ABSTRACT

MOHAN, ANUSHREE. Modification of Nylon 6 Structure via Nucleation. (Under the direction of Dr. Alan E. Tonelli.)

For nearly two decades inclusion compounds (ICs) have been formed by threading polymer chains into the cyclic starches, cyclodextrins (CDs). Non-covalently bonded crystalline ICs have been formed by threading CDs, onto guest nylon-6 (N6) chains. When excess N6 is employed, non-stoichiometric (n-s)-N6-CD-ICs with partially uncovered and dangling N6 chains result. We have been studying the constrained crystallization of the N6 chains dangling from (n-s)-N6-CD-ICs in comparison with bulk N6 samples, as a function of N6 molecular weights, lengths of uncovered N6 chains, and the CD host used. While the crystalline CD lattice is stable to ~ 300°C, the uncovered and dangling, yet constrained, N6 chains may crystallize below, or be molten above ~225°C. In the IC channels formed with host α- and γ-CDs containing 6 and 8 glucose units, respectively, single and pairs of side-by-side N6 chains can be threaded and included. In the α-CD-ICs the ~ 0.5nm channels are separated by ~ 1.4nm, while in γ-CD-ICs the ~ 1nm channels are ~ 1.7 nm apart, with each γ-CD channel
including two N6 chains. The constrained dangling chains in the dense (n-s)-N6-CD-IC brushes crystallize faster and to a greater extent than those in bulk N6 melts, and this behavior is enhanced as the molecular weights/chain lengths of N6 are increased. Furthermore, when added at low concentrations (n-s)-N6-CD-ICs serve as effective nucleating agents for the bulk crystallization of N6 from the melt. Because of the biodegradable/bioabsorbable nature of CDs, (n-s)-polymer-CD-ICs can provide environmentally favorable, non-toxic nucleants for enhancing the melt crystallization of polymers and improving their properties.
Modification of Nylon 6 Structure via Nucleation

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University as partial fulfillment of the requirements for the Degree of Doctor of Philosophy

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DEDICATION

To

My Father the Beacon
My Mother the Pillar
My Brother the Madcap

and

Sanjay

The Master of the Universe
BIOGRAPHY

Anushree Mohan was born in Kerala, India. She attended Osmania University for her Bachelors degree and graduated with honors in the Textile Technology program.

In 2003 she joined the MS program in Textile Engineering at North Carolina State University under the guidance of Dr. Warren J. Jasper. After graduation she continued with the PhD program in Fiber and Polymer Science under the guidance of Dr. Alan E. Tonelli.
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I feel a very unusual sensation - if it is not indigestion, I think it must be gratitude.

~Benjamin Disraeli

It is a funny feeling to remember all those people who have left an indelible mark on one’s life. I would like to thank everybody who has helped me in time of need.

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Chapter 1

1. Introduction

1.1. History

In 1924, Wallace Hume Carothers (1896-1937) was recruited by the DuPont Company to investigate the chemistry of an acetylene polymer (1). In 1930 one of Caruthers’s assistants, isolated a new liquid compound known as chloroprene, which spontaneously polymerized to produce a rubber-like solid, chemically similar to natural rubber. This product, later known as Neoprene, became the first commercially successful specialty rubber. Carothers’s group went on to create strong, elastic synthetic fibers called polyesters, by reacting glycols and diacids, with the catalytic addition of strong acids, under reduced pressure. Since they had very low melting points and high solubility in dry cleaning solvents they were not commercially viable then (2).

After many attempts to work around the problems surrounding polyesters, this team of
scientists from DuPont went on to use diamines rather than glycols to produce polyamides rather than polyesters (3). Polyamides are synthetic proteins that prove to be much more stable than polyesters. The ability of the polyamide to form crystalline domains through hydrogen bonding gives them the much required boost in mechanical properties. Therefore they are capable of producing a “synthetic silk” that would be practical for everyday use. Carother’s research resulted in the invention of a number of new polyamides. His group went on to later discover an amazing polyamide fiber, a material with a structure similar to silk, called nylon 6-6 in 1931 (4).

DuPont decided to commercialize nylon by creating stockings in 1939. Other applications of nylon followed in the years to come, particularly during World War II when nylon was used to make parachutes and other items needed by the military. The very first nylon product was a toothbrush with nylon bristles (5; 6).

1.2. **Specifics**

The aliphatic polyamides made from $\alpha$, $\omega$-amino acids are called n-nylons, where n stands for the number of main chain carbon atoms in the monomer, while m,n-nylons are created from aliphatic diamines and aliphatic diacids. The number of main chain carbon atoms originating from diamines is denoted by m and those from diacids is denoted by n (7).
It is important to understand the significance of the amide bond in nylons, as the hydrogen bonding capability of the amide linkage influences most of the solution, and crystalline and amorphous solid-state properties. The amide group in all nylons is present in the trans-configuration, where the oxygen and hydrogen atoms are trans to each other across the C-N bond, and all four atoms in the amide group are present in the same geometrical plane (8). The direction of the amide group dipole moment in its common trans-configuration was shown to be inclined by 39.6° relative to the N-H-C=O central amide bond, rendering the dipole moment to be more or less parallel to the N-H and C=O bonds (9).

The backbone bonds play a major role in the solution and solid state behavior of nylons. These covalent bonds are strong and specific: the average energies involving C-C and C-N single bonds fall in the neighborhoods of 350 and 290kJ/mol respectively. On the other hand non-bonded van der waal’s interactions are weak and non-specific. A balance between attractive and repulsive interactions determines the average distances between the non-bonded atoms. Many atoms may interchangeably participate in such non-bonded interactions. These are very short range forces and may fall to below 1kJ/mol over intermolecular distances as short as 0.1 nm. In between these two extremes is the hydrogen bond where the average energy of a N-H---O=C- type bond is 29-30 kJ/mol (10; 11).
The smaller the concentration of methylene groups in nylon repeat units, the larger the amide group fraction and the higher the crystal density. The higher the H-bonded amide bond concentration in the crystal the higher its melting point. The overall bulk density and glass transition temperature also increase with the density of amide groups (12).
1.3. References


3. Carothers, W. H. *Diamine-Dicarboxylic acid salts and process of preparing the same*. 2130947 USA, July 1, 1936.


Chapter 2

2. 6-Nylons

Of all the 6-nylons, 6-nylon is most widely manufactured, used and studied.

![Figure 2.1 Schematic structure of Nylon 6](image)

2.1. Monomer and its Polymerization

Nylon 6 is industrially prepared from ε-caprolactam (See Figure 2.2) (1). At room temperature, ε-caprolactam is a colorless crystalline solid. Its white appearance is caused by multiple refractions and reflections of light at the many interfaces between the higher-refractive index caprolactam particles and the lower-refractive-index interleaving air. ε-caprolactam is soluble at room temperature in water and organic solvents, such as methanol, ethanol, chloroform and benzene, none of which dissolve the polymer. The melting point of caprolactam is $71\pm1^\circ C$ and its boiling point under
normal atmospheric pressure is 270°C. The molecular weight of ε-caprolactam comes to 113.6g/mol (2).

![Caprolactam](image)

**Figure 2.2 Caprolactam**

Caprolactam is prepared in many ways. In one of the methods developed and patented by an Italian company, SNIA Viscosa (Figure 2.3), toluene serves as the starting material. The liquid toluene is oxidized to benzoic acid by air oxidation using a soluble cobalt salt as a catalyst. The total conversion of toluene is about 30% per each oxidation cycle, and the unreacted toluene is recycled to increase the total yield to over 90%. The benzoic acid is hydrogenated at 170°C under hydrogen in the presence of palladium on activated charcoal in a quantitative yield. The cyclohexane carboxylic acid is then treated with nitrosyl sulfate in concentrated sulfuric acid, leading directly to the ε-caprolactam (3).
This method has, however, met with limited economic success (4). A more popular route is to start with phenol (Figure 2.4) and then convert the phenol to cyclohexanone. The cyclohexanone is then reacted with hydroxylamine to produce cyclohexone oxime, and the oxime rearranged to ε-caprolactam in the presence of sulfuric acid. The Beckmann rearrangement, by which the cyclohexanone oxime is converted to ε-caprolactam, requires sulfuric acid or oleum at temperatures in the neighborhood of 90°C (5).
All unsubstituted lactams are capable of polymerizing by hydrolytic ring-opening or by alkaline catalytic initiation, at temperatures of about 250°C and higher (6). There are three types of initiation for polymerization of 6-nylons:

1. Hydrolytic Polymerization

2. Anionic Polymerization

3. Cationic Polymerization


**2.1.1. Hydrolytic Polymerization**

The ability of the chains to adopt conformations favorable to ring closure creates equilibrium between the growing chains and the cyclic lactams, termed as the ring-chain equilibrium (6). This is due to the chain flexibility in *n*-nylons, which can be reduced by adding substituents along the chain to increase the chain rigidity. This reduces the probability of back-biting and formation of cyclic products. The amount of cyclic monomer and oligomers reflects the ease of cyclization.

The amounts of cyclic oligomers present at equilibrium with the linear polymer decrease as the size of the oligomeric rings increase (2).

Table 2.1 shows the concentrations of cyclic monomers (*M*₁), dimers (*M*₂), trimers (*M*₃), and more coexist in equilibrium at 280°C for linear nylons-6, 11 and 12.

<table>
<thead>
<tr>
<th></th>
<th><em>M</em>₁</th>
<th><em>M</em>₂</th>
<th><em>M</em>₃</th>
<th><em>M</em>₄</th>
<th><em>M</em>₅</th>
<th><em>M</em>₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon-6</td>
<td>7.80</td>
<td>1.13</td>
<td>0.78</td>
<td>-</td>
<td>0.59</td>
<td>0.45</td>
</tr>
<tr>
<td>Nylon-11</td>
<td>0.15</td>
<td>1.08</td>
<td>0.55</td>
<td>0.09</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nylon-12</td>
<td>0.33</td>
<td>0.94</td>
<td>0.25</td>
<td>0.18</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The hydrolytic or the water-initiated polymerization is governed by three reactions (5; 7; 8):

1)

\[
\text{HN-}(\text{CH}_2)_3\text{C}=\text{O} + \text{H}_2\text{O} \xrightleftharpoons[k_1']{k_1} \text{NH}_2-(\text{CH}_2)_5\text{C}=\text{OH}
\]

ring opening

2)

\[
\text{NH}_2 + \text{HOOC} \xrightleftharpoons[k_2']{k_2} \text{H}_2\text{O} \rightarrow\] \[\text{CONH} \rightarrow
\]

polycondensation

3)

\[
\text{NH}_2 + \text{HN-}(\text{CH}_2)_5\text{C}=\text{O} \xrightleftharpoons[k_3']{k_3} \text{NHCO (CH}_2)_5\text{NH}_2
\]

Polyaddition
When 6-aminocaproic acid is heated alone, or in low concentrations as polymerization initiator for dry caprolactam, it undergoes ring closure with generation of water.

\[
\text{caprolactam} + \text{water} \rightleftharpoons 6\text{-aminocaproic acid}
\]

The generation of water becomes very noticeable at about 230°C, and at around 280°C half the aminocaproic acid is converted to caprolactam and water (2). Under such conditions of high pressure, both water and aminocaproic acids exert catalytic effects on the polymerization (8). Due to the amphoteric nature of the amide groups in lactams, carboxylic acid and amine groups belonging to polymer chain ends of linear oligomers and the free aminocaproic acid all serve as catalysts for polymerization (9).

A dynamic equilibrium exists between the most probable molecular weight distribution, of linear chains, monomer and some oligomers. For Nylon-6 a broad distribution is present with higher amounts of caprolactam and the amount of cyclic oligomers decreases with increases in their size. Also the cyclic oligomers are not formed from the monomer, but by polymerization of the linear polymer (10). As it comes out of the reactor nylon-6 contains about 10% weight residual monomer and it is generally extracted twice in water to remove as much monomer as possible.
An underlying issue with nylons, especially nylon-6, is that even after extraction, when it is heated up for processing it undergoes re-equilibration. The higher the temperature and the longer the residence time at this temperature the larger the amount of monomer and cyclic oligomers produced, until equilibrium is attained (2).

During re-equilibration of nylon-6, the strongest influence on the appearance of monomer and cyclic oligomers at each equilibration temperature is exerted by the chain-end groups (11; 12). Various researchers employed several techniques to study these effects. The principle mechanism of de-polymerization is assumed to be due to the interaction of free amino groups or carboxyl end-groups with the closest amide residues along the chain, with the liberation of caprolactam (13; 14; 15).

To summarize, the rate of generation of caprolactam is dependent upon the temperature, the chain length, the concentration of reactive amino and carbonyl end-groups, and the concentration of water in the equilibrated system.

2.1.2. **Anionic Polymerization**

N-substituted lactams can be anionically polymerized in the presence of alkaline catalysts (6; 16). Anionic polymerization occurs rapidly under anhydrous conditions and can achieve higher conversions when compared to hydrolytic or cationic processes.
High molecular weights have been achieved in the presence of catalysts made from Grignard reagents and co-catalysts made from acyllactams (17; 18).

Joyce and Ritter were the first to describe anionic polymerization. They used several alkali and alkaline earth metals as catalysts, specifically Na, Li and Ca, while Hanford and Joyce were the first ones to describe the mechanism. A plethora of catalysts were subsequently investigated, including hydrides, hydroxides, alkali metals, grignard reagents, alkoxides etc (19; 20).

Anionic polymerization starts out with the reaction of a lactam ring with the catalyst to form lactam anion and hydrogen (21; 7; 5):

\[
X^\ominus + (\text{CH}_2)_5\text{NH} &\xrightarrow{\text{C}=\text{O}} HX + (\text{CH}_2)_5\text{N}^\ominus \\
\text{anionic initiation}
\]

The lactam anion then reacts with a lactam monomer at higher temperatures to form an imide anion, which quickly reacts with another monomer to form a new lactam anion and an acyllactam.
The polymerization propagates by nucleophilic attack of a lactam anion on the carboxyl group of the imide. The polymeric anion then subtracts a hydrogen atom from other lactams to continue the process.
In this mechanism the polymerization and depolymerization occur largely at the imide group which is the strongest electrophilic group. The addition of imides to the initial reaction mixture greatly accelerates the polymerization, while addition of imides to the initiation reaction eliminates the disproportionation reaction.

N-acyllactams have been given various names, but Sekiguchi calls them ‘chain initiators’ as they initiate polymerization and are built into the growing chain. The alkaline catalyst must be present to create the lactam anion, such that the catalyst and the initiator act together in the anionic polymerization. The N-acyllactams are so efficient in promoting the reaction that the polymerization occurs in the range of 100-200°C, while without them it occurs only above 200°C and the reactions take place only after a long induction period (21).
Acylactam initiated polymerization

A few additional points associated with anionic polymerization are:

1. Effects of counter ions

The effects of counter ions arise from interactions between the cationic catalyst and monomer units along the chain or at the ends.
These effects vary with both the cations and lactams (22). It has been shown that when cation trapping crown ethers or cryptands were added to the anionic polymerization, the rates were affected favorably or adversely depending on the lactams, and the dissociation and dielectric constants of the reaction medium (23; 24).

2. Low temperature bulk polymerization

Low temperature bulk polymerization has commercial importance as lactams may be polymerized in the bulk without any special precautions (25).

3. Low monomer content

The most important aspect is the low monomer content in the polymer, even though the polymerization is conducted at temperatures much lower than the polymer crystallization temperature. This mostly occurs due to the exclusion of the cyclic monomer from the growing crystalline regions of the polymer. The amount of the residual monomer is the product of the amount of residual monomer expected at equilibrium at the polymerization temperature times the volume fraction of the polymer that is in the amorphous state during the polymerization. Since the monomer is mostly present in the amorphous regions it has the possibility to
polymerize into new chains or add to growing chains when the system is at temperatures higher than $T_g$, where chain and monomer translational motions take place with high probability (2; 26).

2.1.3. Cationic Polymerization

Under anhydrous conditions, lactams may be protonated and these lactam cations may initiate and propagate polymerization. It is characterized by the absence of an induction period and can be initiated in the presence of cationic catalysts such as protic acids, lewis acid derivatives, salts of acids with amines or ammonia. A constant concentration of polymer chains, equivalent to the concentration of the initiator is obtained (27; 21).

An interesting feature of the active lactams in cationic polymerization is in the tautomeric equilibrium. The lactam monomer is the most nucleophilic species in the reaction mixture; it is acylated to give the aminoacyllactam dimer (28).
Cationic polymerization

The aminoacyllactam dimer contains two different sites: the ammonium ion and the \( N \)-acyllactam. Both can participate in chain growth reactions, but each involves a different propagation mechanism. In the first instance, the ammonium ions of the aminoacyllactam dimer exchanges a proton with a lactam molecule, creating a primary amino group and a lactam cation (29).

The amino dimer is immediately acylated by the lactam molecule (due to its strong nucleophilicity), resulting in the insertion of one monomer unit.
The extra proton is exchanged with another lactams to form lactam cation, and the chain grows by one repeat unit for each repeat of the reaction cycle (30).

In another set of reactions, the free amino group reacts with the \( \text{N-acyllactam} \) group. The attack on the carbonyl in the open chain is favored more than the opening of the terminal ring (31; 32).

It has been demonstrated that cationic polymerization can also be initiated by amine hydrochlorides. Further, lactams can form complexes with Lewis acid metal halides and with complexing cations, such as zinc in zinc diacetate (6). The Lewis acids coordinate themselves with the carbonyl oxygen rather than the nitrogen atom. The activation of the lactams for polymerization is proportional to the charge and electronegativity of the coordinating metal atom and the initiation reaction produces the \( \text{N-acyllactam} \) dimer (33).

### 2.2. Molecular Weight and its Distribution

A fundamental characteristic of linear polymer chains is their molecular weight as it influences many properties of the polymer. For low molecular weight flexible polymer chains, the glass transition temperature \( T_g \) shows a strong dependence on \( M \), while at high molecular weights the dependence asymptotically vanishes (34). The melt viscosity is also directly dependent on the molecular weight.
At low molecular weights the melt viscosity depends proportionally on the molecular weight, but as entanglements occur it becomes fully dependent on the entanglement concentration (35). In the intermediate range of molecular weight the bulk mechanical properties show a dependence on the molecular weight, even though this dependence is affected by the interchain entanglements. The entanglements strongly affect rheological properties (36). For \( n \)-nylons where \( n \geq 3 \), the main chain flexibility combines with interchain H-bonding to control the behavior of the polymers. To impart strength to a solid bulk polymer, each chain must be involved in at least two entanglements. Due to the existing molecular weight distribution in all industrially produced polymers a higher \( M_c \) is desired as it results in a balance between the ultimate mechanical properties and processability. \( M_c \) is the characteristic molecular weight necessary to form the average chain entanglement (2; 34).

### 2.2.1. Molecular Weight Determination

As is the case with every synthetic polymer, \( n \)-nylons are not monodisperse, but polydisperse. Several methods can be used to measure the molecular weights. The number average molecular weight is defined by:

\[
M_n = \frac{w}{\sum n_i} = \frac{\sum n_i M_i}{\sum n_i}
\]
Where, \( w \) is the total weight of the molecules and \( n_i \) is the number of molecules with Molecular weight \( M_i \).

The methods used for measurement of \( M_n \) are end group analysis, membrane osmometry, and vapor pressure osmometry. All these methods have their own range of accessible molecular weights, accuracy, and limitations. Molecular weight distributions are also obtained from size exclusion chromatographs, where measurements of polymer diffusion through a packed column by photon-correlation spectroscopy gives the sizes of the macromolecules and these results may be converted to molecular weights using relationships between size and molecular weight. The weight average molecular weight, \( M_w \), is mainly measured by light scattering.

\[
M_w = \sum w_f(i)M(i) = \frac{\sum n_iM_i^2}{\sum n_iM_i}
\]

where \( w_f(i) \) is the weight fraction of molecules with molecular weight \( M(i) \).

Solution viscosity measurements are used to measure \( M_v \) and to estimate \( M_w \) (37).

### 2.3. Structure, Morphology and Properties

Polymer properties to a large extent are dependent on their physical structure, in other words the arrangement of molecules.
The ability to rotate about the covalent backbone bonds in a polymer chain lends it the flexibility to attain a vast number of molecular conformations. In the bulk state these chain molecules need to coexist in harmony with each other in the limited space available to them (38).

Polymer chains tend to be in either of two states (See Figure 2.5) (39):

Random coil state/Amorphous State

If the molecules have the slightest bit of flexibility, they prefer to adopt a state of configurational/conformational disorder. It is this state of disorder that gives the polymer its ability to sustain large amounts of stress. It complies to stress by a small readjustment in bond rotation angles. The state of parallel order is only preferred when polymer chains cannot move without expending high amount of energy.

Ordered State/Crystalline

The crystalline state in polymers is the state of order. The molecules are presumed to occur in fully extended zigzag or in helical conformations depending upon the stereochemical requirements. The order mostly occurs due to the forces operating between the chain molecules; for example a regularly repeating structure with polar groups or substituents that occur at regular
intervals tend to align the adjacent chains, such that the polar groups or the substituent occur in regularly spaced planes intersecting the molecular axes.

The chain molecules with ordered conformations pack themselves in a regular three dimensional lattice. This close packing of molecules maximizes the force of attraction between the chains therefore maximizing interactions that favor ordering of polymer chains (39).

Structure consists of various hierarchical levels: the unit cell, the crystallite, the non-crystalline region and the supermolecular structure. The term ‘morphology’ refers to the size, shape of crystals, crystal aggregates, and the arrangement of crystalline and amorphous regions. It has been well established that the lamellar-like crystallite habit is the characteristic gross morphological form developed by homopolymers during crystallization from the melt (40; 41).
Two extremes have been noted for the lamellar structures: the regularly folded adjacent re-entry structure and the switchboard model with the distinct, disordered amorphous layer (See Figure 2.6). The character of lamellae and their arrangement relative to one another are dependent on the molecular weight and the crystallization temperature. Low molecular weight samples exhibit stacked lamellae while curved lamella are observed for higher molecular weights (40).

Supermolecular structure is concerned with the arrangement of these individual lamellar crystallites into a large scale organization. These structures depend upon the molecular weight, the crystallization conditions, such as the isothermal crystallization temperature, the cooling rate, the molecular constitution, and the polydispersity of the molecular weight (42).
Spherulite growth occurs in concentrated solutions where the lamella are radially arranged. (See Figure 2.7) The shish-kebab structure is observed both in concentrated solutions and in melts. It consists of a centrally extended chain core and lamelle radially attached to the core.

As a semicrystalline polymer, bulk nylon-6 contains two well-defined states: the amorphous and crystalline state. Depending upon the crystallization conditions, the crystallites may be assembled as large spherulitic entities, where lamellar growth occurs from a central nucleus and extends in all directions (43). The spherulites (See Figure 2.8) are quite stable and retain their overall form during annealing and swelling in water even after the crystallites undergo transition from one crystal form to another (44).
In the crystalline phase the chains are aligned either parallel or anti-parallel to one another and the hydrogen bonds between them are all connected to each other in sheets. The crystals grow on faces that are called growth faces, and the flat faces where the chains fold and reenter are called basal planes.

The chains tend to grow into the amorphous phase and back in to the same lamellar crystal or into another lamella (2). (See Figure 2.9)

The lamellar crystallites are interspersed with randomly oriented amorphous polymer between their fold surfaces, depending upon the overall degree of crystallization. These growth surfaces aid in aligning some or most of the disordered amorphous regions. These regions do not take part in crystallization, but, since their motion is curtailed by
the existence of adjacent crystal growth surfaces, a measure of alignment arises. Upon drawing, these chain sections stretch out and tend to orient themselves in the draw direction (40) n.

![Figure 2.9 (A) Amorphous and Crystalline regions (B) Strain Induced crystallization (38)](image)

When heated, the crystalline regions reach a point where the thermal motions of the atoms are high enough to overcome the forces holding the crystals together. At that temperature the solid crystal falls apart and starts flowing, this transition from a crystalline solid to an amorphous flowing liquid is termed as melting and the temperature at which this transition occurs is called the melting temperature, $T_m$ (45). Upon cooling, non-isothermally, most materials solidify into a crystalline solid and the temperature at which they 'freeze' is called the freezing temperature, $T_f$. For low
molecular weight materials the melting and freezing changes mostly occur at the same
temperature. The randomly-coiling entangled polymer melt crystallizes at \( T_{cc} (\leq T_m) \),
producing semi-crystalline polymers with crystalline and amorphous phases. With
further cooling through a narrow temperature range the chains in the amorphous
phases undergo a glass-transition \( T_g \), where they become immobile. The melting
behavior of the crystallizable polymer is related to its chemical structure depending on
three factors (46; 39):

a. Chain geometry and regularity

The ability of chains to form and exist in an ordered 3-dimensional array is
influenced by the tacticity of the system. This regularity of the chains favors
packing in parallel arrays which causes crystallization, defines the crystal
geometry and the diffraction pattern.

b. Chain stiffness

Main-chain stiffness imparts a highly helical geometry which facilitates the
parallel packing of the extended chains. The lateral ordering of these extended
chains increases till a point is reached where the proximity of the side groups of
the helices forces them to organize in order to maximize their packing density.
c. Intermolecular forces

When the hydrogen bonds are intermolecular in nature the chains prefer to crystallize in parallel arrays of molecular sheets, where the H-bonding exits with in the sheets and not between them. When hydrogen bonds are intermolecular in nature, the chains usually adopt a rigid helix shape. The shape and rigidity is maintained by the intramolecular hydrogen bonding. The selection of molecular sheet or molecular helix depends upon the geometrical shape and size of the side groups and the conformation of the main chain, all leading to the minimization of conformations, which results in a decrease in the conformational entropy.

Crystallization occurs when $T\Delta S_f < \Delta H_f$. Hence crystallization occurs at a higher temperature than the quiescent condition. The crystallization of an already oriented polymer results in a reduction in the retractive force (See Figure 2.10). This phenomenon can be explained by the rubber elasticity theory, which states that the force exerted by a fixed chain is inversely proportional to the number of chain segments and the magnitude of the end to end distances. Hence the reduction in force occurs due to a lesser number of statistical units available in the amorphous regions and also because the end to end distances of chains in the amorphous regions are smaller than in the crystal (38; 47; 48).
a. **Under quiescent conditions** (50):

Crystallization under quiescent conditions can be classified into two types:

a. Crystallization from dilute solutions:

    Crystallization from dilute solution offers a fundamental approach for structural analysis, as the crystals can be isolated and studied.

b. Crystallization from melt:

    It offers an understanding of the overall level of crystallinity, required for practical purposes.

### 2.4. **Crystallinity and Its Characterization**

Various characterization techniques have been used to carefully understand the structures and properties of nylons.

Wide Angle X-Ray studies have been conducted to study the crystalline phases in nylon.
Infrared Spectroscopy or Raman Spectroscopy can be used to clearly identify the chemical composition of a polymer.

Nuclear Magnetic Resonance can also be used for understanding and characterizing polymers. The resonance frequencies of $^1$H, $^{15}$N, and $^{13}$C nuclei in a strong magnetic field are measured and depend upon the resonating atom-type, its bonding; and the local electronic/structural/conformational environment.

To begin with every crystalline material belongs to one of the seven major crystal systems shown in Table 2.2 (51).

**Table 2.2 Crystal Systems**

<table>
<thead>
<tr>
<th>System</th>
<th>Axes</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>$a\neq b\neq c$</td>
<td>$\alpha \neq \beta \neq \gamma$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a\neq b\neq c$</td>
<td>$\alpha = \gamma = 90^\circ \neq \beta$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a\neq b\neq c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Tetrogonal</td>
<td>$a=b\neq c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Trigonal</td>
<td>$a=b=c$</td>
<td>$\alpha = \beta = \gamma \neq 90^\circ$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a=b\neq c$</td>
<td>$\alpha = \beta = 90^\circ, \gamma = 120^\circ$</td>
</tr>
<tr>
<td>Cubic</td>
<td>$a=b=c$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
</tbody>
</table>
Polyamides generally tend to pack themselves in triclinic and monoclinic unit cells (52; 53). Nylon-6 consists of three polymorphic crystalline forms (See Figure 2.11 and Table 2.3):

The α-phase is most commonly observed at room temperature and can be obtained by slowly cooling from the melt state (54; 55). The crystal structure of the α-phase is monoclinic, and the hydrogen-bonded sheets are composed of neighboring chains traversing in opposite or antiparallel directions. In the X-ray diffraction pattern of Nylon 6, 2 peaks characteristic of the α phase at room temperature are at about 2θ=20 and 23.7° and are indexed as (200) and (002)/(202) reflections, respectively (56). The α-form has a density of about 1.235 g/cm³ (57; 58; 59).

The γ phase can be obtained by fast quenching from the melt state or by treating α phase in iodine-potassium iodide aqueous solution, followed by removal of the absorbed iodine by sodium thiosulfate. For the γ phase, the diffraction peaks at about 2θ=10.7 and 21.4° are indexed as (020) and (001), respectively (58).
Figure 2.11 Nylon 6 Alpha form (a) Gamma form (b) Crystals (56)
Table 2.3 Crystalline properties of nylon 6 (60; 61; 62)

<table>
<thead>
<tr>
<th>Property</th>
<th>α</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Structure</td>
<td>Monoclinic</td>
<td>Hexagonal/pseudohexagonal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a = 0.956 \text{ nm})</td>
<td>(a = 0.472 \text{ nm})</td>
</tr>
<tr>
<td></td>
<td>(b = 1.724 \text{ nm (fiber axis)})</td>
<td>(c = 1.688 \text{ nm})</td>
</tr>
<tr>
<td>Lattice Constants</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(c = 0.801 \text{ nm})</td>
<td>(\gamma = 120^\circ)</td>
</tr>
<tr>
<td></td>
<td>(\beta = 67.5^\circ)</td>
<td></td>
</tr>
<tr>
<td>Crystallographic</td>
<td>(200)</td>
<td>(001)</td>
</tr>
<tr>
<td>reflection(s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(002/202)</td>
<td>(200/201) –minor</td>
</tr>
<tr>
<td>Characteristic d-spacings</td>
<td>(d_{200} \approx 0.370 \text{ nm})</td>
<td>(d_{001} \approx 0.413 \text{ nm})</td>
</tr>
<tr>
<td>Density, (\rho) (g/cm(^3))</td>
<td>1.23 (experimental)</td>
<td>1.16-1.19 (experimental)</td>
</tr>
<tr>
<td></td>
<td>1.23 (calculated)</td>
<td>1.16(calculated)</td>
</tr>
<tr>
<td>Heat of fusion (\Delta H_f^{\alpha} (J/g))</td>
<td>241</td>
<td>239</td>
</tr>
</tbody>
</table>

The β phase (or pleated α) is generally formed in quenched samples, which is identified by a single strong lateral diffraction and a strong chain-directional diffraction.
The d-spacings corresponding to the two crystalline peaks are about 0.42 and 0.85 nm, respectively. The β crystal is assumed to be a metastable phase with variable degree of disorder or stacking faults: it includes stacking of parallel and antiparallel chains, paracrystalline disorder, faults in the hydrogen bond sheet-like setting, and hydrogen-bonded layers normal instead of parallel to the chain axis (56).

Depending upon the number of main chains atoms a point net notation can also be described as follows $A^* u / t$, where $A$ is the number of main chain atoms in the crystal motif, $u$ is the number of repeat units or main-chain atoms for full translational identity period; $c$, along the helix axis; $z$, and $t$ is the number of full turns the chain makes per full translational identity period. The planar zigzag structure of 6-nylon in both $\alpha$ and $\gamma$ crystal forms maybe denoted by $7^*2/1$, each repeat unit consists of 7 main chain atoms and 2 such repeat units participate in 1 turn per translational identity period (2; 52).
2.5. References


34. **Aharoni, S. M.** Correlations between chain parameters and failure characteristics of polymers below their glass transition temperature. Macromolecules, Vol. 18, 12, 1985, pp. 2626-2630.


3. Nucleated Crystallization

3.1. Introduction

Nucleated crystallization has been widely studied over the years (1-9). A nucleating agent shortens the induction time, as well as enhancing the rate of transformation from the molten state to solid crystalline state (10). Nucleating agents are generally crystalline and insoluble in the polymer melt. They usually consist of parallel layers of molecules with non-polar exteriors and polar groups inside (11; 12).

Primary nucleation is a time-dependent phenomenon; hence the function of a nucleating agent is to provide active sites to initiate the crystallization process (13). Melt crystallized polymers consist of chain-folded lamellar crystallites, radiating in all directions to form spherulites. Large spherulites result in poor transparency and poor impact properties. When the spherulites start growing on the active sites created by finely dispersed nucleating agents they quickly encroach upon each other, thereby
arresting the growth of larger spherulites and improving transparency/clarity, density, and tensile and impact properties (14).

3.2. Crystallization Thermodynamics

Thermodynamic studies are concerned with the way in which the crystalline structure is laid down with increase or decrease in temperature. The temperature above which a polymer loses all of its crystallinity is called the melting temperature (See Figure 3.1). The nucleation theory was first proposed by Gibbs (1).

![Figure 3.1 Thermal Behavior for (1) Crystalline Material and (2) Amorphous Material (15)](image)

In the liquid to glass transition the molecules lose their mobility and freeze in their disordered positions, while in crystallization the loss in translational freedom occurs...
along with the uniform packing of molecules. The glass transition temperature is the temperature at which the amorphous part of the polymer turns glassy. Unlike melting, at $T_g$ there is no change in volume but a change in rate of change in volume with respect to temperature, that is, a change in the coefficients of thermal expansion $\alpha$ and of bulk compressibility, $\kappa$ (See Figure 3.1). The glass transition temperature is affected by the coexistence of the crystalline phase and the amorphous phase, the amount of moisture present, the heating rate and the molecular weight of the polymer. As the molecular weight increases $T_g$ eventually becomes independent of molecular weight (16).

The melting temperature could be referred to as the characteristic temperature of transformation between the crystalline and the amorphous states i.e. a phase transition. As seen from Figure 3.1, crystallization involves a ‘significant’ discontinuous volume change while the formation of the glassy state does not (17).

The first law of thermodynamics states that the sum of all energies in an isolated system is constant.

Which implies,

$$\Delta E = \Delta Q - \Delta W$$

where,

$\Delta E =$ Internal Energy
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$\Delta Q =$ Heat Exchange

$\Delta W =$ Work done by/on the system

Work done on a system can be the product of pressure and the change in the volume.

\[ \Delta W = P \Delta V \]

\[ \Rightarrow \quad \Delta E = \Delta Q - P \Delta V \]

\[ \Delta Q = \Delta E + P \Delta V = \Delta H \]

Gibbs free energy is given by:

\[ \Delta G = \Delta H - T \Delta S \]

If we consider melting as a change of state then \( \Delta G = 0 \) at \( T = T_m \)

\[ T_m = \frac{\Delta H_m}{\Delta S_m} \]

\( \Delta H_m = \text{Change in enthalpy on melting} \)

\( \Delta S_m = \text{Change in entropy on melting} \)
Crystallization occurs when $\Delta H \leq T \Delta S$ (See Figure 3.2)

For a polymer system the equilibrium state considered is given by a model in which the end portions of the molecules are disordered and the melting temperature for such a system is expressed as (19):

$$\frac{1}{T_{me}} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \left\{ \left( \frac{1}{x} \right) + \left( \frac{1}{x - \zeta_e + 1} \right) \right\} \quad \text{where,}$$

\[ x = \text{number of repeat units} \]

\[ T_{me} = \text{melting temperature for a fraction consisting of } x \text{ repeat units} \]

\[ T_m^0 = \text{equilibrium melting temperature for an infinite molecular weight chain} \]

\[ \zeta_e = \text{crystallite length} \]
When phase equilibrium thermodynamics is applied to evaluate the depression in melting temperature by a low molecular weight diluent; the expression is given as (20):

\[
\frac{1}{T_m^*} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \left\{ \left( \frac{V_u}{V_1} \right) \left( \vartheta_1 - \chi_1 \vartheta_1^2 \right) \right\},
\]

where,

\( T_m^0 = \text{equilibrium melting temperature of the pure system} \)

\( T_m^* = \text{melting temperature corresponding to the volume fraction of diluent } \vartheta_1 \)

\( \frac{V_u}{V_1} = \text{ratio of the molar volume of the chain repeating unit to that of the diluent} \)

\( \chi_1 = \text{polymer – diluent thermodynamic interaction parameter} \)

\( \Delta H_u = \text{the enthalpy of fusion per chain repeating unit of the completely crystalline polymer} \)

\( \Delta H_u \) is obtained for a given polymer system with a series of different diluents.
3.3. Crystallization Kinetics

Dilatometry, calorimetry, various spectroscopies and light scattering microscopy are used to study the overall rate of crystallization (19). Initially crystallization of polymers had been shown to follow the general mathematical theory that was developed many years ago for the crystallization of metals and other low molecular weight substances (21). In the original formulation there was no termination step, which was resolved by the postulation that when two crystals collided or made contact their growth ceased (22-24).

The basis for this theory can be explained using Avrami’s approach, which states that the fraction $1 - \lambda(t)$ transformed at time $t$ can be expressed as (23; 24):

$$1 - \lambda(t) = 1 - \exp \left( -\frac{\rho_c}{\rho_l} \int_0^t V(t, \tau) N(\tau) d\tau \right)$$

$N(\tau)$ is the nucleation frequency per unit of the untransformed volume

$V(t, \tau)$ is the corresponding volume of the growing center

$\rho_c$ and $\rho_l$ are the densities of the crystalline and liquid phases respectively

This equation describes the kinetics of phase transformation of a one component monomeric system. One set of conditions that leads to a specific derived Avrami
equation is that, the steady state nucleation rate is achieved at \( t=0 \) and remains invariant with the fraction of the material transformed and that \( N(\tau) \) is treated as a constant. Also the rate of crystal growth is assumed to be linear and constant.

The Avrami equation can then be written as:

\[
1 - \lambda(t) = 1 - \exp(-kt^n)
\]

*\( k \) is the rate constant and \( n \) is termed as the Avrami constant*

At low extent of transformation the equation reduces to:

\[
1 - \lambda(t) = kt^n
\]

Prior to the onset of crystallization, the polymer melt is composed of randomly coiled entangled chains that loop, knot and form other structures. These structures cannot participate in crystallization and the region around such defects are also uncrystallizable. The concentrations of such units are dependent on the molecular weight, and as crystallization progresses the availability of the crystallizable units decreases relative to the total number of non crystallizable units. Hence molecular weight not only influences the level of crystallinity it also influences the rate of crystallization (19; 25; 26).
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The crystallization temperature also has a significant influence on crystallinity. As the crystallization temperature is lowered the rate of growth of crystallites becomes less dominant relative to the nucleation rate. The nucleation rate increases rapidly as the temperature is lowered, while the rate of transport of chain segments to growing crystallites is reduced.

It's the balance between the competitive rates of these two mechanisms that results in the maximum rate of crystallization (26).

Nucleation is the process by which a new phase is initiated within a parent phase. A nucleus is a small structural entity of the new phase. Hence two different types of nucleation can be observed. The initiation of crystallization involves primary nucleation and crystallite growth could be considered as nucleation controlled (25; 27). Therefore the decrease in Gibbs free energy that normally characterizes the development of a large macroscopic phase is offset by the contributions from the surfaces of the small entities. Initially there will be an increase in the free energy as the entity grows due to the dominance of the surface contribution. As the growth proceeds a maximum in the free energy $\Delta G^*$ is determined by the dimensions of the geometry reached. As it grows to a critical size there is a decrease in the free energy that eventually becomes negative. The magnitude of the $\Delta G^*$ will depend on the shape assumed (19).
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For homogeneous crystallization the steady state nucleation rate can also be expressed as (28):

$$N = N_0 \exp \left( -\frac{E_D}{RT} - \frac{\Delta G^*}{RT} \right)$$

$N$= Steady State Crystallization rate per unit volume and time

$N_0$= Constant

$E_D$= Transport Energy at Solid-Liquid Interface

$\Delta G^*$= Free Energy of formation of a nucleus.

Homogeneous nucleation occurs in the melt due to thermal fluctuation. In heterogeneous nucleation, the nucleation agent reduces the free energy barrier so as to increase the nucleation rate (See Figure 3.3).
3.4. Nucleating Agents

Talc has been known to be an effective nucleating agent for Nylon 6. Although talc has been known and used as an effective nucleating agent in various semicrystalline polymers, it does restrict the application of the polymers in biomedical applications as it is related to asbestos, a carcinogen (29). Other nucleating agents such as I\(_2\), KCl, and modified clays have also been used as nucleating agents for Nylon 6.

Cyclodextrins are natural compounds and previous studies have shown that they can act as an effective nucleating agent for various polymers (30-32).
It has been shown by Yong et al that partially included α-cyclodextrin compounds can also act as nucleating agents. According to them the inclusion compound of a given polymer greatly enhanced the nucleation and crystallization of the polymer itself (31).

The authors presume that the limited mobility of the uncovered part of the guest polymer partially threaded through cyclodextrin, as indicated in Figure 3.5, leads to the nucleation of the polymer (31).
The nucleation effects of α-cyclodextrin and its inclusion complexes with Poly(ε-caprolactone) (PCL), Poly(ethylene glycol) (PEG) and Poly(butylene succinate) (PBS) were investigated by differential scanning calorimetry, fourier transform infra red spectroscopy and wide angle X-ray diffraction. The polymer chains in the bulk phase can not only contact the outer regions of the α-CD molecule but also the uncovered polymer chains protruding from the α-CD molecule. As seen in Figure 3.4 above, the α-CD-IC of a given polymer can influence the crystallization of the polymer. The CD-IC greatly enhanced the crystallization temperature and reduced the crystallization temperature range (31).
The isothermal crystallization kinetics is given by the Avrami equation:

\[ X_t = 1 - \exp(-kt^n) \]

where, \( n \) is the dimensional growth index

\( k \) = overall rate constant for nucleation and growth.

\[ \log[-\ln(1-X_t)] = \log k + n \log t \]

The values for \( n \) and \( k \) are obtained by plotting \( \log[-\ln(1-X_t)] \) vs. \( \log t \). The crystallization half time, \( t_{1/2} \), is given by:

\[ t_{1/2} = \left( \frac{\ln 2}{k} \right)^{1/n} \]
Crystallization rate tends to decrease with increase in crystallization temperature, while $t_{1/2}$ decreases. The isothermal crystallization of PCL and PBS, with and without nucleating agents, and reported by Yong et al. (31), are presented in Figure 3.6. The Avrami constant $n$ shows no significant change with the addition of nucleating agent.
These authors also studied the spherulitic morphologies of these polymers when melt-crystallized with talc, cyclodextrin and 2wt% cyclodextrin inclusion compound. The PCL samples were quenched from 90°C and crystallized at 42°C. As seen in Figure 3.7, the addition of nucleating agents resulted in the increase of the number of nuclei and decrease in the diameter of the spherulites (31).
3.5. References


Chapter 4

4. High Molecular Weight Poly (ε-caprolactam)

4.1. Introduction

Anionic polymerization of ε-caprolactam gains its importance due its fast reaction rates, relatively low temperature and the better mechanical properties of the resulting nylon 6 (1-5). For our research purpose it enables us to obtain a broad range of molecular weights. The catalytic system consists of a catalyst and an initiator. The former is a strong base, such as an alkaline metal, metal anhydride, amide or an organo-metallic compound, which produces the source of Lactam anion (C) on reaction with monomer, as seen below. The initiator could be an acid chloride, anhydride or isocyanate, to produce an imide-containing species (I) when it reacts with a lactam monomer (1).

Among the N-acyl-caprolactams, N-acetyl-caprolactam has been found to be one of the better initiators, as the size of the acyl group determines the ease with which the catalyst can approach the initiator molecule close enough to break the amide linkage and initiate a polymer chain reaction.
It has also been noted that the rate and the degree of polymerization were directly proportional to the cocatalyst/initiator concentration (2). The initiation takes place by a rapid addition reaction between (I) and (C) and then followed by a rapid proton exchange reaction to reproduce a monomeric anion and an imide containing species (1).

\[ \text{Initiation} \]
\[
\begin{align*}
R-\overset{\text{C-N-C}}{\text{O}} & \quad + \quad \overset{\text{N-C}}{\text{O}} \\
\underset{k_1}{\text{R-C-N-C}} & \quad \underset{k_1'}{\text{R-C-N-C}} 
\end{align*}
\]

\[ \text{Propagatation} \]
\[
\begin{align*}
R-\overset{\text{C-NCH}_{2}\text{CH}_{2}}{\text{O}} & \quad \overset{\text{N-C}}{\text{O}} \\
\underset{k_2}{\text{R-C-N-C}} & \quad + \quad \overset{\text{N-C}}{\text{O}} \\
\overset{\text{H}}{\text{R-C}} & \quad \overset{\text{N-C}}{\text{O}} \quad \underset{k_3}{\text{R-C-N-C}} \\
\end{align*}
\]
Chapter 4

High Molecular Weight Poly-Caprolactam

The propagation takes place by repeated addition and hydrogen abstraction reactions (1). This is a regular linear reaction mechanism without the deactivating and branching side reactions which produce side products, heterogeneity in the resultant polymer chain structure and a broad molecular weight distribution (3; 2).

Depending upon the concentration of the catalytic system, a minimum temperature of 140°C is usually required for adiabatic reaction conditions, without crystallization, as the exothermic polymerization can give a temperature rise of up to 51°C. For isothermal reaction conditions a temperature of 180°C or greater is essential to be free of crystallization before the equilibrium conversion is reached (2).

The low temperature (i.e. below melting point of semi-crystalline nylon 6), activated anionic polymerization of ε-caprolactam is further complicated by the crystalline nature of nylon 6. Heterogeneous reaction conditions have been encountered if the polymer crystallizes during polymerization process. Thus higher temperatures are preferred (4).
Chapter 4

High Molecular Weight Poly-Caprolactam

Anionic polymerization is of primary importance in this research as the high molecular weight polymer obtained will further be used for spinning of high modulus fibers. The polymer chain length has a significant influence on the mechanical properties of the fiber formed. Melt spinning can only be accomplished up to a certain molecular weight. As high molecular weight nylon possesses higher viscosity, it will be used in gel-spinning rather than melt-spinning. High viscosity also implies lower solution concentrations required for spinning of fibers. Gelation would enable reduction in entanglements and enhance stretching along the fiber axis. Hence the first objective of this research is to observe the influence of anionically polymerized high molecular weight nylon on gelation and polymer properties compared to a commercial lower molecular weight nylon sample.

4.2. Experimental Methods

The experimental procedures followed, to synthesize high molecular weight Nylon 6 were obtained from Ueda et al (5). The monomer 99% pure ε-caprolactam was obtained from BASF. At first moisture was removed from ε-caprolactam by bubbling nitrogen gas for an hour at 120°C in a pre-dried reactor vessel. The temperature was then raised to 150°C, the chain initiator, N-acetyl-caprolactam obtained from Sigma-Aldrich, was injected into ε-caprolactam and nitrogen was bubbled for 15 minutes more.
The catalyst, ethyl magnesium bromide obtained from Sigma-Aldrich, was then injected into the $\varepsilon$-caprolactam for the polymerization to take place. The polymer obtained was then shaved and extracted in hot water twice for 5 hours to remove all the extractables.

The extraction method validated by Ueda et al shows low oligomer content in anionically polymerized high molecular weight Nylon 6 when compared to other processes. The formation of cyclic oligomers in hydrolytically polymerized nylon is due to back-biting of the amino terminal group. The amino end group attacks the internal amide group to form cyclic oligomers. The limited reactions between lactam and lactam-anion and the scarce hydrolysis of the polymer result in a low content of amino terminal groups, and in low back biting by them. The oligomer content also changed with the amount of initiator and catalyst. It was seen that the cyclic oligomer content increased with initiator concentration and decreased with catalyst concentration (5).

The polymerization was conducted at various temperatures and initiator concentrations to understand and characterize the polymer obtained.

The catalyst concentration was kept constant at 0.5 mol%. Figure 4.1 illustrates the polymerization system employed.
4.3. Solution and Melt Properties

4.3.1. Molecular Weight and Its Distribution

Solution viscosity measurements are the simplest and most popular method of molecular weight characterization. The conventional method of measuring solution viscosity is by using a constant volume of several solutions with decreasing concentrations of the studied polymer and measuring the length of time it takes for each of these solutions to flow through a capillary tube of a fixed diameter and length.
These time periods are then compared with the efflux time of the pure solvent. The flow time is proportional to the viscosity, and inversely proportional to the density (6).

\[
    t_{\text{solvent}} = \frac{\eta_{\text{solvent}}}{\rho_{\text{solvent}}}, \quad t_{\text{soln}} = \frac{\eta_{\text{soln}}}{\rho_{\text{soln}}}
\]

The relative viscosity is defined as the ratio \( \eta_{\text{soln}} / \eta_{\text{solvent}} \). For most polymer solutions at the concentrations of interest, \( \rho_{\text{soln}} / \rho_{\text{solvent}} \approx 1 \). Thus, to a very good approximation, the relative viscosity is a simple time ratio:

\[
    \eta_{\text{rel}} = \frac{t_{\text{soln}}}{t_{\text{solvent}}}
\]

and the specific viscosity:

\[
    \eta_{sp} = \eta_{\text{rel}} - 1
\]

The intrinsic viscosity is then given by:

\[
    [\eta] = \left( \eta_{sp}/c \right)_{c \to 0}
\]

where, \( c \) is the solution concentration.
Chapter 4

High Molecular Weight Poly-Caprolactam

The molecular weights were determined from the intrinsic viscosities of the polymer in formic acid at 25°C using an Ubbelohde viscometer. The Mark-Houwink's equation and the constants \( K \) and \( a, 22.6 \times 10^{-5} \text{ dL/g} \) and 0.82, respectively were applied (7).

\[
[\eta] = KM^a
\]

Table 4.1 presents the molecular weights of several nylon 6 samples determined from their intrinsic viscosities.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150AC1%</td>
<td>~200,000</td>
</tr>
<tr>
<td>150AC0.5%</td>
<td>~300,000</td>
</tr>
<tr>
<td>150AC0.1%</td>
<td>~450,000</td>
</tr>
<tr>
<td>150AC0.03%</td>
<td>~550,000-650,000</td>
</tr>
</tbody>
</table>
4.3.2. Gel Permeation Chromatography

Gel permeation chromatography was carried out on trifluoroacetylated-nylon dissolved in THF. Trifluoroacetylation was conducted based on the experimental method proposed by Jacobi et al (8). 0.1gm of nylon 6 was suspended in 3 ml of pure CH₂Cl₂ and an excess of Trifluoroacetic Anhydride (TFA) (CF₃CO)₂O was added to the solution in the molar ratio of 1:2 (N₆:TFA). The mixture was stirred until the solution became clear and colorless. The solution was then reduced in volume and dried in vacuum to remove any trace of CF₃COOH to avoid possible corrosion of the chromatograph. The dried complex was then redissolved in 10ml of CH₂Cl₂.

Inaccurate molecular weight data were obtained for high molecular weight polymer, when 1% solution concentrations were used for SEC measurements, as indicated in Table 4.2. Therefore for high molecular weight measurements reduced concentrations were used, with improved results shown in Table 4.3. Not all high molecular weight polymer solutions gave good results, which could be due to lack of proper acetylation of the high molecular weight samples with TFA.
Table 4.2 SEC Molecular weight measurements at 1% concentration

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Mw</th>
<th>Mn</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>150AC1</td>
<td>45,148</td>
<td>21,220</td>
<td>2.12</td>
</tr>
<tr>
<td>150AC0.03</td>
<td>81,772</td>
<td>30,338</td>
<td>2.69</td>
</tr>
<tr>
<td>170AC1</td>
<td>33,965</td>
<td>16,925</td>
<td>2.006</td>
</tr>
<tr>
<td>170AC0.5</td>
<td>51,158</td>
<td>23,274</td>
<td>2.19</td>
</tr>
</tbody>
</table>

Table 4.3 SEC molecular weight measurements

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Soln</th>
<th>Mw</th>
<th>Mn</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc.</td>
<td>(g/mol)</td>
<td>(g/mol)</td>
<td></td>
</tr>
<tr>
<td>150AC0.1a</td>
<td>0.2%</td>
<td>488,904</td>
<td>212,569</td>
<td>2.299</td>
</tr>
<tr>
<td>150AC0.1b</td>
<td>0.2%</td>
<td>481,346</td>
<td>209,843</td>
<td>2.293</td>
</tr>
<tr>
<td>150AC0.1c</td>
<td>0.2%</td>
<td>484,235</td>
<td>210,438</td>
<td>2.301</td>
</tr>
<tr>
<td>150AC0.1a</td>
<td>0.1%</td>
<td>449,719</td>
<td>198,174</td>
<td>2.269</td>
</tr>
<tr>
<td>150AC0.1b</td>
<td>0.1%</td>
<td>450,316</td>
<td>198,817</td>
<td>2.264</td>
</tr>
<tr>
<td>150AC0.1</td>
<td>0.06%</td>
<td>445,958</td>
<td>228,394</td>
<td>1.95</td>
</tr>
</tbody>
</table>
The most probable molecular weight distribution for nylon 6 as predicted by Flory is \( M_w/M_n = 2 \) (9). The PDI value of 2 is not unexpected as the polymerization occurs in the molten state and the reaction time is long not only for polymer-monomer-oligomer equilibria, but also transamidation and interchain equilibria. When initiated anionically, the distribution depends upon the reaction conditions. If the polymerization occurs at elevated temperatures say over 200°C for an extended period of time then the distribution tends to broaden over time. This broadening is mainly caused by transamidation reactions. The analysis also shows that the higher the catalyst to initiator ratio, the narrower the distribution. When the ratio of catalyst to initiator reaches 1 distributions of about 5 were obtained (10).

The anionically polymerized high molecular weight nylon 6 was characterized and compared with a low molecular weight nylon 6 obtained from BASF with molecular weight of 60,000g/mol. The high molecular weight nylon used for modification and characterization was obtained at 150°C with an initiator concentration of 0.03 mol% and catalyst concentration of 0.5 mol%.
4.3.3. Melt Rheology

A constant stress was applied by a load cell placed on top of the piston pushing the molten polymer out of the capillary rheometer. As seen in Figure 4.2, the melt viscosity is directly dependent on the molecular weight. Slight instability was observed in the viscosity at 240°C for high molecular weight nylon due to non-uniform melting.

![Melt Rheology of Nylon Samples](image)

Figure 4.2 Melt Rheology of Nylon Samples
4.4 Properties

Nylons are identified by three distinct IR absorption bands: a hydrogen bonded N-H band at 3300 cm\(^{-1}\), an amide band at 1640 cm\(^{-1}\) associated with the C=O bond and another amide band around 1545 cm\(^{-1}\) (11). Figure 4.3 presents a comparison of FTIR spectra for commercial low and anionically polymerized high molecular weight nylon 6 samples.

![FTIR Absorption Bands](image)

**Figure 4.3 FTIR Absorption bands for (a) 600,000g/mol (b) 60,000 g/mol Nylon 6**

The differential scanning calorimeter thermograms were recorded on a Perkin-Elmer Pyris Diamond DSC. The samples were heated to above the melting temperature of...
polymer (240°C) at 10°C/min, annealed for 5 minutes and cooled to 25°C, and after 5 minutes heated back to 240°C at 10°C/min. Selective DSC results are presented in Table 4.4. The higher the degree of molecular order, the higher is the melting temperature. The longer the chains the harder it gets to establish order at the molecular level. It has been reported that the crystallization rate of Nylon 6 is maximum at 150°C (12). A nucleating agent could be used to shorten the induction time and to increase the overall rate of crystallization from melt to a crystalline solid. It has also been suggested that crystallization is slower at higher temperature. Increasing catalyst concentration increases the rate of polymerization, but retards crystallization. Initiator concentration does not affect the degree of crystallinity in the polymer (13).
Table 4.4 Comparison of thermal properties of different nylon samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Nylon</td>
<td>58</td>
<td>220</td>
<td>175</td>
</tr>
<tr>
<td>High Molecular Weight Nylon</td>
<td>45</td>
<td>224</td>
<td>174</td>
</tr>
</tbody>
</table>

4.5. Gel Spinning of High Molecular Weight Nylon-6

Nylon 6 is a widely used engineering thermoplastic. It can be melt-processed to make a series of commercial products such as tire cords, parachutes, carpets and it can also be spun to make filaments for clothing, automotive interiors and sutures for surgery. The mechanical properties of specific polymers are generally enhanced at higher molecular weights. The conventional approach of extruding polymers into filaments applies only to low molecular weight polymers, while studies have shown that gel spinning has been used to spin high molecular weight polyethylene to obtain high strength high modulus fibers. This technique was first applied on ultra high molecular weight polyethylene to produce high modulus fibers.
Chapter 4  

High Molecular Weight Poly-Caprolactam

The main principle behind gelation is the reduction of molecular entanglements in the gel which give rise to increased stretching that allow processing and formation of fibers (14). Several publications and patents have been filed for the gel spinning of ultra high molecular weight polyethylene (15-20).

The high melting temperature of nylon 6 permits applications over a wider temperature range when compared to polyethylene. Therefore gel spinning of nylon 6 could result in finer fibers with improved mechanical properties. This was first applied to nylon 6 by Cho et al. Nylon 6 was dissolved in benzyl alcohol and the fibers were stretched to a draw ratio of 5-6 (15). The modulus obtained was 6.2GPa with a low tenacity of 0.5-0.6GPa. Similar work was conducted in a Japanese patent where Nylon 66 chips were dissolved in N-methyl-2-pyrrolidone at 10% concentration in LiCl at 180°C, stretched 7 times, and gave a tenacity of 13.2g/denier and 16% elongation (15).

This method was applied to the high molecular weight nylon 6 we obtained by anionic polymerization to obtain high modulus fibers. The presence of intermolecular hydrogen bonds in nylon inhibits the ability to draw fibers to a higher ratio. Amit Gupta, PhD student in our research group focused on reducing the influence of hydrogen bonds in nylon 6 by thermoreversible gelation.
4.5.1. Materials and Methods

Two molecular weights of nylon 6 were applied in this study. The low molecular weight sample was obtained from BASF (LMWN6) and the anionically polymerized high molecular weight sample (HMWN6) was made in our lab.

Gelation and Gel Spinning

The Nylon samples were dissolved in N-methyl pyrrolidinone at 175-180°C in nitrogen atmosphere. Different concentrations of gels were made for spinning and Amit found that best results were obtained at 33% concentration for low molecular weight Nylon and 15% for high molecular weight Nylon. The hot solution was then transferred to the fiber extrusion device, as shown in Figure 4.4, and spun at 180°C. A single-hole spinneret with diameter 250 µm and length to diameter ratio 1:1 was used. After extrusion the fiber gel was cooled in a mineral oil bath at room temperature and then wound onto a bobbin under tension. Amit was able to spin the fibers at a draw ratio of 3.86 for LMW Nylon and at 4.26 draw ratio for the HMW sample.
To completely remove NMP and regenerate nylon 6, the as spun gel fiber was immersed in hexane for 3 days. The fibers were drawn at 180° C on a hot plate and two sets of rollers. Tensile properties were measured on an Instron Tensile Tensile tester. The fiber samples were further characterized by Amit using Wide angle X-Ray Diffraction, Differential Scanning Calorimetry, Scanning Electron Microscopy etc.
4.5.2. Results and Discussion

Tensile Properties

Amit observed that the as spun fibers from the samples showed high elongation at break and therefore low tenacity and modulus. Upon hot drawing he observed a reduction in elongation at break while the tenacity and modulus increased. He concluded that the stress-strain behavior shown by the samples was analogous to the stress-strain curves typical for highly oriented ultra high molecular weight polyethylene fibers (16-19). For both nylon samples the tensile strength and modulus increased while the % strain at break decreased sharply with increasing draw ratio. This behavior is typical of semi crystalline polymeric fibers before and after hot drawing (22). He achieved a maximum draw ratio of 6.65 for LMW Nylon-6 fibers and a higher draw ratio of 8.97 for HMW nylon 6 fibers. The high molecular weight samples could be drawn further in the cooling bath due to the presence of longer chains (17; 21; 23). At similar low draw ratios the tensile strengths of the two fibers were similar, but for higher draw ratios both tensile strength and modulus for HMW Nylon 6 fibers were significantly higher.

When compared to Pennings work, (dry-spinning fibers with co-solvent mixtures of formic acid and chloroform), Amit obtained higher values for tensile strength and modulus of up to 1.23 GPa and 25 GPa respectively for HMW Nylon 6 fibers (24).
Pennings reported a high tensile strength of 1.0 GPa and modulus up to 19 GPa in their work from a high molecular weight N-6 (~ 3.5 million g/mole). The nylon samples were able to attain higher draw ratios with the gel spinning approach than those obtained via the melt spinning process. The high molecular weight samples were also used in crystallization studies, which will be discussed in subsequent chapters.
4.6 References


Chapter 5

5. Cyclodextrin Inclusion Compounds

5.1 Introduction

Cyclodextrins (CDs) are cyclic-oligosaccharides obtained from starch. They were first discovered by A. Villiers who published the isolation of a crystalline substance from starch in 1891 (1). It was Schardinger’s work that laid the foundation for CD chemistry. He was able to separate α and β dextrins He also mentioned the production of dextrins from different starches, such as potato, wheat, rice, and identified the formation of dextrin with the type of bacteria digesting the starch (2). γ-CD was discovered by Freudenberg and Jacobi in 1935 (3). Cramer in his book, Inclusion Compounds, extensively described the structural and physiochemical characteristics of cyclodextrins.
The three industrially known CDs are: α-, β-, γ-CDs and consist of six, seven and eight glucopyranose units, respectively, as seen in Figure 5.1, they have inner diameters of 5, 7 and 9 Å respectively and a channel depth of 7-8 Å (4).

Figure 5.1 Cyclodextrin-Chemical structures

As indicated in Figure 5.2, CD development occurred in three stages (a) Its discovery, (b) Characterization of properties and (c) Production and Application. Over the last decade CD production has increased from several hundred to several thousand tons. Most CD research is concentrated in pharmaceutical applications.
Drug molecules usually have low water solubility and hence have lower absorption. CD complexation of drug molecules has shown significant productivity and drug efficiency (6; 7). CDs have also shown prominence in food, cosmetics, pesticide formulation, analytical chemistry applications and in the textile industry. (8-14).

5.2. Production of Cyclodextrins

Starch is liquefied at elevated temperatures and then cooled down to an optimum temperature to add CD glucosyl transferase enzyme (CGT-ase)(See Figure 5.3).
CGT-ase is produced by a large number of microorganisms, like *Bacillus macerans*, *Klebsiella oxytoca, Bacillus circulans,* and *Alkalophylic bacillus* etc. If toluene is added to the solution, β-CD/toluene complex can be separated from the mixture for further β-CD formation. 1-decanol can be used to produce α-CD and cyclohexadecanol produces γ-CD (5). The solvents are generally removed by suspension in water, by distillation, or by extraction. The aqueous solution obtained after removal of the complexing solvent is treated with activated carbon and filtered. The CDs are then separated from this solution by crystallization and filtration (5).

![Figure 5.3 Formation of cyclic and acyclic dextrins (5)](image)

### 5.3. Cyclodextrin Chemistry

In CDs the glucose units form rigid building blocks, with a $^4C_1$-chair conformation, as the endocyclic torsion angles in the rings are confined to plus and minus gauche values within a narrow range. (15-17).
The inner cavity is lined with carbons and ether oxygens, rendering it distinctly hydrophobic, while the hydroxyl groups on the outer edges provide the hydrophilic character (9). The cavity is lined with hydrogen bonds and glycosidic oxygen bridges (See Figure 5.4).

As seen there, the primary hydroxyl groups reside at the narrow edges and the secondary hydroxyl groups are found at the wider edges. The chair conformation of the glucopyranose gives CDs their unique cone structure. The properties of CDs are compared in Table 5.1 and their dimensions indicated in Figure 5.5.
### Table 5.1 Cyclodextrin properties (9)

<table>
<thead>
<tr>
<th>Cyclodextrin</th>
<th>α</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of glucose units</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>972</td>
<td>1135</td>
<td>1297</td>
</tr>
<tr>
<td>Inner Diameter (nm)</td>
<td>0.45-0.57</td>
<td>0.62-0.78</td>
<td>0.79-0.95</td>
</tr>
<tr>
<td>Outer Diameter (nm)</td>
<td>1.37</td>
<td>1.53</td>
<td>1.69</td>
</tr>
<tr>
<td>Height (nm)</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td>Cavity Volume (nm$^3$)</td>
<td>0.174</td>
<td>0.262</td>
<td>0.472</td>
</tr>
<tr>
<td>Crystal Forms</td>
<td>Hexagonal plates</td>
<td>Monoclinic parallelograms</td>
<td>Quadratic Prisms</td>
</tr>
</tbody>
</table>
5.4 Crystal Structures

The crystal structures of CDs can be broadly classified into (15):

a. Cage Structure

b. Channel Structure

In the cage structure the cavities in CDs are blocked by the adjacent cyclodextrins. Two kinds of cage structure have been observed and proposed: the herring bone structure and the layer structure (Figure 5.6) (16). The as-received (pure) α-, β-, and γ-CDs have cage structures with just water molecules residing in their cavities.
CDs adopt cage or channel type crystal structures in their inclusion complexes (ICs) depending on the characteristics of the guest molecules. Crystalline α-CD ICs form cages with small guests, whereas long molecular, ionic and polymer guests prefer channels. The channel structure formed by α-CD is mostly of the head-to-head: tail-to-tail form (Figure 5.7). By contrast, β-CD molecules are arranged head-to-head:tail to head:tail to tail. The crystalline state in inclusion complexes can be characterized by various techniques. Wide angle X-ray diffraction shows the transition between the cage structures of pure cyclodextrin to the channel structure attained by the polymer CD-ICs.
Polymer-γ-CD IC shows a major peak at $2\theta=7.5^\circ$, while pure γCD has reflections at $2\theta=12.4, 16.5, 18.8$ and $23.4^\circ$ (Figures 5.8 and 5.9). While major peaks for pure α-CDs have been seen at $9.6, 12.03, 19.5$ and $21.8^\circ$, the channel structure showed a major peak at $20.0^\circ$ (18). Nuclear Magnetic Spectroscopy (NMR) also shows a shift in the resonance peaks for cyclodextrins (19), as a result of transition from cage to channel structure.

Figure 5.7 Channel crystal structures (a) head to head:tail to tail (b) head to head-tail to head:tail to tail
Figure 5.8 X-Ray Diffraction for α, β, γ CDs (5)

Figure 5.9 WAXD pattern for (a) as received γ-CD and (b) PolyMethyleneMethacrylate- γ-CD IC (20)
5.5 Cyclodextrin Complexation

Freudenberg discovered that CDs could form inclusion complexes with organic molecules (Figure 5.10) (3). In an aqueous solution the hydrophobic cavities of CDs is occupied by water molecules (a polar solvent), which is energetically unfavorable. Hence the driving force of the complexation is the replacement of the highly polar water molecule by a less polar guest molecule (21; 22). The molecular encapsulation can be obtained in various host to guest ratios depending upon the requirement and application. Therefore small molecule inclusion in CDs is dependent upon the stoichiometry, speed of formation, complex stability and water solubility.

Figure 5.10 Schematic representation of cyclodextrin inclusion formation
A large number of guest molecules have been included into the cyclodextrins, they range from polar reagents, halogen anions to apolar hydrocarbons. The inclusion compounds can be soluble or crystalline solids (4;16;23- 29).

5.6 Cyclodextrin-Polymer Inclusion Compounds

For nearly two decades CD-polymer ICs have been studied all over the world (30-38). Harada and Kamachi were the first to report inclusion complexes formed between CDs and Poly-ethylene glycol (PEG) (See Figure 5.11) (30).

Harada et al and Tonelli et al have conducted extensive research on CDs and the polymer inclusion compounds they form. They have incorporated various polymers and observed the influence of characteristics such as crystallinity, hydrophobicity, hydrophilicity, molecular weight, aliphatic chains, aromatic chains etc (39-46).
A model was proposed by Baglioni et al describing the formation of polymer-CD complexes, which consists of five prominent steps (See Figure 5.12) (46):

1. Diffusion of polymer chains and CD molecules
2. Threading of polymer chain ends into the CD cavities
3. Movement of CD molecules through the polymer chains
4. De-threading of CD molecules off of the polymer chains
5. Precipitation of the final aggregate
The driving force behind the host-guest complexation was believed to be due to van der waal's forces and the hydrophobic interactions (47). Tonelli et al recently concluded that electrostatic, van der Waals, and hydrogen-bonding interactions and relief of conformational strain in CDs are not important, while hydrophobic interactions, exclusion of high energy, cavity-bound water, and crystalline packing of host CDs are important in the formation of polymer-CD-ICs (48). Hydrogen bonding ability of the guests, the substituent groups on the aromatic and aliphatic chains and the flexibility of the chains also, have an effect on the formation of complexes.
Furthermore the nano-threading of polymers appears to be a general phenomenon characteristic of their long-chain natures, or polymer physics, and not their specific chemical structures (48).

Tonelli et al have coalesced the guest polymers out of their CD inclusion complexes and observed changes in their resultant structures, morphologies, and chain conformations. The coalesced samples exhibited properties distinctly different from the normal bulk samples (49; 50).

Figure 5.13 Comparison of the consolidation of polymers from their solution or melts vs. coalescence from their CD-ICs.
They were also able to coalesce well-mixed polymer-drug blends from the CD-ICs. Coalescence may occur in vivo by amylase digestion of CD, followed by the subsequent release of the drug as the biodegradable/bioabsorbable matrix polymer is in turn digested (See Figure 5.14) (49).

5.7 (n-s)-Nylon 6 Inclusion Compounds

More recently it has been demonstrated that crystalline non-stoichiometric (n-s)-polymer-CD-ICs can be obtained if an excess of the guest polymer is used during their formation (51-54).
Note in Figure 5.15 that incomplete coverage of the threaded guest polymers results in the dangling of unincluded portions of the polymer chains from the (n-s)-polymer-CD-IC crystal surfaces. If the guest polymer is crystallizable, then the portions of the chains dangling from the (n-s)-polymer-CD-IC may also crystallize. As a consequence, it has been demonstrated that when small amounts of (n-s)-polymer-CD-ICs are added to the same neat bulk polymer, they function as very effective nucleation agents during melt crystallization (52).

This is presumably due to the ability of the dangling chains to readily crystallize and provide nuclei for the crystallization of the bulk polymer chains. This approach is limited to polymers with melting temperatures $T_m$ that are below the decomposition temperature ($\sim$250–300$^\circ$C) of polymer-CD-IC crystals. Because of the biodegradable/bioabsorbable nature of CDs, (n-s)-polymer-CD-ICs provide environmentally favorable, non-toxic nucleants for enhancing the melt crystallization of polymers and improving their properties.
In addition, (n-s)-polymer-CD-ICs with crystallizable guest polymers have also been demonstrated to exhibit shape-memory. If they are heated between the $T_m$ of the included polymer and the decomposition temperature of the polymer-CD-IC, they may be deformed into a new shape, which is retained following a rapid quench. When this newly-shaped sample is heated above $T_m$ it reverts back to its original shape (55).
5.8 References


2. Schardinger, F. *About thermophile bacteria from different food and milk and about implementation of some products in the same carbohydrate solution including crystalline polysaccharides (Dextrins) from starch*. Zeitschrift für Untersuchung der Nahrungs- und Genußmittel, Vol. 6, 1903, pp. 865-880.


Chapter 5  

Cyclodextrin Inclusion Compounds


Chapter 6

6. Nylon 6-Cyclodextrin Inclusion Compounds

6.1 Introduction

In this chapter we are concerned with comparing the melt crystallization of neat bulk nylon-6 (N6) samples and those portions of N6 that are constrained by and dangle from their non-stoichiometric-N6-cyclodextrin-inclusion compounds [(n-s)-N6-CD-ICs] (See Figures 6.1 and 6.2). Anionically initiated ring-opening polymerization of ε-caprolactam produced N6 samples with molecular weights ($MW = M_w$, with $M_w/M_n \sim 2$) ranging from 100,000 to 600,000 Da, providing the opportunity to compare the effects of MW on the melt crystallization of “free” neat bulk and dangling constrained (n-s)-CD-IC N6 chains. α- and γ-CDs were selected as the hosts, because single and pairs of side-by-side N6 chains are, respectively, threaded through their ICs, and so produce different constraints on the N6 chains that dangle from their (n-s)-CD-ICs. In addition, several different N6:CD ratios were employed in the formation of (n-s)-N6-CD-ICs. The
N6 samples were also coalesced from their ICs and the change in their crystallization behaviors were observed and compared.

Figure 6.1 Schematic Representation of Polymer-Cyclodextrin Inclusion Compound (1)

Figure 6.2 Polymer crystallization from unconstrained (neat) and (n-s)-polymer-α-CD-ICs

6.2 Experimental

6.2.1 Materials

The N6 samples with MW = 30,000 and 60,000g/mol were commercial samples obtained from BASF. The 300,000 and 600,000g/mol, N6 samples were obtained by the
anionically initiated ring-opening of ε-caprolactam and characterized with intrinsic viscosity and SEC/GPC measurements described previously in Chapter 4. All solvents and reagents were obtained from Sigma Aldrich. α-Cyclodextrin and γ-Cyclodextrin were obtained from Cerestar Co.

6.2.2. Methods

Formation of N6-CD-ICs followed from Wei, Huang et al, with the following example given for the stoichiometric 1:1 N6-α-CD-IC (See Figure 6.3). 0.5g of N6 was dissolved in 15ml of 90% formic acid at room temperature and 60ml 99% acetic acid was added to the solution. 4.27g of α-CD was dissolved in 21ml of 99% dimethyl-sulfoxide (1; 2). The dissolved α-CD was then added to the N6 solution. The mixture was stirred and heated on a hot plate at 50°C for two hours. After being heated, it was cooled to room temperature and continuously stirred for another six hours. The precipitate was vacuum-filtered and dried in a vacuum oven. Later on hydrochloric acid was added to the samples to precipitate N6 out of the ICs. The coalesced nylon samples were then dried, characterized and compared with their ICs.

Infra Red spectral studies were conducted with a Nicolet 510P FTIR spectrometer, in the range between 4000 and 400 cm⁻¹, with a resolution of 2 cm⁻¹. Differential scanning calorimetric (DSC) thermal scans were performed with a Perkin-Elmer DSC-7 instrument.
Chapter 6 (n-s)-N6-CD-ICs

The measurements were run in the range of 25-250°C at heating and cooling rates of 10°C/min. Nitrogen was used as the purge gas.

**Figure 6.3 (non-stoichiometric) polymer-α-CD IC formation**

Wide Angle X-Ray Diffraction studies were performed with a Siemens type –F X-ray diffractometer with a Ni-filtered CuKα radiation source (λ=1.54Å). The supplied current voltage was 30 kV and 20 mA respectively, and diffraction intensities were measured every 0.1° from 2θ=5 to 30° at a rate of (2θ=3°)/minute.
6.3. Results and Discussion

As seen from the FTIR spectra in Figure 6.4, both N6 and CDs are present in (n-s)-N6-CD-ICs. The DSC scans in Figure 6.5 shows that none, some of the N-6 chains in the 1:1 and 3:1 N-6-α-CD-ICs are crystallizing, so portions of the N6 chains in the 3:1 N-6-α-CD-IC are not included, are dangling, and able to crystallize.

Figure 6.4 FTIR spectra for (a) α-CD, (b) 600,000 g/mol Nylon-6, and their (b) 1:1 and (c) 3:1 ICs.

From Figure 6.6 we see that upon cooling from the melt these dangling N6 chains crystallize at a higher temperature than neat bulk N6. In addition, from Table 6.1 it is observed that a higher fraction of the N6 chains dangling from the (n-s)-α-CD-IC
crystals are able to crystallize compared to the N6 chains in the neat melt. As seen from the DSC scan in Figure 6.7, the constraint on the N6 chains enables them to recrystallize back and forth without any change in the heats of fusion. This is possible because of the orientation and the orientation memory of the N6 chains due to the restriction produced by the host cyclodextrin crystalline lattice (3).

Figure 6.5 DSC cooling scans (10⁰ C/min) for (a) 1:1 and (b) 3:1 (n-s)-N6-α-CD-ICs (Mw = 600,000 g/mol)
Table 6.1 Enthalpy or Heat of Crystallization ($\Delta H_c$, J/g of Sample) upon cooling neat N-6s and their 3:1 (N-S)-N-6-\(\alpha\)-CD-ICs from the melt.

<table>
<thead>
<tr>
<th>N6 (Mw) g/mol</th>
<th>3:1 (n-s)-N6-IC Bulk (Total)</th>
<th>3:1 (n-s) CD-IC (Dangling N-6 only)</th>
<th>Crystallization Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>30,000</td>
<td>-53</td>
<td>-12</td>
<td>-73</td>
</tr>
<tr>
<td>60,000</td>
<td>-56</td>
<td>-15</td>
<td>-90</td>
</tr>
<tr>
<td>300,000</td>
<td>-43</td>
<td>-15</td>
<td>-88</td>
</tr>
<tr>
<td>600,000</td>
<td>-46</td>
<td>-19</td>
<td>-116</td>
</tr>
</tbody>
</table>

*Only ~17 wt% of 3:1 (n-s)-N-6-\(\alpha\)-CD-ICs is contributed by the 2/3 of the N6 chains that are not threaded and included, but are dangling and can crystallize.

\[
\Delta H_c \text{ (J/g dangling N-6)} = \Delta H_c \text{ (J/g total IC)}/0.17.
\]
Figure 6.6 DSC cooling scans from the melts of (a) 600,000g/mol bulk N-6 and its (b) 3:1 (n-s)-N6-α-CD-IC.
Figure 6.7 DSC scan for 3:1 (n-s)-N6-\(\alpha\)-CD-IC, (Mw=600,000g/mol).

Table 6.2 below shows the melting and crystallization of all the ICs formed with alpha cyclodextrin.
Table 6.2 DSC data for Nylon samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tm</th>
<th>Tc</th>
<th>ΔHc</th>
<th>Xc</th>
</tr>
</thead>
<tbody>
<tr>
<td>30,000</td>
<td>221.6</td>
<td>173</td>
<td>53</td>
<td>27</td>
</tr>
<tr>
<td>2:1 αCD-N6IC</td>
<td>213</td>
<td>176</td>
<td>7 (41)⁺</td>
<td>21.5</td>
</tr>
<tr>
<td>3:1 αCD-N6IC</td>
<td>214</td>
<td>180</td>
<td>12 (71)</td>
<td>37</td>
</tr>
<tr>
<td>60,000</td>
<td>222</td>
<td>175</td>
<td>56</td>
<td>29.4</td>
</tr>
<tr>
<td>2:1 αCD-N6IC</td>
<td>217</td>
<td>174</td>
<td>8 (47)</td>
<td>25</td>
</tr>
<tr>
<td>3:1 αCD-N6IC</td>
<td>219</td>
<td>178</td>
<td>15 (88)</td>
<td>46.3</td>
</tr>
<tr>
<td>300,000</td>
<td>222</td>
<td>174</td>
<td>43</td>
<td>23</td>
</tr>
<tr>
<td>2:1 αCD-N6IC</td>
<td>214</td>
<td>173.8</td>
<td>7 (41)</td>
<td>22</td>
</tr>
<tr>
<td>3:1 αCD-N6IC</td>
<td>220</td>
<td>178.2</td>
<td>16 (94)</td>
<td>49.4</td>
</tr>
<tr>
<td>600,000</td>
<td>223</td>
<td>174</td>
<td>46</td>
<td>24</td>
</tr>
<tr>
<td>2:1 αCD-N6IC</td>
<td>216</td>
<td>173.3</td>
<td>5 (29)</td>
<td>15</td>
</tr>
<tr>
<td>3:1 αCD-N6IC</td>
<td>222</td>
<td>182</td>
<td>19 (111)</td>
<td>58</td>
</tr>
</tbody>
</table>

⁺% Crystallization values for the dangling chains.

As the Mw increases the melt-crystallization temperatures Tc and levels of crystallinity ΔHc decrease for bulk N6 samples, while in (n-s)-α-CD-ICs both show an increase. In the case of neat molten polymers, the increased entanglement between higher MW chains is usually cited as the reason that they crystallize more slowly and not as completely as lower Mw samples. As the opposite behavior is observed here for the dangling yet constrained chains in 3:1-(n-s)-N6-α-CD-ICs, their degree of entanglement, if any, is apparently unimportant to their ability to crystallize.
On the otherhand, the N-6 chains dangling from 2:1 (n-s)-N-6-α-CD-ICs do not exhibit crystallization that is enhanced compared to bulk N6.

The WAXD diffractograms in Figures 6.8-6.10 show the formation of columnar structure by cyclodextrins when including the nylon 6 chains. The completely covered 1:1 stoichiometry shows a strong peak at 2θ=20 for the α-CD columnar crystal structure.
Because their relative center-of-mass diffusion is limited by the constraining \( \alpha \)-CD-IC crystals from which they emanate, entanglement and unentanglement of the
dangling chains would be significantly retarded in comparison to that in unconstrained neat N6 samples. Therefore, a major factor resulting in the enhanced crystallizability observed for the dangling N6 chain is likely due to the increase in their extension and orientation with respect to the α-CD-IC crystal surfaces. This may at first be discordant with the well known behavior of polymer brushes, whose chains lose orientation perpendicular to and extension from their surfaces as their MW increases, i.e., brush-to-mushroom transition (4). However, it must be remembered that polymer brushes are generally formed with non-crystallizable polymers and at much lower surface densities than the dangling N6 chain brushes emanating from the (n-s)-N6-CD-IC crystal surfaces. At higher brush densities, it has been observed that the chains in non-crystallizing brushes are highly extended perpendicular to the surfaces of their attachment, and increasingly so as MW increases (4), as indicated in Figure 6.11.
Figure 6.11 Extended and highly oriented chains in (n-s) polymer-α-CD ICs

Figure 6.12 Channel structure, α-CD-IC.
In the α-CD-ICs the ~0.5nm channels are separated by ~1.4nm, (See Figure 6.12) with 0.6 N-6 chains/nm² protruding from the IC crystal surface.

We also formed stoichiometric and non-stoichiometric N6-CD-ICs with gamma cyclodextrin. While all the samples (30,000; 60,000; 300,000; 600,000 g/mol) formed stoichiometric ICs with γ-CD, only high molecular weight samples (300,000 and 600,000g/mol) could successfully form non-stoichiometric ICs with γ-CDs. While α-CD-ICs can hold one nylon chain in their 0.5 nm channels, ~1nm γ-CD-IC channels, separated by ~ 1.7nm, can include two closely paired nylon-6 chains.

The N6 chains protruding from their 6:1-(n-s)-γ-CD-ICs were found to be only slightly more crystallizable (higher T_c's, but comparable ΔH_c's) than bulk N6 and significantly less crystallizable than the N-6 chains protruding from their (n-s)-α-CD-ICs (See Figure 6.13). As seen for (n-s)-α-CD-ICs with less than 6:1 stoichiometric slowed dangling N6 whose crystallization was not enhanced compared to bulk N6.
Figure 6.13 DSC cooling scans from the melts of 600,000g/mol (a) bulk Nylon-6 and its (b) 6:1 (n-s)-N6-γ-CD-IC.
Figure 6.14 DSC cooling scans for (a) 6:1 (n-s)-N6-γ-CD IC and (b) 3:1 (n-s)-N6-α-CD-IC (Mw=600,000g/mol)

As seen from the DSC scans in Figure 6.14, the 3:1-(n-s)-N6-α-CD-IC crystallized more and faster than the 6:1-(n-s)-N6-γ-CD-IC. This may be due to the larger distance between the pair of N6 chains protruding from the γ-CD-IC channels and the possible intermolecular hydrogen bonding between the paired N6 chains within the channels, as indicated in Figure 6.15, which may lower the overall crystallization of chains protruding from the (n-s)-γ-CD-ICs.
Table 6.3 below shows the melting and crystallization of all the ICs formed with gamma cyclodextrin and alpha cyclodextrin for the high molecular weight N6 samples.

WAXD diffractograms were also obtained for the γ-CD-ICs (Figures 6.16 and 6.17) and the channel structure was observed. The inclusion compound shows a strong peak at 2θ=7.5° is characteristic for the columnar structure (10).
Table 6.3 DSC data for high molecular weight with N6 (n-s)-CD-IC samples (* % Crystallization values for the dangling chains).

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_m$</th>
<th>$T_c$</th>
<th>$\Delta H_c$</th>
<th>$X_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300,000</td>
<td>222</td>
<td>174</td>
<td>43</td>
<td>23</td>
</tr>
<tr>
<td>2:1 $\alpha$-CD-N6IC</td>
<td>214</td>
<td>173.8</td>
<td>7 (41)$^+$</td>
<td>22</td>
</tr>
<tr>
<td>3:1 $\alpha$-CD-N6IC</td>
<td>220</td>
<td>178.2</td>
<td>16 (94)</td>
<td>49.4</td>
</tr>
<tr>
<td>4:1 $\gamma$-CD-N6IC</td>
<td>214.5</td>
<td>168.4</td>
<td>6.6 (28)</td>
<td>15</td>
</tr>
<tr>
<td>5:1 $\gamma$-CD-N6IC</td>
<td>214.5</td>
<td>166.4</td>
<td>8.5 (37)</td>
<td>19</td>
</tr>
<tr>
<td>6:1 $\gamma$-CD-N6IC</td>
<td>212</td>
<td>171.6</td>
<td>12 (52)</td>
<td>27</td>
</tr>
<tr>
<td>600,000</td>
<td>223</td>
<td>174</td>
<td>45</td>
<td>24</td>
</tr>
<tr>
<td>2:1 $\alpha$-CD-N6IC</td>
<td>216</td>
<td>173.3</td>
<td>5 (29)</td>
<td>15</td>
</tr>
<tr>
<td>3:1 $\alpha$-CD-N6IC</td>
<td>222</td>
<td>182</td>
<td>19 (111)</td>
<td>58</td>
</tr>
<tr>
<td>4:1 $\gamma$-CD-N6IC</td>
<td>216</td>
<td>162</td>
<td>7 (30)</td>
<td>16</td>
</tr>
<tr>
<td>5:1 $\gamma$-CD-N6IC</td>
<td>214</td>
<td>171</td>
<td>7.6 (33)</td>
<td>17</td>
</tr>
<tr>
<td>6:1 $\gamma$-CD-N6IC</td>
<td>215</td>
<td>174</td>
<td>15 (65)</td>
<td>34</td>
</tr>
</tbody>
</table>
As a continuation from our previous works, the N6 samples were coalesced from their stoichiometric and non-stoichiometric CD-ICs to understand the influence of cyclodextrin coverage on the chain extension (5-10).
The FTIR spectra for both coalesced samples (Figures 6.18 and 6.19) showed no traces of cyclodextrin.

As seen from the DSC scans in Figure 6.20, the coalesced samples from both the 1:1 N-6-α-CD IC and the 3:1 (n-s)-N-6-α-CD-IC show more and faster crystallization when compared to the bulk sample. Therefore it can be stated that the completely covered IC and the partially covered non-stoichiometric IC, when coalesced, give the same amount of orientation and extension to the N6 chains.

As stated previously, it has been shown that (n-s)-polymer-CD ICs do act as effective nucleating agents for the polymer itself (11-14). Consequently these (n-s)-N6-CD-ICs and N6 coalesced from them were added in small quantities back into the bulk sample with the results shown in the next chapter.
Figure 6.18 FTIR spectra for (a) alpha cyclodextrin (b) 1:1 N6-α-CD-IC (c) Neat Nylon-6 Sample (d) Coalesced Nylon-6 Sample
Figure 6.19 FTIR spectra for (a) alpha cyclodextrin, (b) 1:1 N6-α-CD-IC, (c) Neat Nylon-6 Sample and (d) Coalesced Nylon-6 Sample

Figure 6.20 DSC cooling scan for (a) as-received Nylon 6, (b) Nylon 6 coalesced from 1:1 N6-α-CD IC (c) Nylon 6 coalesced from 3:1 (n-s) N6-α-CD IC
6.4. References


Chapter 7


7.1. Introduction

The tremendous development in polymer processing and engineering has led to polymer materials with various prominent applications in all fields. But it has also given rise to a major concern in the polymer industry; the constant build up of polymeric materials and waste. Environmental and health safety is a critical issue during the processing of polymers. More and more research is being conducted to obtain ecologically safe materials that can be easily recycled and efficiently reused. Based on the end use of the polymer, various additives are added during processing. It is important to mention here that most of the polymers processed contain additives and many that are toxic and potentially hazardous to health and the environment. One such vital additive delivered to polymer during processing is a nucleating agent which controls the crystallization and morphology of the polymer obtained.
Chapter 7  

BioNucleation

Talc, which is related to the asbestos family, is a commonly used nucleating agent. It is potentially toxic and a probable carcinogen (1). In our effort to reduce hazardous waste build up and to impart eco-friendly reuse of polymers, we propose the use of Nylon-6:Cyclodextrin inclusion compounds (N6-CD-ICs) as *biologically-safe nucleating agents* for the bulk crystallization of N6. We use N6 in our research due its high performance capability and ecological effectiveness, because it can be depolymerized back to its monomer ε-caprolactam and repolymerized to N6 with ease (2; 3).

Recently it has been demonstrated that crystalline non-stoichiometric (n-s)-polymer-CD-ICs can be obtained if an excess of the guest polymer is used during their formation (4-7). If the guest polymer is crystallizable, then the portions of the chains dangling from the (n-s)-polymer-CD-IC may also crystallize. As a consequence, it has been demonstrated that when small amounts of (n-s)-polymer-CD-ICs are added to the same neat bulk polymer, they function as very effective nucleation agents during melt crystallization. This is presumably due to the ability of the dangling chains to more readily crystallize and provide nuclei for the crystallization of the bulk polymer chains (7; 8). Because of the biodegradable/bioabsorbable nature of CDS, (n-s)-polymer-CD-ICs provide environmentally favorable, non-toxic nucleants for enhancing the melt crystallization of polymers and improving their properties (9-11).
7.2. Experimental Methods

N6 was dissolved in 90% formic acid, obtained from Sigma Aldrich, and 2 wt% of each insoluble nucleant was added to the solution. The solution was dried and the films were characterized. The inclusion compounds and the coalesced nylons from them, α- and γ-CDs and talc were used as nucleants. DSC measurements were performed with a Perkin-Elmer Diamond DSC-7 in the range of 25-250° C at heating and cooling rates of 10° C/min, and nitrogen was used as the purge gas. The micrographs of crystallized N6 films were obtained with a Nikon Eclipse 50i POL Optical Microscope and the images were captured by a CCID-IRIS/RGB color video camera made by Sony Corp.

7.3. Results and Discussion

All the inclusion compounds formed were added to the neat nylon sample and their melt crystallization was observed (See Figures 7.1 – 7.4). The DSC scans for nylon samples with ICs as nucleating agents showed higher levels of crystallinity and faster crystallization (higher crystallization temperatures, $T_c$), when compared to talc. It is interesting that even though the dangling N6 chains in the 6:1 (n-s)-γ-CD IC showed lower crystallizability (Figure 7.2) than those in the 3:1 (n-s)-α-CD IC (See Figure 7.1), when added to bulk N6 it was a better nucleating agent (See Figure 7.3). This could possibly be attributed to the greater distance between the channels in γ-CD ICs, when
compared to (n-s)-α-CD-ICs, and from which pairs of N6 chains emerge and might enhance their interactions with free nylon chains.

The coalesced samples also showed higher, faster and more uniform crystallization (See Figures 7.4), which makes them better nucleating agents, as in this case the reorganized coalesced N6 itself acts as the nucleant!

Table 7.1 summarizes the melting temperatures and the % crystallization attained by these samples. This data is confirmed by the micrographs (Figure 7.5) obtained for the melt crystallized neat N6 sample and the N6 samples containing the various nucleants. The nucleants clearly produce finer and more uniform melt crystallized morphologies when compared to the neat bulk N6 sample.
Figure 7.1 DSC cooling scan for (a) neat N6 sample (600,000 g/mol), (b) N6 with 2 wt% 3:1 (n-s)-N6-α-CD IC, and (c) 3:1 (n-s)-N6-α-CD IC.
Figure 7.2 DSC cooling scan for (a) neat N6 sample (600,000 g/mol), (b) N6 with 2 wt% 6:1 (n-s)-N6-γ-CD IC, and (c) 6:1 (n-s)-N6-γ-CD IC
Figure 7.3 DSC cooling scan for (a) neat N6 sample (600,00 g/mol), (b) N6 with 2 wt% 3:1 (n-s)-N6-\(\alpha\)-CD IC, (c) N-6 with 2 wt% talc, and (d) N6 with 2 wt% 6:1 (n-s)-N6-\(\gamma\)-CD IC
Figure 7.4 DSC cooling scan for (a) neat N6 sample (600,000 g/mol), (b) N6 with 2 wt% of N6 coalesced from the 1:1 (n-s)-N6-α-CD IC, (c) N6 with 2 wt% N6 coalesced from the 3:1 (n-s)-N6-α-CD IC, and (d) N6 with 2 wt% talc.
### Table 7.1 Crystallization of N6 with Nucleating Agents

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_m$</th>
<th>$T_c$</th>
<th>$\Delta H_c$</th>
<th>$X_c$</th>
</tr>
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<tbody>
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<td>60,000</td>
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<td>175</td>
<td>58</td>
<td>31</td>
</tr>
<tr>
<td>60+ACD</td>
<td>217.3</td>
<td>183.5</td>
<td>55</td>
<td>29</td>
</tr>
<tr>
<td>60+1:1 ACD</td>
<td>217.4</td>
<td>183.5</td>
<td>60</td>
<td>32</td>
</tr>
<tr>
<td>60+3:1 ACD</td>
<td>220.4</td>
<td>185</td>
<td>62</td>
<td>33</td>
</tr>
<tr>
<td>60+Talc</td>
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<td>64</td>
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<td>60+GCD</td>
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<td>180.5</td>
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<td>600+3:1 ACD</td>
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<tr>
<td>600+3:1 ACD Coal</td>
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<td>182</td>
<td>56</td>
<td>30</td>
</tr>
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<td>600+Talc</td>
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Figure 7.5 Melt crystallized films of (a) neat N6, (b) N6 with 2 wt% 3:1 (n-s)-N6-α-CD-IC, (c) N6 with 2 wt% α-CD, (d) N6 with 2 wt% talc, (e) N6 with 2 wt% γ-CD, (f) N6 with 2 wt% 6:1 (n-s) -N6-γ-CD-IC, (g) N6 with 2 wt% N6 coalesced from 1:1 N6 α-CD-IC, and (h) N6 with 2 wt% N6 coalesced from 3:1 (n-s)-N6-α-CD-IC.
Therefore it is plausible to report that (n-s)-CD-ICs influence the orientation, nucleation and crystallization of N6 chains. The channel structure attained by CD molecules in (n-s)-polymer-CD-ICs enables the N6 chains to extend out and orient themselves. These oriented chains then enhance the crystallization of the bulk N6 when used as a nucleating agent. It has also been seen that the N6 chains coalesced from their CD-ICs retain their orientation and work as effectively as the (n-s)-ICs to nucleate the melt crystallization of bulk polymers.
7.4. References


Chapter 8

8. Conclusions and Future Work

8.1 Conclusions

Nylon-6 (N6), with a wide range of molecular weights, were used to form non-covalently bonded inclusion compounds with cyclodextrins (N6-CD-ICs). When an excess of N6 is employed non-stoichiometric ICs [(n-s)-N6-CD-ICs] are formed, as illustrated in Figure 8.1. Interestingly, as the molecular weight of N6 increased, the crystallizability of the N6 chains dangling from (n-s)-N6-CD-ICs also showed an increase. This has been explained by the behavior shown by dense polymer brushes with extended and oriented chains (1).
Because the constrained N6 chains dangling from the (n-s)-N6-CD-ICs crystallize more effectively, they work as good nucleating agents for N6. They provide sites for the free bulk N6 chains to crystallize, increase the crystallization temperature, reduce the spherulite size and increase the rate of crystallization. N6 samples coalesced from their CD-ICs also showed similar results, as they retain the enhanced orientation and extension attained in their CD-ICs. Both types of N6 samples serve as environmentally and biologically safe nucleants.

In addition, recently (n-s)-polymer-CD-ICs have been shown to exhibit shape-memory (2,3). When heated between the $T_m$ of the included polymer and the decomposition temperature of the (n-s)-polymer-CD-IC, they may be deformed into a
new shape, which is retained following a rapid quench below $T_m$. When this newly-shaped sample is heated above $T_m$ it reverts back to its original shape in response to the constraining CD-IC crystals.

8.2. Future Work

It would be interesting to study the mechanical and other properties of N6 samples produced with ICs and coalesced nylon as nucleants. In future work we will melt mix (n-s)-N6-CD-IC and coalesced nylon 6 nucleants into neat bulk N6 to obtain films which will be tested for strength, toughness, permeabilities, and other properties. Because (n-s)-polymer-CD-ICs are environmentally responsible and non-toxic additives, their use in polymer processing will not hinder their recycling.
8.3 References