amide –N-CO- bond. Because of the different sources of the contributions and the coupling between them, the amide II band is rather sensitive to the details of PA chain packing and the interactions between amide groups. When the amide I and amide II bands are considered
together, a pattern is noticed according to which the amide II band shifts downfield when the amide I band shifts upfield. These shifts are associated with the level of disorder in the sample; the more disordered is the sample, the higher is the amide I and the lower is the amide II band [102].

IR spectral processing can be employed in other fields of polymer analysis [141] such as:

a) Detection and identification of additives [144].
b) End group analysis [145]: the detection and identification of end groups is of considerable importance for the determination of molecular weight and degree of branching. If a standard polymer of very high molecular weight and low degree of branching is available, its FTIR spectrum can be subtracted from the spectrum of any low molecular weight analogue, thereby accentuating the absorptions of the end groups.
c) Study of oxidation and degradation reactions [146], and molecular interactions [144]: as a consequence of molecular interactions arising from chemical or physical effects (e.g. H-bonds or dipole association) shifts in the absorption frequency and/or changes in the absorptivity of particular absorption bands will be observed.
d) Crystallinity [147]: absorption bands originating from regular intermolecular interaction in polymer chains of a certain conformational regularity can be used for the determination of crystallinity. Generally with increasing crystallinity or state of order, absorption bands originating from interactions between conformationally regular units show a decreasing bandwidth, while bands due to vibrations of amorphous regions with random conformations decrease in intensity.

Light incident on a system may suffer transmission, reflection, scattering, and absorption. For the portion of radiation effectively entering the sample, the Lambert-Bouguer law of absorption holds under the assumption of a homogeneous medium and monochromatic radiation:

\[ T = \frac{I}{I_o} = 10^{-\alpha b} \quad \text{or} \quad A = \log \frac{I_o}{I} = \alpha b \quad \text{eq. 2.27} \]

where \( T \) is transmittance, \( A \) is absorbance, \( I_o \) is intensity of radiation entering the sample, \( I \) is intensity of radiation after passing through the sample, \( \alpha \) is absorption coefficient, and \( b \) is pass length of radiation within the sample. Beer showed that the absorption coefficient, \( \alpha \), is proportional to the concentration of the absorbing medium:
where \( c \) is expressed in moles per \( \text{dm}^3 \) then \( a \) is called the molar absorptivity (cm\(^2\)/mmol). Thus, the combined law of Lambert-Bouguer-Beer, the basis of quantitative absorption spectroscopy is stated as:

\[
A = \log \frac{I_0}{I} = acb
\]  
\[eq. 2.29\]

The difficulty of obtaining accurate values for the thickness of solid samples (polymer films or KBr pellets) necessitates the use of comparative methods. The absorbance \( A \) of the analytical band is compared to the absorbance \( A' \) of an internal standard which is either present or added to the sample in known concentration:

\[
\frac{A}{A'} = \frac{acb}{a'c'b} = kc
\]  
\[eq. 2.30\]

In analogy the composition of a binary system can be determined from the ratio of isolated absorption bands characteristic of each component:

\[
\frac{A_1}{A_2} = \frac{a_1c_1b}{a_2c_2b} = k \frac{c_1}{c_2}
\]  
\[eq. 2.31\]

Care has to be taken in the choice of analytical and reference bends because their intensity should be independent of molecular order phenomena (e.g. crystallinity, sequence distribution in copolymers) [141]. Free N-H and C=O groups generate absorption bands at 3400 and 1740 cm\(^{-1}\), respectively. As these are mutually hydrogen bonded, the absorption bands shift to lower wavenumbers. The stronger the hydrogen bonding is, the lower the wave number of the absorption band would be [148]. Other FTIR qualitative and quantitative measurements are reported in literature [149-151].

### 2.6.2 X-ray diffraction

Wide-angle x-ray diffraction (WAXD, \( 2\theta > 3^\circ \)) is used in determining crystallinity, phase composition, crystallite size and perfection, and orientation. Crystallite size and perfection
both have an effect on the intensity of the diffracted beam. The effect of heat on a material will usually result in growth of crystallites and at the same time relieve any strain in them. By heating, the peak intensity increases and the width at half maximum decreases which is because of considerable growth of crystallite that takes place. Crystalline structure has been widely investigated using X-ray diffraction [152-160].

A typical, semicrystalline PA is usually regarded as a two phase system consisting of crystalline and amorphous regions. The diffraction pattern of a completely amorphous PA would be a broad diffuse halo with an intensity maximum at \(2\theta\). The diffraction pattern of a fully crystalline PA would be a series of sharp diffraction peaks, corresponding to diffraction from the various crystalline planes. The XRD diffraction of a semi-crystalline PA consists of both and the degree of crystallinity can be determined as follow:

\[
\text{Crystallinity \%} = \frac{A_c \times 100}{A_c + A_a}
\]

where \(A_c\) and \(A_a\) are the respective areas of the crystalline peaks and amorphous halo [143]. Therefore, an important step in calculating crystallinity is to separate the amorphous halo from crystalline peak. To do this a 100% amorphous sample must be used in XRD and this amorphous template must be subtracted from the semi-crystalline peak to measure \(A_c\).

The width of a crystalline peak is inversely related to the size of the crystals. The crystalline reflections in polymers are broadened additionally by the defects and distortions of the crystal lattice. A measure of both the crystallite size and perfection (CSP) can be determined from the Scherrer equation [133,153,155]:

\[
\text{CSP} = \frac{k\lambda}{\beta \cos \theta}
\]

where \(\beta\) is the width of the crystalline peak at \(2\theta\), and \(k\) is a constant equal to 1.0 or 0.9 depending on whether \(\beta\) is the integral breadth or full width at half maximum respectively. In many instances CSP can be a more useful parameter than crystallinity and a sample with a large CSP is usually brittle [143]. In many polymers higher CSP is associated with higher crystal density. For routine measurements, the change in unit cell volume of PA can be readily followed by measuring the positions of the various crystalline reflections. For instance, the \(d\)-spacings, \(d\alpha_1\) and \(d\alpha_2\) of the two most intense equatorial reflections of the \(\alpha\)
crystalline phase ($\alpha_1$ and $\alpha_2$) can be used to calculate an index of crystalline perfection (ICP) defined as:

$$ICP = \Delta d = d\alpha_1 - d\alpha_2$$  \hspace{1cm} eq. 2.34

Variations of the above relations are routinely used to monitor small changes in the unit cell volume in chain axis projection [153]. ICP correlates well with CSP and lamellar spacing, density, and other parameters that are related to the degree of crystalline perfection.

The position $2\theta$ of the peak is normally used to obtain the distance, $L$, between the lamellae using the following equation:

$$L = \frac{(2 \sin \theta)}{\lambda}$$  \hspace{1cm} eq. 2.35

The $d$ spacing can be calculated with the aid of the Bragg equation [133]:

$$d = \frac{\lambda}{2} \cdot \frac{1}{\sin \theta}$$  \hspace{1cm} eq. 2.36

Ricco [50] chose the reciprocal of the width at half-height (A) for the $\alpha$ form (200) reflection as an index of the order level attained by PA6 samples at the different conditions of synthesis. They used the 1/A parameter in the Scherrer equation because, for less perfect crystals, the intensity profile is also affected by lattice distortions. This parameter, i.e. the sharpness of a crystalline reflection in the WAXS intensity profile, is directly related to the size and/or perfection of the crystallites and increases with the increasing structural order of the polymers. They showed the 1/A values for all PA6 samples are a function of polymerisation temperature and this diagram showed a trend very similar to that of crystallinity degree, decreasing with increasing polymerisation temperature, thus indicating a reduction of the crystal size and/or a loss of crystalline perfection [50].

Yeh et al. [148] measured the difference of the $d$-spacing for both the $\alpha_1$ and $\alpha_2$ peaks, $\Delta d$, and the ratio $d\alpha_2/d\alpha_1$. Because $\Delta d$ is a measure of the index of chain packing [156], a smaller $\Delta d$ shows that the PA6 chains forming regular chain packing is inhibited. The ratio $d\alpha_2/d\alpha_1$, which represents the ratio $c/a$ of unit cell [157], of PA6 is around 0.841. This indicates the distance between hydrogen bonded sheets (i.e. $d\alpha_2$) in the unit cell.
2.6.3 Scanning electron microscope (SEM)

Scanning electron microscopy (SEM) permits the observation and characterisation of heterogeneous organic and inorganic materials on a nanometer (nm) to micrometer (µm) scale. The popularity of the SEM stems from its capability of obtaining three dimensional like images of the surfaces of a very wide range of materials.

The types of signals produced from the interaction of the electron beam with the sample include secondary electrons, backscattered electrons, characteristic x-rays, and other photons of various energies. These signals are obtained from specific emission volumes within the sample and can be used to examine many of its characteristics.

The imaging signals of greatest interest are the secondary and backscattered electrons because these vary primarily as a result of differences in surface topography. The secondary electron emission, confined to a very small volume near the beam impact area for certain values of beam energy, permits images to be obtained at a resolution approximating to the size of the focused electron beam. The three dimensional appearance of the images is due to the large depth of field of the scanning electron microscope as well as to the shadow relief effect of the secondary and backscattered electron contrast.

In the SEM, characteristic X-rays are also emitted as a result of electron bombardment. The analysis of the characteristic X-radiation emitted from samples can yield both qualitative identification and quantitative elemental information from regions of a specimen nominally 1 µm in diameter and 1 µm in depth under normal operating conditions. The X-rays emitted from a specimen bombarded with the finely focused electron beam of the SEM can be used to identify which electrons are present. Using flat polished samples and an appropriate experimental setup and data reduction procedure, the measured X-rays from the identified elements can be used to quantitatively analyse chemical composition with an accuracy and precision approaching 1%. The required energy for this is usually more than 10 keV [161].

2.6.4 Gel permeation chromatography (GPC)

Gel chromatography [162,163] is a method for the separation, purification, and analysis of mixtures of substances. The separation is based on difference in molecular size; thus gel chromatography lends itself also to the determination of MWs.

Gel permeation chromatography (GPC) is the generic name given to liquid chromatographic separation of macromolecules by molecular size. The term size exclusion chromatography (SEC) is commonly used interchangeably with GPC. The primary purpose of the GPC is to
provide MWD information about a particular polymeric material. The molecular size measurements provide MW information by using the relationship between linear dimension and MW in a freely jointed polymeric chain (random coil). Either the root mean square end-to-end distance or the radius of gyration is proportional to the square root of the MW [164]. It follows that the log of either distance is proportional to (one-half) the log of the MW [165]. Polyamides have been investigated in hexafluoroisopropanol (HFIP) containing 0.05 M potassium or sodium trifluoroacetate as solvent [166,167]. This highly polar eluant is needed in order to interact with the very polar amide groups in polyamides. Sodium trifluoroacetate destroys the intermolecular hydrogen bonding between the amide groups, thus single polymers appear as single molecules and not as polymeric associations. One of the most important applications of MW sensitive viscometry detectors is in the characterisation of branched polymers. A branch molecule in solution has a smaller size than a linear molecule of the same MW. This smaller size also means a correspondingly smaller intrinsic viscosity. By comparing the measured intrinsic viscosity of the branched molecule at each elution volume increment to the intrinsic viscosity of the linear molecule with the same MW, a branching factor \( g' \), can be determined as follow:

\[
g' = \left( \frac{[\eta]_b}{[\eta]_l} \right)_M
\]

where the subscripts b and l correspond to the branched and linear polymers respectively. For a branched polymer \( g' \) decreases as the number of branch points per molecule increases. Light scattering detectors can be also used to study branching. The branching factor can then be rewritten as follow:

\[
g' = \left( \frac{M^*}{M_b} \right)^{\alpha+1}
\]

where \( M^* \) is the MW of the linear molecule with the same hydrodynamic volume as the branched molecule and \( \alpha \) is the Mark-Houwink exponent for the linear molecule [168]. The presence of monomers with more than two groups capable of reacting (functionality > 2) results in branched, nonlinear polymers. Branching can lead to gelation, defined as that point where the MW is infinity. Below the gel point, branched polymers have a broader MWD than linear polymers of comparable MW [169].
Since the weight average molecular weight, $\overline{M_W}$, is most influenced by the high MW portion of the distribution whereas the $\overline{Mn}$ is influenced by low MW portion [165], the polydispersity or MWD of samples can be determined as:

$$MWD = \frac{\overline{M_W}}{\overline{M_N}}$$  \hspace{1cm} eq. 2.39

When the residual monomer of PA6 is largely removed by careful washing, a polydispersity slightly narrower than 2 are usually obtained. The narrower than 2 polydispersity appears to be a clear reflection of the absence of monomer and cyclic oligomers in the polymer. When the polymer remains unwashed and the extractables are included in the MWD, then polydispersity higher than 2 are usually obtained [102]. Analysis of polymers obtained by anionic polymerisation indicated that when a high ratio of catalyst to activator was present, very narrow MWDs were obtained, but when the ratio of catalyst to activator approached 1, broad MWDs were obtained [170].

Four methods have been reported for determination of number and weight averages of MW, $\overline{M_n}$ and $\overline{M_w}$, of polymers respectively [171]. $\overline{M_n}$ is usually obtained by end group analysis [172] or osmometry [173], while $\overline{M_w}$ can be obtained using light scattering [174]. However, the most popular method of molecular characterisation of PAs is viscosity average molecular weight, $\overline{M_v}$, determination, which is called viscometry [175]. The definitions of $\overline{M_n}$, $\overline{M_w}$, and $\overline{M_v}$ are as follows [176]:

$$M_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{1}{\sum (w_i / M_i)}$$  \hspace{1cm} eq. 2.40

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \sum w_i M_i$$  \hspace{1cm} eq. 2.41

$$M_v = \left[ \frac{\sum N_i M_i^{1+\alpha}}{\sum N_i M_i} \right]^{\frac{1}{\alpha}} = \left[ \sum w_i M_i^a \right]^{\frac{1}{\alpha}}$$  \hspace{1cm} eq. 2.42

where $N_i$ is the number of molecules, $w_i$ is the weight fraction of molecules with MW $M_i$, and $a$ is a constant in the Mark-Houwink equation, which is defined in the Experimental Chapter. The $a$ and $K$ values of polyamide solutions in good solvents fall in the range expected for
flexible coil polymers. They appear to be rather insensitive to the number of \(-\text{CH}_2-\) groups between the amides along the chain. The lower \(a\) values and the commensurate larger \(K\) values may be explained by poor polymer-solvent interactions in these instances [102]. It should be noted that \(\overline{M}_n < \overline{M}_v < \overline{M}_w\).

Biernacki et al. [177] used osmometric and light scattering methods to measure the \(\overline{M}_n\) and \(\overline{M}_w\) of PA6 respectively. They reported \(\overline{M}_n\) of 31,300 and \(\overline{M}_w\) of 57,300 for their samples which is far higher than for hydrolytic polycaproamide.

In 1994, Hornsby et al. [178], determined the \(\overline{M}_v\) of PA6 by solution viscometry according to ISO 307:1984. Their procedure was applied to the analysis of PA6 made by APCL in a co-rotating twin-screw extruder, using 90\% formic acid solution with a polymer concentration of \(\leq 0.005\ \text{g\ ml}^{-1}\) [178]. They checked the validity of their results using a GPC method and found good agreement with viscometry. The \(\overline{M}_v\) obtained for PA6 has been reported to be strongly dependent on screw speed of extruder, varying from 49,000 to 122,000 gmol\(^{-1}\). Viscometry has been used by Chaupart et al. [179] to characterise the MW of PA11 during hydrolysis. They used \(m\)-cresol as the solvent, which was also suitable solvent for PA6.

In general, the breadth of a GPC curve is the most common method to obtain the polydispersity of polymers [180,181].

### 2.7 Objectives

Previous sections included a discussion of the main parameters which have influence on the APCL and the common methods for characterisation of PA6. The main objectives of the project are mentioned in the Introduction Chapter. However, the aim of this work is to optimise the polymerisation conditions in APCL on both bulk and smaller scales. These are catalyst-activator type and concentration, polymerisation temperature (and heating strategy) and influence of environment. Comparing results from bulk and small scale polymerisation, and also achieving polymerisation after jetting the polymerisation mixtures are the other objectives of this work. This project also deals with characterisation of polymerisation materials and developing polymerisation methods which could be used in relation with jetting.
CHAPTER THREE: EXPERIMENTAL

3.1 Materials

A wide range of materials have been used in this work. All materials were used as received.

*Monomer*: Caprolactam (CL) (C\textsubscript{6}H\textsubscript{11}NO) as the monomer is obviously the major raw material in this work. Among the different grades of CL which are available in the market, the 99% pure \(\varepsilon\)-caprolactam (MW = 113.16) was purchased from Sigma-Aldrich.

*Catalysts*: The two common components to make the catalysts for anionic polymerisation of caprolactam (APCL), sodium hydride 95% (NaH) and ethyl magnesium bromide (CH\textsubscript{3}CH\textsubscript{2}MgBr) 3.0 M in diethyl ether were both purchased from Sigma-Aldrich.

*Activators*: Among the wide range of activators that can be used in APCL, N-acetylcaprolactam (ACL) 99% (C\textsubscript{8}H\textsubscript{13}NO\textsubscript{2}, MW = 155.19) is the most common one. In addition, two other types of activators, 4,4’-methylene-bis-phenyl isocyanate (MDI) (CH\textsubscript{2}(C\textsubscript{6}H\textsubscript{4}NCO)\textsubscript{2}, MW = 250.25) and 1,3-bis(1-isocyanato-1-methylethyl)benzene (TMXDI) (C\textsubscript{6}H\textsubscript{4}[C(CH\textsubscript{3})\textsubscript{2}NCO]\textsubscript{2}, MW = 244.29) have been used. All the activators were supplied by Sigma-Aldrich.

*Commercial catalyst/activator*: Sodium caprolactamate (CLNa) in CL (C10) and N-N’-hexane-1,6-diylbis(hexahydro-2-oxo-1H-azepine-1-carboxamide) in CL (C20P) were kindly provided by Bruggemann Chemicals in Germany.

*Solvent*: m-Cresol 98% has been used as the solvent, purchased from Fisher Scientific.

*Drying agent*: Phosphorus pentoxide 98% was used as drying agent (in the process of nitrogen treatment), supplied by Fisher Scientific

*Nitrogen*: A cylinder of nitrogen (oxygen free, N\textsubscript{2}) 99.998% was supplied by BOC Industrial, and used as the inert atmosphere.
3.2 Concentrations

3.2.1 Molar concentration measurements

Molar concentration (also called molarity, amount concentration or substance concentration) is a measure of the concentration of a solute in a solution, or of any molecular species in a given volume. Molarity (mol/kg, molar, or m) denotes the number of moles of solute per kilogram of solvent (not solution). For instance: adding 1.0 mole of solute to 2.0 kilograms of solvent constitutes a solution with a molarity of 0.50 mol/kg. Such a solution may be described as "0.50 molar". The term molar solution is used as shorthand for a "one molar solution", i.e. a solution which contains one mole of the solute per 1000 grams of the solvent. The mole fraction \( \chi \), (also called molar fraction) denotes the number of moles of solute as a proportion of the total number of moles in a solution. For instance: 1 mole of solute dissolved in 9 moles of solvent has a mole fraction of 1/10 or 0.1. Mole fractions are dimensionless quantities, (the mole percentage or molar percentage, denoted "mol %" and equal to 100% times the mole fraction, is sometimes quoted instead of the mole fraction). Concentrations of the various chemicals used are described below.

**N-acetylcoprolactam**: CL MW: 113g/mol, ACL MW: 155g/mol

Required amount of ACL (99% purity) in equal molarity with 1g CL: 

\[
\frac{155}{113} \times \frac{100}{99} = 1.38 \text{ml} \text{ (density is 1.094g/ml at 25\(^\circ\)C)}
\]

**NaH**: CL MW: 113g/mol, NaH MW: 24g/mol

Required amount of NaH (95% purity) in equal molarity with 1g CL: 

\[
\frac{24}{113} \times \frac{100}{95} = 0.22 \text{g}
\]

**EtMgBr**: CL MW: 113g/mol, EtMgBr MW: 133g/mol

Concentration of EtMgBr in diethyl ether: 3 molar or 40%

\[
\frac{\text{EtMgBr}}{\text{Caprolactam}} = \frac{133}{113} = 1.177
\]

Required amount of EtMgBr 3 molar solution in diethyl ether in equal molarity with 1g CL:
1.177 \times \frac{100}{40} = 2.94\text{ml} \text{ (density is 1.02g/ml at 25}^\circ\text{C)}

**Example:** Caprolactam weight: 5g, EtMgBr solution: 1.5ml,

\[
\text{The} \quad \frac{\text{EtMgBr}}{\text{Caprolactam}} \text{ molar ratio is} \quad \frac{1.5}{5 \times 2.94} = 0.102 = 10\%molmol^{-1} \text{ (or 10 mole\%)}
\]

**C10:** The molar concentration of catalyst component in C10 was estimated by evaporation of CL from C10 in a vacuum oven at 130\(^\circ\text{C}\) for 10h as follows:

- Weight before evaporation (W1): 10.141g
- Weight after evaporation (W2): 2.323g
- Weight percent of CL in C10: \((10.141 - 2.323)/10.141 \approx 77\%\)
- Weight percent of CLNa in C10: 100 - 77 \approx 23\%

Molar ratio of CLNa/CL in C10:

\[
\frac{\text{Weight fraction of CLNa}}{\text{Mw of CLNa}} \quad \frac{\text{Weight fraction of CL}}{\text{Mw of CL}} = \frac{23}{135} \approx 0.25\text{molmol}^{-1} = 25\%\text{molmol}^{-1} \text{ (or 25 mole\%)}
\]

**C20:** Equal molar ratios of catalyst and activator are claimed to be used in C10 and C20 respectively. However, since a di-functional activator is being used in C20, the molar ratio of activator/CL in C20 must be half of CLNa/CL in C10. So, the estimation for molar ratio of activator/CL in C20 is about 0.125molmol\(^{-1}\) or 12.5 mole%.

### 3.2.2 Molar concentrations of materials used in this work

Generally in this work, the mixtures of catalyst and CL, and activator and CL are called mixture A and B respectively. Caprolactam magnesium bromide (CLMgBr) - ACL and C10 - C20 were the two combinations that resulted in the best performance. These components are used in different concentrations in this work; thus, to make it easier to follow each concentration has been allocated a code. The molar concentrations of catalyst-activator and their allocated codes are presented in Table 3.1.
Table 3.1: Molar concentrations and compositions of mixtures used in this work.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Molar ratio (mol&lt;sup&gt;-1&lt;/sup&gt; CL)</th>
<th>Code</th>
<th>Chapter</th>
<th>Application</th>
</tr>
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<tbody>
<tr>
<td>CLMgBr+CL</td>
<td>1 to 4%</td>
<td>Mixture A</td>
<td>4</td>
<td>Polymerisation</td>
</tr>
<tr>
<td>CLNa+CL</td>
<td>1 to 6%</td>
<td>Mixture A</td>
<td>4</td>
<td>Polymerisation</td>
</tr>
<tr>
<td>ACL+CL</td>
<td>0.5 to 1%</td>
<td>Mixture B</td>
<td>4 and 5</td>
<td>Polymerisation</td>
</tr>
<tr>
<td>CLMgBr+CL</td>
<td>3%</td>
<td>Complex3</td>
<td>5</td>
<td>DSC, FTIR</td>
</tr>
<tr>
<td>CLMgBr+CL</td>
<td>6%</td>
<td>Complex6</td>
<td>5</td>
<td>DSC, FTIR</td>
</tr>
<tr>
<td>CLMgBr+CL</td>
<td>10%</td>
<td>Complex10</td>
<td>5</td>
<td>DSC, FTIR</td>
</tr>
<tr>
<td>CLMgBr+CL</td>
<td>50%</td>
<td>Complex50</td>
<td>5</td>
<td>DSC, FTIR</td>
</tr>
<tr>
<td>CLMgBr+CL</td>
<td>&gt;50%</td>
<td>Complex50+</td>
<td>5</td>
<td>DSC, FTIR</td>
</tr>
<tr>
<td>CLMgBr+CL</td>
<td>1.5 to 2%</td>
<td>Mixture A</td>
<td>5</td>
<td>Polymerisation</td>
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<tr>
<td>C10 in CL</td>
<td>2.5%</td>
<td>10%C10</td>
<td>6</td>
<td>SEM</td>
</tr>
<tr>
<td>C10 in CL</td>
<td>5%</td>
<td>20%C10</td>
<td>6</td>
<td>DSC, SEM</td>
</tr>
<tr>
<td>C10 in CL</td>
<td>10%</td>
<td>40%C10</td>
<td>6</td>
<td>SEM</td>
</tr>
<tr>
<td>C10</td>
<td>25%</td>
<td>C10</td>
<td>6</td>
<td>SEM, FTIR</td>
</tr>
<tr>
<td>Concentrated</td>
<td>N/A</td>
<td>Conc. C10</td>
<td>6</td>
<td>DSC, FTIR</td>
</tr>
<tr>
<td>C10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C10 in CL</td>
<td>0.5 to 2.5%</td>
<td>Mixture A</td>
<td>6</td>
<td>Polymerisation</td>
</tr>
<tr>
<td>C20 in CL</td>
<td>1.25%</td>
<td>10%C20</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>C20 in CL</td>
<td>2.5%</td>
<td>20%C20</td>
<td>6</td>
<td>DSC</td>
</tr>
<tr>
<td>C20 in CL</td>
<td>5%</td>
<td>40%C20</td>
<td>6</td>
<td></td>
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<tr>
<td>C20</td>
<td>12.5%</td>
<td>C20</td>
<td>6</td>
<td>FTIR</td>
</tr>
<tr>
<td>Concentrated</td>
<td>N/A</td>
<td>Conc. C20</td>
<td>6</td>
<td>DSC, FTIR</td>
</tr>
<tr>
<td>C20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C20 in CL</td>
<td>0.25 to 1.25%</td>
<td>Mixture B</td>
<td>6</td>
<td>Polymerisation</td>
</tr>
</tbody>
</table>

CLMgBr in CL (mixture A) and ACL in CL (mixture B) are discussed in Chapter 5. These are the two mixtures required for polymerisation and therefore jetting. Mixtures A and B were produced according to the optimised concentrations which were obtained in chapter 4. It was found in this work that mixture A had totally different properties compared with mixture B, and CL. These differences created significant problems in jetting making it impossible to jet mixture A. Therefore, mixtures of CLMgBr in CL were produced in different molarities.
(i.e. CLMgBr-CL molar ratio) for a more detailed study. These mixtures were named according to their CLMgBr molar ratio in CL and are in Table 3.1. For instance, mixture A with CLMgBr-CL molar ratio of 6% molmol\(^{-1}\) was named as complex6. Mixtures with molar ratios of 10 and 50% molmol\(^{-1}\), which are complex10 and 50 respectively, were also produced. Another mixture with higher CLMgBr concentration was produced by evaporation of CL from complex50 in a vacuum oven at 130\(^\circ\)C for 6h (i.e. complex50+). The molar ratio of ACL-CL in mixture B was 2% molmol\(^{-1}\). These concentrations were halved when mixture A and B are mixed together in equal weight prior to polymerisation.

It is shown in Chapter 5 that CLMgBr in CL mixture (i.e. mixture A) could not be jetted. Therefore, commercial materials were also studied in detail. C10 in CL (mixture A) and C20 in CL (mixture B) are discussed in Chapter 6. Mixture A and B were produced using different molar concentrations of C10 and C20 in CL. Mixtures with higher concentrations of catalyst and activator were produced by evaporation of CL in a vacuum oven at 130\(^\circ\)C for 6h from C10 and C20 respectively. As mentioned before, these concentrations have halved when mixture A and B were mixed together in equal weight prior to polymerisation.

3.3 Polymerisation in bulk

3.3.1 Polymerisation rig

Small samples of CL (30±0.3 g) were melted in standard tall 150ml glass beakers, which were a close fit inside a cylindrical cavity machined in a heater block made from aluminium to provide a steady and reasonably uniform temperature. The block was placed on a standard laboratory hot plate, which is the source of heat. The temperature of the block was monitored by means of a thermocouple and that of the molten CL in the beaker by a separate thermocouple. A lid also made from aluminium was placed on top of the heater block to prevent contact of the molten CL with air. An inert atmosphere of dry nitrogen was maintained above it from a feeder pipe in the lid. A port was provided in the lid fitted with a stopper to allow the injection of small measured quantities of the activator for initiating the polymerisation reaction.

The progress of the polymerisation reaction was monitored by measuring the viscosity changes taking place as the reaction proceeded. This was achieved by measuring the torque required to rotate a glass paddle immersed in the molten CL. The paddle was rotated by means of a small D.C. motor of the ironless rotor type which gives an indication of the drag
on its spindle from a measurement of the motor current (see Fig. 3.1). Results were shown in the form of graphs on a computer screen by using an analogue to digital interface. Graphs of current against time allowed comparisons to be made for different catalyst concentrations, activator concentrations, and initial reaction temperatures.

![Figure 3.1: Schematic of experimental rig](image)

**Figure 3.1**: Schematic of experimental rig (a) reaction chamber, (b) nitrogen cylinder, (c) computer, (d) analogue to digital converter, (e) power supply, and (f) glass paddle.

### 3.3.2 Polymer synthesis

* Catalyst formation: *A quantity of CL, usually 30g, in the form of a white powder or granules at room temperature, was first weighed out into a glass beaker. The required quantity of the catalyst was then added and the beaker put in the reaction chamber at 80 to 90°C (i.e. as
recommended in the literature [20,21]). This stage was carried out under a nitrogen blanket to exclude moisture and oxygen. The catalyst concentration has a significant impact on the solidification time of the polymer, so the weight of the compound was carefully controlled. The mixture was then heated up to the initial polymerisation temperature. This stage took a few minutes for the reaction of CL and catalyst to take place. During the reaction, depending on the type of catalyst, hydrogen or ethane gas was evolved from sodium hydride and ethyl magnesium bromide, respectively (eq. 2.3 and 3.1).

\[ \text{EtMgBr} + \text{CL} \leftrightarrow \text{CLMgBr} + \text{Ethane} \uparrow \]  

\textit{eq. 3.1}

\textit{Polymerisation:} On reaching the desired temperature, the activator was added to the above mixture in order to form the polymer. This was done by the injection of activator through a port in the top of the reaction chamber. A micro-litre syringe was used to measure an accurate amount of activator. As soon as the activator had been injected into the mixture the polymerisation reaction commenced and after a period of time it was observed that the viscosity rose quickly and the solid PA6 had been formed.

\textit{Process monitoring:} The glass stirrer allowed the progress of polymerisation to be monitored, since the drag experienced by the stirrer increased as the viscosity increased during the reaction. This is reflected in the rising current in the motor winding which was easily measured and recorded. When the liquid mixture solidified, the stirrer became trapped in the solid PA6. Usually the solid PA6 could be removed from the beaker because of polymer shrinkage on cooling.

\subsection*{3.3.3 Measurements}

\subsubsection*{3.3.3.1 Polymerisation half-time (t_{1/2})}

Results from this experiment are shown in the format of current versus time graphs. As seen in Fig. 3.2, no specific time can be considered as the polymerisation time. Half-time\textsuperscript{3} of polymerisation is a variable which can be used to represent the influence of polymerisation conditions on solidification time. This value was obtained for each experiment run as shown in Fig. 3.2. The rate of bulk polymerisation was measured using eq. 3.2

\textsuperscript{3} Polymerisation half-time, (t_{1/2}), here is the time taken for a polymerisation solidification process to be half completed.
Polymerisation rate \( (s^{-1}) = \frac{1}{t_{\frac{1}{2}}} \)  \hspace{1cm} \text{eq. 3.2}

where \( t_{\frac{1}{2}} \) is the half-time of solidification as shown in Fig. 3.2.

![Graph showing polymerisation rate over time](image)

**Figure 3.2:** measurement of the half-time of polymerisation.

3.3.3.2 Polymerisation temperature

A K-type thermometer coupled with a stainless steel penetration probe was used to measure the temperature inside the polymerisation chamber.

3.3.4 Polymerisation atmosphere

Oxygen-free nitrogen was used in this work as the inert atmosphere of reaction. For selected experiments which investigated influence of environment on the rate of polymerisation, 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 to freeze the moisture content in the nitrogen, then led to a U-shaped glass tube containing phosphorus pentoxide to absorb any remained moisture in the nitrogen.

3.3.5 Experimental design

Designs of experiments were performed several times in this work using experimental design software, ECHIP 7. ECHIP\(^4\) software provides the most capable design of experiments solution (DOE) which is designed for use by experimenters in all fields (e.g. plastic and paint

formulation). This software can be applied to optimise any process and/or product design in a timely cost effective manner. Randomised standard partial cubic design was used in all the experimental designs.

3.3.5.1 Optimisation of conditions in CLNa-ACL and CLMgBr-ACL systems

The influence of different polymerisation parameters (such as temperature, concentration, and types of catalyst-activator) is described in detail in the literature review. However, understanding the influence of these parameters on the synthesised polymer was essential to optimise conditions. This section discusses the influence of polymerisation conditions on some of the processing parameters and polymer properties. The optimisation was performed with the aid of ECHIP software for the three design variables: catalyst concentration, activator concentration, and initial polymerisation temperature. Half-time of polymerisation, monomer conversion, crystallinity, and viscosity average molecular weight, $\bar{M}_v$, were the response variables.

27 polymerisation experiments were carried out with at least 5 repeated experiments. The best catalyst-activator concentration range for each catalyst-activator combination was found by doing some extra polymerisation experiments prior to experimental design. For instance, the best catalyst-activator concentration range for the CLNa-ACL combination was 1.1 to 6.5 mole% and 0.39 to 0.97 mole% catalyst and activator respectively. These ranges for the CLMgBr-ACL combination were 1 to 3.4 mole% and 0.39 to 0.97 mole%. Table 3.2 and 3.3 show the trials carried out for each system.

3.3.5.2 C10-C20 concentration effect

The influence of catalyst, activator concentration and initial polymerisation temperature on APCL is described in Chapter 4 (Sections 4.3 and 4.4). For the commercial catalyst-activator, only concentrations were optimised as described in Section 6.2.1. The effect of catalyst/activator ratio on APCL was also studied. Response variables were the same as in Section 3.3.5.1. The list of experiments carried out in this section is in Table 3.4. The catalyst-activator concentration range used in this experimental design was from 0.5 to 2.5 mole% catalyst and from 0.25 to 1.25 mole% activator.
<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Trials for CLMgBr-ACL system</th>
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<tbody>
<tr>
<td>1</td>
<td>8.90 11.2 7.2 1.1 0.9</td>
</tr>
<tr>
<td>2</td>
<td>1.1 0.8 0.9 1.1 1.1</td>
</tr>
<tr>
<td>3</td>
<td>1.1 0.9 1.1 1.1 0.8</td>
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<td>4</td>
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Table 3.4: Trials for C10-C20 system

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3.3.6 Other heating strategies

It is shown in Chapter 4 that polymerisation temperature had an essential effect on polymerisation and the properties of synthesised PA6 (S-PA6). Therefore, the heating mechanism of polymerisation mixtures after jetting is one of the challenges in this project. Since the first S-PA6 layers can behave as heat isolators for upper jetted layers, hot surface heating from bottom will not be a suitable technique for uniform heating. The feasibility of using infrared heating (i.e. IR heating) was investigated as an alternative heating technique.

Figure 3.3: Schematic of heating setups; (a) existing heating setup for bulk polymerisation, and (b) IR heating using an IR lamp.
An IR lamp was used to heat the polymerisation mixture from the top. Figs. 3.3 (a) and (b) show the existing heating set up and an IR heating set up respectively. A digital thermometer fitted with a K-type thermocouple, was used to measure the temperature increase.

In another experiment, the IR lamp was used to heat 15g of polymerisation mixture from the solid state in a Petri dish. As the consequence of IR heating, the mixture started to melt quickly (i.e. in less than 5 minutes) and solidified after about 15 minutes and finally the IR lamp was removed after 20 minutes. This procedure was carried out both in air and nitrogen atmosphere and the solid materials produced were analysed by DSC.

### 3.4 Small scale polymerisation

In jetting, the polymerisation mixtures would be deposited in the form of very small droplets (about 50µm diameter) and then be polymerised by heating. Thus, investigating the polymerisation using much smaller amounts of the polymerisation mixtures (i.e. in comparison with 30g) was one of the main objectives of this project.

It must be mentioned here that, except for hot stage microscopy and experiments described below in Section 3.4.1.1, all of the small scale polymerisations were carried out in DSC pans. Unless it is mentioned in the text, open DSC pans (without lids) were used in majority of experiments.

### 3.4.1 Polymerisation methods

DSC, drop on drop polymerisation on a hotplate, and hot stage microscopy were used to study small scale polymerisation of CL.

#### 3.4.1.1 Drop on drop polymerisation on a hotplate

A hotplate was covered with an aluminium foil film and set at 170°C. Small plastic syringes with very fine needle size (i.e. gauge 25) were employed to generate tiny droplets of mixtures A and B. One droplet of mixture B was deposited on one droplet of mixture A which was already deposited on the hotplate. This procedure led to fast polymerisation of CL. The mixture’s colour was observed to change from white to yellow and from a liquid to a solid droplet.
3.4.1.2 Small scale polymerisation in DSC

Small scale APCL was also investigated using DSC. The full description of the DSC equipment used for a number of purposes in this project is in Section 3.5.1.1. One droplet of each mixture (i.e. about 7mg of A and B) in the molten state were deposited using the plastic syringes into a cold DSC pan and solidified quickly without undergoing any polymerisation reaction between the components. Since different heating strategies were used in various experiments, further details of experiments are described in their associated sections in results and discussion chapters.

In an experiment in Section 5.3.2, the small scale polymerisation was carried out isothermally using a temperature range of 110 to 150°C (with 5° intervals). The polymerisation rate was measured using eq. 3.3 and Fig 3.4. For comparison, the rate of bulk polymerisation was measured using eq. 3.2. Both polymerisations were carried out using 3 mol% of CLMgBr and 1 mol% of ACL.

![Figure 3.4: Small scale polymerisation using isothermal heating in DSC.](image)

*Equation 3.3:

\[
\text{Polymerisation rate (s}^{-1}\text{)} = \frac{1}{\text{Width of half peak of polymerisation}}
\]

**eq.3.3**

Equations 3.2 and 3.3 were defined in this work only for comparison of small scale and bulk polymerisation and do not necessarily produce the same results.

3.4.1.3 Small scale polymerisation using hot stage microscopy

Hot stage microscopy is a good method to monitor material behaviour during heating. The equipment consists of an optical microscope equipped with a hot stage which is connected to
a temperature control unit, (models and makes are in Section 3.5.1.3). This facility enables the user to heat up the hot stage and the material on it to any temperature at different heating rates with good accuracy. This microscope is also equipped with a set of polarising filters in order to observe the crystalline and spherulitic structure in crystalline materials. Amorphous regions in polymers and molten crystals are isotropic and cannot be observed.

![Micrograph of a, left: thick sample layer, right: thin sample layer under a polarised microscope.](image)

**Figure 3.5:** Micrograph of a, left: thick sample layer, right: thin sample layer under a polarised microscope.

Sample preparation is one of the most important challenges that must be considered in hot stage microscopy. A small amount of test material was spread to make a thin layer on a microscope slide. The crystalline structure can only be seen when very thin layer of material is being observed under a polarised microscope otherwise different crystallised layers interact into each other and this results in an unclear image. Fig. 3.5 shows micrograph of a thick polymerisation mixture layer on microscope slide in the left and a thin polymerisation mixture layer in the right. A cover slip is used to protect the hot stage and also help to produce a thin uniform layer on the microscope slide.

Observing the crystallisation process was important in order to monitor initial crystallisation temperature and initial melting temperature. The APCL was carried out on a hot stage. The polymerisation progress was visualised using the optical microscope fitted with a digital camera. The crystalline structure was observed using crossed polars. The temperature controller was set to heat the hot stage to 220°C, at four different heating rates (i.e. from 3 to 20°C/min; 20°C/min was the maximum possible rate with this equipment). Heating to 200°C was also carried out at a heating rate of 20°C/min after samples were cooled down to about 100°C. The heating profiles (heat/cool/heat cycles) for this experiment are shown in Fig.3.6.
A heating rate of 10°C/min was chosen to illustrate the polymerisation process on the hot stage because all of the processes which occur during heating were observed clearly at this heating rate. Results from other heating rates were also used for comparison with DSC results.

3.4.2 Experimental design

3.4.2.1 Influence of heating rate, maximum heating temperature, and cooling rate using EtMgBr-ACL

The effect of heating strategy, which includes heating rate, maximum heating temperature, and cooling rate, on final properties of S-PA6 (i.e. monomer conversion, weight loss during polymerisation, crystallinity, and melting point ($T_m$)) were studied. Since heating has a significant influence on the properties of the final product in the APCL, this experiment was designed to identify a suitable heating strategy after jetting the polymerisation mixtures in order to synthesise polymers with good properties.

ECHIP was used to design a set of experiments including heating/cooling rate, and maximum heating temperature as the variables. The effect of heating strategy on polymerisation enthalpy (or exothermic peak), peak temperature, crystallinity (measured using eq. 3.5), $T_m$, weight loss during polymerisation (WLDP), and monomer conversion (measured using eq. 3.18) were investigated. The heating and cooling rate limits were in the range of 5 to 30°C/min. The maximum heating temperature range was from 140 to 200°C. A second DSC run with a heating rate of 20°C/min to 250°C was carried out after every experiment. The list
of experiments carried out is shown in Table 3.5. Fig. 3.7 shows typical first and second run DSC thermograms.

### Table 3.5: Tests carried out in Section 3.4.2.1

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![First DSC run](image1.png)  ![Second DSC run](image2.png)

*Figure 3.7:* Typical first and second run DSC thermograms in this experiment.
3.4.2.2 Influence of polymerisation temperature, isothermal time, and concentration using C10-C20

Small scale APCL was carried out using C10-C20 as an alternative catalyst-activator system for jetting. The major parameters which control the polymerisation and the synthesised PA6 (S-PA6) were investigated using ECHIP. These were the influence of heating temperature, heating time, and mixture composition.

**Table 3.6:** Tests carried out for this experiment

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Mixture composition (i.e. concentration effect), isothermal heating time, and isothermal temperature were the condition variables and monomer conversion, polymerisation temperature and enthalpy, Tm and heat of fusion, re-crystallisation temperature and enthalpy, and final crystallinity of the S-PA6 were the response variables in the design experiment using ECHIP. Polymerisation mixtures with different concentrations (i.e. 5 to 30%) were placed in hermetic sealable pans and were put in an oven at isothermal temperatures ranging.
from 140 to 180°C for 5 to 60 minutes. The hermetic pans were then used for DSC experiments with a heating and cooling range of 30 to 240 to 30°C at heating/cooling rate of 20°C/min. The list of experiments carried out is shown in Table 3.6.

Fig. 3.8 is an example to show how response variable were measured in DSC. As seen, there are five exothermic and endothermic peaks in this thermogram. Peaks I, III, and V correspond to melting of CL, PA6, and PA6 on second heating respectively. Peaks II and IV correspond to polymerisation and crystallisation in heating and re-crystallisation of PA6 in cooling respectively. The presence of these peaks depended on the polymerisation conditions.

![Figure 3.8: Method for measuring the response variables.](image)

The monomer conversion for each sample was measured using eq. 3.4. It must be mentioned that eq. 3.4 was only used in this part of the work for measuring the monomer conversion and the other methods for measuring the monomer conversion are discussed in Section 3.5.2.3.

\[
\text{Monomer conversion(\%)} = \left[ 1 - \frac{\text{Peak (I) area}}{100\% \text{ CL melting area (125J/g}^{-1})} \right] \times 100 \quad \text{eq. 3.4}
\]

Polymerisation enthalpy, \( \Delta H_p \), was measured by subtracting peak (III) from (II) and polymerisation temperature, \( T_p \), was measured from peak (II) temperature. Re-crystallisation
enthalpy, $\Delta H_c$, and temperature, $T_c$, were measured using peak (IV) and finally the crystallinity of S-PA6 part was measured as follows:

\[
\text{Crystallinity}(\%) = \left[ \frac{\text{Peak (V)area}}{100\% \text{ crystalline PA6 melting enthalpy} \ (190 J g^{-1})} \right]^{190} 
\]

Further details of the method of measuring crystallinity are described in Section 3.5.2.2.

3.5 Characterisation and analysis

The characterisation and analysis of raw materials, polymerisation mixtures, and synthesised polymers have been done in this work using the following equipment and techniques.

3.5.1 Characterisation techniques

In this section there is a brief description of the various techniques that were used to obtain a good understanding of the chemical, physical, and thermo-mechanical behaviour of the materials used and produced in this work.

3.5.1.1 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is commonly used to detect transitions and sub-transitions such as the melting temperature (Tm) and the glass transition temperature (Tg) of polymeric materials. In this work DSC measurements were carried out with a TA Instrument DSC Q200. Since different heating conditions were applied for each experiment, the experimental specifications are provided in Chapters 4 to 6.

In DSC the sample contained in an aluminium pan and the reference, usually an empty pan, are placed on raised platforms on the sensors. A preheated purge gas, normally nitrogen, is present to provide additional baseline stability as well as the desired sample-atmosphere interaction [184]. DSC is widely used to measure the crystallinity of semi-crystalline polymers as shown in Section 3.5.2.2. DSC can also be used to study chemical reactions, as discussed in Chapters 5 and 6. The ability to determine transition temperatures and enthalpies makes DSC an invaluable tool in producing phase diagrams for various chemical systems [185]. DSC was used also in this work to study the small scale APCL (see Sections 3.4.1.2,
3.4.2.1 and 3.4.2.2). The final application of DSC in this project was to measure the monomer conversion as described in Section 3.5.2.3.

3.5.1.2 Thermogravimetric analysis (TGA)
Thermogravimetric analysis (TGA) is commonly utilised to study thermal stability of polymeric materials. TGA experiments were carried out using a TA-Instruments SDT 2960 Simultaneous TGA/DSC. All samples were heated from room temperature to 600°C at a heating rate of 10°C/min.

3.5.1.3 Hot stage optical microscopy (HOM)
A Leica-DMLM optical microscope fitted with polarising filters was used to observe the polymerisation progress. The heating process was carried out using a Mettler-Toledo-FP82HT type hot stage and a FP90 type temperature controller. Video data were recorded on a Leica-Q5501W PC using a Leica-DFC350FX digital camera.

3.5.1.4 Attenuated total reflectance infrared spectroscopy (FTIR-ATR)
IR spectra were recorded on a Shimadzu-8400-S type FTIR spectrometer, over a range of 600 to 4000cm⁻¹ at a resolution of 4cm⁻¹ and accumulation of 64 scans, using thin KBr/caprolactam discs. IR spectra were recorded for solid PA6 samples using a Specac-MKII-Golden Gate single reflection ATR system. The Lambert-Bouguer-Beer law can be used to measure the concentrations of different components in any mixtures as follows:

\[
\frac{A_1}{A_2} = \frac{a_1 c_1 b}{a_2 c_2 b} = k \frac{c_1}{c_2}
\]

eq. 3.6

Definitions of the terms in eq. 3.6 are given in Section 2.6.1.

3.5.1.5 Rheometer
The viscosity of CL at 85°C at 30s⁻¹ shear rate with and without CA/AC was measured using a rheometer (Anton Paar: physica, MCR 101). Viscosity is one of the properties which is important for setting the jetting parameters.
3.5.1.6 Wide-angle x-ray scattering (WAXS)
In this work wide-angle x-ray investigation was used to provide information about the morphological properties and study the compositional structure of polymerisation mixtures. X-ray diffraction measurements were performed in the reflected radiation mode, using a Bruker D8 system with Cu Kα radiation source operating at 40kV and 50mA. Ranges investigated were from 5 to 35° and 5 to 60° for PA6 samples and polymerisation mixtures respectively and the step increment was 1°min⁻¹. The measurements were carried out under ambient conditions.

3.5.1.7 Dynamic mechanical thermal analysis (DMA)
Dynamic mechanical thermal analysis (DMA) was carried out using a TA Instruments DMA Q800 using dual grips and central oscillating rod to perform sinusoidal tensile deformation at a frequency of 1Hz and heating rate of 5°C/min. Samples in the form of strips 35mm long, 10 to 12mm wide, and 1.5 to 2mm thick were clamped between the grips. DMA results were used to measure the temperature at which tan δ peak occurs. This temperature represents the Tg of the PA6 samples.

3.5.1.8 Scanning electron microscopy (SEM)
In scanning electron microscopy (SEM) the radiation that interacts with the specimen is a beam of high energy electrons, produced from a filament and accelerated by a high voltage. Three imaging signals can be used [186]: back scattered electrons, secondary electrons and X-rays. Characteristic X-rays have well defined energies from different atoms. Thus analytical information can be obtained from an X-ray spectrum. Back scattered electrons are primary beam electrons that have been elastically scattered by the nuclei in the sample and escape from the surface. Thus they can be used to obtain compositional contrast in the sample. Secondary electrons are emitted with low energy from top few nanometers of the materials. This technique yields topographic images of the sample surface. Non-conductive samples, such as CL and polymerisation mixtures that were tested in this work were gold coated before analysis in order to make the scanned surface conductive. The instrument used was a Carl Zeiss (Leo / Cambridge) Stereoscan 360.
3.5.2 Properties measurements

In this section there is a brief description of the three techniques that were used to measure properties of synthesised polymers.

3.5.2.1 Molecular weight measurement

Solution viscometry: Viscometry is based on the following principle: the higher the polymer MW, the more viscous the polymer solution. Therefore a definite relationship exists between a polymer MW and its solution viscosity. In solution viscometry, the rate at which a dilute polymer solution flows through a capillary is measured. Temperature and concentration of the polymer are carefully controlled. The parameter most often determined by dilute solution viscometry is intrinsic viscosity, which is related to molar mass through a semi-empirical relationship, called the Mark-Houwink equation.

![Solution viscometry set up](image)

**Figure 3.9:** solution viscometry set up: (i) heater and water circulator (ii) suspended viscometer (iii) water bath.

The viscosities of PA6 solutions were measured using the experimental set up shown in Fig. 3.8. Here a suspended level viscometer, range 6 to 30 cp (from Fisher Scientific), is immersed in a temperature controlled bath of water (25 ± 0.1°C). Selection of size of the viscometer depends on the viscosity of pure solvent, which was found to be about 13 cp at 25°C [187]. Different PA6 concentrations in m-cresol, in the range of 0.001 to 0.005 (g/ml) were prepared for each polymer sample. Using a stopwatch, the efflux times for PA6 solutions at varying concentrations to flow between two pre-defined levels (indicated as (a) and (b) on the viscometer in Fig. 3.9) were measured. Also, the efflux time for the pure
solvent (m-cresol) was measured. The relative viscosity ($\eta_r$) and specific viscosity ($\eta_{sp}$) can be determined using the efflux times obtained for pure solvent and different PA6 solutions, as follows:

$$\text{Relative viscosity } (\eta_r) = \frac{\text{solution efflux time}(t)}{\text{solvent efflux time}(t_0)} \quad \text{eq. 3.7}$$

$$\text{Specific viscosity } (\eta_{sp}) = \frac{\text{solution efflux time}(t) - \text{solvent efflux time}(t_0)}{\text{solvent efflux time}(t_0)} \quad \text{eq. 3.8}$$

The data were plotted in forms consistent with the Huggins and Kramer’s equations:

$$\text{Huggins equation: } \frac{\eta_{sp}}{c} = k' [\eta]^2 c + [\eta] \quad \text{eq. 3.9}$$

$$\text{Kramer equation: } \frac{\ln(\eta_r)}{c} = -k' [\eta]^2 c + [\eta] \quad \text{eq. 3.10}$$

where $c$ is the concentration of PA6 in its solvent. $\bar{M}_v$ for each PA6 solution was determined using the Mark-Houwink equation after substituting the obtained intrinsic viscosity value in eq. 3.11:

$$\text{Mark – Houwink equation: } [\eta] = kM_c^a \quad \text{eq. 3.11}$$

where $k$ and $a$ are Mark-Houwink constants, which depend on temperature and polymer-solvent combination in question. For a PA6/m-cresol system at 25$^\circ$C, the above constants were used as follows: $k = 0.058$ (cm$^3$/g), and $a = 0.73$ [188,189].

Gel permeation chromatography (GPC): Gel permeation chromatography (GPC) was carried out on selected samples (9 samples) kindly by Smithers Rapra. The samples were analysed using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the solvent. It was observed that many of the samples included polymer with MWs greater than the exclusion limit of the columns used. This excluded polymer all eluted at the same retention
volume and gave a sharp front to the MWDs. This exclusion distorted the computed MW data but still allowed some comparison of the MWDs, the size of the excluded peak or shoulder being an indication of the proportion of polymer with MWs greater than the exclusion limit. It is probable the calculated MW averages reflected the value that would be obtained if polymer were not excluded. If the columns had a greater MW range, a more symmetric shaped distribution, extending to a higher MW, would be expected.

3.5.2.2 Crystallinity, melting point and structural regularity

**Crystallinity:** DSC is an easy technique for measuring the polymer crystallinity by quantifying the heat associated with melting (fusion) of the polymer. This heat is used to determine percent crystallinity by normalising the observed heat of fusion to that of a 100 % crystalline sample of the same polymer. As 100 % crystalline polymers do not exist, literature values are usually used for this value.

In this study, samples of PA6 were analyzed over the temperature range from 30 to 230°C. A heating rate of 10°C/min was used with the sample in a nitrogen atmosphere. Samples were pre-weighed to be in the range of 10 to 15 mg. The crystallinity of each sample determined using the following equation:

\[
\%\text{Crystallinity} = \frac{\Delta H_{mp}}{\Delta H_{mp}^0} \times 100
\]

*eq. 3.12*

where \( \Delta H_{mp} \) is heat of fusion of polymer (J/g), and \( \Delta H_{mp}^0 \) is heat of fusion (J/g) of 100% crystalline sample, obtained from literature. The value for \( \Delta H_{mp} \) is the area under the melting peak in the DSC thermograms. Universal analysis software was used in this work to calculate the area under each peak. The degree of crystallinity was calculated from heat of fusion using 190 Jg\(^{-1}\) as the heat of fusion of 100% crystalline PA 6 [190,191]. Melting point (Tm) was measured using the peak temperature of the fusion peak (see Fig. 3.7).

**Crystalline structure:** The following equations can be used to characterise the crystalline structure of polymers using X-ray diffraction method:
Scherrer equation:

\[ CSP = \frac{k\lambda}{(\beta \cos \theta)}: \text{crystallite size and perfection (CSP)} \quad \text{eq. 3.13} \]

\[ ICP = \Delta d = d\alpha_1 - d\alpha_2: \text{index of crystalline perfection (ICP)} \quad \text{eq. 3.14} \]

Bragg equation [133]:

\[ d = \frac{\lambda}{2} \cdot \frac{1}{\sin \theta} \quad \text{eq. 3.15} \]

3.5.2.3 Monomer conversion (DSC checked with TGA results, and vacuum oven extraction)

There are various methods for determining the monomer conversion during polymerisation (online methods) and after its completion. Among these methods, gravimetry [52,85,192-195], gas chromatography [196], enthalpy of polymerisation (kinetics) [197], and on-line infrared spectroscopy [198], have been proposed to determine the conversion of CL. Following in this section, there are some techniques which have been used by different groups to measure the monomer conversion.

The residual monomer was extracted from the synthesised polymer using distilled water [193]. After drying in a vacuum oven at 90°C over night, the percentage of monomer conversion was calculated using the following equation:

\[ \text{Percent monomer conversion} = \frac{\text{polymer weight after extraction}}{\text{polymer weight before extraction}} \times 100 \quad \text{eq. 3.16} \]

Using kinetics of polymerisation is another way to measure the monomer conversion. Under adiabatic conditions, with certain assumptions, (e.g. constant heat capacity, constant heat of reaction, and homogeneous reaction [33]), fractional conversion was obtained from the temperature data by the relationship below [33]:

\[ \beta = \frac{[M]_0 - [M]}{[M]_0} = \frac{T - T_0}{T_f - T_0} \quad \text{eq. 3.17} \]
where $T$ is temperature at time $t$, $T_0$ is initial temperature, $T_f$ is the final polymerisation temperature, and $[M]_0$ and $[M]$ are the initial monomer concentration and monomer concentration at time, $t$, respectively.

According to Zhang and co workers [195] monomer extraction by solvent, residual monomer extraction by vacuum drying at 140°C [199], and thermogravimetric analyses (TGA) [200] are all suitable for measuring monomer conversion of PA6. These results were used to create a new technique for measuring the monomer conversion in the current project.

The main technique for measuring the monomer conversion in this work was to weigh the sample before and after heating in the DSC up to 250°C. Since the boiling point of CL is below the Tm of PA6, the residual monomer in PA6 samples will be evaporated when temperature reaches 230°C (near the melting point of PA6). Thus, the PA6 sample after the DSC run is expected to be free of CL.

$$\text{Monomer conversion} = \frac{\text{sample weight after DSC}}{\text{sample weight before DSC}}$$

\textit{eq. 3.18}

Results obtained using this technique were compared with results from the extraction technique to evaluate the accuracy of the DSC method. Table 3.7 presents this comparison.

\textbf{Table 3.7:} Comparison between two monomer conversion determination methods

<table>
<thead>
<tr>
<th>Sample</th>
<th>Monomer conversion from DSC$^*$</th>
<th>Monomer conversion from extraction$^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>83</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>91</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>93</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>98</td>
<td>97</td>
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<tr>
<td>5</td>
<td>87</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td>90</td>
<td>89</td>
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<tr>
<td>7</td>
<td>92</td>
<td>93</td>
</tr>
<tr>
<td>8</td>
<td>93</td>
<td>92</td>
</tr>
<tr>
<td>9</td>
<td>96</td>
<td>95</td>
</tr>
</tbody>
</table>

$^*$ measured using the eq. 3.18  
$^{**}$ measured according to ref [195]

In Section 5.2.2 the feasibility of having a single jetting mixture instead of two mixtures was studied by measuring the degree of monomer conversion at temperatures below the normal polymerisation temperature (i.e. at the jetting temperature). The degree of monomer conversion of the polymerisation mixture was determined by extraction of CL from S-PA6 (i.e. water reflux at 95°C for 24 hs). Specimens were dried in a vacuum oven for 10 hrs. Dried
specimens were weighed out to determine the monomer conversion using eq. 3.16 after being heated for 5, 15, 30, and 60 minutes at 70, 80, and 90°C. Comparison between the results of the two monomer conversion determination methods showed a close similarity which means that DSC is a suitable method for measuring the monomer conversion.

3.6 Mechanical testing

3.6.1 Mould preparation

The mould that was used to cast PA6 to produce test samples is shown in Fig 3.10. It was produced from aluminium and the mould surface was polished in order to get a very smooth surface finish for the cast polymers. Using this mould, the thickness of the synthesised sheet could be easily adjusted using a different amount of material. However, as the mould is open, the top surface of the cast PA6 will be irregular. This effect has been investigated and will be discussed in the next section. In general, polyamides do not tend to stick to metal surfaces; however, a silicone release agent was used to reduce the surface energy of the mould even more.

Figure 3.10: Schematic of the mould used.

3.6.2 Sample preparation

Sample preparation for testing consisted of three stages; mixture preparation, casting and polymerisation, and making the dog-bones for mechanical testing. As before, there were two polymerisation mixtures (i.e. mixtures A and B). Each pair of mixtures was prepared at the required initial polymerisation temperature under nitrogen for fast polymerisation. The mould was put in an oven for 30 minutes to reach to the initial polymerisation temperature. Mixtures A and B were heated and mixed together and then immediately cast into the mould. The synthesised polymer was removed from the mould after the required polymerisation time.
Dog-bones were all cut out with the following dimensions: neck length: 45mm, width: 4mm, and total length of 75mm.

3.6.3 Sample analysis

Mechanical properties are very sensitive to any sort of defect such as micro-cracks, bubbles and notches in the sample. The most common type of defect in PA6 samples is existence of bubbles which make the samples more brittle. This is probably because of production of gases during the polymerisation reactions. Therefore, de-gassing the polymerisation mixtures before casting reduces the amount of bubbles. Optical microscopy was used to detect any surface roughness and defects inside the dog-bones. Obviously samples with micro-cracks or bubbles inside were not suitable for mechanical testing.

The following shows an example of a poor sample which was not suitable for mechanical testing. A PA6 sheet was cast into the tray mould and polymerised. Dog-bones were then cut out from that PA6 sheet. Fig. 3.11 shows the top and bottom surface of a prepared dog-bone using an optical microscope.

![Microscopy photograph of a PA6 dog-bone synthesised in the tray mould (a) bottom surface, (b) top surface.](image)

**Figure 3.11:** Microscopy photograph of a PA6 dog-bone synthesised in the tray mould (a) bottom surface, (b) top surface.

Fig. 3.11 (a) shows the bottom surface of the PA6 sample which was in contact with the mould. There are some small scratches on this surface from the surface of the mould. These scratches were found not to be deep enough to have a significant influence on the mechanical properties and were neglected. On the other hand, there were too many micro-cracks and bubbles on the top surface of the synthesised polymer which made this sample useless for mechanical testing. There are two reasons for existence of these defects on the surface of the
PA6 sheet; the first was due to the residual gases in the polymerisation mixture which escaped from the top surface during the polymerisation and got trapped on the surface because of the fast polymerisation. The second reason was due to the interaction between the polymerisation mixture and air. Moisture in the surrounding air reacted with the polymerisation mixture and deactivated the catalyst in the mixture. This resulted in the reduction in the monomer conversion and production of a non-uniform structure with micro-cracks on the surface of the polymer. In practice, the first reason could not be true because when a higher concentration of catalyst-activator was used (i.e. causing a faster polymerisation) the top surface of the sample became smoother.

3.6.4 Mechanical testing results

Tensile testing was carried out using a Lloyd Instruments LR50K plus at the cross head speed of 50mm/min (ASTM D 638 [129]). DMA testing was done at a frequency of 1 Hz and heating rate of 3 to 5°C/min under nitrogen atmosphere [201]. Young’s modulus, strain at break, stress at maximum load, and temperature at which tanδ occurs were measured from the tensile testing and DMA respectively. Fig. 3.12 shows a typical tensile test (i.e. two regular samples) and DMA graph and the points of interest in the relevant graphs.

![Figure 3.12: (a) tensile testing graph (b) DMA graph.](image)

3.7 Experiments related to jetting

3.7.1 Feasibility of a single jetting mixture

Mixing of polymerisation mixtures (i.e. deposited droplets of mixtures) after jetting is one of the main challenges in this project. Using a single jetting head would solve this problem.
Since APCL occurs at elevated temperatures (i.e. above 110°C), the possibility of having all polymerisation components as a single polymerisation mixture (i.e. catalyst, activator, and monomer in one container) at the jetting temperature (i.e. 80°C) was investigated. The single polymerisation mixture contained 1% ACL and 3% CLMgBr in CL. The degree of monomer conversion at the jetting temperature was determined to evaluate the feasibility of using a single jetting mixture. Results are discussed in Section 5.2.2.

3.7.2 Caprolactam evaporation

Evaporation is one of the important parameters which control the size and shape of droplets after deposition. Evaporation of CL at high temperatures was studied for different sample sizes. Since polymerisation mixtures will be heated up to the polymerisation temperature (i.e. 140 to 180°C), there will be some evaporation of mixtures before the polymerisation initiation step. The rate will be different at different temperatures and for different initial sample weights.

For large scale evaporation, CL was weighed out in specific quantities (i.e. 1.25, 2.5, 5, and 10 g) and heated up to specific temperatures (i.e. 140, 150, 160, 170, and 180°C) using a controllable heater. After reaching to the desirable temperature samples were weighed again and a stop watch started. Samples were then weighed out after 2, 6, and 12 minutes and data were recorded.

Thermogravimetric analysis (TGA) was used to study CL evaporation from small samples (i.e. less than 20mg).

3.7.3 Other deposition methods

One, two, three, and four droplets of catalyst solution (i.e. 40% EtMgBr in diethyl ether) was deposited (injected) into mixture B at 160°C, using a syringe. The same experiment was carried out with deposition of activator (N-acetylcaprolactam) into mixture A in Section 5.2.5.2. This was done to study the polymerisation propagation.

In a similar experiment in Section 5.2.5.2, droplets of catalyst solution were dropped on a bed of mixture B and droplets of activator were dropped on a bed of mixture A at 160°C. The purpose of this was to find out whether jetting activator or catalyst solution on a bed of mixture A and B respectively layer by layer could be used to make a PA6 3D part.
3.7.4 Characterisation of polymerisation mixtures after jetting

Jetting of polymerisation mixtures was carried out in a separate project [202]. Problems were experienced in jetting mixture A containing commercial materials and CL (20%C10). Concentration changes which occurred during jetting of this mixture were therefore investigated using SEM and optical microscopy in Section 6.2.3.2.

The feasibility of polymerising the polymerisation mixtures (20%C10 and 20%C20) after being jetted was studied in Section 6.3.5.

Quantitative identifications were carried out to obtain elemental information from different regions of mixture A before and after jetting, using SEM. The X-rays emitted from bombardment of mixtures with the focused electron beam of the SEM was used to identify and quantify the elements. Hot stage microscopy was also used to compare mixture A before and after jetting. Results are shown in Section 6.2.3.2.

In addition, about 14mg of polymerisation mixtures (A and B) in equal quantities were jetted in a DSC pan in air to carry out the polymerisation. The DSC experiment were carried out, after sealing the DSC pan, in the range of 20 to 240°C with heating rate of 5°C/min (see Section 6.5).
CHAPTER FOUR: POLYMERISATION IN BULK

4.1 Introduction

The anionic polymerisation of caprolactam (APCL) in bulk is discussed in this chapter. Polymerisation thermodynamics and influence of conditions on polymerisation are discussed here in the introduction.

In the next sections of this chapter, the influences of various parameters on APCL are described individually. According to the literature [11-25,29-38], there are four parameters which could have a major effect on the polymerisation. These are catalyst-activator concentration and type, initial polymerisation temperature, and polymerisation atmosphere.

An experimental design software (ECHIP) was used to design a set of polymerisation experiments at different conditions. The properties of synthesised-PA6 (S-PA6) produced using different polymerisation conditions were measured and used to optimise the process. Polymerisation (or solidification) half-time, crystallinity, final degree of monomer conversion, melting point ($T_m$), and viscosity average molecular weight, $\overline{M_v}$, were the variables which were measured and used for optimising the polymerisation conditions. The optimisation was carried out for APCL using two different catalysts which were sodium caprolactamate (CLNa) and caprolactam magnesium bromide (CLMgBr), both activated by N-acetylcaprolactam (ACL).

The properties of S-PA6s using each catalyst were compared in order to find the most efficient combination. Two commercial cast PA6 samples were also used to compare with the properties of polymers synthesised in this work.

4.1.1 Exothermic measurements

As discussed in Section 2.4, the APCL is exothermic. The temperature increase during polymerisation in these experiments was measured using a K-type thermocouple. The final results for three different initial polymerisation temperatures and three different catalyst-activator concentrations are shown in Fig. 4.1 (a) and (b) respectively.

As seen in Fig. 4.1, the final polymerisation temperature reached 218°C during polymerisation. Fig. 4.1 (a) shows that the final polymerisation temperature depended on the initial polymerisation temperature. A temperature rise of about 58°C was measured. This was due to the exothermic polymerisation reaction and simultaneous crystallisation.
Figure 4.1: Temperature increase during polymerisation catalysed and activated by CLNa and ACL respectively (all concentrations used in this work are mol% of catalyst-activator per 1 mol of CL).

The rate of polymerisation can be determined using the exothermic nature of polymerisation. Fig. 4.1 (a) shows that the rate of polymerisation was higher when the initial polymerisation temperature was higher. Increasing catalyst and activator concentrations also resulted in increasing the polymerisation rate as seen in Fig. 4.1 (b).

Figure 4.2: Monomer conversion versus time.
4.1.1.1 Monomer conversion
The monomer conversion can be measured using the temperature rise during polymerisation. Eq. 3.17 was used to calculate the monomer conversion during polymerisation. Results are shown in Fig. 4.2 for the same polymerisation experiments as Fig. 4.1.

4.1.1.2 Catalyst-activator combination
As discussed before, the exothermic nature of polymerisation was used to measure the polymerisation rate. This method was used in this work to compare the efficiency of different catalyst-activator combinations in APCL. The influence of catalyst-activator type on the rate of reaction was discussed in Section 2.3.3., where it was indicated that by using the best combination, the polymerisation time would be minimised [53]. Figure 4.3 shows the influence of different catalyst-activator combinations on the rate of polymerisation.

![Figure 4.3: The influence of catalyst-activator combination on the rate of polymerisation.](image)

The CLNa-ACL combination which was initially used in this work did not result in the fastest polymerisation. Approximately the same result was obtained when CLNa-TMXDI (1,3-bis(1-isocyanato-1-methylethyl)benzene) was used. The fastest and slowest polymerisations occurred when CLMgBr-ACL and CLNa-MDI (4,4'-methylene-bis-phenyl isocyanate) combinations were used, respectively. It must be mentioned that finding the best
combination also depended on the final properties of the synthesised polymer. It is shown that using di-functional activator (e.g. TMXDI) results in increasing the molecular weight (MW) and at the same time enhancing the branching rate [52] and consequently reducing the crystallinity.

4.1.1.3 Repeatability of the experiments

The repeatability of experiments using the same polymerisation conditions is illustrated in this section. Three experiments were carried out at 160°C using CLNa and ACL as the catalyst and activator respectively. Viscosity and temperature changes were both measured. Fig. 4.4 shows the viscosity change against time for these three experiments.

As seen in Fig. 4.4 the viscosity of polymerisation mixtures rose after 80 seconds and solidified after 120 seconds, which means that all experiments had almost the same solidification time.

Fig. 4.5 shows the temperature rise and consequently calculated monomer conversion for the three experiments. Figs. 4.4 and 4.5 showed that using a single polymerisation condition resulted in very similar solidification time and also temperature, and monomer conversion rise. Although temperature measurements resulted in a more accurate determination of monomer conversion, because of the difficulties that this technique caused (i.e. thermocouple
stuck in the synthesised polymer), the viscosity measurement method was selected as a technique to monitor the polymerisation progress in the rest of the work.

Figure 4.5: Left: mixture temperature versus time, right: monomer conversion versus time.

4.1.2 PA6 characterisation

The crystalline structure, morphology, Tm, and chemical structure of PA6 are discussed in this section using DSC, XRD, optical microscopy, and ATR.

4.1.2.1 Differential scanning calorimetry (DSC)

Fig. 4.6 shows a DSC thermogram of a typical S-PA6 at a heating and cooling rate of 10°C/min. Two endothermic and exothermic processes are observed. The peak temperatures and peak areas were measured.

As seen in Fig. 4.6 there was an endothermic peak on heating which corresponded to melting of PA6 at about 217°C (i.e. corresponds to α crystalline structure). A small drop in the DSC base line was observed before melting at about 41°C which was believed to be the glass transition temperature (Tg) for this PA6. An exothermic peak was observed on cooling at about 175°C which was due to re-crystallisation of PA6. Comparing melting and re-crystallisation peak areas showed that the amount of released heat in re-crystallisation was almost equal to heat of fusion. It was also seen that re-crystallisation in cooling occurred about 45°C below melting point.
4.1.2.2 Optical microscopy

The crystalline structure of a typical S-PA6 was observed using a polarised optical microscope. Fig. 4.7 shows the crystalline structure and PA6 spherulites. PA6 spherulites with diameters of approximately 30µm were observed.

Figure 4.6: DSC thermogram of a typical S-PA6 in this work.

Figure 4.7: Crystalline structure of a typical S-PA6 under an optical microscope.
4.1.2.3 WAXS structure investigation

The crystalline structure of PA6 was determined using x-ray diffraction. Fig. 4.8 shows WAXS intensity profiles of the top (was facing air when solidified) and the bottom (was attached to the reactor when solidified) of a typical S-PA6 in the range 5 to 35° 2θ. As seen in the figure, it is difficult to resolve the WAXS intensity profile into areas attributed to crystalline and amorphous phases.

![Figure 4.8: X-ray diffraction pattern of a typical S-PA6.](image)

Fig. 4.8 showed the typical α-form crystalline diffraction pattern of PA6 in which the diffraction maxima occurred at 2θ=20° and 23.8°. The former peak (i.e. α₁) represents the diffraction of the (200) and the latter (i.e. α₂) represents the (002) and (202) plates [50,134-140].

4.1.2.4 IR studies

The IR spectra of a typical S-PA6 is shown in Fig. 4.9. The essential structural group in PA6, including the amide group (CO-NH) stretching and bending vibrations [81], =N-H stretch vibration, amide I, =C=O, and amide II, =N-H, deformation were seen in Fig. 4.9. These were characteristic of the amide groups existing in the trans planar conformation [81,142]. The amide II was sensitive to the crystalline structure corresponding to the α-phase. In addition,
the out-of-plane bend of NH (amide V) group which appears at 692 cm$^{-1}$ indicates that the form of the crystalline phase of polymer was $\alpha$-type [148].

![Figure 4.9: IR spectra of a random S-PA6.](image)

Therefore, DSC, WAXS, and IR studies were in an agreement and showed $\alpha$ form as the major crystalline structure in the S-PA6 produced in this work.

### 4.2 Influence of polymerisation atmosphere

As discussed in the literature [21,53], APCL is usually carried out in a dry oxygen-free environment. Introducing moisture and oxygen to the polymerisation mixture can cause inhibition by killing the active centres (i.e. free anions). Therefore, APCL was carried out in different atmospheres using two different catalytic systems to study the influence of polymerisation atmosphere on APCL.

#### 4.2.1 Influence of polymerisation atmosphere on APCL catalysed by CLNa

Four different reaction atmospheres were used to study the influence of oxygen and moisture on the polymerisation catalysed and activated by CLNa and ACL respectively. Fig. 4.10 shows the viscosity of polymerisation mixtures at 160°C against time for different polymerisation atmospheres.
Figure 4.10: solidification time at four different atmospheres for CLNa-ACL combination: (a) air, (b) nitrogen, (c) N$_2$ dried with phosphorus pentoxide (PP), and (d) N$_2$ dried with PP and liquid nitrogen.

As seen in Fig. 4.10 (a) the viscosity of the mixture in air did not change even after 400 seconds. Therefore, the glass paddle in the polymerisation mixture never stopped rotating which is a sign of lack of polymerisation and solidification. Fig. 4.10 (b), shows the polymerisation in a nitrogen atmosphere. The viscosity rose rapidly after 110 seconds and the glass paddle stopped rotating after 160 seconds, so that solidification began after 110 seconds and the solid polymer was obtained after 160 seconds. Dry nitrogen was used as shown in Fig. 4.10 (c) and (d). It can be seen that the polymerisation solidification time was reduced using dry nitrogen. The solidification onset in Fig. 4.10 (c) is after 65 seconds which was reduced to 50 seconds in (d). In addition, the slope of viscosity increase is higher for (d) compared with (b) and (c) which shows that the polymerisation rate is highest when using dried nitrogen. It is obvious from these results that oxygen and moisture behaved as inhibitors for polymerisation as reported in the literature [88,89].

It was shown that the APCL was very sensitive to moisture, oxygen, and carbon dioxide [88,89] when CLNa was used as the catalyst. Moisture and oxygen attacked the free anions
which are released in the reaction between monomer and catalyst [21]. Therefore, these active sites reacted with air before reacting with activator. As the amount of moisture decreased in the reaction atmosphere, the number of initiating sites which had the chance to react with activator increased. This led to a higher polymerisation rate and formation of the polymer in a shorter time. When the concentration of oxygen and moisture in air was too high, most of the initiating sites were killed before participating in polymerisation, thus there was little catalysed monomer (i.e. initiating sites) to start polymerisation when the concentration of activator was still high. In this case, each activator molecule was only able to react with a limited number of initiating sites and monomers resulting in the production of very low molecular weight oligomers and polymer chains which do not change the viscosity of the mixture (see Fig 4.10 (a)).

4.2.2 Influence of polymerisation atmosphere on APCL catalysed by CLMgBr

Influence of polymerisation atmosphere on the solidification time of APCL at 160°C, catalysed and activated by CLMgBr and ACL respectively was also investigated. Atmospheres that were used in this experiment were normal air (ambient atmosphere) and oxygen free nitrogen (99.998% minimum). Results are shown in Fig. 4.11. Fig. 4.11 showed that polymerisation and solidification occurred in air when CLMgBr was used as the catalyst. It is also reported in the literature that a magnesium based catalyst has the ability to overcome the effect of moisture on the polymerisation [21]. It was seen that the solidification time in air and nitrogen were closer to each other when the speed of reaction was higher (compare (a), (b), and (c)). This was because at higher reaction rates, less initiating points were deactivated by air before getting involved in the polymerisation. As discussed before, atmospheric elements deactivated the free anions. These free anions could be a free catalyst-monomer-activator complex or a growing polymer chain. It is obvious that killing a polymer chain anion resulted in preventing that chain from growing and consequently lowering the MW of that chain. Besides, if the deactivated free anion was a catalyst-monomer-activator complex, the final degree of monomer conversion would drop because that monomer could not participate in polymerisation any more. So, the next study was to investigate the influence of polymerisation atmosphere on the MW, crystallinity, and monomer conversion of the polymer.
Figure 4.11: MgBr (ml), N-acetylcaprolactam (µl), and temperature (°C): (a) 1, 380, 150 (b) 2, 500, 180 (c) 2.5, 450, 180.

Fig. 4.12 shows a comparison of the properties of three polymers synthesised in air and N₂. Three typical PA6 synthesised using different polymerisation conditions were used for this study. The polymerisation conditions were as follows:

i. Catalyst-activator concentration: 2.4-1.1 molmol⁻¹, polymerisation temperature: 180°C.

ii. Catalyst-activator concentration: 1.0-0.94 molmol⁻¹, polymerisation temperature: 150°C.

iii. Catalyst-activator concentration: 2.7-1.1 molmol⁻¹, polymerisation temperature: 180°C.
It can be seen that the properties of polymers synthesised in air were similar in all cases to the polymers synthesised in a nitrogen environment.

![Graphs showing molecular weight, monomer conversion, crystallinity, and melt flow rate for samples synthesised in air and nitrogen environments.]

**Figure 4.12:** the comparison of the properties of synthesised polymer in air and N₂.

Polymerisation was less sensitive to moisture and oxygen when CLMgBr was used as the catalyst; so, APCL could be carried out under normal atmospheric conditions in the presence of CLMgBr but not with CLNa. Results shown in Fig. 4.12 confirmed that the anions generated through catalyst formation took part in the polymerisation reaction and were not deactivated by moisture or oxygen. This was due to the high affinity of the generated complex (i.e. between CLMgBr and ACL) for monomer molecules, which resulted in a high polymerisation rate.

### 4.3 CLNa-ACL system

The influence of polymerisation conditions (i.e. initial polymerisation temperature, catalyst and activator concentrations) on APCL catalyst and activated by CLNa and ACL was studied in this section. Half-time of solidification, monomer conversion, crystallinity, and $M_v$ were measured for PA6 samples produced at different polymerisation conditions. ECHIP software was used for the experimental design. Results obtained from the tests carried out in Table 3.2 are in appendix A (Table A-1).
4.3.1 Influence of initial polymerisation temperature on APCL catalysed by CLNa

Fig. 4.13 shows the effect of initial polymerisation temperature on solidification half-time, crystallinity, monomer conversion, and $M_v$. The influence of polymerisation temperature on polymerisation is shown at catalyst and activator concentrations of 4.7 and 1% molmol$^{-1}$ respectively.

![Graphs showing the influence of polymerisation temperature on solidification half-time, crystallinity, monomer conversion, and molecular weight.](image)

**Figure 4.13:** Influence of polymerisation temperature on APCL catalysed and activated by CLNa and ACL respectively.

The solidification half-time and crystallinity of the synthesised polymer against initial polymerisation temperature, is shown in Figs. 4.13 (a) and (b) respectively. The solidification half-time decreased with increase in the initial polymerisation temperature. This occurred
because, according to Arrhenius equation\(^5\), when the polymerisation temperature was higher, the reaction rate constant, \(k\), was higher. This means that the rate of polymerisation increased with increasing polymerisation temperature as reported previously [43,52,75] and consequently the solidification time shortened. It is known that the crystallinity of the polymers has one of the major effects on the final properties of each polymer: generally higher crystallinity results in higher stiffness and strength [116]. The crystallinity against initial polymerisation temperature graph showed a maximum at about 160°C. The reason for this trend can be described as follows: the S-PA6 was kept in the heater, which was set at the initial polymerisation temperature, for about 15 minutes after polymerisation was completed. During this time, the secondary crystallisation [133] could progress at that temperature. It is well known that the rate of crystallisation is maximum at \(T_{\text{max}}\) (i.e. about 135°C for PA6 [131]) which lies between glass transition temperature, \(T_g\), (i.e. about 55°C) and \(T_m\) (i.e. about 220°C) of the polymer. Near \(T_m\), the probability of nucleus formation and growth is governed by two factors. For growth to occur, the nucleus must reach a critical size. This is prevented by thermal agitation leading to the dispersion of molecules, so nuclei do not form. As temperature decreased from \(T_m\) kinetic energy of molecules decreased, so crystallisation rate increased. In addition, at temperatures near \(T_m\) the rate of branching reactions is too high which results in a reduction in the regularity and packing of the synthesised polymer. Near \(T_g\), viscosity was high, so movement of molecules to allow growth of crystals was inhibited. As temperature increased, viscosity decreased, so transport became easier, and growth rate increased. However, the maximum crystallinity was obtained at about 160°C which was higher than \(T_{\text{max}}\). This was because the rate of polymerisation was too slow at lower temperatures, so that less polymer chains could form and consequently crystallise. Therefore the plot of crystallinity versus initial polymerisation temperature went through a maximum.

Generally, in APCL, increasing initial polymerisation temperature results in decreasing the crystallinity of synthesised polymer, which is caused by the higher thermal motion of the polymer chains.

As a consequence of increasing the polymerisation temperature, the rate of reaction increased as did the degree of monomer conversion. However, it is reported in the literature the amount of residual CL in PA6 depends on the ring-chain equilibrium which is characteristic for the CL at different temperatures [26]. It has also been reported [77,78] that by increasing the

\[\ln(k) = \ln(A) - \frac{E_a}{R} \left(\frac{1}{T}\right),\]

where \(k\) is reaction rate constant, \(A\) is pre-exponential factor, \(E_a\) is activation energy, \(R\) is gas constant, and \(T\) is absolute temperature (K).
initial polymerisation temperature, the ring-chain (or monomer-polymer) equilibrium shifted
towards the ring (i.e. monomer) side. This is the reason for the decrease in monomer
conversion against initial polymerisation temperature graph, as seen in Fig. 4.13 (c) above
160°C. The influence of initial polymerisation temperature on $\overline{M_v}$ of polymer synthesised is
shown in Fig. 4.13 (d). It can be seen that the $\overline{M_v}$ has been increased by raising the initial
polymerisation temperature. This trend is in agreement with what has been reported in
literature [48]. One reason for this can be due to the high energy available during
polymerisation at higher temperatures which results in condensation reactions (branching)
[40] between polymer chains.

4.3.2 Influence of catalyst concentration on APCL catalysed by CLNa
Fig. 4.14 shows the effect of catalyst concentration on solidification half-time, crystallinity,
monomer conversion, and $\overline{M_v}$. The influence of catalyst concentration on polymerisation is
shown at initial polymerisation temperature and activator concentrations of 160°C and 1%
molmol$^{-1}$ respectively.

In addition to initial polymerisation temperature, catalyst-activator concentration has one of
the greatest influences on the rate of polymerisation. The catalyst concentration against the
half-time of solidification graph in Fig. 4.14 (a) shows that increasing catalyst concentration
resulted in decreased half-time of solidification. Increasing the catalyst concentration resulted
in production of more anions to initiate the polymerisation, which resulted in increasing the
polymerisation rate [75] and consequently reducing the solidification time. The crystallinity
of S-PA6 decreased with increasing the catalyst concentration. Increasing catalyst
concentration results in increasing the polymerisation temperature as a consequence of
increasing the polymerisation rate (i.e. exothermic polymerisation). The polymerisation
temperature influences the process in two ways. At high temperatures, it increases the
polymerisation rate, whereas it decreases the rate of crystallisation [70]. At low temperatures,
the crystallisation rate is very high and reactive groups can become trapped inside growing
crystals before they can polymerise. At polymerisation temperatures above 180 °C, the rate of
polymerisation is high but the rate of crystallisation is decreased (see Section 4.3.1) [53].

The influence of catalyst concentration on the final degree of monomer conversion is shown
in Fig. 4.14 (c). The final degree of monomer conversion decreased with increasing catalyst
concentration. This behaviour was due to the monomer molecules that have been consumed
to compensate for the cations which have been released after addition of each catalyst
molecule [76]; therefore complete monomer conversion is impossible in this polymerisation. In addition, due to the exothermic nature of the polymerisation, adding more catalyst to the polymerisation mixture results in a shift of the ring-chain equilibrium to the monomer side. At lower catalyst concentrations, the rate of polymerisation was low but crystallisation occurred at a higher rate [48], so monomer molecules became trapped inside the PA6 crystals. On the other hand, increasing the catalyst concentration caused the rate of polymerisation to increase and consequently the rate of crystallisation decreased. Therefore the fewer monomer molecules were trapped inside the crystals.

Figure 4.14: Influence of CLNa concentration on APCL activated by ACL at 160°C.
Fig. 4.14 (d) showed that $\overline{Mv}$ against catalyst concentration passed through a maximum at about 3% molmol$^{-1}$ and decreased afterward. Three reasons can explain the decreasing trend: first, by increasing the catalyst concentration the final degree of monomer conversion decreased, so fewer monomer molecules were added to the polymer chains which resulted in a reduction in molecular weight. Second, increasing catalyst concentration caused a higher number of anions to be released and all anions could start new chain growth simultaneously. Therefore, the higher number of chains resulted in lower molecular weight of the synthesised polymer. Finally, side reactions and branching, which reduce the molecular weight, happens when the concentration of catalyst is high [49].

4.3.3 Influence of activator concentration on APCL catalysed by CLNa

Fig. 4.15 shows the effect of activator concentration on solidification half-time, crystallinity, monomer conversion, and $\overline{Mv}$. The influence of catalyst concentration on polymerisation is shown at initial polymerisation temperature and catalyst concentrations of 160°C and 4.7% molmol$^{-1}$ respectively. The half-time of solidification decreased with increasing activator concentration as expected. The reason is because activator molecules form initiating points for chain growth in APCL [52], thus increasing the activator concentration resulted in increasing the chain growth points and an increase in the polymerisation rate. As seen in crystallinity against activator concentration graph in Fig. 4.15 (b), the crystallinity of S-PA6 decreased with increasing activator concentration. This occurred for two reasons; first, increasing activator concentration resulted in increasing the polymerisation rate and temperature consequently decreasing the crystallinity. The second reason may be because of an enhanced rate of branching at high activator concentration [49] which could prevent the polymer chains from being able to crystallise easily (i.e. branches increase the irregularities in polymer chains).

Fig. 4.15 (c) demonstrates that the monomer conversion strongly depends on activator concentration in APCL and is increased by increasing the activator concentration. Increasing activator concentration resulted in increasing the initiating points which were adding centres for monomer molecules to participate in polymerisation. In other words, by adding more activator molecules to the polymerisation mixture, the number of initiating points from which polymer chains can start growing, increases. $\overline{Mv}$ is decreased by increasing the activator concentration because the number of initiating points increased and so did the number of polymer chain growing centres. Therefore, more polymer chains could grow simultaneously
which resulted in a drop in MW of polymer. However, it was observed that the $\bar{M}_W$ increased by increasing activator concentration before about 0.65% molmol$^{-1}$. It can be concluded that below this concentration, the activity and number of initiating points were not adequate to let all monomers participate in polymerisation so the MW of polymer increased with adding more initiating points.

**Figure 4.15:** Influence of ACL concentration on APCL catalysed by CLNa at 160°C.

### 4.3.4 Optimisation of polymerisation conditions

Polymerisation conditions were optimised in this section to achieve the best properties and fastest reaction at the same time. Optimisation was carried out individually for each property
and also in the form of overall optimisation in which all properties were considered. The optimisation was carried out using graphs which were produced by ECHIP.

**Figure 4.16:** The variation of (a) solidification half-time, (b) crystallinity, (c) the final degree of monomer conversion, and (d) viscosity average molecular weight ($\text{gmol}^{-1} \times 10^{-3}$) with CLNa-ACL concentration.
4.3.4.1 Individual optimisation

Fig. 4.16 shows the influence of catalyst-activator concentrations on APCL. Optimised conditions in which each variable has the maximum value (i.e. except for half-time of solidification for which the minimum value is desirable) are presented in the bottom section of Fig. 4.16. It is shown that the fastest solidification occurred in the top right quarter of Fig. 16 (a) where high concentrations of catalyst and activator were used for polymerisation. The shortest reaction time is achievable at 4.5% (i.e. mole% per 1 mole CL) catalyst, 0.9% activator and at 180°C. In Fig. 4.16 (b), crystallinity of S-PA6 was decreased by increasing catalyst-activator concentrations. Unlike activator, increasing catalyst concentration resulted in a decrease in monomer conversion as seen in Fig. 4.16 (c). According to this figure, the maximum degree of monomer conversion would be achieved when 2% catalyst, and either 0.76% or 0.92% activator were used at 170°C. $\overline{Mv}$ decreased with increasing the catalyst concentration as seen in Fig. 4.16 (d); however, there was a peak at about 0.65% for activator concentration. The reason for this behaviour has already been discussed in the previous sections.

Although equal molar concentration of catalyst and activator is reported for polymerisation in literature, it can be seen here that there is a large difference between the molar concentration of catalyst and activator. Two reasons can account for this difference; first, the nitrogen used contained moisture (about 0.002 %) which could react with a proportion of the catalyst and deactivate the free anions. The second reason is that, not all of the NaH molecules were successful in reacting with CL to form active catalyst, (i.e. CLNa). This will lead to no further reaction with the activator.

4.3.4.2 Overall optimisation

The optimised values in Fig. 4.16 corresponded to each variable individually. Fig. 4.17 shows optimum ranges for polymerisation conditions in which all the variables had a reasonable value at the same time. This procedure was called “overall optimisation”. ECHIP software was again used to produce these graphs. The influence of catalyst-activator concentrations and initial polymerisation temperature on half-time of solidification, melting point, monomer conversion, and $\overline{Mv}$ were also studied individually. These variables have different units and it was not possible to allocate y axes to all of them, so a nominal scale from 0 to 1 which reflected the observed range of actual values was used. This shows how each variable changes with the corresponding parameter on the x-axis. Using these plots changes caused by
varying different parameters can be compared. The filled rectangles in Fig. 4.17 show the best range for each of the polymerisation condition parameters. Overall optimisation ranges, to obtain the optimum polymerisation temperature, catalyst and activator concentration, are shown in Fig. 4.17 for each of the polymerisation parameters.

**Figure 4.17:** Overall optimisation of polymerisation conditions; (a) influence of CLNa concentration, (b) influence of ACL concentration, and (c) influence of initial polymerisation temperature.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Optimised range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst concentration</td>
<td>3.7-4.0 (molmol⁻¹)</td>
</tr>
<tr>
<td>Activator concentration</td>
<td>0.79-0.81 (molmol⁻¹)</td>
</tr>
<tr>
<td>Initial temperature</td>
<td>177-180 (°C)</td>
</tr>
</tbody>
</table>

Fig. 4.17 (a) showed that increasing catalyst concentration resulted in a faster solidification as a consequence of higher polymerisation rate due. On the other hand, as seen in Fig. 4.17 (a) adding more catalyst caused the final degree of conversion to decrease. Increasing the catalyst concentration resulted in a slightly decrease in $\bar{M}v$ as seen in Fig. 4.17 (a). The crystallinity of S-PA6 decreased with increasing catalyst concentration as discussed before. Therefore, the optimised catalyst concentrations were in the range of 3.7-4.0% molmol⁻¹. Fig. 4.17 (b) showed that increasing activator concentration resulted in a decreased half-time of solidification. $\bar{M}v$ decreased by increasing activator concentration after about 0.65 mol%. However, $\bar{M}v$ increased by increasing activator concentration below 0.65% molmol⁻¹ of activator because of very low degree of monomer conversion at low concentrations of
activator. The final monomer conversion was increased by increasing the activator concentration, as seen in Fig. 4.17 (b). Since monomer conversion is one of the factors which influence melting point of S-PA6 [102], melting point also increased with increasing activator concentration. Finally, crystallinity decreased with increasing activator concentration. The optimised range for activator concentration was found to be 0.79-0.81 mole%. It is seen in Fig. 4.17 (c) that increasing the initial polymerisation temperature resulted in decreasing half-time of solidification. Fig. 4.17 (c) also showed that increasing polymerisation temperature resulted in increased $\bar{M}v$. There was a peak in monomer conversion against initial polymerisation temperature diagram in Fig. 4.17 (c). Fig. 4.17 (c) showed that the melting point of PA6 decreased with increase in the initial polymerisation temperature due to the decrease in crystalline perfection with increasing temperature [26]. Monomer conversion and crystallinity pass through a maximum at 160°C as the temperature increases. After 165°C the crystallinity drops rapidly when the rate of reaction has reached almost 90% of its maximum value. Thus, the best value for initial polymerisation temperature will be in a range of 160 to 165°C, and if the crystallinity is not in the first order of importance, it is in the range of 165 to 170°C.

### 4.4 CLMgBr-ACL system

CLMgBr-ACL was used as another combination in APCL. Obviously some properties of polymer will be different by changing the catalyst. The influence of polymerisation condition on the response parameters (e.g. half-time, crystallinity, monomer conversion, and $\bar{M}v$) was discussed and defined in the previous sections. In this section the behaviour of this system (CLMgBr-ACL) using different polymerisation conditions is discussed. Results obtained from the tests carried out in Table 3.3 are in appendix A (Table A-2).

#### 4.4.1 Influence of initial polymerisation temperature on APCL

Fig. 4.18 shows the effect of initial polymerisation temperature on solidification half-time, crystallinity, monomer conversion, and $\bar{M}v$. The influence of polymerisation temperature is shown at catalyst and activator concentrations of 2.4 and 0.94 mole% respectively. The influence of initial polymerisation temperature on the half-time of solidification is shown in Figure 4.18. As expected and described in previous sections, Fig. 4.18 (a) showed that the half-time of solidification decreased by increasing initial polymerisation temperature. The
influence of initial polymerisation temperature on the degree of crystallinity of the synthesised polymer is shown in Fig. 4.18 (b). Unlike Fig. 4.13 (b), in Fig. 4.18 (b) the degree of crystallinity decreased with increasing initial polymerisation temperature from 150°C to 180°C. This showed that fast polymerisation resulted in fast crystallisation when CLMgBr was used, when crystallisation process mainly occurred simultaneously with polymerisation. The reduction in crystallinity of S-PA6 by increasing the initial polymerisation temperature is because of the competitive nature of polymerisation and crystallisation in this process, the higher thermal motion of the polymer chains, and also enhanced rate of branching at higher temperatures [50,52].

Figure 4.18: Influence of polymerisation temperature on APCL catalysed and activated by CLMgBr and ACL respectively.
The influence of initial polymerisation temperature on the degree of monomer conversion of the synthesised polymer is shown in Fig. 4.18 (c), which shows that the degree of monomer conversion decreased with increase in initial polymerisation temperature as described before (i.e. the ring-chain equilibrium of the anionic ring opening polymerisation shifts towards the monomer side at high temperatures). The initial polymerisation temperature against $\overline{M_v}$ diagram in Fig. 4.18 (d) shows that the MW of the synthesised polymers increased with increase in the initial polymerisation temperature, as reported in the literature [86].

### 4.4.2 Influence of catalyst concentration on APCL catalysed by CLMgBr

![Graphs showing influence of CLMgBr concentration on APCL activated by ACL at 160°C.](image)

**Figure 4.19:** Influence of CLMgBr concentration on APCL activated by ACL at 160°C.
Fig. 4.19 shows the effect of catalyst concentration on solidification half-time, crystallinity, monomer conversion, and viscosity average molecular weight ($\overline{M_v}$). The influence of catalyst concentration on polymerisation is shown at initial polymerisation temperature and activator concentrations of 165°C and 0.94% molmol$^{-1}$ respectively.

Fig 4.19 (a) shows that the half-time of polymerisation decreased by increasing catalyst concentration. The degree of crystallinity decreased with increasing catalyst concentration for the same reason as described in Section 4.3.2. Fig. 4.19 (c) shows that the degree of monomer conversion decreased with increasing catalyst concentration. There were two reasons for reduction in the degree of monomer conversion with increasing catalyst concentration. The first reason was because of the increase in the exothermic heat of polymerisation by adding more catalyst to the system which shifted the ring-chain equilibrium to monomer side. The second reason was due to the fact that for each catalyst molecule added a cation is introduced which needs to be compensated for by a CL anion. Finally, as discussed in Section 4.3.2, the $\overline{M_v}$ of synthesised polymers decreased with increasing catalyst concentration.

### 4.4.3 Influence of activator concentration on APCL catalysed by CLMgBr

Fig. 4.20 shows the effect of activator concentration on solidification half-time, crystallinity, monomer conversion, and $\overline{M_v}$. The influence of catalyst concentration on polymerisation was shown at initial polymerisation temperature and catalyst concentrations of 165°C and 2.4% molmol$^{-1}$ respectively.

As expected and described in previous sections it was shown that the half-time of polymerisation was decreased by increasing initial polymerisation temperature, activator concentration, and catalyst concentration. The degree of crystallinity also decreased with increasing activator concentration. Adding more activator resulted in the production of more initiating points from which monomers participated in polymerisation. Therefore, increasing the concentration of activator resulted in a higher degree of monomer conversion. This trend would be true as long as the ring-chain equilibrium is not shifted toward the monomer side because of a large amount of released heat of polymerisation. The $\overline{M_v}$ of synthesised polymers decreased with increasing activator concentration. This was because of the increase in the number of initiating points which resulted in the formation of more polymer chains.
Figure 4.20: Influence of ACL concentration on APCL catalysed by CLNa at 160°C.

4.4.4 Optimisation of polymerisation conditions

Polymerisation conditions were again optimised to achieve the best properties and fastest reaction at the same time. Optimisation was carried out individually for each property and also in the form of overall optimisation in which all properties were involved.

4.4.4.1 Individual optimisation

Fig. 4.21 (a) shows that increasing catalyst-activator concentrations resulted in reduction in half-time of solidification. The maximum crystallinity was achieved at the lowest catalyst and activator concentrations as shown in Fig. 4.21 (b). Fig. 4.21 (c) shows the same trend as Fig. 4.16 (c) (i.e. monomer conversion decreased with increasing catalyst concentration and
increased with increasing activator concentration). The maximum value for monomer conversion could be achieved at 1.5% catalyst, 1% activator, and 170°C. Finally, Fig. 4.21 (d) shows that maximum $\bar{M}$ is achievable at the lowest catalyst-activator concentrations.

**Figure 4.21:** The variation of (a) polymerisation half-time, (b) crystallinity, (c) the final degree of monomer conversion, and (d) viscosity average molecular weight (g mol$^{-1} \times 10^3$) with CLMgBr-ACL concentration.
4.4.4.2 Overall optimisation

Fig. 4.22 (a) showed that increasing catalyst concentration resulted in a faster solidification and decrease in the final degree of monomer conversion. Increasing the catalyst concentration resulted in a sharp drop in $M_v$ as seen in Fig. 4.22 (a) whereas in Fig. 4.17 (a) it decreased slightly. This is because the combination of CLMgBr and ACL generated a more efficient complex for initiating new polymer chains compared with CLNa-ACL. According to Fig. 4.17 (a) and 4.22 (a), the optimised catalyst concentrations were in the range of 3.7-4.0% and 1.7-1.9% for CLNa and CLMgBr respectively.

![Figure 4.22](image)

**Figure 4.22:** Overall optimisation of polymerisation conditions; (a) influence of CLMgBr concentration, (b) influence of ACL concentration, and (c) influence of initial polymerisation temperature.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Optimized range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst concentration</td>
<td>%1.75-%1.90 (%mol mol⁻¹)</td>
</tr>
<tr>
<td>Activator concentration</td>
<td>%0.78-%0.82 (%mol mol⁻¹)</td>
</tr>
<tr>
<td>Initial temperature</td>
<td>167 to 172°C</td>
</tr>
</tbody>
</table>

Fig. 4.22 (b) showed that increasing activator concentration resulted in a decreased half-time of solidification and $M_v$. The final monomer conversion was increased by increasing the activator concentration, as seen in Figs. 4.17 (b) and 4.22 (b). The reason is due to the very slow polymerisation rate at lower concentrations of activator; therefore as the polymer chains get formed and start to crystallise, the active sites will be trapped inside the crystals [23]. Also, there are less active addition centres for monomers at lower activator concentrations.
Therefore the best range in which all parameters had a reasonable value was 0.78-0.82\% mol/mol\(^{-1}\). All properties (i.e. except for \(\bar{M}_n\)) decreased with increasing initial polymerisation temperature as seen in Fig 4.22 (c). The best polymerisation temperature range was found to be 167 to 172\(^\circ\)C.

### 4.5 Comparison between the properties of the PA6 samples synthesised in this work

The properties of S-PA6 in the two systems were compared in order to find the more efficient system. The produced samples were also compared with commercial cast PA6 grades.

#### 4.5.1 Comparison between CLNa-ACL system and CLMgBr-ACL system

<table>
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<th>Table 4.1: Average values for all the parameters</th>
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</thead>
<tbody>
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<td>Response parameters</td>
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<tr>
<td></td>
</tr>
<tr>
<td>(t_{1/2}) (s)</td>
</tr>
<tr>
<td>(T_m) ((^\circ)C)</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
</tr>
<tr>
<td>Mon. Con. (%)</td>
</tr>
<tr>
<td>(\bar{M}_n) (g/mol)</td>
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</table>

<table>
<thead>
<tr>
<th>Table 4.2: Optimised values for all the parameters</th>
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</thead>
<tbody>
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<td>Response parameters</td>
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<td></td>
</tr>
<tr>
<td>(t_{1/2}) (s)</td>
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<tr>
<td>(T_m) ((^\circ)C)</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
</tr>
<tr>
<td>Mon. Con. (%)</td>
</tr>
<tr>
<td>(\bar{M}_n) (g/mol)</td>
</tr>
</tbody>
</table>

The properties of S-PA6 using CLNa and CLMgBr are compared in this section. Twenty seven synthesis and property measurements using different conditions were carried out for each system (in the case of CLNa, polymerisation did not occur in some of the experiments).
Average properties values and optimised properties values are presented in Tables 4.1 and 4.2. The average half-times of solidification were 123s and 38s while the minimum solidification half-times predicted by ECHIP were 36s and 7.5s for CLNa and CLMgBr respectively. The average degree of monomer conversion was 94% and 86% and the maximum monomer conversion predicted by ECHIP was 95% and 98% for CLNa and CLMgBr respectively. The comparison between two systems shows that higher MW polymers were synthesised using CLMgBr as the catalyst. The $\bar{M}_v$ were 27,000 and 31,000 and the maximum $\bar{M}_v$ predicted by ECHIP was 46,000 and 51,000 for CLNa and CLMgBr respectively. The average and optimised values for crystallinity and $T_m$ for the two systems were as follows; 30% against 34% (i.e. average crystallinity), 40% against 44% (i.e. optimised crystallinity), and 210°C against 218°C (i.e. average $T_m$) and 218°C against 223°C (i.e. optimised $T_m$).

Comparison of Figs. 4.17 and 4.22 and Tables 4.1 and 4.2 clearly shows that when CLMgBr was used as the catalyst, even at low concentrations of activator or low polymerisation temperature the rate of reaction was high enough to prevent decrease in monomer conversion. This behaviour can be explained in two possible ways: firstly, magnesium cations are less electropositive than sodium cations. Therefore, magnesium cations would have a weaker bond to the CL anions than sodium cations [6]. Secondly, the rate of dissociation and therefore the activity of the catalyst decreases with increasing size of the cation due to a decreasing ionisation potential and restricted mobility. An alternative way to generate anions is through complex formation between the activator and the cation of the catalyst [8]. However, not all combinations of activator and catalyst are able to form a complex (i.e. CLNa-ACL combination). If no complex were formed, anions would only be generated at low concentrations due to dissociation, so the rate of reaction would be low.

4.5.2 Comparison between CLMgBr-ACL system and a commercial cast PA6

In order to check the quality of the synthesised polymers in this work, some of the important parameters (e.g. monomer conversion, crystallinity, molecular weight, and melting point) of the polymers synthesised in our laboratory were compared with a commercial cast PA6. Two typical commercial parts, supplied from Nylacast, were used in this experiment. Three S-PA6 samples were synthesised using the following conditions:
i. CLMgBr: 1.7molmol$^{-1}$, ACL: 0.75molmol$^{-1}$, polymerisation temperature: 170°C, half-time of solidification: 42s

ii. CLMgBr: 1.7molmol$^{-1}$, ACL: 0.82molmol$^{-1}$, polymerisation temperature: 170°C, half-time of solidification: 34s

iii. CLMgBr: 1.7molmol$^{-1}$, ACL: 0.75molmol$^{-1}$, polymerisation temperature: 160°C, half-time of solidification: 51s

Results are shown in Fig. 4.23.

Figure 4.23: Comparison of a commercial cast PA 6 with synthesised polymers.

Fig. 4.23 illustrated that there was a good similarity between the properties of synthesised polymers in this work and commercial cast PA6 samples. It must be noted that the polymerisation time in this work is expected to be much less than that obtained commercially (i.e. from casting to de-moulding takes about 15 minutes depends on the size of mould).
CHAPTER FIVE: POLYMERISATION FOR INKJETTING

5.1 Introduction

This chapter deals with jetting issues such as small scale polymerisation, and jetting head specifications. Jetting of polymerisation mixtures and setting up the jetting equipment was carried out in a separate project [202]. However, sample preparation for jetting and studying polymerisation on a small scale is of the main aims of this work. It was shown in Chapter 4 that CLMgBr-ACL system made a better and more efficient combination for the polymerisation; therefore only CLMgBr-ACL system was used to continue the work in this chapter. As discussed before, droplets of catalyst-caprolactam (CL) mixture (mixture A) and activator-CL mixture (mixture B) are supposed to be deposited on a substrate using two jetting heads at 80°C. Anionic polymerisation of CL (APCL) is then expected to occur after heating the polymerisation mixtures to 150 to 180°C. Small scale polymerisation was carried out to study drop on drop polymerisation which will occur in the jetting process. Because of the jetting head specifications, some limitations are applied to polymerisation mixtures in terms of suitability for jetting. The definition of small scale polymerisation and jetting head specifications are mentioned in the following sections.

5.2 Jetting issues

This section deals with the issues that are related to jetting such as jetting material characterisation, material evaporation after jetting, jetting of mixtures, heating mechanism, and other deposition methods.

5.2.1 Mixture characterisation

DSC, X-ray diffraction, FTIR, TGA, rheometry, and optical and electron microscopy were used to study the properties and characteristics of polymerisation mixtures (as described in Chapter 3).

5.2.1.1 DSC thermograms

It was found that the use of (CLMgBr) as the catalyst in mixture A presented problems because of the possibility of clogging the jetting heads by CLMgBr microcrystals. Thermal behaviour of this mixture was therefore studied. Fig. 5.1 shows DSC thermograms of mixture
A at four concentrations using a heating/cooling rate of 10°C/min. Different heating ranges were used as required for each mixture. Complex50+ (trace iv) was heated and cooled down three times to study the influence of heating on CLMgBr structure.

![DSC thermogram of (I) complex6, (II) complex10, (III) complex50, and (IV) complex50+.

Figure 5.1: DSC thermogram of (I) complex6, (II) complex10, (III) complex50, and (IV) complex50+.

Endothermic and exothermic peaks which correspond to melting and crystallisation of mixtures can be seen in Fig. 5.1. The first endothermic peak at about 70°C obviously correspond to melting of CL. Since CL has a single melting peak (see Fig. 5.2(a)), existence
of two different melting peaks confirmed the existence of two different crystalline structures in mixture A. The second endothermic peaks in all traces are associated with melting of CLMgBr crystals which melt at higher temperatures than CL. However, the peak temperatures and enthalpies for CLMgBr melting were different depending on the concentration of CLMgBr in CL. It is shown in Fig. 5.1 that the peak temperature and endothermic area of CLMgBr melting increased from 103°C to 169°C and from 2.5J/g to 53J/g respectively with increasing CLMgBr concentration in CL (i.e. with increasing the CLMgBr concentration in CL the second melting peak shifts toward the melting point of CLMgBr at ~167°C). Therefore, the melting temperature of CLMgBr crystals present at high concentrations was found to be about 167°C. In cooling only one exothermic peak was observed at 33°C for complex6. This temperature was about 12°C below the re-crystallisation temperature of CL. Since no re-crystallisation occurred for complexes 10, 50, and 50+ on cooling, it was seen that CLMgBr had a retarding influence on CL re-crystallisation. This might suggest a co-crystallisation process in mixture A. X-ray diffraction was used to study the existing crystalline structures in mixture A (see Fig. 5.12).

In the DSC thermogram for complex50+, the CLMgBr melting peak was much bigger compared with CL, which showed that the proportion of CLMgBr in complex50+ is very high. No sharp exothermic peak, which is evidence of re-crystallisation, was observed during the first cooling. However, a small endothermic peak for melting of CLMgBr was observed in the second heating. This means that re-crystallisation of CLMgBr occurred to some extent during the first cooling. The melting peak decreased in size even more in the third heating. CLMgBr decomposition at high temperatures could be a reason for this. So, the decomposition temperature was investigated further as discussed in section 5.2.1.2.

Fig. 5.2 (a) and (b) show DSC thermograms of CL and mixture B respectively. 10 cycles of heating and cooling of CL using DSC in the temperature range from 25°C (room temperature) to 90°C (maximum jetting temperature) at a heating rate of 10°C/min are shown in Fig. 5.2 (a). The probability of decomposition or change in melting point (Tm) of CL during cooling and heating was investigated. This heating/cooling loop test was carried out because in a real situation, CL may be heated for jetting and cool down to room temperature several times. As seen in Fig. 5.2 (a), there was no change in melting point of CL, even after 10 heating cycles. This confirmed that the composition of CL did not change in these reheats. The exothermic peak which relates to re-crystallisation of CL showed a small shift to lower temperatures until reaching the steady point. This was because of melting of residual nuclei
by repeating the melting stage. Residual nuclei increase the crystallisation rate; thus the re-
crystallisation initially occurred at higher temperatures.

![Figure 5.2: DSC thermogram of (a) caprolactam, and (b) mixture B.](image)

Unlike mixture A, mixture B DSC thermograms in Fig 5.2 (b) showed a close similarity to
CL DSC thermogram, in which a single melting peak and re-crystallisation peak were
observed at the same temperature as for CL. These results suggested that N-
acetylcaprolactam (ACL) did not change the crystalline structure of CL in mixture B. The
main reason for this is because ACL was liquid at room temperature and dissolved in CL
when they were mixed.

### 5.2.1.2 TGA of mixture A

Fig. 5.3 is a simultaneous DSC/TGA thermogram of complex50+ in the heating range of 20-
600°C and using a heating rate of 10°C/min.

As seen in the derived weight (%) diagram, complex50+ showed a series of significant
weight losses; the first was at about 100°C and corresponded to onset of evaporation of
residual CL and any absorbed moisture. The second peak was between 236 to 259°C,
however, the onset of this peak was at 170°C. This and following peaks are believed to be
due to decomposition of CLMgBr. CLMgBr melted at 169°C and started to lose weight at
170°C according to the heat flow and weight (%) diagrams respectively. This showed that
CLMgBr is an unstable substance in the molten state, melting and decomposing
simultaneously at about 170°C. The heat flow diagram showed major exothermic reactions at
400°C and above which can be associated with oxidation or other exothermic reactions. It has
been reported that CLMgBr is stable up to 180°C, and then a two stage decomposition becomes evident [182].

![TGA thermogram of complex50+](image)

**Figure 5.3:** TGA thermogram of complex50+.

### 5.2.1.3 IR spectra of mixtures

Fig. 5.4 shows FTIR spectra of (a) CL, (b) mixture B, and (c) mixture A within the range of 600 to 4000cm\(^{-1}\). As seen in Fig. 5.4 (a) and (b), CL and mixture B showed similar results and there was not any noticeable difference between their IR spectra. The difference between IR spectra of CL and complex10 was considerable in the ranges of 600 to 900cm\(^{-1}\) and 2931 to 3600cm\(^{-1}\). In addition, the bands at 1417cm\(^{-1}\), corresponding to CH\(_2\)-(NH) deformation vibration [182], and at 1365cm\(^{-1}\) mostly disappeared in the complex.

A strong sharp IR peak was observed for samples (i.e. CL, mixtures A and B) at 1670cm\(^{-1}\) which was due to the carbonyl absorption of CL [203]. Secondary amides also exhibit a band near 1300cm\(^{-1}\) (amide III) which corresponds to NH deformation mode, a C-N stretching mode and as a mixed vibration involving both types of motion. The strong band at 2962cm\(^{-1}\) and smaller band at 2853 were due to the CH\(_2\) groups in the structure. Mixture B IR spectrum also showed a series of bands in the range of 3400 to 3100cm\(^{-1}\) which correspond to the different NH stretching modes [203]. As seen in the IR spectra of mixture A, there was an
overlap between the bands in the range of 3400 to 3100cm$^{-1}$ and another broad band which arises from the substitution of hydrogen for MgBr in CLMgBr.

Fig. 5.4: IR spectra of (a) caprolactam, (b) mixture B, and (c) complex10.

Fig. 5.5 shows the FTIR spectra of CLMgBr in CL at different concentrations (i.e. complex6, 10, 50, and 50+). As seen in Fig 5.5, there was a broad peak at 3370cm$^{-1}$ which corresponds to N-MgBr in CLMgBr. CH$_2$ group bands at 2931 and 2865cm$^{-1}$ and carbonyl absorption band at 1627cm$^{-1}$ were used for comparison with the N-MgBr band at 3370cm$^{-1}$. Clearly comparing (a) to (d) shows that the intensity of N-MgBr band increased by increasing the CLMgBr concentration in CL mixture. The intensity of carbonyl absorption band was almost two times higher than CLMgBr in Fig. 5.5 (a) where as for Fig. 5.5 (c) it was equal to N-CLMgBr band.
The concentration of CLMgBr in CL (i.e. concentration of catalyst in mixture A) can be estimated using eq. 3.6 (Beer-Bouguer-Lambert law [141]). A calibration graph can be plotted using data from Fig. 5.5 to measure the $k$ value in eq. 3.6. The intensity of each band was measured as shown in Fig. 5.5 (d).

The ratio of the absorption band of the N-MgBr group of CLMgBr to the carbonyl absorption band was plotted versus CLMgBr-CL molar ratio in Fig. 5.6. The concentration of catalyst (CLMgBr) in mixture A with an unknown concentration of CLMgBr can be measured using the equation in Fig. 5.6. Since CLMgBr micro-crystals can be blocked in the jetting heads,
the concentration of CLMgBr in mixture A after jetting (which would be different from its initial concentration before jetting) can be measured using this equation.

**Figure 5.6:** Using IR spectrum to estimate CLMgBr molar concentration in mixture A.

### 5.2.1.4 Optical microscopy

An optical microscope fitted with crossed polarisers and a hot stage was used to observe the crystalline morphology of CL, mixture B, and mixture A. In order to study the crystalline morphology of different components in each sample, micrographs of samples were taken at different temperatures.

Fig. 5.7 shows the crystalline morphology of CL and mixture B at room temperature (RT).

**Figure 5.7:** Crystalline morphology of (a) caprolactam, and (b) mixture B at RT.
Both samples had big spherulites in their crystalline structure, typical of low molecular weight components. Comparing these micrographs showed that there was no specific difference between the crystalline structure of CL and mixture B at RT, which meant that ACL did not have a significant effect on the crystallisation of CL, as shown by the DSC results. CL and mixture B crystalline structures melted at about 70°C; thus the camera screen turned dark as no light could pass through the polarisation filters.

The crystalline morphology of complex10 at RT and 90°C is shown in Fig. 5.8 (a) and (b) respectively. The CLMgBr crystalline structure interfered with CL crystalline structure at RT in Fig. 5.8 (a); therefore, this micrograph was different that of CL in Fig. 5.7 (a). CL was molten at 90°C leaving the CLMgBr crystalline structure which was observed in Fig 5.8 (b). Agglomerations of single CLMgBr crystals were observed when the concentration of CLMgBr in CL was high. Destroying these structures would be necessary before jetting to reach the maximum acceptable size of 5µm for jetting.

![Figure 5.8: (a) crystalline structure of complex10 at room temperature, and (b) crystalline structure of CLMgBr at 90°C.](image)

Melting and re-crystallisation processes of CLMgBr in complex50 are seen in Fig. 5.9. Onset of melting was first observed in Fig. 5.9 (a) at about 155°C and was complete at 165°C using a heating rate of 10°C/min heating. In Fig. 5.9 (b), complex50 was cooled down straight after the melting process finished (i.e. at 165°C) using a cooling rate of 10°C/min. It was seen that re-crystallisation occurred at 120°C on cooling. The observed CLMgBr melting point in hot stage microscopy was in a good agreement with DSC results. Although CLMgBr re-crystallisation could not be monitored using DSC (i.e. re-crystallisation exotherm was not
detected), hot stage microscopy enabled the re-crystallisation temperature of CLMgBr to be measured.

**Figure 5.9**: Complex50 (a) melting at 155°C, and (b) re-crystallisation at 120°C.

The filtration units in the jetting heads used in this work have an average pore size of about 5µm. Therefore, small solid particles bigger than 5µm may cause clogging problems or at least change the concentration of components in the jetted mixture. Since the ACL in mixture B was a liquid and dissolved easily in molten CL, it was expected that mixture B had the same characteristics as CL would be jetted successfully. However, the CLMgBr micro-crystals have the potential to get trapped in filters. This work was therefore concerned with studying the possibility of eliminating the micro-crystals in mixture A at the jetting temperature.

Fig. 5.10 shows the images from mixture A taken under a polarised microscope and a hot stage using a heating rate of 5°C/min. Fig. 5.10 (a) shows the crystalline structure of mixture A at 50°C. In Fig. 5.10 (b) the temperature was raised to 67°C, which was the onset of CL melting. Therefore it was observed that the image became darker. At 75°C the CL portion of mixture A was completely molten, producing a black background. Some white dots could be still observed in Fig. 5.10 (c). It is believed that these dots are micro-crystals of CLMgBr (which have a melting temperature of 169°C as seen in Fig. 5.1 (IV)). However, these micro-crystals started to vanish at 95°C and disappeared completely at about 101°C in Fig. 5.10 (f). As shown by DSC in Fig. 5.1 (I), CLMgBr melted at a lower temperature, when its concentration was low, than its real melting point.

In another experiment mixture A was heated up to 110°C to melt both components. It was then cooled down to 80°C, which was assumed to be the jetting temperature, and held
isothermally for 60 minutes. No re-crystallisation was observed which means that the CLMgBr did not re-crystallise separately at 80°C.

It can be concluded from these experiments that mixture A should be heated up to 110°C prior to jetting in order to melt all the components in the mixture. The mixture can then be cooled down to 80°C and be ready for jetting. Using this procedure, should be possible to avoid the presence of solid CLMgBr micro-crystals.

**5.2.1.5 Scanning electron microscopy**

Scanning electron microscopy (SEM) was also used to observe the crystalline structure of CLMgBr at room temperature. The SEM micrograph of CLMgBr crystalline structure, in complex10, is shown in Fig. 5.11.
A continuous crystalline structure is seen in Fig. 5.11, which corresponds to CLMgBr crystal agglomerations. Since 5µm is the maximum permitted size of any solid particle in polymerisation mixtures for jetting, it will be impossible to jet the above composition. The dark portion of image in Fig. 5.11 corresponds to CL crystalline structure.

5.2.1.6 X-ray diffraction

Figure 5.12: X-ray diffraction of (a) CL and (b) mixture A.
X-ray diffraction was used as a comparison method between CL and mixture A crystalline structure as seen in Fig. 5.12. It clearly shows that there is an additional crystalline phase in mixture A, which corresponds to CLMgBr crystals. The \( d \) spacing value corresponding to each major band is also shown in Fig. 5.12.

### 5.2.1.7 Viscosity measurement

Dynamic viscosity of jetting materials is one of the significant factors in jetting process. It is recommended by the jetting head producer company to keep the viscosity of jetting materials within the range of 9 to 13 mPa.s. Dynamic viscosity of polymerisation mixtures and CL at 80\(^\circ\)C were measured using a shear rate of 300s\(^{-1}\) and results are shown in Fig. 5.13.

![Dynamic viscosity of caprolactam, mixture A, and mixture B.](image)

**Figure 5.13:** Dynamic viscosity of caprolactam, mixture A, and mixture B.

As seen in the Fig. 5.13, viscosity of mixture B, 0.011Pa.s, was close to viscosity of CL, 0.009Pa.s, at 80\(^\circ\)C because ACL is a liquid at room temperature and was present at low concentration in mixture B. However, the viscosity of mixture A at 80\(^\circ\)C was almost twice as high as mixture B (i.e. about 0.02Pa.s). This was due to the existence of the CLMgBr solid crystals at this temperature which resulted in an increase in viscosity. Mixture A viscosity showed a higher value (i.e. 0.028Pa.s) at about 200s which tended to decrease to a steady level after 700s. This is thought to be because CLMgBr micro-crystal agglomerates were broken by shear with time.
5.2.2 Feasibility of a single jetting mixture

Mixing the droplets of polymerisation mixtures after jetting is one of the challenges in this project. Having a single jetting mixture containing catalyst and activator could solve this. An experiment was therefore carried out to find if any polymerisation would occur at jetting temperatures. Fig. 5.14 shows the degree of monomer conversion versus time at different polymerisation temperatures.

![Figure 5.14: Monomer conversion versus time at low polymerisation temperatures.](image)

As seen in Fig 5.14, the degree of monomer conversion increased with time at all polymerisation temperatures. The monomer conversion increase was significantly greater at 90°C, a temperature which would be reached during jetting. These results confirmed that the polymerisation occurred even at temperatures below 100°C. Therefore, having one mixture instead of two mixtures could cause jetting problems such as clogging.

For comparison the monomer conversion of this polymerisation mixture would be about 95% when the polymerisation temperature exceeded 150°C.

5.2.3 Caprolactam evaporation

Evaporation is one of the important parameters which control the size and shape of droplets after deposition by jetting. Evaporation of CL at high temperatures was studied for different sample sizes. Since polymerisation mixtures will be heated up to the polymerisation
temperature (i.e. 140 to 180°C), there will be some evaporation of mixtures before initiation of polymerisation. The rate will be different at different temperatures and for different initial sample weights.

Fig. 5.15 is a DSC thermogram of CL at 10°C/min, which shows onset of CL evaporation. As seen, there are two endothermic peaks in Fig. 5.15, which correspond to melting and evaporation of CL at 69 and 174°C respectively. CL evaporation started at 100°C.

![DSC thermogram of caprolactam](image)

**Figure 5.15:** DSC thermogram of caprolactam

### 5.2.3.1 Evaporation from large samples

Fig. 5.16 and 5.17 show the rates of evaporation of CL at different temperatures and different initial sample weights respectively.

![Graphs showing evaporation rates](image)

**Figure 5.16:** (a) Influence of temperature on evaporation rate of CL and (b) evaporation rate of CL at different temperatures (initial sample weight 10g).
Figure 5.17: (a) influence of initial sample weight on evaporation rate of CL (b) evaporation rate of CL at different initial sample weights and at 160°C (i.e. evaporation rate here is the ratio of weight loss of sample with time to its initial weight).

Interpolation between points led to prediction of the evaporation rate of CL at different temperatures or different initial weights (i.e. as seen in Fig. 5.18 and 5.19). As seen, the evaporation rate of CL increased with increase in initial polymerisation temperature and decrease in initial weight of sample.

5.2.3.2 Evaporation from very small samples

Fig. 5.18 and 5.19 show evaporation of CL at two isothermal temperatures of 160 and 180°C respectively, measured by TGA.

Figure 5.18: TGA thermogram of caprolactam at 160°C.
Figs. 5.18 and 5.19 show the weight% of CL and temperature profile versus time. As seen in these figures, the weight loss because of evaporation started at about 130°C in both tests. If the initial polymerisation temperature was 150°C, the polymerisation mixture would reach to initial polymerisation temperature more quickly at 180°C compared to 160°C. This resulted in less loss of material because as soon as the polymerisation starts the evaporation will be suppressed. On the other hand, higher temperature enhanced the rate of evaporation which was -16%/min at 180°C compared to -10%/min at 160°C. So, the longer the polymerisation takes to initiate, the more evaporation of material would be expected especially at higher temperature.

All the experiments carried out in this section (i.e. DSC, hotplate, TGA), showed that CL evaporated quickly at the polymerisation temperature. Therefore, it is essential to have a fast polymerisation in order to reduce the rate of material lost in the process. Since polymerisation temperature enhances the polymerisation rate and material evaporation rate at the same time, an optimum point must be measured in which the material loss is minimum. Work was carried out using DSC to study the influence of heating strategy on small scale polymerisation and results are discussed in Section 5.4.1.

### 5.2.4 Infrared heating

Other heating techniques such as microwave heating has been used in APCL and it was proved to be more rapid and efficient [204]. For monomers containing polar groups that favour the absorption of microwaves, polymerisation has been dramatically accelerated by
microwave irradiation. In previous work, CL exhibited effective absorption of microwaves which induce fast chemical reactions, and PA6 was produced [205]. However this is the first time that IR heating has been used for APCL.

The efficiency of the IR heating technique was compared with the existing heating technique and results are shown in Fig. 5.20. CL as the main component in the polymerisation mixture was used in both techniques. Although the influence of lamp to heating surface distance was not studied in this work, it was realised this distance has a major effect on the heating rate and final temperature reached.

![Figure 5.20: Studying the efficiency of IR heating technique.](image)

IR heating was shown to be a reasonable method for heating CL as seen in Fig. 5.20. The CL temperature was about 190°C and 175°C after 45 minutes when the IR lamp and a cylindrical heater set at 180°C were used respectively. However, the rate of heating in the first 20 minutes was higher in latter case. The heating rate and maximum temperature were higher when an IR lamp was used compared with the heater set at 140°C.

Fig. 5.21 (a) and (b) show the DSC thermograms of the solid materials which were produced in air and nitrogen respectively using an IR lamp. Two endothermic peaks were observed in the DSC experiment which corresponded to melting of CL and PA6. These peaks were used to measure monomer conversion, crystallinity, and melting point of the S-PA6. Monomer conversion was measured using eq. 2.4 and the values were 94% and 98% for the PA6 produced in air and nitrogen respectively. Crystallinity was measured using eq. 3.5 and the
values were 27% and 42% and Tm values were 215°C and 217°C for the PA6 produced in air and nitrogen respectively. As expected, the PA6 produced in nitrogen had better final properties compared with the PA6 produced in air in case of monomer conversion, crystallinity, and melting point. These results showed that PA6 can be synthesised using IR heating.

Figure 5.21: DSC thermograms of IR synthesised PA6s; (a) in air, and (b) in nitrogen.

5.2.5 Feasibility of other deposition methods

Although the heating method, which was described in 5.2.1.4, could result in melting all the solid particles at 80°C, it was not possible to jet mixture A with the available jetting heads. It is believed that even the molten CLMgBr has a higher viscosity than molten CL and makes a heterogeneous mixture (emulsion) with molten CL, which is not suitable for jetting. This is discussed in more detail in ref [202]. Therefore, other jetting techniques were studied. Section 3.7.3 describes the experimental procedures in detail.

5.2.5.1 Lowest limit of CLMgBr concentration for polymerisation

Since CLMgBr could not be jetted, preparing mixture A with a lower CLMgBr concentration was considered as another solution to the jetting problem (i.e. low concentration results in less agglomeration which can break down more easily). Therefore, the lowest concentration of CLMgBr required for monomer conversion was studied. Fig. 5.22 shows the influence of low concentrations of CLMgBr on monomer conversion versus time.
As expected, monomer conversion increased with increasing CLMgBr concentration and time. Monomer conversion did not exceed 20% after 60 minutes when the CLMgBr molar concentration was 0.22%. The values for monomer conversion were 55%, 85%, and 92% after 60 minutes at 160°C when CLMgBr concentration were 0.3%, 0.45%, and 0.6% respectively. It was seen that the concentration of CLMgBr was not high enough below 0.6% for the polymerisation to occur rapidly. Since there was a significant difference between 0.45 and 0.6% concentration of CLMgBr in rapid polymerisation, the minimum acceptable concentration of CLMgBr was found to be 0.6% or higher. If this concentration was too high for jetting, this material therefore could not be used in the jetting process.

### 5.2.5.2 Polymerisation propagation

This experiment was carried out to investigate how much polymerisation would propagate if few droplets of catalyst or activator are deposited into the heated mixtures B and A respectively. The idea of this work was to evaluate the feasibility of having localise polymerisation. Fig. 5.23 shows S-PA6 when 1, 2, 3, and 4 droplets of catalyst solution (EtMgBr) were deposited into mixture B at 160°C.

As seen in Fig. 5.23, localised polymerisation occurred at the point where catalyst solution droplets were deposited (i.e. without mixing). This showed that polymerisation propagation was inhibited at some point when monomer molecules were still available. It was also observed that the size of S-PA6 in the heated mixture B increased proportionately with increasing number of deposited droplets (i.e. 1 droplet covered smallest area in comparison
with 2, 3, and 4 droplets). The same experiment was carried out but activator droplets were deposited into molten mixture A.

![Deposition of catalyst solution droplets in hot mixture B.](image)

**Figure 5.23:** Deposition of catalyst solution droplets in hot mixture B.

Fig. 5.24 shows the relationships between S-PA6 weight (i.e. obtained after washing the specimens in Fig. 5.23 with water and drying in vacuum oven for 10 h) and the deposited catalyst and activator weights.

![S-PA6 weight versus catalyst and activator weights.](image)

**Figure 5.24:** S-PA6 weight versus (a) catalyst, and (b) activator weight.

As mentioned above, the size of S-PA6 depended on the number of deposited catalyst or activator droplets. Both graphs showed that S-PA6 weight increased with increasing catalyst or activator weight. However, the exponential nature of both curves showed that monomer conversion increases rapidly at higher concentrations of catalyst and activator. This experiment showed that small-size PA6 specimens could be synthesised by deposition of
droplets of catalyst or activator on mixture B and A respectively. It was also shown that the amount of S-PA6 depended on the number and amount of deposited droplets of catalyst or activator.

The effect of dropping activator and catalyst onto a hot bed of mixture A or B is shown in Fig. 5.25 and 5.26 respectively. PA6 was synthesised by adding one droplet of activator onto a bed of mixture A at 160°C. The synthesised polymer was round (i.e. just like the droplet) and had a smooth surface. Comparing images (a) and (b) in Fig. 5.25 showed that diameter of the S-PA6 was almost twice as big as the original droplet. However, dropping catalyst onto a hot mixture B bed produced unacceptable results as shown in Fig. 5.26.

**Figure 5.25:** (a) Dropped activator droplet on a bed of mixture A at 160°C, (b) activator droplet size after being dropped on a glass slide.

**Figure 5.26:** Dripping EtMgBr solution droplets on a bed of mixture B at 160°C.

White bubbles were produced on the top surface of mixture B where the EtMgBr solution was dropped. This was due to the reaction between EtMgBr and CL on contact to produce CLMgBr which has a white colour. Hydrogen and ethylene gases were evolved in the
reaction which made the synthesised CLMgBr appeared fluffy. The consequence of this was that PA6 could not be synthesised successfully by this route.

5.3 Small scale polymerisation

Since polymerisation in the jetting process will involve very small samples, this section is directly related to jetting. Firstly, the feasibility of drop on drop polymerisation is discussed in Section 5.3.1. The influence of heating strategy on the small scale polymerisation was studied using DSC. The best heating strategy will be used later in jetting process to obtain the best properties. In addition to DSC, hot stage microscopy was employed to give a better understanding of small scale polymerisation.

5.3.1 Drop on drop polymerisation on a hotplate

Fig. 5.27 shows the small scale S-PA6 by deposition of one droplet of mixture A on mixture B on a hotplate.

![Figure 5.27: S-PA6 in drop on drop polymerisation on a hotplate](image)

The synthesised polymer weighed 7mg which was equal to 6µl (i.e. assuming 1.16g/cm$^3$ as the density of PA6). Fig. 5.28 shows IR spectra of the S-PA6 prepared using this process. The same procedure was carried out with two and three droplets of each mixture, which all produced the same results.

Clearly, there was a considerable difference between the IR spectra from mixtures A and B, as seen in Fig. 5.6, and the spectrum in Fig. 5.28. Comparing Fig. 5.28 with the spectrum of S-PA6 obtained in bulk polymerisation (see Fig. 4.9) confirmed that APCL occurred when one droplet of mixture A was deposited on one droplet of mixture B on a hotplate.
5.3.2 Small scale polymerisation in DSC

The small scale APCL was carried out using DSC to study the thermal phenomena during polymerisation. There are similar investigations in the literature [55-60] in which DSC has been used to determine some of the polymerisation characteristics such as heat of polymerisation, and study the effect of different chemical compounds on the polymerisation. Fig. 5.29 is a typical example of DSC thermogram in which the polymerisation process and re-melting of the synthesised polymer are shown.

Five peaks exist in Fig. 5.29 which can be described as follows; peak I corresponds to melting of CL at about 70°C, peak II shows that an exothermic process occurred during the
heating (i.e. onset of this peak is at 110°C). This peak is associated with the anionic polymerisation and crystallisation of CL which are both exothermic processes. Peak III corresponds to the melting of PA6 (i.e. 190°C to 220°C) and confirms that crystallisation occurred during heating. This means that the polymerisation and crystallisation processes occurred simultaneously. There is another exothermic peak (i.e. IV) in Fig. 5.29 (a), which corresponds to re-crystallisation of S-PA6 on cooling. Re-melting of this synthesised polymer was then carried out in second DSC run. Peak V corresponds to the melting of unconverted residual monomer in PA6. Finally, peak VI shows melting of PA6. This was at a lower temperature than the usual melting point for PA6 (i.e. about 215°C), and showed that the rapid polymerisation-crystallisation has led to poor and imperfect crystallinity.

The significant difference between the heat of fusion of PA6 in the first DSC run and the second DSC run (i.e. 35 J/g against 65 J/g) showed that, although both the polymerisation and the crystallisation processes occurred simultaneously during the first DSC run, a significant portion of crystallisation occurred during and after the cooling stage of the first DSC run.

The influence of heating rate on crystallisation during polymerisation is also discussed in this section. Fig. 5.30 shows polymerisation, crystallisation, and melting of PA6 at five different heating rates. The synthesised polymers in Fig. 5.30 were cooled down to room temperature and heated up again in the DSC to measure the final amount of crystallinity and crystallisation during polymerisation. Results are shown in Fig.5.31 and Table 5.1.

As seen in Fig. 5.30 the endothermic peak corresponding to melting of PA6 became smaller when the heating rate was increased and disappeared at a heating rate of 50°C/min. This means the amount of crystallisation simultaneous with polymerisation was decreased by increasing the heating rate because the heating rate was too fast for the PA6 crystallisation. On increasing the heating rate the synthesised polymer did not have enough time to crystallise before it reached to its melting point.

The percentage of crystallinity of each polymer was then measured in a second DSC run in order to study the influence of heating rate on the crystallinity of final polymer. As seen in Fig. 5.31 and Table 5.1, the percentage of crystallinity of the final product after cooling was almost independent of the heating rate. The crystallinity during polymerisation was also compared with the final crystallinity. As expected, crystallisation during polymerisation decreased with increasing the heating rate which means that at higher heating rates, crystallisation mainly occurred during cooling. Fig. 5.31 showed that 98% of the crystallisation process occurred simultaneously with polymerisation when the heating rate was 3°C/min; however the amount was zero when the heating rate was 50°C/min.
Figure 5.30: Polymerisation of caprolactam in DSC at five different heating rates.

Table 5.1: Influence of heating rate on the crystallinity of synthesised PA6.

<table>
<thead>
<tr>
<th>Heating rate (°C/min)</th>
<th>3</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallisation during polymerisation(%) (^a)</td>
<td>29</td>
<td>27</td>
<td>12</td>
<td>5</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Crystallinity(%) (^b)</td>
<td>30</td>
<td>29</td>
<td>27</td>
<td>22</td>
<td>27</td>
<td>28</td>
</tr>
<tr>
<td>First/second(%) (^c)</td>
<td>98</td>
<td>92</td>
<td>46</td>
<td>23</td>
<td>17</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) Peak III in Fig. 5.30 divided by 190J/g;
\(^b\) Peak V in Fig. 5.30 divided by 190; this is the final crystallinity of synthesised polymer.
\(^c\) Peak III divided by Peak V in Fig. 5.30; it shows the percentage of final crystallinity which occurred simultaneously with polymerisation.
Figure 5.31: Influence of heating rate on the crystallinity of synthesised PA6.

The influence of isothermal polymerisation temperature on the polymerisation rate in small scale experiments is shown and compared with results from bulk polymerisation in Fig. 5.32. The rates of small scale and bulk polymerisation were measured using eq. 3.3 and 3.2 respectively.

Figure 5.32: Isothermal polymerisation in small scale and bulk.

Comparison between small scale and bulk polymerisations in Fig. 5.32 showed a good agreement between the two polymerisations. This showed that the polymerisation mechanism did not change significantly when the quantity of materials were much smaller than bulk
polymerisation. Thus, it is expected that the small scale polymerisation would show almost the same behaviour as bulk polymerisation.

5.3.3 Small scale polymerisation using hot stage microscopy

Polymerisation was also visualised using a hot stage microscopy at four different heating rates. The experimental procedure is discussed in Section 3.4.1.3. Fig. 5.33 shows 12 micrographs from the polymerisation process at different temperatures.

![Polymerisation of caprolactam on a hot stage at heating rate of 10°C/min.](image)

**Figure 5.33:** Polymerisation of caprolactam on a hot stage at heating rate of 10°C/min.

Fig. 5.33 (a-i) were obtained during the first heating, Fig. 5.33 (j,k) were obtained during cooling and Fig. 5.33 (l) was obtained during the second heating. The crystalline structure of
the polymerisation mixture can be seen at room temperature in Fig. 5.33 (a). The boundary between mixture A and mixture B is clear in this micrograph. Fig. 5.33 (b), at 82°C, shows that crystalline structure of CL had melted as expected at this temperature. Although CL was molten at this temperature, there were still some micro-crystals which scattered light. These dots were believed to be CLMgBr crystalline particles (i.e. discussed in Section 5.2.1.4). At 103°C, the mixtures were molten including the CLMgBr crystals. PA6 crystallisation initiated at 115°C as seen in top right of Fig. 5.33 (d) and developed simultaneously with polymerisation on increasing the temperature. The crystalline structure started to disappear at about 180°C and melted completely at 200°C in Fig. 5.33 (i). During cooling the onset of crystallisation was found to be at 150°C (see Fig. 5.33 (j)) and during the second heating the sample melted at about 190°C.

Fig. 5.34 includes 9 micrographs from the polymerisation of CL at a heating rate of 3°C/min.

**Figure 5.34:** Polymerisation of caprolactam on a hot stage at heating rate of 3°C/min.

Fig. 5.34 (a), at 50°C, is a micrograph of both the mixtures. The black circles at the right side and top of each micrograph are due to trapped air bubbles. At 73°C CL was molten and CLMgBr crystals could be observed. In Fig. 5.34 (c), unlike Fig. 5.33 (c), increasing the
temperature did not result in disappearance of all of the crystalline structures. Because of the very slow heating rate polymerisation which was followed by crystallisation occurred at a very low temperature (i.e. below 100°C which is in a good agreement with DSC results), therefore PA6 started to crystallise even before CLMgBr crystals melted. The melting temperature of PA6 at this heating rate was observed to be similar to that at 10°C/min. Crystallisation occurred at 155°C during cooling and melted again at the same temperature. Fig.5.35 (c) shows the onset of crystallisation with a heating rate of 15°C/min at 128°C followed by onset of melting at 180°C. The crystallisation occurred at 150°C during cooling and melted at 190°C during the second heating.

![Figure 5.35](image)

**Figure 5.35:** Polymerisation of caprolactam on a hot stage at heating rate of 15°C/min.

Finally Fig.5.36 shows the polymerisation process at a heating rate of 20°C/min. During the first heating, unlike the other heating rates, only a blurry picture was observed after melting of CLMgBr. This means that because of very fast polymerisation the crystallisation could not occur properly resulting in a poor and imperfect crystalline structure which could not be observed clearly. However, as seen in Fig.5.36 (e), the crystallisation occurred properly during cooling and, as for the other samples, melted at about 190°C during second heating. Results from hot stage microscopy are presented in Table 5.2. These results showed that increasing the heating rate resulted in increased crystallisation temperature. At higher heating rates, the time difference between onset of crystallisation and melting was shorter and the crystallisation process did not get enough time for completion. These results were consistent with DSC results in which the amount of crystallinity during the first heating decreased with
increasing the heating rate. However, it was observed that despite different heating rates, all samples re-crystallised (i.e. after melting) at the same temperature (i.e. around 150°C) during the cooling stage which shows that changing heating rate did not result in changing the crystalline structure of S-PA6.

![Figure 5.36: Polymerisation of caprolactam on a hot stage at heating rate of 20°C/min.](image)

<table>
<thead>
<tr>
<th></th>
<th>3°C/min</th>
<th>10°C/min</th>
<th>15°C/min</th>
<th>20°C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disappearing of catalyst microcrystals (°C)</td>
<td>N/A</td>
<td>104</td>
<td>112</td>
<td>120</td>
</tr>
<tr>
<td>Initial crystallisation temperature (°C)</td>
<td>90</td>
<td>115</td>
<td>125</td>
<td>N/A</td>
</tr>
<tr>
<td>First-run melting point (°C)</td>
<td>193</td>
<td>191</td>
<td>191</td>
<td>N/A</td>
</tr>
<tr>
<td>Crystallisation during cooling (°C)</td>
<td>153</td>
<td>152</td>
<td>152</td>
<td>149</td>
</tr>
<tr>
<td>Second-run melting point (°C)</td>
<td>192</td>
<td>193</td>
<td>190</td>
<td>187</td>
</tr>
</tbody>
</table>

### 5.4 Effect of heating strategy on polymerisation

The influence of heating rate on crystallinity of S-PA6 was discussed in Section 5.3.2. Section 5.4.1 is a discussion of the effect of heating strategy, including heating rate, maximum heating temperature, and cooling rate, on final properties of S-PA6 (i.e. polymerisation enthalpy, monomer conversion, weight loss during polymerisation, crystallinity, and $T_m$). Some of the DSC curves are considered in more detail in Section 5.4.2.
5.4.1 ECHIP results

The effect of heating strategy on polymerisation enthalpy, peak temperature, crystallinity, $T_m$, weight loss during polymerisation, and monomer conversion is discussed in this section. Results obtained from the tests carried out in Table 3.5 are in appendix B (Table B-1).

5.4.1.1 Influence of heating strategy on polymerisation enthalpy and peak temperature

As seen in Fig. 5.37 (a), the exothermic peak area decreased rapidly on increasing the heating rate; however, there was a slight increase in peak area when the heating rate increased from 5 to 12°C/min. This was because at low heating rates polymerisation initiated at low temperatures, before all CLMgBr crystals melted (see Fig. 5.34). Since polymerisation and crystallisation occurred at the same time, CLMgBr and CL molecules get trapped inside PA6 crystals before participating in polymerisation. This resulted in lowering the monomer conversion and also polymerisation enthalpy. The exothermic peak area decreased when heating rate was increased from 12 to 30°C/min because time for polymerisation decreased with increasing heating rate.

![Figure 5.37: The influence of heating strategy on (a) polymerisation and crystallisation enthalpy and, (b) the exothermic peak temperature (maximum temperature: 200°C).](image)

The APCL is exothermic and once it starts, depending on initial polymerisation temperature, the adiabatic temperature can rise up to 200°C [33]. Therefore, the exothermic peak area increased when the maximum temperature increased from 140 to 200°C (see Fig. 5.37 (a) and Fig. 5.41 (i)). Fig. 5.37 (b) shows that peak polymerisation temperature increased with

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increasing heating rate. This was due to the fact that, at high heating rates, polymerisation mixtures do not get sufficient amount of time at that temperature to progress polymerisation. In general, peak temperature increases with increasing heating or cooling rate because the temperature difference between the thermocouple and sample gets bigger.

5.4.1.2 Influence of heating/cooling strategy on crystallinity and Tm
Since S-PA6 crystallised during cooling, the crystallinity of the S-PA6 was independent of heating rate. However, when cooling rate was fast, S-PA6 quenched before completing crystallisation process, which means that crystallisation process only occurred during heating (see Fig. 5.38 (a)). Figs. 5.38 (b) and (c) show that the melting point of S-PA6 reduced by increasing the heating and cooling rate. This means that increasing the heating and cooling rate resulted in production of a poorer crystalline structure.

Figure 5.38: The influence of heating strategy on (a) crystallinity, (b) and (c) melting point. The maximum temperature in (a) was 200°C, cooling rate in (b) was 17°C/min, and maximum temperature and heating rate in (c) were 170°C and 17°C/min respectively.

5.4.1.3 Influence of heating strategy on monomer conversion and weight loss during polymerisation (WLDP)
Monomer conversion refers to the final degree of monomer conversion in the S-PA6 samples. Fig. 5.39 (a) shows that monomer conversion increase in with increasing the maximum temperature up to about 180°C and decreased afterwards. This is because at lower temperatures fewer active anions were produced to participate in polymerisation (i.e. in propagation stage); however, increasing the temperature above 180°C resulted in a shift in the ring-chain equilibrium of the anionic ring opening polymerisation toward the monomer side.
[77,78]. Fig. 5.39 (a) also shows that monomer conversion increased at lower heating rates because the polymerisation mixtures were heated for a longer time.

![Figure 5.39](image)

**Figure 5.39:** The influence of heating strategy on (a) monomer conversion, and (b) weight loss during polymerisation. Cooling rate was 17°C/min in both figures.

Weight loss during polymerisation (WLDP) is the amount of material which disappears after the first DSC and the second DSC runs. This material loss is because of monomer (i.e. CL) evaporation, as discussed in Section 5.2.3. Since the optimum heating rate in which the exothermic peak area of polymerisation-crystallisation had the highest value was 12°C/min, the WLDP was reduced by increasing heating rate up to about 12°C/min (see Fig. 5.39 (b)). A change in behaviour was observed in all plots in Fig. 5.39 (b) at about 16°C/min. This change was different for low maximum temperature and high maximum temperature plots. WLDP increased above a heating rate of 16°C/min when the maximum temperature was 140°C. This was because of the low monomer conversion achieved during polymerisation (i.e. fast heating and low polymerisation temperature). This resulted in high evaporation of residual monomer in the second DSC run. The final degree of monomer conversion increased with increase in the maximum temperature up to 170°C (see Fig. 5.39 (a)), so there was less evaporation of residual monomer in the second DSC run. Finally, depolymerisation at very high temperatures (i.e. 200°C) due to the shift in ring-chain equilibrium resulted in a high amount of WLDP. However, increasing heating rate reduced depolymerisation time and consequently reduced WLDP.
5.4.1.4 Relationships between all properties

Relationships between all properties are shown in Figs. 5.40 (a) and (b). As explained above, increasing maximum temperature caused increasing exothermic peak area, monomer conversion and WLDP. The influence of heating rate on these parameters has also been described. As seen in Figs. 5.40 (a) and (b), the melting point of S-PA6s followed the same trend as monomer conversion. The reason is the shift in melting point to lower temperatures due to overlap between monomer evaporation and polymer melting peaks (see Fig. 5.41 (ii) in Section 5.4.2).

![Graphs showing properties vs. heating strategy](image)

**Figure 5.40:** The influence of heating strategy on all of properties, (a) maximum temperature and (b) heating rate effects.

Figs. 5.40 (a) and (b) were used to find the optimum heating rate and maximum temperature. The best processing ranges in which all of the properties were optimised are shown by grey lines in Figs. 5.41 (a) and (b) which were 175°C and 13°C/min for maximum heating temperature and heating rate respectively. It was noted that cooling rate did not have a major effect on most of the properties. Melting point and crystallinity decreased slightly with increasing cooling rate when heating rate was very fast. However, when heating rate was slow enough, the crystallisation process was completed during heating, and cooling rate did not have significant influence.

5.4.2 Curve resolution in DSC

The endothermic and exothermic processes during polymerisation have been monitored using DSC in previous sections. However, DSC was not able to distinguish and separate the
overlapped peaks when simultaneous processes occurred. For instance, only one exothermic peak was observed during heating in most of the cases, when two simultaneous processes (i.e. polymerisation and crystallisation) occurred. An attempt to separate these simultaneous processes is described below. There were two main pairs of processes which occurred at the same time; these were polymerisation/crystallisation and monomer evaporation/PA6 melting processes.

The DSC traces (i.e. polymerisation and crystallisation) for APCL catalysed with CLMgBr and activated with ACL are shown in Fig. 5.41 (i). It is claimed in the literature [60] that the separation of polymerisation and crystallisation processes can be achieved in a slow reaction. However, this separation also occurred when CLMgBr and ACL (i.e. which result in a fast polymerisation) were used at lower concentrations (i.e. half of the optimum concentrations in the polymerisation mixtures).

![DSC traces](image)

**Figure 5.41:** (i): Curve resolutions of the exothermic peaks are indicated; curve for polymerisation (●) and for crystallisation (○). (a) 5°C/min, (b) 10°C/min, (c) 15°C/min, and (d) 20°C/min. (ii): Curve resolution of the endothermic peaks are indicated; curve for melting of residual caprolactam (●), for PA6 melting (○) and for evaporation of caprolactam (■). Monomer conversion: (a) 71%, (b) 81%, (c) 90%, and (d) 96%.
Although polymerisation and crystallisation processes were separated into two different exothermic peaks in the first two diagrams in Fig. 5.41 (i), the exothermic polymerisation and crystallisation effects were still superimposed. The components of the overall exothermic peak can be separately established by curve resolution as illustrated by dots in Fig. 5.41 (i). The separate peak areas were estimated using hot stage optical microscopy results (the initial crystallisation temperatures were measured at different heating rates, using hot stage microscopy) from the previous work (see Table 5.3) and a curve fitting method described in ref [56]. In this work, curve resolving was carried out by estimating the position of the peaks and they are not necessarily accurate. Effect of heating rate on polymerisation and the subsequent crystallisation process can also be seen in Fig. 5.41 (i). When the heating rate was below 10°C/min, the polymerisation peak was followed by another exothermic peak which corresponds to crystallisation. However, hot stage microscopy showed that crystallisation started before the polymerisation process was complete and continued after completion of the polymerisation. When the heating rate was 15°C/min, polymerisation and crystallisation processes occurred almost simultaneously and when the heating rate was 20°C/min, crystallisation only occurred to a limited extend. This was because of fast heating which reduced polymerisation-crystallisation time. In addition, when the heating was fast, the polymerisation process occurred at high temperatures at which crystallisation process was inhibited because of high kinetic energy of polymer chains.

Two endothermic peaks were observed during the second DSC run which were associated with melting of residual monomer and S-PA6. As seen in Fig. 5.41 (ii) the endothermic peak areas were larger at low monomer conversions. This is due to melting and evaporation of residual CL in the first and second peaks respectively. Residual monomer in S-PA6 also resulted in a small shift of melting point of S-PA6 to lower temperatures. The onset of melting of S-PA6 samples with different degrees of monomer conversion are shown in Table 5.3.

<table>
<thead>
<tr>
<th>Heating rate</th>
<th>5°C/min</th>
<th>10°C/min</th>
<th>15°C/min</th>
<th>20°C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial crystallisation temperature (°C) from hot stage microscopy</td>
<td>105</td>
<td>118</td>
<td>125</td>
<td>N/A</td>
</tr>
<tr>
<td>Monomer conversion</td>
<td>71%</td>
<td>81%</td>
<td>90%</td>
<td>96%</td>
</tr>
<tr>
<td>$T_m$ (°C) from curve resolution</td>
<td>205</td>
<td>207</td>
<td>210</td>
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</table>
CHAPTER SIX: BULK AND SMALL SCALE POLYMERISATION USING A COMMERCIAL CATALYST-ACTIVATOR COMBINATION

6.1 Introduction

Although anionic polymerisation of caprolactam (APCL) catalysed and activated by caprolactam magnesium bromide (CLMgBr) and N-acetylcaprolactam (ACL) respectively resulted in good PA6 specimens, the problem with jetting the CLMgBr-CL mixture (mixture A) led to the need to investigate another catalyst-activator combination. The new system must provide an equivalent or better performance for APCL and at the same time be suitable for jetting. Having considered various available catalysts and activators, it was decided to use a commercial catalyst-activator combination for this purpose. This chapter deals with characterisation of these commercial materials and an investigation of their performance in APCL. The commercial materials are mainly identified by their company code in this work (i.e. C10: CLNa in CL; C1: CLMgBr in CL (was used for comparison); and C20: di-functional activator in CL). The chapter is divided into three sections and each section includes sub-sections. The first section focuses on the characterisation of new materials by thermal analysis (DSC), IR studies, microscopy, and rheometry. The APCL in bulk is described in section two and influence of experimental conditions on polymerisation is reported. Finally in the last section, small scale polymerisation catalysed and activated by C10 and C20 was carried out using DSC, small droplets in an oven, and hot stage microscopy.

6.2 Materials characterisation

DSC, FT-IR, rheometry, and optical and electron microscopy were used to study the properties and characteristics of polymerisation mixtures.

6.2.1 DSC thermogram

DSC thermograms of the commercial catalyst (C10) and activator (C20) in the range of 20 to 160°C and heating rate of 5°C/min are shown in Fig. 6.1 (a) and (b) respectively. The first diagram (i) in each figure is a DSC thermogram of the mixture which was prepared for jetting (i.e. 5 and 2.5 mole% catalyst and activator respectively in CL (20%C10 and 20%C20, see Table 3.1)) and diagram (ii) is a DSC thermogram of the concentrated catalyst and activator.
The concentrated catalyst and activator samples were produced using a vacuum oven to evaporate the CL present.

As seen in Fig. 6.1 (a), 20%C10 had a single melting peak at 69°C which corresponded to melting of CL. No melting peak was observed for catalyst component in the mixture because the endothermic heat of fusion was not high enough to be detected by DSC. The recrystallisation peak on cooling occurred at 28°C which was about 15°C below the recrystallisation temperature of CL (i.e. about 43°C). Therefore, it can be concluded that catalyst component in C10 had a retarding effect on re-crystallisation of CL. Two overlapped melting peaks were observed in diagram (ii) that were associated with melting of residual CL and concentrated catalyst. The concentrated catalyst had a single re-crystallisation peak at 88°C on cooling. 20%C20 melted at 64°C and did not re-crystallise in cooling. In a separate experiment, this mixture was cooled down to sub zero temperatures but still did not re-crystallise. The concentrated activator melted at 82°C and did not re-crystallise on cooling.

**6.2.2 IR spectra**

Fig. 6.2 shows FT-IR spectra of (a) C10, (b) concentrated C10, (c) C20, and (d) concentrated C20 within the range of 600 to 4000cm⁻¹. As seen in Fig. 6.2 (a) and (b), the IR spectrum of
C10 (CLNa in CL) was similar to a CLMgBr in CL mixture especially in the ranges of 600 to 900 cm\(^{-1}\) and 2931 to 3600 cm\(^{-1}\) (compared with Fig. 5.7). This showed that the molecular composition of CLNa in CL and CLMgBr in CL were similar.

**Figure 6.2:** IR spectrum of (a) C10, (b) concentrated C10, (c) C20, and (d) concentrated C20.

The bands in the region of 1560 to 1600 cm\(^{-1}\) (i.e. the band at 1566 in Fig 6.2 (b)) are associated with the benzoyl group or fused ring systems. In most compounds this band is very weak in IR and appears as a weak shoulder on the side of the 1600 cm\(^{-1}\) band [203].
Since C20 had a complex molecular structure, it was not easy to interpret the spectrum. As seen in Fig. 6.2 (c) and (d), there were some significant differences and distinguishable peaks in C20 which did not exist in C10, CL, etc. For instance, there was a peak at 1687 cm\(^{-1}\) in C20 which shifted to 1707 cm\(^{-1}\) in the concentrated C20. This peak did not exist in any other component in this work. This may correspond to another nitrogen which is attached to the amide nitrogen (i.e. the compounds R-CO-NH-NH-CO-R gave multiple bands in the region 1683 to 1707 cm\(^{-1}\)). The sharp band in the range of 1150 to 1170 cm\(^{-1}\) could be associated with single bond vibrations in the aromatic group and the band just after 1500 cm\(^{-1}\) might correspond to double bond vibrations in aromatic group. Any of these peaks can be used to identify this component in the polymerisation mixture [206].

6.2.3 Microscopy

Hot stage optical microscopy and SEM were used to observe crystalline structure and any other solid particles in the polymerisation mixture at room and jetting temperatures. The feasibility of jetting mixture A was also evaluated in this work using both microscopes.

6.2.3.1 Morphology

The crystalline structure of 20%C10 at room temperature and 80\(^{\circ}\)C are shown in Fig. 6.3 (a) and (b) respectively using hot stage optical microscopy. SEM micrographs of C10 and 20%C10 are also shown in Fig. 6.3 (c) and (d) respectively. As seen in Fig. 6.3 (a), the crystalline structure of 20%C10 at room temperature was similar to neat CL. Fig. 6.3 (b) showed that the catalyst component in C10 had a smaller crystalline size and less agglomeration compared to CLMgBr (see Fig. 5.10). This was also shown using SEM images. Although large crystalline structures were observed in C10, 20%C10 had a very fine crystalline size and good distribution. The star shaped particles in Fig. 6.3 (d) were believed to be the catalyst component which had a size distribution of 2 to 4 µm. This would allow jetting of this component without clogging the filtration unit in the jetting head (i.e. filtration unit pore size is 5 µm).

Fig. 6.4 shows the thermal behaviour of concentrated C10 (i.e. catalyst component) using hot stage optical microscopy. The continuous black and white areas in Fig. 6.4 were due to molten CL and the catalyst crystalline structure respectively. Comparing Fig. 6.3 (b) and Fig. 6.4 (a) shows high agglomeration and concentration of white spots in concentrated C10
which correspond to the catalyst crystalline structure. The onset of melting of the catalyst crystalline structure was at 175°C and melting was completed at 200°C. The mixture re-crystallised at 140°C on cooling. However, quite different results were obtained from DSC in Fig. 6.1 (i.e. in a separate experiment, concentrated C10 was heated up to 240°C in the DSC without producing a melting peak at 170°C). Since the melting point of the catalyst component strongly depended on the concentration and agglomeration of crystals (as shown in Section 5.2), this temperature varied a lot in different experiments. The second reason was that the low heat of fusion of the catalyst which was not detected by DSC.

**Figure 6.3:** (a) and (b): optical image of 20%C10 at room temperature and 80°C, (c) and (d) SEM image of C10 and 20%C10.

Fig. 6.5 shows the thermal behaviour of concentrated C20 using hot stage optical microscopy. As seen in Fig. 6.5, the activator component melted at about 80°C, but did not re-crystallise on cooling. Unlike concentrated C10, results from DSC totally agreed with results from hot
stage microscopy. This showed that activator component had a separate solid crystalline structure at room temperature. It was shown by DSC that this component melted with CL at about 65°C when 20%C20 was used (see Fig. 6.1 (b)).

**Figure 6.4:** Thermal behaviour of concentrated C10.

**Figure 6.5:** Thermal behaviour of concentrated C20.
6.2.3.2 Concentration of CLNa in mixture A after jetting

This section contains a discussion on the possibility of jetting catalyst mixture which was problematic when CLMgBr was used as the catalyst. Solid micro-crystal particles were observed in 20%C10 using a polarised optical microscope (see Fig. 6.6). The effect of these micro-crystals on jetting was investigated. Fig. 6.6 shows 20%C10 before and after jetting.

![Figure 6.6: Micrograph of 5 mole% catalyst in CL (a) before jetting and (b) after jetting.](image)

Since the micro-crystals in C10 (i.e. CLNa) were much smaller than CLMgBr micro-crystals, maximum microscope illumination was used to observe them. For the same reason, the micro-crystals in 20%C10 were passed through the filtration unit in jetting system and were deposited on a glass slide using the available jetting heads in this work. However, the intensity of white spots in Fig. 6.6 (b) was less than Fig. 6.6 (a) which showed that concentration of these micro-crystals reduced after jetting. Therefore, some of the CLNa micro-crystals in 20%C10 were trapped by the filtration unit despite their small size (i.e. agglomeration of micro-crystals increased their size above the jetting limit).

SEM was used also to observe and measure the intensity of CLNa particles. Fig. 6.7 (a) and (b) show SEM micrographs of CL and C10 respectively. The crystalline structure of CLNa in C10 is shown in Fig. 6.7 (b). It can be seen that CLNa micro-crystals agglomerated when the concentration of CLNa in CL was high. The element composition of each sample was also observed using SEM in Fig. 6.7. The weight % and average weight % (i.e. average of three sample and three different positions), of each element in the different compositions are listed below each micrograph. As expected, CL had two main peaks corresponding to C and O in its composition. However, another peak was seen in Fig. 6.7 (b) which corresponded to the sodium (Na) in CLNa molecules.
Figure 6.7: SEM micrograph (a) CL and (b) C10.

Figure 6.8: SEM micrograph of 20% C10 (a) before jetting and (b) after jetting.
SEM was used to measure the CLNa concentration change in 20% C10 after jetting. Fig. 6.8 (a) and (b) show the SEM micrographs of 20% C10 (i.e. containing 5 mole% catalyst in CL which is equal to 23 weight% CLNa in CL) before jetting and after jetting respectively. As seen in Fig. 6.8, the intensity of Na peak decreased by almost half its size after jetting, which showed that the concentration of this composition was decreased in the jetting process. This confirmed the results from optical microscopy and showed that CLNa micro-crystals only partially passed through the filtration unit in the jetting system. The feasibility of breaking the micro-crystal agglomerations prior to jetting and its influence on the jetting of mixture A was not studied in this work and could be an interesting aspect for future work.

6.2.4 Viscosity

Fig. 6.9 shows the dynamic viscosity of the commercial materials, CLMgBr-ACL catalyst-activator in CL and neat CL against time (in this experiment shear rate was also increased from 5 to 500 s\(^{-1}\) with time simultaneously). Although viscosities of the latter ones were reported before in Chapter 5, they are presented again for comparison.

![Dynamic viscosity of CL, 5mole% N-acetylcaprolactam in CL, 20% C20, 20% C10, and complex6 (see Table 3.1).](image)

As seen in Fig. 6.9, dynamic viscosity of activator mixtures (i.e. ACL in CL and C20 in CL) were similar to each other and were just above CL viscosity. However, the catalyst mixtures
had quite different dynamic viscosity in the beginning of the experiment which decreased to reach a steady state after 1700s. The dynamic viscosity of complex6 and 20%C10 were about 0.3 and 0.15Pa.s respectively at the beginning of the test and both reached a similar value of about 0.025Pa.s after shearing for a specific period of time. This showed that the solid particles in the mixtures had a significant effect on the dynamic viscosity. Complex6 had a higher value than 20%C10 because there were more agglomerates and a bigger crystalline structure in complex6. However, the agglomerates and crystalline structure of both catalysts were reduced by applying a high shear rate.

6.3 Polymerisation in bulk
APCL catalysed and activated with C10 and C20 respectively was studied in bulk. In this section, the optimised catalyst-activator concentration was estimated and then the influence of polymerisation atmosphere on APCL was studied.

6.3.1 Catalyst-activator concentration influence
The influences of catalyst-activator concentrations and catalyst/activator ratio on APCL are discussed below. ECHIP was used in this section and results obtained from the experiments carried out (see Table 3.4) are in appendix C (Table C-1).

6.3.1.1 Concentration optimisation
Fig. 6.10 shows the influence of catalyst-activator concentrations on APCL. Optimised conditions in which each variable has the maximum value (i.e. except for half-time of solidification for which a minimum value is desirable) are presented in the bottom section of Fig. 6.10. It is shown that the fastest solidification occurred when a high concentration of catalyst and an intermediate concentration of activator were used for polymerisation. The solidification was very slow when the catalyst concentration was low but the activator concentration was high. The shortest time was achieved at 1.92 mole% catalyst and 0.77 mole% activator. Crystallinity of S-PA6 was decreased by increasing activator concentration and increased by increasing catalyst concentration as shown in Fig. 6.10 (b). The highest crystallinity was at 1.97 mole% and 0.34 mole% of catalyst and activator respectively. Unlike previous systems (i.e. in Chapter 4), increasing activator concentration resulted in a decreasing monomer conversion as seen in Fig. 6.10 (c). According to this figure, the
maximum degree of monomer conversion was achieved when 2 mole% catalyst and 0.27 mole% activator were used.

### Table

<table>
<thead>
<tr>
<th>Optimised point</th>
<th>Catalyst (mole%)</th>
<th>Activator (mole%)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>1.92</td>
<td>0.77</td>
<td>12(s)</td>
</tr>
<tr>
<td>(b)</td>
<td>1.97</td>
<td>0.33</td>
<td>45(%)</td>
</tr>
<tr>
<td>(c)</td>
<td>2</td>
<td>0.27</td>
<td>99(%)</td>
</tr>
<tr>
<td>(d)</td>
<td>0.5</td>
<td>0.25</td>
<td>106,000(g/mol)</td>
</tr>
</tbody>
</table>

**Figure 6.10:** The variation of (a) half-time of solidification, (b) crystallinity, (c) the final degree of monomer conversion, and (d) viscosity average molecular weight (gmol\(^{-1} \times 10^{-3}\)) with catalyst-activator concentration.
Viscosity average molecular weight, $\bar{M}_V$, had similar trend to the other systems decreasing with increasing the catalyst and activator concentration as seen in Fig. 6.10 (d); however, the rate of decrease in $\bar{M}_V$ with increasing catalyst concentration was much lower than with activator. The highest value for $\bar{M}_V$ was 106,000 (g/mol) which was almost double the value of the commercial cast PA6 sample used in Section 4.5.2.

It can be seen in Fig. 6.10 that the catalyst/activator ratio which had a significant influence on the polymerisation was always higher than 1. The influence of catalyst/activator ratio will be discussed in more detail later. The reason for this difference is due to the moisture that reacts with a proportion of catalyst and deactivates the free anions, as the nitrogen used for polymerisation contained moisture (about 0.002%).

Overall optimisation was carried out using Fig. 6.11. The influence of catalyst-activator concentrations on half-time of solidification, melting point, monomer conversion, and $\bar{M}_V$ are also shown individually in Fig. 6.11. The filled rectangles in Fig. 6.11 show the best range for each of the concentrations.

![Figure 6.11](image.png)

**Figure 6.11:** Overall optimisation of polymerisation conditions; (a) influence of catalyst concentration, (b) influence of activator concentration, and (c) influence of initial polymerisation temperature.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimized range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst concentration (C10)</td>
<td>1.65-1.85 (Mole%)</td>
</tr>
<tr>
<td>Activator concentration (C20)</td>
<td>0.5-0.62 (Mole%)</td>
</tr>
</tbody>
</table>
As mentioned above, the catalyst/activator ratio had a significant influence on ACPL; therefore, the trends for each parameter in Fig. 6.11 (a) depend on activator concentration. In other words, the optimised concentration for each component is highly dependent on the concentration of the other component. It is shown in Fig 6.11 (a) that all parameters passed through a maximum with increasing catalyst concentration. Although these maxima had different positions for different characterisations, all of them were located above a 1.5 mole% concentration of catalyst. This means that the catalyst/activator ratio must be always equal or greater than 1 (the concentration of difunctional activator was 0.75 mole% × 2), however, the best catalyst and activator concentration ranges in which all properties were optimised found to be 1.62 to 1.87 and 0.5 to 0.62 mole% respectively.

6.3.1.2 Influence of catalyst/activator ratio

It was noticed that the catalyst/activator ratio as well as their individual concentrations had an important influence on APCL. The influence of catalyst/activator ratio is discussed in this section and may possibly also relate to other catalyst-activator systems.

Fig. 6.12 shows the activator (difunctional activator) concentration effect on APCL at different concentrations of catalyst (CLNa). As expected, all properties decreased and polymerisation solidification time increased by increasing activator concentration when the catalyst concentration was 0.5 mole%. However, at the highest concentration of catalyst (i.e. 2.5 mole%) solidification time decreased with increasing activator concentration. This showed that the polymerisation rate was increased by increasing activator concentration as long as catalyst/activator ratio was higher than 1. Crystallinity of S-PA6s decreased with increasing activator concentration because of the enhanced rate of branching which occurs when using a di-functional activator. Monomer conversion decreased with increasing activator concentration when catalyst concentration was 0.5 to 1.5 mole%, however, there was a peak in monomer conversion against activator concentration when the catalyst concentration was 2.5 mole%. The monomer conversion increased with increasing activator concentration up to 0.56% when the catalyst concentration was 2.5 mole%. $\bar{M}_v$ started to decrease with increasing activator concentration straight away when the catalyst concentration was 0.5 mole% for the same reason as described in Chapter 4. However, it started to decrease above 0.62 and 0.75 mole% of activator concentration when the catalyst concentration was 1.5 and 2.5 mole% respectively which clearly showed the influence of catalyst/activator ratio.
Figure 6.12: Influence of activator concentration and catalyst/activator ratio on all properties.

Fig. 6.13 shows properties of all S-PA6 samples versus their catalyst/activator ratio for all experiments that carried out in this section. For instance, catalyst/activator ratio of 1 can be either catalyst: 2.5mole%-activator: 1.25mole% or catalyst: 0.5mole%-activator: 0.25% (i.e. because activator is di-functional and its molar concentration was doubled).

Fig. 6.13 clearly shows that solidification half-time dropped sharply when catalyst/activator ratio was higher than 1, which means that polymerisation rate was very low at ratios lower than 1. All other properties increased rapidly by increasing catalyst/activator ratio over 1. However, further increase in the ratio did not result in improving the properties consequently and it even reduced $M_v$ when the catalyst/activator ratio went above 3.

It was reported [37] that the initial rate of the APCL is not proportional to the concentration of the activator and that in some cases it even decreases with its increasing concentration. These facts are sometimes explained by the fast decay of the catalytic components or by the
participation of ion pairs or adducts of the activator growth centres with alkali metal lactamates (e.g. CLNa). It is quite possible therefore that a significant amount of catalyst disappears as soon as polymerisation starts. Addition of activating components above their equivalent ratio may slow down or even stop the reaction proportionally to their amount because compared with CL they are strong acids and thus reduce the concentration of the CLNa. Greenley et al. [34] suggested that when using di-functional activators, if an activator to catalyst ratio of two is employed, there may be simultaneous growth of two molecules from one catalyst site. Otherwise, if ratios less than two are employed, because of the excess of activator, degradative and branching processes would be enhanced, (i.e. reactions of active sites with polymer chains instead of monomer).

![Graphs showing influence of catalyst/activator ratio on various properties of APCL.](image)

**Figure 6.13:** Influence of catalyst/activator ratio on APCL.

### 6.3.2 Influence of polymerisation atmosphere

The influence of polymerisation atmosphere (i.e. moisture, oxygen, and CO₂) on APCL has been discussed in Chapter 4. It was found that this effect varied dependent on the types of catalyst and activator which were used for polymerisation.
Three sets of conditions were selected from the previous experiments to study the influence of polymerisation atmosphere on APCL using the commercial catalyst-activator system (i.e. C10-C20). Each experiment was carried in nitrogen, air-nitrogen (i.e. mixture A and B were heated to the polymerisation temperature in nitrogen and mixed together in the mould in air), and air, and results are presented in Table 6.2.

Table 6.2: List of experiments carried out for polymerisation atmosphere effect study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Half-time (s)</th>
<th>Crystallinity (%)</th>
<th>Monomer Conversion (%)</th>
<th>$M_n$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2*</td>
<td>88</td>
<td>42</td>
<td>98</td>
<td>80000</td>
</tr>
<tr>
<td>2 nitrogen-air</td>
<td>90</td>
<td>35</td>
<td>93</td>
<td>65000</td>
</tr>
<tr>
<td>2 air</td>
<td>156</td>
<td>38</td>
<td>89</td>
<td>30000</td>
</tr>
<tr>
<td>12**</td>
<td>44</td>
<td>36</td>
<td>95</td>
<td>78000</td>
</tr>
<tr>
<td>12 nitrogen-air</td>
<td>72</td>
<td>25</td>
<td>88</td>
<td>62000</td>
</tr>
<tr>
<td>12 air</td>
<td>163</td>
<td>20</td>
<td>75</td>
<td>25000</td>
</tr>
<tr>
<td>14***</td>
<td>14</td>
<td>43</td>
<td>97</td>
<td>69000</td>
</tr>
<tr>
<td>14 nitrogen-air</td>
<td>31</td>
<td>37</td>
<td>94</td>
<td>58000</td>
</tr>
<tr>
<td>14 air</td>
<td>40</td>
<td>33</td>
<td>91</td>
<td>48000</td>
</tr>
</tbody>
</table>

*Catalyst: 1.5 mole%-activator: 0.25 mole%
**Catalyst: 1 mole%-activator: 0.5 mole%
***Catalyst: 2.5 mole%-activator: 0.75 mole%

As seen in Table 6.2 for all experiments, introducing more air during polymerisation resulted in increasing the solidification half-time as a consequence of decreasing the polymerisation rate. All other properties decreased significantly when air was replaced by $N_2$ in any stage of the polymerisation. The acceptable properties for an S-PA6 are shown in Section 4.5.2 using the commercial cast PA6 samples.

Since the catalyst component in C10 was CLNa, it was expected from Chapter 4 atmosphere experiment (Section 4.2) to see some deactivation in the catalyst when air was used. These results confirmed that the commercial catalyst-activator system was essentially sensitive to air. It was shown in the previous section that the catalyst/activator ratio must be equal or more than 1 and any ratios below 1 resulted in very poor polymerisation and S-PA6. Therefore, as seen in Table 6.2, the influence of using air as the polymerisation atmosphere on APCL was more significant in experiment no.12 in which catalyst/activator ratio was 1 (i.e. by deactivating catalyst in air the ratio was reduced down to less than 1). It was also
observed that when the concentrations of catalyst-activator were high (i.e. experiment 14) the influence of air on APCL was less noticeable.

6.3.3 Influence of polymerisation temperature on properties

In PA6 casting, there are two important temperatures; mixing temperature, and mould temperature (i.e. oven temperature). This section deals with studying the influence of the above parameters on the properties of S-PA6. The measured properties were monomer conversion, viscosity average molecular weight, $\bar{M}_v$, $T_m$, crystallinity and crystalline perfection. Fig. 6.14 shows the mixing and mould temperature effects on the APCL catalysed and activated by C10 and C20 respectively. 1.65 mole% catalyst and 0.62 mole% activator in CL were used in all experiments. The mould temperature was left constant at 180°C when studying the mixing temperature effect and the mixing temperature was 130°C when studying the mould temperature influence.

Figure 6.14: Influence of polymerisation temperatures on physical properties of S-PA6.
As seen, all properties improved by increasing the mixing temperature from 80°C to 160°C. Low monomer conversion was achieved when the mixing temperature was below 110°C. The highest values for monomer conversion and $\bar{M}_v$ were obtained when the mixing temperature was 160°C, (i.e. even more than the value that was obtained when the oven temperature was 190°C). The crystallinity decreased slightly when the mixing temperature exceeded 130°C. Tm was the only property which showed a different trend when the x-axis changed from mixing temperature to oven temperature. Tm decreased because branching rate was enhanced by increasing the oven temperature and consequently the irregularity in chain structure increased (see Fig. 6.15). However, increasing the oven temperature resulted in increasing $\bar{M}_v$ and monomer conversion. Crystallinity first increased with increasing oven temperature to 170°C and then decreased afterwards. This was because monomer conversion and MW were low at low oven temperatures and at higher oven temperatures the crystallinity was reduced because of the branches and irregular structure.

Fig. 6.15 shows the influence of mixing and oven temperatures on crystallite size and perfection (CSP) and index of crystalline perfection (ICP) using eq. 2.33 and eq. 2.34 respectively.

![Figure 6.15](image)

**Figure 6.15:** Influence of mixing and oven temperatures on the size and perfection of crystalline structure.

According to the literature, samples with a large CSP are usually brittle [143] and higher CPS is associated with higher crystal density. ICP is a measure of the index of chain packing [156], a smaller ICP shows that the regular packing of PA6 chains is inhibited. Fig. 6.15 clearly shows that the CSP and ICP values for S-PA6 samples are functions of polymerisation temperature and this diagram showed a trend very similar to that of crystallinity degree.
decreasing with increasing polymerisation temperature, thus indicating a reduction of the crystal size and/or a loss of crystalline perfection as reported by Rico [50]. This was due to the enhanced rate of branching and consequently reduction in structural order of the S-PA6. Although the polymerisation process mainly occurred after mixing in the mould, it was shown that the initial mixing temperature had an even more significant influence than oven temperature on most of the properties. Initial polymerisation temperature was the temperature which provided the activation energy for polymerisation reactions, and oven temperature mainly affected the crystallinity and polymer structure.

Fig. 6.16 shows IR spectra of PA6 samples synthesised at different oven temperatures in the range of 600 to 1700cm$^{-1}$.

The IR bands for out-of-plane bends of the N-H (amide V) appears as relatively sharp band at 690cm$^{-1}$ for the $\alpha$-phase [143]. The $\alpha$ phase also shows characteristic absorbance peaks at 928 and 959cm$^{-1}$ [159]. The bands at 1200 and 1170cm$^{-1}$ are present only in the $\alpha$-phase and the lower cm$^{-1}$ band (i.e. 1170cm$^{-1}$) indicates amorphous components. The broad band at 1120cm$^{-1}$ is useful for monitoring the amorphous content [143].

As seen in Fig. 6.16, the bands corresponding to $\alpha$-phase crystalline structure decreased in intensity and broadened by increasing the oven temperature above 170°C. However, the band at 1170cm$^{-1}$ which associated with amorphous component did not change significantly. This suggested that the crystallinity of S-PA6 decreased with increasing the oven temperature.
above 170°C as seen in Fig. 6.14 (b). Bands at 800, 1080, and 1120 cm\(^{-1}\) are also seen in CL in Fig. 5.6 (a). These peaks decreased and almost disappear with increasing the oven temperature. This was because at the low oven temperatures the amount of residual unconverted monomer in S-PA6 was high enough (see Fig 6.14 (a)) to be reflected in the IR spectrum of PA6.

### 6.3.4 Comparison between the properties of PA6 produced in this work using different catalyst-activator

The effect of four different catalyst-activator combinations using optimised concentrations on the properties of PA6 produced was studied. The combinations were as follows: CLMgBr-ACL (1.7-0.81 mole%), CLNa-ACL (3.7-0.81 mole%), CLMgBr-C20 (1.7-0.62 mole%), and C10-C20 (1.65-0.62 mole%). Physical and mechanical properties of the S-PA6 produced using each of these combinations were measured and results are shown in Table 6.3.

#### Table 6.3: Influence of catalyst-activator type on physical properties and mechanical properties of S-PA6 polymerised at 130-180°C (mixing-oven)

<table>
<thead>
<tr>
<th>Properties</th>
<th>CLMgBr-ACL</th>
<th>CLNa-ACL</th>
<th>CLMgBr-C20</th>
<th>C10-C20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer conversion (%)</td>
<td>95</td>
<td>93</td>
<td>85</td>
<td>96</td>
</tr>
<tr>
<td>Molecular weight(^*) (g/mol)</td>
<td>74</td>
<td>65</td>
<td>142</td>
<td>210</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
<td>35</td>
<td>30</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>Tm (°C)</td>
<td>225</td>
<td>219</td>
<td>220</td>
<td>221</td>
</tr>
<tr>
<td>Young’s modulus (MPa)</td>
<td>2020</td>
<td>1640</td>
<td>1560</td>
<td>1450</td>
</tr>
<tr>
<td>Tg ** (°C)</td>
<td>80</td>
<td>62</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>Strain at break (%)</td>
<td>15</td>
<td>18</td>
<td>22</td>
<td>174</td>
</tr>
<tr>
<td>Stress at maximum load (MPa)</td>
<td>67</td>
<td>63</td>
<td>55</td>
<td>60</td>
</tr>
</tbody>
</table>

\(^*\) Mw×10\(^{-3}\): measured using gel permeation chromatography  
\(^{**}\) measured using Tanδ peak temperature in dynamic mechanical analysis thermogram

As discussed in Chapter 4, the catalyst-activator combination had significant influences on the APCL. The best properties were obtained using combinations in which the catalyst and activator could make an efficient complex for initiating the polymerisation. On the other hand, unsuitable combinations resulted in poor polymerisation and low monomer conversion and MW. It is seen in Table 6.3 that despite the individual composition of catalyst or activator, an incorrect combination of these could produce a polymer with poor performance.
For instance CLMgBr and C20 were shown to be efficient as catalyst and activator when they were used with the appropriate activator and catalyst respectively. However, the combination of CLMgBr and C20 resulted in an unacceptable S-PA6 with monomer conversion of 85% and crystallinity of 15%. On the other hand, when CLMgBr was used with ACL a good polymer with the highest Young’s modulus, stress at maximum load, Tg, and Tm was produced. C20 was also a very efficient activator when it was used with C10 which produced polymer with highest strain at break, monomer conversion and MW. A big difference was observed in the MW of S-PA6 when polymerisation was activated with C20 compared with ACL. This is because the polymer chains can grow simultaneously from two sites on a single activator molecule when it is di-functional (C20). This also enhances the branching and irregularity in polymer structure which results in a decrease in crystallinity, Tm, and Young’s modulus.

Fig. 6.17 and Table 6.4 show GPC traces and corresponding results of the above S-PA6 and five other selected samples.

![Figure 6.17](image)

**Figure 6.17:** Influence of catalyst-activator type on molecular weight and molecular weight distribution of PA6.

Bimodal curves were observed in Fig. 6.17 when a di-functional activator was used in APCL. This would suggest a high amount of branching as a consequence of using a di-functional activator, resulting in synthesis of polymers with some ultra high MW and even in the case of
CLMgBr-C20 gelation. The presence of monomers with more than two groups capable of reacting (functionality > 2) results in branched, nonlinear polymers. Branching can lead to gelation, defined as that point where the MW is infinity. Below the gel point, branched polymers have a broader MWD than linear polymers of comparable MW [169]. As expected, the MW of S-PA6 increased with increasing polymerisation temperature and decreased with increasing the catalyst-activator concentrations.

**Table 6.4: Mn, Mw, and polydispersity of selected S-PA6 samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLNa-ACL*</td>
<td>13,300</td>
<td>62,400</td>
<td>4.7</td>
</tr>
<tr>
<td>CLMgBr-ACL**</td>
<td>12,700</td>
<td>74,400</td>
<td>5.9</td>
</tr>
<tr>
<td>CLMgBr-C20***</td>
<td>17,100</td>
<td>142,000</td>
<td>8.3</td>
</tr>
<tr>
<td>C10-C20</td>
<td>23,000</td>
<td>210,000</td>
<td>9.1</td>
</tr>
<tr>
<td>1.0-0.5 mole%</td>
<td>21,100</td>
<td>277,000</td>
<td>13</td>
</tr>
<tr>
<td>1.5-0.75 mole%</td>
<td>26,400</td>
<td>218,000</td>
<td>8.3</td>
</tr>
<tr>
<td>2.0-1.0 mole%</td>
<td>22,000</td>
<td>142,000</td>
<td>6.5</td>
</tr>
<tr>
<td>130-150 ++</td>
<td>19,900</td>
<td>136,000</td>
<td>6.8</td>
</tr>
<tr>
<td>130-170</td>
<td>21,900</td>
<td>207,000</td>
<td>9.4</td>
</tr>
<tr>
<td>130-190</td>
<td>32,100</td>
<td>245,000</td>
<td>7.6</td>
</tr>
</tbody>
</table>

* Polymerisation temperature: 130-180°C, catalyst-activator concentrations: 3.7-0.81 mole%  
** Polymerisation temperature: 130-180°C, catalyst-activator concentrations: 1.7-0.81 mole%  
*** Polymerisation temperature: 130-180°C, catalyst-activator concentrations: 1.7-0.62 mole%  
* Polymerisation temperature: 130-180°C, catalyst-activator type: C10-C20  
** Catalyst-activator concentrations: 1.65-0.62 mole%, catalyst-activator type: C10-C20  

### 6.4 Small scale polymerisation

Small scale polymerisation was also investigated by polymerising small droplets using DSC, and hot stage microscopy. The influence of catalyst-activator concentrations and heating strategy on small scale APCL was studied. Finally, small scale polymerisation was carried out by DSC using jetted polymerisation mixtures in a DSC pan.

#### 6.4.1 Small scale polymerisation in hot stage microscopy

Small scale APCL was observed in Chapter 5 using CLMgBr and ACL as catalyst and activator respectively. The same experiment was carried out using the commercial materials
with 2.5-1.25 mole% catalyst-activator and 10°C/min heating rate from room temperature to 220°C. The whole process of polymerisation was recorded and 9 micro-graphs were used to show the process as seen in Fig.6.18.

Figure 6.18: Polymerisation of CL using commercial materials on a hot stage at heating rate of 10°C/min.

The process of polymerisation using commercial materials was very similar to what was described in Section 5.3.3. The very thin film of polymerisation mixture melted at 70°C and started to crystallise at 110°C. The process was followed by more crystallisation and melting of crystallised PA6 at 215°C. Finally re-crystallisation was observed at 160°C which was developed and completed at 125°C.

6.4.2 Small scale polymerisation in DSC
Small scale polymerisation of CL catalysed and activated by C10 and C20 respectively was investigated using DSC. Polymerisation mixtures with different concentrations of catalyst-
activator were deposited in an aluminium DSC pan. Fig. 6.19 shows a sample with 2.5-1.25 mole% catalyst-activator which was heated 5°C/min up to 250°C.

Figure 6.19: Small scale polymerisation of CL catalysed and activated by C10 and C20 respectively in DSC using standard aluminium pan.

Four endothermic peaks (i.e. I, II, III, and V) corresponding to melting and evaporation of CL and melting of PA6 and one exothermic peak (i.e. IV) corresponding to re-crystallisation of PA6 are seen in Fig 6.19. It has been shown previously that this polymerisation was sensitive to moisture when C10-C20 was used. Consequently, the rate of polymerisation was reduced and degree of polymerisation was retarded. Therefore, a high proportion of CL evaporated before polymerisation and resulted in disappearance of the polymerisation peak because of the peaks overlapping (evaporation peak was bigger than polymerisation peak). However, Peak III and IV show that polymerisation has occurred partially. Therefore sealed pans were used in this study to prevent CL evaporation before polymerisation so that the polymerisation-crystallisation exothermic peak could be seen.

Fig 6.20 shows the small scale polymerisation of CL catalysed and activated by C10 and C20 respectively using sealed aluminium DSC pans. The repeatability of experiments and influence of heating rate were investigated.

The first endothermic peaks in Fig. 6.20 corresponding to melting of polymerisation mixtures (i.e. in the range of 65 to 75°C) had two peak temperatures which corresponded to melting point of CL and the activator respectively. Although it was attempted to prepare samples with minimum air contact, DSC results in Table 6.5 highly depended on the amount of absorbed
moisture by the polymerisation mixtures prior to pan sealing. If moisture was excluded, a better consistency would be achieved in repeat experiments.

![Figure 6.20](image)

**Figure 6.20:** (a) Experiment repeatability and (b) Influence of heating rate on APCL in DSC.

**Table 6.5:** Experiment repeatability results

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<thead>
<tr>
<th>Sample</th>
<th>$T_{mc}^i$</th>
<th>$\Delta H_{mc}^*$</th>
<th>$T_p^{ii}$</th>
<th>$\Delta H_p^+$</th>
<th>$T_{mp}^{iii}$</th>
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**Table 6.6:** Influence of heating rate on small scale polymerisation in DSC

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$^i$ polymerisation mixture melting point, $^{ii}$ polymerisation temperature, $^{iii}$ melting point of S-PA6, $^{iv}$ re-crystallisation temperature

$^*$ Heat of fusion of polymerisation mixture, $^{**}$ heat of fusion of S-PA6

$^+$ Polymerisation enthalpy, $^{++}$ re-crystallisation enthalpy
As expected, increasing the heating rate resulted in an increase in polymerisation temperature (i.e. exothermic peak temperature) from 90°C at 2.5°C/min to 203°C at 20°C/min (see Table 6.6). This temperature variation was much less when CLMgBr and ACL were used as catalyst and activator respectively (i.e. 117°C at 5°C/min-152°C at 50°C/min, see Fig. 5.32). Although the half-time of solidification in bulk polymerisation was similar to or shorter than CLMgBr-ACL system (compare Table 4.2 with Fig. 6.10), the polymerisation occurred at higher temperatures in the DSC (compare Figs. 6.20 and 5.32). This was because of the retarding and inhibiting effect of absorbed moisture on APCL using C10-C20. Consequently, there was no melting peak for PA6 in DSC thermograms when the heating rate was above 10°C/min. However, the re-crystallisation temperature and enthalpy were not significantly changed by increasing the heating rate, which showed that re-crystallisation was an independent process as expected.

6.4.3 Influence of polymerisation temperature, isothermal time, and concentration

The influence of heating temperature and time on APCL on a small scale is one of the significant challenges for polymerisation after jetting the polymerisation mixtures. Obviously mixture composition (catalyst-activator concentrations) affects the required polymerisation time and temperature. Therefore, the major parameters which control the polymerisation and the S-PA6 were investigated using ECHIP. These were the influence of heating temperature, heating time, and mixture composition (see Section 3.4.2.2 for the experimental procedure). Results obtained from the tests carried out in this section (see Table 3.6) are in appendix C (Table C-2).

6.4.3.1 Influence of catalyst-activator concentration

The influence of catalyst-activator (i.e. C10-C20) concentration on small scale APCL is shown in Fig. 6.21. For the same reason as discussed in Section 4.3.4.2 a nominal scale from 0 to 1 was used as y axes.

According to the literature and previous work, increasing catalyst-activator concentration resulted in production of more initiating points, consequently increasing the polymerisation rate and monomer conversion. However, decreased MW and crystallinity due to enhanced branching were some of the disadvantages. As expected, monomer conversion increased by increasing the catalyst-activator concentration as seen in Fig. 6.21 (a). The polymerisation
exothermic peak area decreased with increasing monomer conversion because a high proportion of monomer molecules had polymerised in the oven at higher concentrations of catalyst and activator.

![Figure 6.21: Influence of catalyst-activator concentration on (a) polymerisation, and (b) crystallisation.](image)

It was shown that the degree of monomer conversion after the first heating in oven was high at high concentrations of catalyst-activator, so less polymerisation occurred in the second heating in the DSC. Since the exothermic peak consisted of simultaneous polymerisation and crystallisation processes (i.e. polymerisation and crystallisation peaks overlapped in one peak), decreasing the polymerisation peak resulted in dominance of the crystallisation peak. Therefore, the exothermic peak temperature shifted to higher temperature because crystallisation occurred at a higher temperature than polymerisation. The exothermic peak temperature decreased again at very high catalyst-activator concentrations due to suppressed crystallisation.

As discussed, increasing concentration of catalyst-activator (i.e. initiating points) resulted in enhancing the amounts of branching because the active sites attack chains when they do not find free anions around them. This was more probable when a di-functional activator was used to activate the polymerisation reaction. The regularity of polymer chains reduced because of branches which caused the intermolecular forces to reduce. Consequently, the re-
crystallisation temperature decreased. For the same reason, on heating less energy was required to overcome the intermolecular forces and melt the crystals. Therefore, crystallinity, re-crystallisation temperature, and melting point of S-PA6 decreased with increasing catalyst-activator concentration as shown in Fig 6.21 (b).

### 6.4.3.2 Influence of isothermal heating temperature and time

Fig. 6.22 shows the influence of isothermal heating temperature and time on the polymerisation and particularly monomer conversion.

![Figure 6.22: Influence of isothermal temperature and time on polymerisation.](image)

Results from APCL in bulk using C10 and C20 as catalyst and activator respectively showed that the rate of polymerisation was reduced when polymerisation mixtures were exposed to air. In addition, the DSC results in 6.4.2 section showed that small scale APCL occurred at higher temperatures when polymerisation mixtures were exposed to air. Having said that, very slow polymerisation occurred at lower temperatures and times and as a result monomer conversion was very low. Fig. 6.22 shows that monomer conversion increased with increasing isothermal temperature and time. However, the magnitude of this influence depended on the concentration of catalyst-activator. Therefore, the influence of heating temperature and time was studied at different catalyst-activator concentrations and results are shown in Fig. 6.23.
Figure 6.23: Influence of isothermal temperature and time on polymerisation at different concentrations.

It was shown that polymerisation condition variables had both direct and interactional effects on properties. Fig. 6.23 (a) shows the influence of isothermal temperature on monomer conversion at different isothermal times. As shown in Fig. 6.22, monomer conversion increased with isothermal temperature and time. It was seen in Fig. 6.23 (a), at the specified concentration, the monomer conversion never exceeded 60% even at 180°C when heating time was 5 minutes; however, it was always above 80% when heating time was 60 minutes. Fig. 6.23 (b) shows that the monomer conversion after 30 minutes heating at 140°C increased from 42% at 1.25-0.62 mole% catalyst-activator to about 80% at 7.5-3.75 mole% catalyst-activator. The maximum value of monomer conversion was about 90% after 30 minutes.
heating at 180°C for concentrations of 4.25-2.12 and 7.5-3.75 mole% catalyst-activator while this value was only about 75% at a catalyst-activator concentration of 1.25-0.62 mole%. Although monomer conversion had a higher value after 5 minutes heating at 160°C compared with 140°C in Fig. 6.23 (c), both lines were similar after longer polymerisation times and did not exceed 90% monomer conversion after 60 minutes heating. However, heating the polymerisation mixture containing 4.25-2.12 mole% catalyst-activator at 180°C resulted in 95% monomer conversion after about 40 minutes. This showed that the polymerisation temperature had a significant influence on the final degree of monomer conversion. In other words, the initial polymerisation temperature for small scale APCL (i.e. exposed to air) must be above 160°C to obtain a reasonable monomer conversion. At lower temperatures than 160°C the rate of polymerisation is too slow to compete with the simultaneous crystallisation and residual monomer gets trapped in crystals. Finally, the influence of isothermal heating time at 160°C on monomer conversion at different concentrations is shown in Fig. 6.23 (d). As expected, the final degree of monomer conversion did not exceed 90% even after 60 minutes heating the mixture with 7.5-3.75 mole% catalyst-activator at 160°C. This confirmed the results in Fig. 6.23 (c), which showed that high monomer conversions would be achieved at temperatures above 160°C.

6.5 Polymerisation and jetting

Small scale APCL using C10 and C20 as catalyst and activator has been discussed. The feasibility of achieving polymerisation after jetting these mixtures is discussed in this section. It was shown in Section 6.2.3.2 that, unlike CLMgBr, CLNa micro-crystals in C10 could be partially jetted. The activator mixture, (i.e. mixture B containing 2.5 mole% activator in CL) was jetted successfully with no problems. Fig. 6.24 shows the DSC thermograms of the sample using a first and second heat/cool cycles. The experimental procedure is in Section 3.7.4.

The polymerisation mixtures jetted into a DSC pan melted at about 69°C in the first DSC run. However, the mixture did not polymerise in the expected polymerisation temperature range seen previously (i.e. 140-210°C). An exothermic process started just before cooling at about 215°C as circled in the right bottom side of Fig. 6.24 (a). This process continued in cooling down to 200°C as circled in right top side of Fig. 6.24 (a). The thermogram was then followed by an exothermic process which would be typical of crystallisation of PA6 on cooling (peak I).
In the second DSC heating, there was a small endothermic peak at 69°C associated with residual CL in S-PA6 in the first DSC run. The CL melting peak was followed by a bigger endothermic peak at 175°C (peak II) from melting of S-PA6 in heating and a recrystallisation exothermic peak at 135°C (peak III) in cooling. The similar values (i.e. peak area values) for peaks I, II, and III suggest that these peaks correspond to a similar process. Although these temperatures were slightly lower than the normal melting point and recrystallisation temperature of PA6, it is strongly suggested that PA6 was synthesised in this process. Lower peak temperatures were due to the lack of regularity in molecular structure and imperfect crystalline structure of S-PA6. The reason for this could be because of the decreased catalyst concentration after jetting which reduced the catalyst/activator ratio below 1.

Fig. 6.24 shows that PA6 was synthesised in heating, using DSC, after jetting polymerisation mixture into a DSC pan. The crystallinity of the S-PA6 produced using the above procedure was about 21% and its monomer conversion was about 96%, measured using eq. 3.4.
CHAPTER SEVEN: CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

7.1 Conclusions
The anionic polymerisation of caprolactam (APCL) was investigated in detail both in bulk and using small scale experiments. Three catalyst-activator combinations were used in this work, which were sodium caprolactamate (CLNa)-N-acetylcaprolactam (ACL), caprolactam magnesium bromide (CLMgBr)-ACL, and C10-C20 (a commercial catalyst/activator combination, refer to Section 3.1 for details). The initial polymerisation temperature, catalyst type and molar concentration, activator type and concentration and polymerisation atmosphere, have been reported to have the most significant influences on the nature of polymerisation. The influence of heating strategy including heating rate, heating temperature, and heating time on small scale polymerisation was also studied. The main conclusions drawn from this work are as follows:

- Moisture behaves as an inhibitor in APCL. The solidification time for a given mixture decreases with decrease in the moisture content in the polymerisation atmosphere. The influence of moisture on polymerisation strongly depends on the type of catalyst used. APCL does not occur in air with CLNa-ACL, but the influence of moisture is negligible when CLMgBr-ACL is used. Polymerisations catalysed and activated by C10 and C20 respectively are also sensitive to moisture but will still occur if higher concentrations of catalysts are used.

The solidification half-time decreased with increasing polymerisation temperature. Crystallinity did not show a steady trend with changing polymerisation temperature; however, it passed through a maximum at a certain temperature in most cases. The viscosity average molecular weight, $\overline{Mv}$, increased with increasing initial polymerisation temperature. The final degree of monomer conversion increased slightly and decreased afterwards with increasing polymerisation temperature. The solidification half-time and $\overline{Mv}$ decreased with increasing catalyst and activator concentrations. Monomer conversion increased with increasing activator concentrations. Other parameters had different responses depending on the type of catalyst-activator used.

The influence of catalyst/activator ratio on polymerisation is significant when C10 and C20 are used as the catalyst and activator respectively. The molar
catalyst/activator ratio should be above 1 to achieve a good polymer. The polymerisation conditions were optimised using ECHIP to obtain the best final product properties and a fast polymerisation at the same time.

- Comparison between the optimised values obtained from polymerisation in bulk using different catalyst-activator combinations shows that CLMgBr-ACL is the best system for fast polymerisation in air. C10-C20 results in fast polymerisation and better final properties when nitrogen was used. CLNa-ACL results in the poorest values both in air and nitrogen atmosphere. C10-C20 and CLNa-ACL systems are sensitive to moisture. CLMgBr in CL cannot be jetted as discussed below, but C10 in CL can be jetted partially using the available jetting head.

Material characterisation was performed using DSC, SEM, WAXS, and optical microscopy. They showed the existence of a separate crystalline phase in mixture A (C10 (CLNa) and CLMgBr in CL) which corresponded to the catalyst component. These micro-crystals do not melt at the jetting temperature (80°C) and can clog the jetting heads. Microscopy showed that CLMgBr had a larger micro-crystals compared with C10 and that was the reason why CLMgBr mixture cannot be jetted (CLMgBr micro-crystals are bigger than the jetting head nozzle size). The activator mixtures (mixture B) have very similar properties to CL and can be jetted easily.

- Drop on drop polymerisation is possible by dripping droplets of mixtures A and B (at 80°C) on top of each other on a hotplate at the polymerisation temperature. Small scale polymerisation can also be carried out using DSC and hot stage microscopy. Small scale polymerisation in DSC showed that increasing the heating rate resulted in an increased exothermic peak temperature. The monomer conversion increased with increase in polymerisation temperature from 140°C to 180°C and decreased from 180°C to 200°C. The crystallinity of the polymer produced in DSC decreased with increase in polymerisation temperature. Hot stage microscopy showed the simultaneous polymerisation and crystallisation processes on heating and also showed that the crystallisation process was retarded by increasing the heating rate. Small scale polymerisation in oven and analysed by DSC showed that increasing catalyst-activator concentration results in increasing monomer conversion and decreased
crystallinity. Monomer conversion also increased with increase in polymerisation temperature and polymerisation time.

- Comparison between small scale and bulk polymerisations shows a good agreement between the two polymerisation rates. This shows that the polymerisation mechanism does not change significantly when the quantity of materials is much smaller than in bulk polymerisation. Thus, it is expected that the small scale polymerisation would show almost the same behaviour as bulk polymerisation and the results from polymerisation in bulk can be relevant for small scale polymerisation.

- Heating polymerisation mixtures after jetting into a DSC pan resulted in an exothermic peak at 135°C in cooling which is a typical of the crystallisation of PA6 and an endothermic peak at 175°C on re-heating associated with the melting of synthesised-PA6 (S-PA6). This showed that polymerisation after jetting polymerisation mixtures (C10-C20) is feasible. Although these temperatures are slightly lower than the normal melting point and re-crystallisation temperature of PA6, it is strongly suggested that PA6 is synthesised in this process. Lower peak temperatures are due to the lack of regularity in molecular structure and an imperfect crystalline structure in S-PA6. The reason for this is possibly because of the decreased catalyst concentration after jetting which reduces the catalyst/activator ratio below 1.

7.2 Suggestions for future work
The main aim of the overall project was investigating the possibility of manufacturing 3D PA6 parts using inkjetting. Most of the work done so far was to investigate the material properties, polymerisation and processing conditions. Therefore, in order to obtain good results in reality, all the results which have been obtained so far must be compared with the results from inkjetting trials. The main challenges which should be investigated in future are as follows:

- Maintaining a neutral atmosphere (e.g. nitrogen) for polymerisation in jetting requires enclosing the whole jetting equipment in a large enclosure and providing a large amount of neutral gas. Therefore, it is essential to establish a catalyst-activator system which is not sensitive to moisture and can be jetted easily
through the available jetting heads. Since it was shown that CLMgBr was an efficient catalyst in APCL and the influence of moisture on it was negligible, an attempt must be done to find a suitable solvent for CLMgBr which does not affect the polymerisation in order to jet CLMgBr without any problem. In case of failure in finding a suitable solvent for CLMgBr, other soluble catalyst components may be used for jetting and polymerisation. As discussed in this work, the composition (i.e. particularly the concentration) of the polymerisation mixture which is provided for jetting may change after jetting. Hence, a further investigation on the effect of jetting on polymerisation mixtures is necessary.

- The APCL was carried out after jetting C10-C20 mixtures. This is a very important achievement that can be studied in more detail in future. Producing PA6 parts or synthesised polymers by inkjetting CL, is the major objective of future work. The polymerisation conditions to achieve the best molecular weight, degree of crystallinity, solidification time and monomer conversion balance were optimised in this work. All these experiments must be carried out again for polymerisation after jetting. The influence of heating mechanism on small scale polymerisation was also studied in this work. However, the influence of different heating techniques such as radiation from the top or heating in a hot chamber (i.e. an oven), on the polymerisation should be investigated. Influence of heating time and heating temperature (or power in the case of using radiation) on polymerisation in jetting should be also studied.
REFERENCES


184. Roger L. Blaine, Ph.D.: Determination of Polymer Crystallinity by DSC, TA Instruments, New Castle DE, USA.


APPENDICES

Appendix A

Table A-1: Results obtained from optimising polymerisation conditions in bulk using ECHIP, catalysed and activated by CLNa-ACL

<table>
<thead>
<tr>
<th>Number of experiments</th>
<th>Trials</th>
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<th>Crystallinity (%)</th>
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<th>Tm (°C)</th>
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Table A-2: Results obtained from optimising polymerisation conditions in bulk using ECHIP, catalysed and activated by CLMgBr-ACL

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1 Polymerisation enthalpy (J/g)
2 Polymerisation peak temperature (°C)
3 Crystallinity (%)
4 Tm (°C)
5 Weight loss during polymerisation (%)
6 Monomer conversion (%)
Appendix C

Table C-1: Results obtained from optimising polymerisation conditions in bulk using ECHIP, catalysed and activated by C10-C20

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<td>21</td>
<td>97</td>
<td>199</td>
</tr>
</tbody>
</table>

1 Polymerisation temperature (°C)
2 Exothermic peak area (°C)
3 Crystallinity (%)
4 Re-crystallisation temperature (°C)
5 Re-crystallisation peak area (J/g)
6 Monomer conversion (%)
7 Tm (°C)