Influence on hydrogen bonding efficiency of structural modification
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Influence on hydrogen bonding efficiency of structural modification

PROEFSCHRIFT

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Secondary interactions have a strong influence on crystallization or self-assembling processes of materials in general. Very often in macromolecular structures, having amide motifs, the presence of hydrogen bonding governs the physical and mechanical behavior. In hydrogen bonded polymers, structural organization is mainly prevailed by the density of hydrogen bonding and length of aliphatic or aromatic units between the hydrogen bonding motifs. In nature, hydrogen bonded polymers, such as proteins, use water with ions as a solvent, and, depending upon the nature of ions, its higher order organization is directed. For an example, a spider spins the silk-protein web using ionic water, where the desired tensile strength depends on the amount of amorphous component in the semi-crystalline silk-protein. During the spinning process of the protein, the presence of water and ions facilitate processing by shielding and de-shielding of the hydrogen bonds. In this thesis, we attempt to unravel the process of shielding and de-shielding of the hydrogen bonded motifs in synthetic polymers and model compounds.

It is also known that hydrogen bonding in water at elevated temperatures, i.e. above its boiling point, is strongly suppressed thus drastically improving the mobility of the water molecules. The presence of ions, either kosmotropic or chaotrophic, also influences the hydrogen bonding leading to the increase or decrease in the boiling point. With the help of solid state NMR and molecular dynamics simulations the influence of hydrogen bonding in water, in the presence of monovalent and divalent ions, has been investigated. It is demonstrated that in the presence of smaller ions, irrespective of charge, water can form a hydration shell due to higher interaction potentials and thus can display hydrophilicity. Whereas, the larger ions cause perturbation in the hydrogen bonding efficiency between the water molecules and exhibit a hydrophobic nature. The molecular insight on the structural variation is summarized in Chapter 2 of the thesis.
The knowledge acquired in the water-ion interaction (chapter 2) is applied to study the dissolution process of synthetic aliphatic polyamides. The time resolved NMR studies are performed to follow the molecular origin of the dissolution process of polyamide (PA46) in water with or without ions. During the dissolution process of PA46 in water, close to the dissolution temperatures of PA46, two distinct $^1$H resonances from water are observed. One of the two resonances is associated with water in the vicinity of PA46 and the other to the bulk state of water. On further heating, the signal from water associated with PA46 dominated. This sudden change in water environment suggested that water molecules, which have escaped the dense hydrogen-bonded network of bulk water, can diffuse into the structure of PA46, and thus trigger the dissolution of PA46. The observed dissolution temperature is more than 100 °C below the melting temperature of the polymer, without any chemical degradation. On cooling, recrystallization of PA46 from the aqueous solution showed incorporation of water molecules into the polymer structure.

Introduction of chaotropic salts based on Hofmeister ions (LiI, CaI$_2$) in different concentrations resulted in overall weakening of the hydrogen-bonded network of the bulk water. On heating, depopulation of the hydrogen bonding between the water molecules took place and this resulted in a decreased chemical shift. This reduced hydrogen-bond efficiency between the water molecules facilitated dissolution of PA46 at much lower temperatures compared to pure water and consequently resulted in complete suppression of crystallization even at room temperature. The influence of ion size in the structural organization of water molecules and on the dissolution process are described in Chapter 3 of this thesis.

Further, in general, interaction of water with amide motifs is investigated. For this purpose a couple of oxalamide based model compounds are synthesized, namely (a) Diethyl 4,5,14,15-tetraoxo-3,6,13,16-tetraazaoctadecane-1,18-dioate (ala oxa (CH$_2$)$_6$ oxa ala ) and (b) N$^1$,N$^2$-bis (3-methoxypropyl) 2,11-dioxo-3,10-diaza-1,12-dodecanamide(Meo oxa (CH$_2$)$_6$ oxa Meo. These compounds are used as model systems to overcome the ambiguity of chain folding in synthetic polyamides.
The structural and conformational changes have been followed with the help of X-ray diffraction and NMR studies. The study revealed that, prior to melting, two phase transitions are present in the melt as well as in the water crystallized model compounds. These low and high temperature phase transitions are associated with crystal-to-crystal modification resulting from the conformational changes at low temperature, and crystallographic changes at high temperature. The two transitions are associated with the crystal to crystal transformations. Changes in the molecular conformation of the model compounds, during the low temperature phase transition, are due to the temperature induced release in the constrained environment of the end groups. The high temperature phase transition is associated with the introduction of gauche conformers in the aliphatic units between the oxalamide motifs. These results are summarized in Chapter 4 of thesis.

Finally, to investigate the influence of rigid and flexible segments on the hydrogen bonding efficiency, poly(amide-aramid)s are synthesized. Chapter 5 of this thesis describes the influence of varying methylene unit length on the thermal properties. Melting in the poly(amide-aramid)s is feasible in the poly(amide-aramid) having at least eight methylene units between the rigid aramid motifs. Polymers having methylene segments below eight degraded prior to melting. A detailed structural investigation using solid-state NMR, FTIR spectroscopy, WAXD, in combination with crystallographic modelling (Cerius software) revealed the cause of lower melting temperature in poly(amide-aramid)s having eight methylene units. These investigations additionally helped in understanding the influence of methylene segment incorporation on the crystal packing and ring dynamics of the aromatic component. Specifically, the presence of longer methylene segments provided an additional degree of freedom, originating from the increased chain flexibility at elevated temperatures which eventually resulted in melting of the polymer.
Chapter 1

Introduction

Molecular configuration strongly depends on the building of the interactions at the atomistic level [1]. These primary interactions are basically short range interactions that can be at the intramolecular or intermolecular level. The strongest intramolecular interaction is the covalent bonding between the atoms, which arises with sharing of the electron cloud at the outermost atomic shell. Relatively weak interactions are the secondary interaction that arises, with some exceptions, mainly between the molecules at the intermolecular length scale and have implications in molecular packing.

Thus the secondary interactions are responsible for the self assembling of the molecules in different physical states of matter [2]. The response of the molecule or material to the external parameters such as pressure and temperature depends upon the magnitude of the secondary interactions. There are many kind of secondary interactions such as ion-ion interaction, dipole-dipole forces (Hydrogen bonding), ion-dipole, induced dipole forces, induced-induced dipole forces (London dispersion forces), and repulsive forces (influenced by van der Waals radii). Nature makes successful use of this secondary interaction, in different forms. For example, the well known examples where the strength or flexible nature of the hydrogen bonding is made use are water, DNA, the spinning of the strongest natural fiber etc [3-6]. It is important to notice that in these cases nature makes use of salts in achieving the desired properties by shielding and deshielding processes of the hydrogen bonding [7]. In this thesis we aim to replicate the tailoring of the hydrogen bonding in synthetic polymers. For this purpose we have made use of ionic solutions – water having monovalent or divalent ions at different concentrations.

The advent of hydrogen bonding in the structural organization of water molecules in the presence of salts was realized by Franz Hofmeister in 1887[8]. In his seminal experiment, Franz Hofmeister recorded the concentration of ionic
aqueous solutions at which precipitation of egg protein was observed. These experiments lead to the important conclusion that interaction of ionic solution with protein promotes the precipitation process, where the interaction is strongly influenced by the nature and concentration of ions in water. Since then, many publications have suggested mechanism of action of these ions in water, called Hofmeister Effect [4,6]. A series of ions, comprising of monovalent and divalent ions, is called Hofmeister series, see Figure 1.1.

<table>
<thead>
<tr>
<th>Hofmeister Ions</th>
<th>most stabilizing strongly hydrates</th>
<th>most destabilizing weakly hydrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>citrate$^{3-}$</td>
<td>sulfate$^{2-}$</td>
<td>phosphate$^{2-}$</td>
</tr>
<tr>
<td>N(CH$_3$)$_4$+</td>
<td>NH$_4$+</td>
<td>Cs$^+$</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>Li$^+$</td>
<td>H$^+$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>Rb$^+$</td>
<td>Ca$^{2+}$</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>Al$^{3+}$</td>
<td>strongly hydrated</td>
</tr>
<tr>
<td>weakly hydrated</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1.1: The classification of Hofmeister ions series. Chaotropic or weakly hydrating ions disrupts, whereas kosmotropic or strongly hydrating ions promote the hydrogen bonding efficiency of water molecules.

Further insight lead to the important conclusion that the hydrogen bonding efficiency between the water molecules can be altered by the size and valency of ions. For an example, the presence of ions such as Li$^+$ can help in structuring of water molecules and is known as kosmotrope, whereas with increasing size of the monovalent ion, the K$^+$ structure between the water molecules is perturbed and is known as chaotrope [9]. The origin of this complexity exists in flexibility of the hydrogen bonding between the water molecules, which makes water a unique material showing inverse density relationship between its solid and liquid state [10].

Just to recall, below the glass transition temperature (~ -196 °C) the ease in compressibility of the crystalline structure (hexagonal packing) lead to the origin of high density amorphous phase. This actually suggests that an amorphous state having density higher than the crystalline state is feasible. Though this subject is out of the scope of this thesis, it implicates variation in hydrogen bonding efficiency that can be realized either in the one component system by increasing pressure at low temperatures or by the addition of Hofmeister ions in water.
Therefore it is of general interest to answer how and why the hydrogen bonding network could be influenced. This question has been addressed in Chapter 2 of this thesis, where a series of monovalent and divalent ions at different concentrations in water at different temperatures have been discussed. For experimental insight use of $^1$H MAS NMR and FTIR spectroscopy has been made. To understand the experimental observation computational methods have been employed. Molecular changes at different length scales as function of temperature have been investigated, among them are the modifications in ionic distance with varying concentration, size and valency.

The understanding in the variations in hydrogen bonding efficiency of the water molecules in the ionic solutions has been exploited to follow the dissolution process of a synthetic polyamide, PA46. To recall, this subject has been of interest our laboratory for more than five years. In their previous studies Vinken and Harings showed the successful dissolution of a range of synthetic polymers in “superheated state” of water [11,12]. Making use of advanced characterization techniques these authors concluded that when given the appropriate conditions water acts as a good solvent for polyamides, and without chemical degradation single crystals of polyamides can be obtained. Harings showed that by making use of the ionic solutions by shielding of the hydrogen bonding amorphous PA46 can be obtained at room temperature. The amorphous polymer, close to its glass transition temperature, can be mechanically deformed to make uniaxially drawn fibers or tapes [13]. The hydrogen bonding can be reinstated by removal of the ions using heated water. The missing part in these studies has been the molecular understanding in dissolution process. To provide this insight we have developed a unique experimental technique; where the ionic solution together with the polymer can be encapsulated in capillary and the molecular conformational changes of water molecules in the presence of polymer can be followed using solid state NMR. These studies have been incorporated in Chapter 3 in of this thesis. The chapter also addresses depression in the dissolution temperature of PA46 in the presence of ions. It is shown that the interaction parameter of water with polyamides is influenced in the presence of ions, which is a probable cause for depression in the
dissolution temperature and the enthalpy contribution during the dissolution process [13]. To follow structural changes of the polymer, for an example Brill transition temperature in the presence of ions, time resolved WAXD studies have been performed.

These studies have been extended to model compounds having oxalamide based hydrogen bonding motifs. The presence of two amide motifs next to each other in reverse fashion promotes hydrogen bonding efficiency compared to the aliphatic polyamides. Oxalamides are actually diamides prepared using oxalic acid, which form intermolecular hydrogen bonding (Figure 1d). These motifs are also known in literature as retro-peptide. Oxalamide motif based polymers were invented by Flory in 1980 know as nylon x, 2 [14]. Due to the stronger hydrogen bonding compared to the aliphatic polyamides, oxalamide based polymers show higher melting temperatures, higher moduli, and low solubility in solvents. Several authors reported the synthesis of polyoxalamide. Gaymans et al reported synthesis of nylon 4,2, having melting temperature ~ 390 °C [15]. Casas et al reported synthesis of polyoxalamide with longer methylene segment, nylon 12,2 [16]. The structural differences in the organization of the oxalamide polymer compared to polyamide are attributed to the difference in the electron charge distributions on the amide motifs. Franco et al reported synthesis of odd polyoxalamide, nylon 9,2 having higher molar mass and melting temperature close to ~240 °C [17]. These findings suggested that, similar to polyamide, melting of polyoxalamide can be significantly influenced by the length of methylene units between the amide motifs.

Another important difference with polyamides is the absence of Brill transition temperature prior to melting of oxalamides. Considering that the Brill transition temperature is the crystallographic modification of the unit cell, these findings are indicative of significant modification in the crystallographic packing due to the oxalamide group. It was predicted by Franco et al that the presence of consecutive amide motifs in oxalamide, causes modification in the molecular conformation due to the formation of hydrogen bonding in two directions. Recently, Feijen et al reported segmented poly (ether-amide) with uniform oxalamide based hard segments. The results demonstrated that alternating block copolymers having
soft polytetrahydrofuran (PTHF) segments and uniform hard segments containing two or three oxalamide groups behave as thermoplastic elastomer, having good combination of thermal and mechanical properties [18]. Oxalamide based model compounds can strongly interact with metal ions or modify rheological behavior of heptylcyclo hexane carboxylic acid [19,20].

In the previous studies performed in our group by making use of model compounds \( N,N'\-1,4\)-butanediyl-bis(6-hydroxy-hexanamide) (BDHA) and \( N,N'\-1,2\)-ethanediyl-bis(6-hydroxy-hexanamide) (EDHA) [21,22], it is shown that the structural organization is facilitated on crystallization from water where the thermodynamically preferred structures can be obtained with ease. In Chapter 4, we investigated the solvent characteristic of water (superheated water) for two oxalamide compounds; having oxalamide motifs separated by aliphatic spacer with polar and non-polar end groups. The changes in the end group lead to differences in crystallization of compounds, eventually the intermolecular hydrogen bonding.

Another way to influence the hydrogen bonding efficiency in polymers is molecular rigidity between the hydrogen bonding motifs. An extreme example is Poly (p-phenylene terephthalamide) (PPTA), where the aromatic molecules provide sufficient chain stiffness leading to extremely high melting temperatures, above the thermal degradation of the polymer (545 °C) [23]. On the contrary the presence of aliphatic units between the hydrogen bonding motifs give all variations in melting temperatures with an ease in processing. The combined effect of aliphatic and aromatic monomers between the amide motifs has been explored in Chapter 5 of this thesis. The adopted synthesis is reported in literature for synthesis of PPTA or segmented block copolymers based and aromatic and aliphatic amides [24-26]. The polymers synthesized in this chapter consist of alternating aromatic and aliphatic units. This objective can be achieved by combining rigid aromatic moieties with flexible moieties, connected through hydrogen bonding motifs. Here we investigate the influence varying methylene segment on hydrogen bonding efficiency of the polymers, considering the factors dissolution in polymerisation medium, melting temperature, crystal packing and chain dynamics the polymers.
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Chapter 2

Implication of Hofmeister ions on the hydrogen bonding efficiency of water molecules

Abstract

Interactions between ions and water are of prime importance that we experience in the development of lifecycle. Bio-macromolecules such as proteins can either dissolve or precipitate in ionic water depending on the ionic valency and size. The flexible nature of hydrogen bonding between water molecules and its adaptation in the presence of ions remains the subject of scientific interest. In this chapter, we investigate the influence of ions on the hydrogen bonding efficiency of water molecules using Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared Spectroscopy (FTIR) and Molecular Dynamic simulations (MD). The influence of monovalent chaotropic (structure breaker) ions based on lithium and sodium halide salts, with increasing anionic radii from Cl\(^{-}\), Br\(^{-}\) & I\(^{-}\) and their concentration, are investigated. Furthermore, the effect of divalent cations, Mg\(^{2+}\) and Ca\(^{2+}\) on the hydrogen bonding efficiency of water molecules, in the presence of halogenic anion, are studied. The kosmotropic nature of Mg\(^{2+}\) ions and the chaotropic behavior of Ca\(^{2+}\) ions, and their dependence on the ionic radii of the counter ions and their concentrations are investigated. Molecular interactions of LiI salt with water molecules is further investigated using MD simulation at low (1MLiI) and high (9MLiI) ionic concentrations. The observations are that in the presence of smaller ions, water can form hydration shell due to higher interaction potentials and thus display hydrophilicity, whereas the larger ions cause perturbation in the hydrogen bonding efficiency between the water molecules and exhibit hydrophobic nature.
2.1 Introduction

One of the most ubiquitous solvents on our planet is water solution having salts. Water also plays an essential role in the evolution and development of living organisms, for example more than 2/3rd of the human body consists of water with various dissolved salts or ions influencing the characteristics of cells and proteins. It has been documented that water can be a solvent for nearly all substances depending upon pressure and temperature, which makes water a unique solvent [1-4]. Different studies have been performed using different modeling techniques such as molecular dynamics (MD) [5-7] and Monte Carlo simulations to investigate the organization of water molecules in solid, liquid, gaseous or intermediate state. The intermediate state that is realized at elevated temperature and pressure is a subject of our interest and will be applied to investigate water hydrogen bonding interactions with and without salts [8]. It is an established concept that in the supercooled state, the hydrogen bonding between water molecules is optimum and hence water molecules are separated by maximum hydrogen bonding distance, structuring them in the crystalline state [4]. While in the liquid state the involved molecular dynamics suppresses the hydrogen bonding efficiency and van der Waal’s forces between the molecules dominate. The latter brings the water molecules closer resulting into the unique density relationship between the crystalline and the liquid state [9]. When water is heated in closed system, above the boiling point, it transforms into “superheated state” that persists between 100 °C to 374 °C [10], where the latter is termed as the super critical temperature [11]. In the “superheated state”, intermolecular distance between water molecules increases with temperature and water molecules stay at liquid/gas interface (the intermediate state) resulting in high mobility compared to the liquid state.

Another entity which significantly influences the hydrogen bonding of water is ions. In 1887, Hofmeister proposed a classification of anions and cations into a series, recognizing the ionic efficiency, now commonly known as Hofmeister series [12]. Depending on the ionic radius and the associated charge, molecular structures based on hydrogen bonding motifs such as proteins or water can be strongly influenced, resulting into ordering or disordering of the molecular structure [13].
The ions that stabilize the secondary structure of molecules based on hydrogen bonding are called kosmotropic ions, whereas the ions that perturb the molecular structure are called chaotropic ions [4]. It is well accepted that the presence of ions in water influences structural reorganization of proteins. For an example during the spinning process of silk, spiders make use of different ions for shielding of the amide motifs in polypeptides to obtain an amorphous peptide solution [14]. Once the amorphous peptide is spun out of the duct, with the removal of the ions, hydrogen bonding is recovered and the desired mechanical properties such as high tensile strength and high modulus are established [15]. Considerable efforts have been made to investigate molecular interactions between water molecules at different temperatures and in the presence of salts – both monovalent as well as divalent ions [1-4].

In this chapter, using $^1$H Magic angle spinning Nuclear Magnetic Resonance (MAS-NMR) and Fourier Transform Infrared Spectroscopy (FTIR), the physical state of water in the presence of ions at ambient and elevated temperature has been investigated. The $^1$H MAS NMR measurements were further strengthened with molecular dynamic simulations. The experimental data obtained from $^1$H MAS NMR has been validated and analyzed with molecular dynamic simulations. Details on the influence of ions, on the structural organization of water molecules in the presence of the monovalent and the divalent ions, are addressed by considering the water-ion interactions.

2.2 Materials and Experiments:

2.2.1 Materials

The salts (LiCl, LiBr, LiI, NaCl, NaBr, NaI, MgCl$_2$, MgBr$_2$, MgI$_2$, CaCl$_2$, CaBr$_2$, and CaI$_2$) obtained from Sigma-Aldrich were used as received. Different ionic solutions at different ionic concentrations, ranging from 0 to 10 mol/l, were prepared using demineralized water.
2.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR measurements on water and ionic solutions were carried out with the help of Varian 670IR spectrometer. The spectrometer was equipped with a microscope. All spectra were measured in the range of 4000 cm\(^{-1}\) to 650 cm\(^{-1}\) at the resolution of 4 cm\(^{-1}\) in Attenuated Total Reflection (ATR) mode. For the purpose the SLIDE-ON ATR selenium crystal was used.

2.2.3 Nuclear Magnetic Resonance (NMR)

Solid state \(^1\)H NMR was performed on a Bruker 800 MHz spectrometer. For all measurements a rotor of 2.5 mm diameter was filled with the sample. The \(^1\)H MAS measurements were carried out using a MAS probe, spun at 5 kHz at room temperature. Proton chemical shifts have been reported relative to tetramethylsilane (TMS).

In situ variable temperature \(^1\)H MAS NMR experiments were performed on a Bruker DSX-spectrometer operating at 500 MHz. \(^1\)H Larmor frequency using a commercial magic-angle spinning (MAS) double-resonance probe (\(^1\)H-X) for rotors with 4.0 mm outside diameter. A MAS spinning frequency of 5.0 kHz and a 4 µs \(\pi/2\) pulse, corresponding to 62.5 kHz rf nutation frequency was chosen. All samples were prepared by placing solvent (water or concentrated LiI solutions) in glass capillaries (from Wilmad Glass) and sealed using LPG gas flame. The temperature was controlled using a Bruker temperature control unit in the range from 30 °C to 220 °C. Reported temperatures were corrected for the induced temperature changes due to sample rotation. For the purpose a rotation dependent temperature calibrant, obtained by \(^{207}\)Pb MAS NMR, recording the temperature dependent chemical shift of Pb(NO\(_3\))\(_2\) was used. The \(^1\)H MAS NMR spectra were recorded at every two minutes during continuous temperature ramp of 2.0 °C/min. \(^1\)H chemical shifts are reported relative to tetramethylsilane (TMS) using adamantane as an external reference[16]. Calibration of \(^1\)H rf-field strength and shimming was performed at ambient conditions.
2.2.4 Computational details:

The MD simulations on the water ion interactions were performed and analyzed in the group of professor Daniel Sebastiani, at Free university Berlin, by Nora P. Salas Illanes and Christoph Allolio.

Initially classical MD simulations were carried out on three boxes of side length 1.184 nm containing 55 water molecules, 53 water molecules and one ion pair, and 37 water molecules and 9 ion pairs. The densities of the boxes were set according to literature values [17]. To obtain an ergodic sampling, the systems were pre-equilibrated using a Kirkwood-Buff type force field, tuned for highly concentrated aqueous solutions of monovalent ions [18-20]. For water, the SPC/E model was used. The trajectories for the three boxes lasted 10 ns and were meant as a pre-equilibration of the systems. GROMACS software package was used [21].

Ab-initio simulations were carried out for each box during 6 to 10 ps, employing a DZVP-MOLOPT [22] basis set with GTH [23,24] pseudopotentials and the GAPW method using a 320 Ry Cutoff (Method I). The simulation was completed with up to 21 ps employing the GPW [25, 26] method, with the BLYP-D dispersion corrected, [27] density functional [28,29]. The basis set employed were augmented wave functions for the hydrogen and oxygen (TZV2PX), and a quadruple zeta (QZV2P) basis set for the cation and DZVP-MOLOPT for anions with a cutoff of 600 Ry (Method II) [22].

The system was kept at constant volume and at constant temperature by means of a CSVR thermostat [30] with a time constant of 100 fs. The simulations ran with deuterated water and used a 1 fs time step. We set the temperature to 350 K to compensate for over structuring of water [31,32]. The NMR chemical shift calculations were carried out using the CP2K package [33] and Method I using 30 randomly sampled snapshots from the last 2 ps of the (Method II)-MD trajectories. The use of deuterated water affects neither the magnetic perturbation Hamiltonian nor the electronic ground state, thereby yielding identical chemical shifts to that of protons [34].
2.3 Results and Discussion

2.3.1 Influence of ionic strength on hydrogen bonding efficiency of water molecules in the presence of monovalent and divalent ions at room temperature

Considerable efforts have been made to understand the structure of water that mainly arises due to variation in hydrogen bonding efficiency between the water molecules with temperature and in the presence of ions. A series of scattering experiments (neutron and x-rays) clearly demonstrate that local order between molecules persists in the liquid state of water [4]. It is beyond the scope of this chapter to elucidate in depth the vast knowledge that exists in this area, because even today strong debates persist on the structure of water at different length scales. However, with the advancement of experimental techniques and theoretical studies, insight into the complexity of the structural organisation of water molecules has become more clear. These findings have been summarised in the recently published excellent reviews of Bakker et al and Marcus [1,4]. These reviews explicitly address the influence of ions on local organisation of water molecules. To recall, in the presence of ions depending upon their size and valency, structural organisation of water molecules is influenced. An agreement persists on the presence of first solvation shell around the ions, where for example Li$^+$ is considered to be kosmotropic (enhances structure between water molecules in their bulk state and is called structure maker) and the I$^-$ is considered to be chaotropic (perturbs the bulk structure of water molecules and is called structure breaker). The kosmotropic ions enhance the hydrogen bonding efficiency, whereas the chaotropic ions perturb the hydrogen bonding. Thus the overall effect of a salt, kosmotropic or chaotropic, depends on the overall efficiency of ionic nature. The persistence of ordering beyond the first solvation shell remains a matter of debate that mainly arises on the time scale to which the ordering is perceived. For an example using femto second techniques Bakker et al question the persistence of ordering in the second shell, whereas Marcus argues on their existence for a certain time scale [13]. The ionic concentration is likely to have the strong influence in ordering beyond the first
solvation shell, especially in the presence of kosmotropic ions. This ordering may arise due to clustering of ion pairs, and it ultimately results in an ordered structure of the water molecules in the second shell. Initially, for simplicity, what follows are our experimental findings in the structural changes of water molecules in the presence of monovalent ions at different concentrations. These studies will be further extended to divalent ions.

To have insight into the organization of water molecules beyond the first shell, Marcus proposed an empirical relation to estimate the distance between ion pairs in a hydrated state of salt or in an aqueous solution that water molecules can occupy [4, 35]. The empirical mathematical relation adopted from electrolyte solution theories, equation 2.1, is applicable for halogenated monovalent salts in aqueous solution.

\[
d(nm)=10^{-3}(m^3/dm^3) \times 10^{27}(nm^3/m^3)/[2c(mol dm^{-3}) N_A (mol^{-1})]^{1/3} \quad \text{equation 2.1}
\]

Where, \(d\) is the distance between the ion pair (nm) in salt having monovalent ions, \(c\) is the ionic strength of the salt solution (mol/l), and \(N_A\) is the Avogadro’s number.

The equation depicts distance between the ion pairs in an aqueous solution as a function of ionic size and ionic strength. Table 2.1 summaries the monovalent ions (Lithium and Sodium halide salts) and their respective radii utilized in this study. Using the ionic radius in equation 1, changes in the available distance between the ion pairs is estimated for different ionic concentrations. The results obtained are depicted in Figure 2.1.
Figure 2.1: Average distance, \( d \), between two ions of a symmetrical electrolyte (having the same valency) as a function of concentration, \( c \). The data points suggest two distinct slopes, related to low and high ionic concentrations. In the low ionic concentrations (approximately lower than 2 mol/l) the possibility of ionic pair formation is less feasible (green dotted circle shows water molecules) compared to the high ionic concentrations (blue and red dotted line circle with positive or negative charge represents the hydrated ion pair). The influence of the ionic concentration on the distance between the ionic pair becomes evident with the change in slope around 2 mol/l. The Figure is adapted from reference [4].

Table 2.1: Ionic radius of an ions and cations

<table>
<thead>
<tr>
<th>Ions</th>
<th>Charge (e)</th>
<th>Radius (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>1</td>
<td>6.60E-11</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1</td>
<td>9.50E-11</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2</td>
<td>6.65E-11</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2</td>
<td>1.14E-10</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1</td>
<td>1.81E-10</td>
</tr>
<tr>
<td>Br⁻</td>
<td>1</td>
<td>1.96E-10</td>
</tr>
<tr>
<td>I⁻</td>
<td>1</td>
<td>2.16E-10</td>
</tr>
</tbody>
</table>

To have insight on the perturbation of the molecular structure of water molecules, in the presence of monovalent salts, \(^1\)H MAS NMR and FTIR studies have been performed. Though such a study will provide qualitative information on the perturbation of hydrogen bonding, quantitative information cannot be extracted. Figure 2.2a depicts \(^1\)H MAS NMR spectroscopy of water in the presence of monovalent ions with increasing ionic concentration. In the absence of salt, in the bulk state of water, a proton chemical shift is observed around 4.6 ppm at room
temperature. With the increasing concentration of salts the chemical shift decreases. The change in the chemical shift suggests changing chemical environment of the water molecules, whereas the decrease in the chemical shift with the increasing concentration is attributed to depopulation of strongly hydrogen bonded states. The latter indicates a decrease in the hydrogen bonding efficiency between water molecules. With the increasing ionic concentration, as the chemical shift moves to lower values, the hydrogen bonding efficiency decreases resulting in a gain in the mobility of water molecules. The influence of ionic concentration, on the chemical shift of the water molecules, is further manifested with the increasing anionic size. For an example, for the same ionic concentration, the comparison between LiCl, LiBr and LiI salts suggests that with the increasing anionic radii the change in the chemical shift from pure water gets more pronounced. These findings clearly indicate that for the same cation, the hydrogen bonding in water is more perturbed with the increasing radii of anion. The difference in chemical shift, with the increasing ionic concentration, is further enhanced by increasing the size of cation, for an example changing from Li$^+$ to Na$^+$. The comparison between LiCl and NaCl further strengthens the concept that in the chosen monovalent ions, ionic radii play an important role in the perturbation of hydrogen bonding, independent of cation or anion.

These observations have been further strengthened by FTIR spectroscopy summarized in the supplementary section (appendix A.2.1). The vibrational spectroscopy complements reduction in the hydrogen bonding between the water molecules with increasing ionic size and ionic strength. To recall, with the increasing ionic concentration and the ionic size the OH bending mode and the symmetric OH stretch mode shift to lower wavenumbers, whereas the anti-symmetric OH stretch mode shifts to higher wavenumbers. The observed shifts of more than 20 cm$^{-1}$ are obvious and pronounced. The FTIR studies are in agreement with the work of Kazarian et al, who observed similar changes in the OH modes with increasing temperature [40], which were attributed to the decrease in the hydrogen bonding efficiency of the water molecules. In this respect it is evident that the presence of salt at room temperature suppresses the hydrogen bonding...
efficiency and thus enhances mobility of water molecules. An observation in agreement with Liu and coworkers who noticed similar changes in water in the presence of NaCl, MgCl₂, AlCl₃, FeCl₃ by employing Raman spectroscopy as a technique [36].

However, considering the complexity of the dynamics in the dipole-dipole interactions to comment on the mobility of the water molecules alone with the FTIR studies is difficult. Moreover, it has also to be realized that the adopted characterization tools are not sensitive enough to provide information on the spectrum of mobility differences that may arise in the same sample. For an example in the same salt, while the chaotropic cation may lead to enhanced water mobility the kosmotropic anion can reduce the water mobility, thus the cation and the anion may cause mobility differences at the local scale in the bulk water. Inspite of these limitations, from the reported data in Figure 2.2a and the FTIR data in the supplementary section, the influence of ionic sizes and ionic concentration is evident. The trend in Figure 2.2a is along the same lines as depicted in Figure 2.1, suggesting decrease in the distance between the ion pairs with increasing ionic concentration and ionic size.

![Figure 2.2](image_url)

**Figure 2.2:** Changes in the proton shift on the incorporation of (a) monovalent cation and anion on the hydrogen bonding efficiency of water molecules, (b) divalent cations and monovalent anions probed with ³¹H MAS NMR at room temperature.
To have further insights into the influence of divalent ions as depicted in Table 2.1, on the organization of water molecules, experiments have been performed in the presence of Mg$^{2+}$ and Ca$^{2+}$ cations in combination with anions with the increasing anionic size Cl$^{-}$, Br$^{-}$, I$^{-}$. Figure 2.2b summarizes changes in the water proton chemical shift with increasing concentration of the divalent ions. The kosmotropic nature of Mg$^{2+}$ is well documented in literature [1,13,36], where the authors by using spectroscopic techniques, conventional and femtosecond Raman spectroscopy, concluded that the first solvation shell in the kosmotropic ion exists. Figure 2.2b illustrates changes in the proton NMR with the increasing ionic strength and ionic radii, from Mg$^{2+}$ to Ca$^{2+}$ of the divalent cations. Important to notice is that, unlike monovalent ions reported in Figure 2.2a, Mg$^{2+}$ ion shows that the chemical shift moves to higher ppm with the increasing concentration. The shift manifests enhancement in hydrogen bonding efficiency thus reduced mobility due to ordering of the water molecules, confirming the kosmotropic nature of Mg$^{2+}$ ions. For the same ionic concentration, the observed shift to higher ppm decreases with the increasing anionic radius from Cl$^{-}$ to I$^{-}$. On increasing the cation size from Mg$^{2+}$ to Ca$^{2+}$, in combination with the halogen anions, the chemical shift reverts and shows shift to lower values with the increasing ionic concentration. In this respect, with the exception of Mg$^{2+}$, the reported salts (monovalent and divalent cations in combination with the halogen anions) show chaotropic behavior that tend to increase with the increasing ionic concentration. The increase in the chaotropic behavior suggests enhanced mobility in water molecules with decreasing distance between the ionic pair of a salt. However, the Mg$^{2+}$ cations in combination with their halides, especially Cl$^{-}$, suggest suppression in mobility of water molecules due to the overall kosmotropic nature of the salt. These findings suggest that in the presence of Mg$^{2+}$, ordering in the water molecules most likely prevail beyond the first solvation shell that tend to increase with the increasing concentration.

In the following chapter, chapter 3, molecular insight on the dissolution and crystallization processes of synthetic polyamides, PA46, in the presence of water and ionic solutions [10,11] has been addressed. The observed perturbation in the hydrogen bonding of water molecules, summarized at room temperature in Figures
2.1 and 2.2, will have consequences in the dissolution process of PA46 in pure aqueous state and in ionic solutions. Considering that the dissolution process requires higher temperatures, with the help of proton NMR changes in the hydrogen bonding of pure water and ionic solutions have been followed as a function of temperature.

2.3.2 Influence of temperature on the hydrogen bonding efficiency of water in the presence of monovalent and divalent ions

As discussed before, water in a closed vessel, between the boiling point (100 °C) and the supercritical temperature (374 °C) [37], is defined as the “superheated” state of water. In these conditions, in spite of increasing vapor pressure, the average intermolecular distance between water molecules increases with temperature and a continuous exchange of water molecules between liquid and/or the gaseous phase occurs. Temperature dependent changes in the electronic structure of water molecules, influencing the hydrogen bonding efficiency between

![Figure 2.3: Temperature dependent changes in $^1$H MAS NMR spectra of (a) water, and (b) 7M LiI aqueous solution. The samples were sealed in glass capillaries. The $^1$H chemical shift indicates changes in the hydrogen bonding efficiency of water molecules during heating and cooling.](image-url)
water molecules in the presence of ions, can be monitored by $^1$H MAS NMR spectroscopy. The temperature dependent chemical shifts are depicted in Figure 2.3a for pure water, and the Figure 2.3b for the ionic solution having 7M LiI in water. In Figure 2.3a, an average chemical shift of 4.6 ppm has been determined at 38 °C for the protons of water. The narrow line observed in the NMR experiment results from more than 10 ppm wide distribution of chemical shifts depicted by Carr-Parinello Molecular Dynamic simulations [38], which is averaged by rapid molecular exchange between different molecular environments in water. The position of chemical shifts thus indicates the hydrogen bonding efficiency of water molecules in the liquid state, although hydrogen bonded water molecules are typically observed between 6 and 10 ppm. On increasing temperature from 38 °C to 210 °C, gradual change in the chemical shift towards lower values is observed, which may result from depopulation of strongly hydrogen bonded states and thus indicate decrease in the hydrogen bonding efficiency between water molecules. At ~210 °C water proton shows the chemical shift of 2.7 ppm and on cooling, from 210 °C to 40 °C, a gradual increase in the chemical shift to higher ppm suggests re-establishment of hydrogen bonding between the water molecules. Conradi et al., with the help of proton NMR, also investigated changes in the chemical shift of water proton at supercritical condition (~400 °C and ~400 bar) [39]. By combining experimental and modeling studies these authors demonstrated that 29% of hydrogen bonds still exist at 400 °C and 400 bar compared to water at room temperature. FTIR studies have been also successfully applied to follow the variations in hydrogen bonding with temperature. By employing Attenuated Total Reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), Kazarian et al have investigated the influence of temperature on hydrogen bonding efficiency of water molecules in the superheated state. The temperature dependent changes in OH stretching and bending mode vibration are associated with the weakening of the hydrogen bonding resulting into an increase in the mobility of water molecules [40]. What follows is the influence of monovalent ions on the hydrogen bonding efficiency of water molecules.
At 38.0 °C, in 7M LiI solution (Figure 2.3b), water $^1$H chemical shift at 4.1 ppm is observed. The shift to a lower ppm, compared to pure water (4.6 ppm), indicates weakening of the hydrogen bonding efficiency between water molecules in the presence of ions. Figure 2.2a also depicts decrease in the chemical shift with the increasing ionic concentration. Similar to Figure 2.3a, Figure 2.3b also shows changes in the chemical shift on increasing or decreasing temperature reflecting changes in the hydrogen bonding efficiency between water molecules with and without ions. However, the rate at which the hydrogen bonding efficiency changes with the increasing temperature is influenced by the presence of ions. Our NMR studies showed that the chemical shift value at 210.0 °C, in the presence of LiI, is 3.1 ppm compared to 2.8 ppm without salt. The higher proton chemical shift, at 210 °C, in the presence of salt could be attributed to the stronger hydrogen bonding between the water molecules that may arise due to localization of water molecules between the ion pairs [4]. Thus it is important to notice is that at lower temperatures, 38 °C, water molecules in bulk water are more organized compared to the ionic solution, whereas at higher temperatures (210.0 °C) the water molecules have lesser mobility in the presence of ionic solution than in the pure water. For LiI solutions with concentrations above 7M, the observed changes at 210 °C in the chemical shift are very similar to that shown in Figure 2.3b. The differences in the chemical shift are at the second decimal place. What follows are the changes in the water molecules hydrogen bonding efficiency in the presence of kosmotropic salt, MgCl$_2$.

Earlier in the chapter, kosmotropic characteristics of magnesium halide salts at room temperature were discussed, Figure 2.2b. In Figure 2.4, influence of temperature on the hydrogen bonding efficiency of water molecules in the presence of 1M MgCl$_2$ is further investigated. At -10 °C, chemical shift of water proton is observed at 5.20 ppm. Compared to the chemical shift of 4.75 ppm at room temperature, the observed value of 5.20 ppm at -10 °C is significantly higher. The higher chemical shift at -10.0 °C may be attributed to increase in the hydrogen bonding of water molecules.
Figure 2.4: Temperature dependent changes in $^1$H MAS NMR spectra of 1M MgCl₂ aqueous solution. The samples were sealed in glass capillaries. The $^1$H chemical shift indicates changes in the hydrogen bonding efficiency of water molecules in the presence of 1M MgCl₂ during heating from -10.0 to 45.0 °C.

Upon heating from -10 °C to 45 °C, with decrease in the hydrogen bonding efficiency between the water molecules, the chemical shift moves to lower ppm. The observed trend in chemical shift with temperature, in the presence of 1M MgCl₂, is in parallel with the results obtained with 7M LiI solution (Figure 2.3b), where reduction in the chemical shift of water proton with increasing temperature is attributed to gain in mobility of the water molecules. What follows are molecular interactions between the water molecules and chaotropic monovalent ion investigated using molecular dynamics simulations.

2.3.3 Molecular understanding of water-ion interactions using MD simulation

2.3.3.1 Case of 1M LiI solution

The influence of monovalent chaotropic ion on local organization of water molecules is investigated using MD simulations at 1M and 9M LiI. The 1M LiI solution represents a straightforward case of ion hydration and their effect on the hydrogen bonding efficiency of water molecules. The interactions between the species in this solution are studied by distinguishing ion-water interaction and water-water interaction. The first interaction applies only to water molecules
involved in ion hydration, while the latter describes the bulk water interactions. On the other hand, ion-ion coordination was not observed at the low concentration. The water-water interaction shapes the hydrogen bonding network and determines the strength of the hydrogen bond. Hydrogen bond between H₂O molecules are define by the distance between the hydrogen bonded oxygen and hydrogen [41-43]. The radial distribution function between oxygen and hydrogen (RDF_{O-H}) for pure water yields a hydrogen bond maximum length of 0.240 nm in this simulation. Both the RDF_{O-H} in figure 2.5 and the chemical shift calculations for the 1M LiI solution depicted in table 2.2, show a small deviation from pure water.

![Figure 2.5: Ionic strength dependent effect of LiI salt on first and second shell of water molecules at room temperature.](image)

**Table 2.2:** ¹H MAS NMR chemical shift (δ¹H) of water in the presence of 1M and 9M LiI.

<table>
<thead>
<tr>
<th>δ¹H (ppm)</th>
<th>1M LiI</th>
<th>9M LiI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental value</td>
<td>4.55</td>
<td>4.16</td>
</tr>
<tr>
<td>Molecular dynamics</td>
<td>4.72</td>
<td>3.62</td>
</tr>
</tbody>
</table>

In order to study the chemical interaction between ion and water molecules, we looked into the hydration of ions. To determine the average ion-oxygen distance within the hydration shell, we analyzed the radial distribution function between ion and oxygen (RDF_{ion-O}) in Figure 2.5. The first solvation shell of lithium is represented by the first peak in the RDF_{Li-O}. This peak extends from maximum at 0.170 to a minimum at 0.270 nm, indicating the spatial limit of the solvation shell. The average number of water molecules associated with the ion, the coordination number (CN), is given by the integral of the peak in the RDF_{Li-O} which yields 4 for lithium (Table 2.3).
Table 2.3: Hydrogen bonding distance between the water molecules without and with ions. The observed values are in good agreement with reported literature.

<table>
<thead>
<tr>
<th></th>
<th>water</th>
<th>1MLiI</th>
<th>9MLiI</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H₁₁₀ hb (Å)</td>
<td>1.8</td>
<td>1.78</td>
<td>1.8</td>
</tr>
<tr>
<td>Li-O₁₋₄ (Å)</td>
<td>-</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>CN₁₋₄(OH)</td>
<td>2.0</td>
<td>2.0</td>
<td>0.6</td>
</tr>
<tr>
<td>CN₁₋₄(O)₅₋₈</td>
<td>-</td>
<td>4.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

The hydration water molecules around ions arrange themselves in geometrical shapes whose vertices are determined by connecting adjacent oxygen atoms. These objects are denominated the hydration polyhedra. Our trajectory shows a tetrahedral solvation shell graphically represented in Figure 2.6. There is a second solvation shell of lithium represented by the second peak in the RDFₐ₋₂, as observed for numerous lithium halides [44].

![Figure 2.6: First solvation shell of lithium in the 1M LiI aqueous solution.](image)

The solvation shell of lithium in the solution maintains its shape through almost all the trajectory, moreover no exchange of hydration water molecules was observed. We only registered a short residence time (2.5 ps at most) of a fifth water molecule seldom entering the solvation shell. Behind the high stability of the lithium solvation shell lies the strong oxophilicity of lithium. The effect of lithium on hydration water is also reflected in the NMR spectrum in Figure 2.7. The average chemical shift of pure water is 4.65 ppm and for the lithium hydration water the average yields 5.50 ppm. The water chemical shift (δ₂H) distribution of lithium hydration water is shifted to the right with respect to bulk water. A higher chemical shift reflects a stronger hydrogen bond, in this case formed between hydration water molecules. Furthermore, on average, 6 of the 8 hydrogens in the first solvation shell is hydrogen-bonded to the second solvation shell.
Figure 2.7: Chemical shift distribution for hydrating water and bulk water in the LiI 1M solution. The average for pure water is marked with a black line, while the chemical shift average of lithium and iodine ion hydration water is marked with the red and green line, respectively.

The hydration shell of iodine ion is far less structured than the lithium shell. Hence the first and only peak of the RDF$_{I-O}$ curve in Figure 2.8 shows a broad distribution, yielding an average I-O distance of 0.360 nm.

![Figure 2.7: Chemical shift distribution for hydrating water and bulk water in the LiI 1M solution.](image)

Figure 2.8: Radial distribution function (g(r)) of I$_{ion}$-I$_{ion}$, I$_{ion}$-H$_{o}$, and H$_{o}$-H$_{o}$ in the 1M LiI solution.

The broad shape of the peak indicates a less defined solvation shell than in the case of lithium, also observed by Szazs in the MD calculations of LiI aq. Solution [45]. The weak hydration of iodine ion has also been observed in other publications [46–48]. After measuring the XAS spectrum of iodine, Tanida [49] concluded that the diffuse solvation shell of iodine ion is due to the weak
electrostatic attraction to iodine on hydration water, compared to the hydrogen bond between water molecules.

From the analysis of iodine ion hydration, it is observed that three fourths of the hydrogens in hydration water molecules are hydrogen-bonded to bulk water. Meanwhile, one fourth of the hydrogens in the solvation shell are free to form hydrogen bonds with I. In addition to our analysis of the iodine ion solvation shell, we examined the electrostatic effect of I ion on the chemical shift of coordination water. Our chemical shift \( \delta^1H \) calculations for iodine ion hydration water in Figure 2.7 return an average chemical shift of 4.27 ppm. The weak hydrogen bonds between water and I ion are reflected in the high field shift in the NMR spectrum. Deviations to the left of the bulk water reflect that hydrogen bonds are weaker between water and I ion than between bulk water molecules.

![Figure 2.9: Distribution of the coordination numbers of I ion in the 1M LiI solution throughout the trajectory. The distribution yields an average of 8.3.](image)

Our results also reproduce the preference of water molecules to coordinate themselves to other water molecules rather than iodine ion. Possibly, due to the large ionic radius and high polarizability of iodine ion, it attracts water molecules very weakly, showing some degree of hydrophobic behavior.

As reported in Table 2.2, the average chemical shift for all hydrogens in the 1M LiI solution does not deviate significantly from pure water. Although ions have an important effect on the chemical shift of hydration water, neither lithium nor iodine ion influences the total average. At this concentration, the effect of ions is short range; the chemical shift of bulk water is not significantly affected by the ions.
The small effect on NMR shifts indicates that the hydrogen bond network in the solution is not strongly perturbed.

2.3.3.2 Case of 9M LiI: absence of bulk water

From the RDF and chemical shift calculations for the 1M LiI solution, we concluded that the electrostatic effect of ions on water is short range. Given the agreement between our results in the previous section and the literature values, we stated the reliability of our calculations. Thereby we proceed with the same method for the LiI solution nearer to the saturation point.

Due to the number of ions at higher concentration, a stronger effect of ions on water was expected. Aiming at a thorough description of highly concentrated salt solutions, analysis of MD trajectory of highly concentrated solution of aqueous LiI has been performed.

The 9M LiI solution presents an example of a complex solution, where the water structure can be referred to the LiI.3H₂O crystal structure. The water molecule in the LiI.3H₂O crystal is coordinated to two lithium atoms, and to two iodine ions via hydrogen bonds [50]. In such compound lithium is placed at the center of a nearly regular octahedron of oxygens of distance 0.214 nm. The iodine ion in the crystal is surrounded by twelve oxygen at a distance between 0.370 and 0.375 nm [51].

![Figure 2.10: Radial distribution function (g(r)) of IonLi, IonI, waterO-H and waterO-O in the 9M LiI solution.](image)
Although the water-ion ratio drops significantly from the 1M solution to the 9M solution, the average coordination number of lithium does not change. In contrast with the octahedron of oxygens around the lithium in the trihydrated LiI crystal, lithium in the 9M LiI solution has a coordination number of 4. In addition, the average distance between lithium and hydration water remains the same despite the increase in concentration (Table 2.2). Lithium in the 9M LiI solution maintains the same coordination number as in the 1M solution despite the low water/ion ratio, because most hydration polyhedra share one water molecule at some point in time. When lithium solvation shells are joint in this fashion, the oxygen of the shared water molecule will be facing both cations, forming what so called as an oxygen bridge. Oxygen bridges have been previously observed in both lithium iodide and lithium chloride [52]. Lithium ions connected through two oxygen bridges like in Figure 2.11 have also been observed in the trajectory, nonetheless their presence count for one of the 36 possible Li-Li pairs. Water molecules forming oxygen bridges count for almost one fifth of water molecules in the whole sample. These water molecules connect almost all lithium ions present in the sample, bringing an important degree of order to the liquid structure. Such structure is comparable to the trihydrated LiI crystal where cations are placed in a chain fashion. In the LiI.3H₂O the lithium ions are connected by an oxygen. In the 9M complex solution, such joint varies in time, occurring between different lithium ions.
On an average the coordination number of lithium does not change with concentration, but it shows variations in time depending on the environment near the cation. In the solution, we recognized a chain built of lithium solvation shells joined by oxygen bridges. Generally, the structure of this chain is far from static. Besides few exceptions, oxygen bridges connecting lithium ions are constantly being formed and broken. Half of the lithium ions in the sample share an oxygen with another lithium only for a few picoseconds before swapping to the next neighboring solvation shell. These events lead to variations in time in the coordination number of each single lithium. Apart from this chain of lithium solvation shells, a small portion of water molecules does not participate in the hydration of lithium at all. In the structure of the trihydrated LiI crystal suggested by West, the lithium ion is at the center of an octahedron of oxygens [51]. This structure was also observed for 2 of the 9 lithium ions, thus it did not last throughout the trajectory. The crystal structure discussed by West presents a distance between lithium and oxygen in the hydration shell of 0.214 nm. Similarly to the proposed Li-O distance, our RDF shows an average distance between lithium and oxygen of 0.200 nm.

The variations in the coordination number of lithium result in modifications to the hydration polyhedra. During the rearrangement of hydration water, the
lithium ion is more exposed and thus free to interact with iodine ion. We looked closer at changes in the RDF of Li and I (RDF$_{Li-I}$) in Figure 2.10, to analyze anion-cation interactions. In this study, an ion pair is defined as two ions at a distance which deviates less than 25% from the sum of their ionic radii. When the concentration increases from 1M to 9M, the RDF$_{Li-I}$ shows an additional peak for the high concentration solution, with a maximum at 0.284 nm. The integral of this peak returns a coordination number of 0.3, which reflects limited presence of anion-cation pair. As observed in the trajectory, an anion-cation pair dissociates after a couple of picoseconds and its constituting ions pair up with a different neighboring ion. From our calculations, iodine ions which pair up with lithium, do it in short intervals and iterate between lithium ions linked through an oxygen bridge. This feature is not found in the crystal structure predicted by West, where iodine ion is surrounded by 12 water molecules [51]. In the crystal structure, the distance between lithium and iodine ion is 0.450 nm. This parameter is in good agreement with the peak at 0.470 nm in the RDF$_{Li-I}$ of our trajectory (Figure 2.10).

The RDF$_{I-I}$ curve in Figure 2.10 has a peak with maximum at 0.450 nm; a distance comparable to the sum of two iodine ion radii, approx. 0.420 nm. Iodine ions, with their large volume and high polarizability, experience a weaker coulombic repulsion than smaller ions. Pairs of iodine ion dissolve and form very fast, constantly changing partner. The iodine ion is frequently readjusting its position depending on the competing forces of the species in the solution. For this reason water molecule around iodine ion are subject to varying forces and change position accordingly, and thus are in constant motion. Meanwhile, those water molecules surrounding lithium ion form a more stable structure. Unlike iodine ions, lithium ions keep distances almost double the sum of two ionic radii.
Figure 2.12: Water molecules in the concentrated solution participate in the hydration of several ions.

Evaluating the environment around all water molecules, we observe that water molecules are coordinated to several ions. An average of 6.5 of 10 water molecules are shared between one lithium and several iodine ions (Figure 2.12). As well, water molecules involved in oxygen bridges tend to be part of the solvation shell of two or more iodine ions at the same time. The latter coordination of water counts for almost 15% of all water molecules. We compared the coordination of water in our solution to water in the tryhydrated LiI crystal, where the water molecule is coordinated to two lithium ions, and to two iodine ions. This structure is also observed in between 5 and 6 water molecules in our trajectory. The crystal-like coordination of water only occurs together with an oxygen bridge, creating crystal-like domains around the oxygen bridge. Since oxygen bridges are constantly being broken and formed, so are the crystalline domains of water.
Figure 2.13: NMR Chemical Shift distribution for all hydrogen atoms in the solution and for iodine ion hydration water, classified by the number of iodine ions surrounding the water molecule. The chemical shift of pure water is marked by a black line at 4.65 ppm.

As shown before in the RDF\textsubscript{O-H} in Figure 2.5 we compared the first peaks, representing hydrogen bonded water molecules, for each solution. The integral under this peak returns 0.6 for water in the 9M LiI solution, whereas for the 1M LiI solution and pure water the integral yields 2. The number of hydrogen bonds in water is drastically reduced when increasing the concentration. This is partly because water molecules are preferably coordinated to several ions, as shown in Figure 2.11. This was also observed in LiCl solutions, revealing a breakdown of the hydrogen bonding network at high concentrations \cite{53,54}.

The average chemical shift for the 9M LiI solution given in table 2 is 3.62 ppm. The shift to the right with respect to the chemical shift of pure water is due to the effect of several iodine ions on a single water molecule. Three fourths of the water molecules in the sample are coordinated to three or two iodine ions at the same time, returning a chemical shift of 3.4 and 4.0 ppm, respectively. The chemical shift of water strongly depends on the number of ions surrounding a water molecule (Figure 2.13).

Near the saturation point, the LiI solution is characterized by the absence of bulk water. Instead, water molecules are surrounded by more than one ion. In addition, water molecules participating in lithium hydration occupy an almost fixed position. At high concentration we did not observe non hydrating water molecules.
As shown in Figure 2.13, the effect of iodine ion in the chemical shift is much greater than in the 1M LiI solution. In the highly concentrated solution more than half of water molecules participate in the hydration of three or more iodine ions. Whereas in the 1M LiI solution only a few water molecules were affected by iodine ions, in the saturated solution the electrostatic effect of iodine ion is determinant.

2.4 Conclusions

The influence of ions on the hydrogen bonding efficiency of water molecules is demonstrated using the $^1$H MAS NMR and ATR-FTIR. In the presence of monovalent salts such as Lithium or sodium halide, decrease in the water proton chemical shift is evident. The changes in the OH stretching vibration, which define the hydrogen bonding efficiency between the water molecules, show a decrease in the overall efficiency in the presence of monovalent ions. Further the influence of divalent ions on hydrogen bonding efficiency is also investigated. Remarkably, in the presence of divalent magnesium halide salt, increase in the hydrogen bonding efficiency is observed. The study conclusively demonstrated that upon the incorporation of smaller ions (ionic radii), hydrogen bonding efficiency can be increased. Whereas in the presence of larger ions, decrease in the hydrogen bonding efficiency representing chaotropic behavior is observed, Figure 2.2. The MD simulation conclusively demonstrated changes in the water-ion interaction in the presence of characteristically different Hofmeister ions. Around smaller ion, water can cluster and minimize the loss in hydrogen bonding efficiency, whereas in the presence of larger ions, water molecules hydrogen bonding efficiency decreases due to higher polarizability and ionic radii. In monovalent ions, at higher concentrations closer to the saturation point of the ionic solution, iodide ion plays determinant role in the perturbation of the hydrogen bonding between the water molecules.
References

Chapter 3
Molecular origin of dissolution and suppression of crystallization in polyamides in the presence of ionic solutions

Abstract
High-resolution Nuclear Magnetic Resonance (NMR) under magic-angle spinning (MAS) conditions is applied to study the dissolution process of polyamide 46 (PA46) in the presence of i) water ii) monovalent, and iii) divalent ionic solutions (LiI and CaI$_2$). The samples are sealed in glass capillaries and employing variable-temperature $^1$H MAS NMR spectroscopy the dissolution process of PA46 as a function of temperature and pressure is followed. The purpose of such a study is to obtain molecular insight on the origin of dissolution, and how the dissolution is influenced in the presence of ions. Without ions, and at temperatures close to the dissolution of PA46, two distinct $^1$H resonances from water are observed. One is associated with water in the vicinity of PA46 and the other with water in the bulk state. On further heating the signal from water associated with PA46 dominates. This sudden change in water environments suggests that water molecules, which have escaped the dense hydrogen-bonded network of bulk water, can diffuse into the structure of PA46, triggering the dissolution of PA46. This happens at a temperature that is more than 100 °C below its melting temperature, notably without chemical degradation. On cooling, recrystallization of PA46 from aqueous solution is observed with water molecules incorporated into the structure. Introduction of salts (LiI, CaCl$_2$) in different concentrations leads to an overall weakening of the hydrogen-bonded network for bulk water as expected for this combination of Hofmeister ions. In the presence of MgCl$_2$, at room temperature strengthening of hydrogen bonding efficiency between water molecules occurs. However, on heating depopulation of the hydrogen bonding takes place, causing decrease in chemical shift. The reduced hydrogen-bond efficiency between the water molecules facilitates dissolution of PA46 at much lower temperatures compared to pure water and ultimately results in complete suppression of crystallization even at room temperature.
3.1 Introduction

In this chapter we aim to combine the know-how on water-ion interactions, to have molecular insight in the dissolution and crystallization of hydrogen bonded aliphatic polyamides. To recall, in analogy to natural polypeptides [1], simple synthetic hydrogen bonded polymers such as polyamides (PAs) can be dissolved in ionic solutions, i.e. monovalent and divalent ions in aqueous solution at different concentrations [2-4]. PAs with decreasing number of hydrogen bonding amide motifs include PA46, PA66, PA6, PA12 etc [5]. PAs are semi-crystalline materials with a crystal structure that is based on intermolecular hydrogen bonding between the amide groups of neighboring chains and van der Waal’s interactions between the hydrogen bonded sheets. The chain-folded crystals adopt triclinic or monoclinic unit cell [6]. By means of X-ray diffraction the *interchain* and *intersheet* characteristics of PAs can be easily identified, since they give rise to two strong characteristic diffraction peaks. The Bragg values, *d*, for these peaks are approximately 0.37 and 0.44 nm, respectively. Upon heating of PAs, the two peaks merge into a single peak and the structure adopts pseudo hexagonal packing. The temperature at which this phenomenon occurs is known as the Brill transition temperature (*T*<sub>B</sub>) and is observed in several polyamides, including PA6, PA66, PA46 etc. [8,7]. On further heating above *T*<sub>B</sub>, the PA crystal retains the pseudo hexagonal packing until melting sets in. However, the onset of the Brill transition temperature depends on the number of methylene units between the amine and carbonyl units of the polyamide and specific crystallization conditions of the polymer. PAs with higher number of methylene groups between the amine and carbonyl group, for example PA12, do not show this transition [8]. Ramesh and coworker observed a relatively high *T*<sub>B</sub> for a solution grown PA66 crystal [9], revealing that the *T*<sub>B</sub> in PA66 is directly related to the crystallization conditions. In the case of PA46, *T*<sub>B</sub> can be observed in the temperature range from 190 °C to 245 °C, again depending on the crystallization condition of the polymer. Further studies on PA46 have revealed that the Brill transition is caused by a crystal-to-crystal transformation in the solid state induced by weakening of *intrachain*
hydrogen bonding and *intersheet* van der Waals forces at elevated temperatures [8,10].

Recently, water or water in the presence of ions in their superheated state has been used for the successful dissolution of hydrogen bonded synthetic polymers even below the Brill transition temperature [2]. This includes PAs, which can be dissolved in the superheated state of water, where typical physical conditions are $T \sim 200$ °C and $P \sim 20$ bar. In the superheated state of water, the weakening of hydrogen bonding between PA chains is likely to be further enhanced due to increased diffusivity of water at higher temperatures, thereby facilitating the dissolution process. Upon cooling from the solution, PA recrystallizes with an improved crystal packing, illustrating the good solvent characteristics of water for dissolution and recrystallization of PAs with improved order [4]. The dissolution and crystallization of polyamides utilizing ionic solutions such as lithium chloride, lithium bromide and lithium iodide has been studied by us recently [2]. It was found that PAs in the presence of the same type of monovalent ions, but with increasing ionic strength of the salt solution, facilitates a lower dissolution temperature. Furthermore, the size of the ions selected from the Hofmeister series can reduce the dissolution temperature of the polyamides. Differences in the dissolution temperatures for PAs at varying ionic strength and ion radii are attributed to changes in the physical state of water due to the presence of ions, as discussed in Chapter 2. However, the mechanism involved during the dissolution process, the interaction between water molecules and/or water-ions, and their interaction with the polymer at higher temperatures prior to dissolution is not well characterized and understood.

In this chapter once again we make use of high-resolution nuclear magnetic resonance (NMR) at variable temperature under magic angle spinning (MAS). The structural changes of water molecules in the presence of ions and their influence on dissolution and crystallization of the polyamide PA46 have been also investigated. To follow the structural changes in the presence of water-ions a specially designed capillary that can be placed at high temperatures (approximately 200 °C) in a MAS rotor has been used. For the study monovalent and divalent ions have been
employed. While the structural changes in the water molecules have been followed by NMR, structural changes in the polymer during dissolution process have been investigated by time resolved X-ray diffraction. What follows are the experimental setup and the results obtained. These time resolved NMR studies confirm our previous findings where the dissolution process of PA46 was observed prior to the Brill transition temperature [2,8] and allowed us to follow molecular mechanism involved during the dissolution process.

3.2 Materials and Experiments

3.2.1 Materials

Monovalent (lithium and sodium halides) and divalent (calcium and magnesium halides) salts used in this chapter were obtained from Sigma-Aldrich and used as received. Different salt solutions ranging from 0 to 12.0 M were prepared from freshly de-mineralized water. The polyamide (PA46 Stanyl®) sample was obtained from DSM and used as received.

3.2.2 Nuclear Magnetic Resonance (NMR)

_in situ_ variable temperature _1^H_ MAS NMR experiments were performed on a Bruker DSX-spectrometer operating at 500MHz _1^H_ Larmor frequency using a commercial magic-angle spinning (MAS) double-resonance probe (_1^H-X_) for rotors with 4.0 mm outside diameter. A MAS spinning frequency of 5.0 kHz and a 4 μs _π/2_ pulse, corresponding to 62.5 kHz rf nutation frequency was chosen. All samples were prepared by placing PA46 powder and solvent (water or concentrated LiI solutions) in glass capillaries (from Wilmad Glass) and sealed using a LPG gas flame. During the sample preparation care was taken to avoid any polymer degradation or water evaporation. The temperature was controlled using a Bruker temperature control unit in the range from 30 °C to 220 °C. Reported temperatures are corrected for sample rotation induced temperature changes using a rotation dependent temperature calibration obtained by _207^Pb_ MAS NMR recording the temperature dependent chemical shift of Pb(NO₃). The _1^H_ MAS NMR experiments
were recorded every two minutes with for a continuous temperature ramp of 2.0 °C/min. $^1$H chemical shifts are reported relative to tetramethylsilane (TMS) using adamantane as an external reference[11]. Calibration of $^1$H rf-field strength and shimming was performed at ambient conditions.

3.2.3 Time-resolved wide-angle X-ray diffraction (WAXD)

Time-resolved Wide-Angle X-ray Diffraction (WAXD) was performed at the high-resolution material science beamline ID11 of the European synchrotron radiation facility (ESRF) in Grenoble, France. Two dimensional diffraction patterns were recorded using a 4M CCD camera at 29.8 keV ($\lambda=0.417$ nm) with an X-ray beam size of 50 x 200 μm$^2$ and an exposure time of 10 s to 12 s. The sample to detector distance was calibrated with lanthanum hexabromide. From the obtained diffraction patterns, background scattering and detector response were subtracted and azimuthal integration was performed on the individual arcs to calculate the intensity against the scattering vector $q$. To convert scattering vector information into the $d$-spacing, $d=2\pi/q$ relationship is used, where $q=\frac{(\omega/\lambda)\sin(\theta)}{2}$ Special experimental setup for obtaining the influence of temperature and pressure was discussed elsewhere. The dried powder material was placed in the capillary with ionic water and the capillary was placed in the pressure cell [4]. The sample was heated/cooled with 10 °C/min till the dissolution/crystallization temperature and X-ray data was collected during heating process of the sample.

3.2.4 Differential scanning calorimeter (DSC)

Thermal behavior of PA46 aqueous solution was prepared with 8M LiI and was investigated using DSC instrument from TA Q1000 under nitrogen atmosphere. The sample was heated and cooled from 20 °C to 300 °C at the rate of 10 °C/min. At the limiting temperatures, 20 °C and 300 °C, the sample was left under the isothermal conditions for 3 mins. Prior to the thermal studies, to remove excess
water the samples were dried at 40 °C under vacuum for 12 hours. Special high pressure “large volume capsule” pans were used for DSC measurements.

3.2.5 Gel permeation chromatography (GPC)

To follow the molecular weight before and after experiments GPC measurements were carried out using MIDAS GPC instrument. The polymer sample was dissolved in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP). The sample for GPC measurements was prepared by dissolving 3.0 mg of the polymer in 1ml of the solvent. The detector of the GPC apparatus was calibrated with PMMA standards, for the GPC measurements. The polymer samples obtained from NMR measurements were thoroughly washed using water to remove the ions and were then used.

3.3 Results and Discussion

3.3.1 Dissolution of PA46 in pure water and ionic solutions

In our earlier studies, superheated water or water-ion solutions are used as solvent for the dissolution of hydrogen bonded aliphatic polyamides. In chapter 2, water-ion interactions are investigated in the presence of Hofmeister ions. Here, we address the questions “What is the molecular origin of the dissolution process? What causes water to be a good or poor solvent in the presence of ions?” Figure 2.2 shows that for the same ionic strength, the size of an ion can enhance/reduce the hydrogen bonding efficiency of water. Depopulation or population of hydrogen bonding between the water molecules, in the presence of ions, will have implications in the dissolution temperature of polyamides. Our previous time resolved X-ray diffraction studies demonstrate that the dissolution temperature of polyamides decreases with the increasing ionic strength of monovalent ions and the dissolution process occurs before the Brill transition temperature. On cooling the solution, depending on the ionic concentration and ionic size crystallization can be fully suppressed. These studies were limited to monovalent LiI and LiBr salts. In this chapter, changes in the hydrogen bonding efficiency of water as a function of
temperature, in the presence of ions and the polymer, has been explored by using $^1$H MAS NMR. To follow the structural changes during the dissolution process, time resolved WAXD studies complemented with $^1$H MAS NMR, $^{13}$C CP/MAS NMR and FTIR studies have been performed. To have molecular insight on the dissolution process it is a requisite to investigate modifications in the hydrogen bonding of PA46 on heating. What follows are the conformational changes in methylene segments, and the resultant changes in the hydrogen bonding efficiency between the amide motifs, during heating of PA46. For these studies $^{13}$C CP/MAS NMR has been employed.

### 3.3.2 Conformational changes in PA46 on heating

Figure 3.1: Variable temperature $^{13}$C($^1$H) CP/MAS NMR spectra depicting the conformational changes of carbonyl and methylene segments in PA46. Assignment of the methylene groups between amine-amine ($\alpha_N$, $\beta_N$) and carbonyl-carbonyl ($\alpha_C$, $\beta_C$) moieties of PA46 is shown in (a).

Figure 3.1a shows peak assignment of methylene segments between the amine and carbonyl group, and carbonyl carbon (CO) for PA46 [3]. Figure 3.1b shows $^{13}$C($^1$H) CP/MAS spectra, revealing changes in the $^{13}$C chemical shifts of the
methylene groups along the PA46 polymer chain as a function of temperature. At
41.0 °C, $^{13}$C spectra shows relatively broad peaks for the carbon atoms assigned to
$\alpha_N$, $\alpha_C$, $\beta_N$ and $\beta_C$, indicating broad conformational distributions and very low
molecular mobility along the polymer backbone. The observed chemical shifts
assigned to the methylene units are characteristic for the crystalline state of PA46
[12]. On heating, the changes in $^{13}$C chemical shift of specific PA46 sites acquired
from Figure 3.1b, are summarized in Table 3.1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$^{13}$C CP/MAS NMR chemical shifts (ppm) of PA46 in the solid state.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha_N$ CH$_2$</td>
</tr>
<tr>
<td>41.0</td>
<td>42.0</td>
</tr>
<tr>
<td>69.5</td>
<td>41.2</td>
</tr>
<tr>
<td>107.3</td>
<td>41.0</td>
</tr>
<tr>
<td>145.2</td>
<td>40.9</td>
</tr>
<tr>
<td>183.1</td>
<td>40.9</td>
</tr>
<tr>
<td>211.5</td>
<td>40.9</td>
</tr>
</tbody>
</table>

In general, the interchain hydrogen bonding in polyamides weakens on
heating, due to the decrease in the electron exchange efficiency between amid
motifs. On increasing temperature, CO signal shifts from 173.5 ppm (41.0 °C) to
175.2 ppm (211.0 °C). The increase in the chemical shift value of the CO signal
indicates better shielding of carbonyl site due to reduction of the electron exchange
between the amid motifs causing an increase in electron density around the
carbonyl site. Considerable changes in the chemical shift are also observed for the
methylenic segments between the amide motifs. Broad peaks of $^{13}$C methylene
carbon, in the range of 45.0 to 20.0 ppm, are indicative of a broad conformational
distribution and very low molecular mobility at 41.0 °C. On heating, the narrowing
of the peaks indicates temperature induced mobility within the methylene units of
PA46. However, the temperature response of the chemical shift for individual
aliphatic carbon sites along the PA46 chain differs. The aliphatic carbon $\alpha_N$ shows
chemical shift at 42.0 ppm (41.0 °C), which upon heating moves to a lower value of
41.2 ppm (69.5 °C). The decrease in the chemical shift is associated to the sudden
release of constraint to the aliphatic diamine segment that is likely to be imposed
during crystallization of the polymer [13]. Unlike $\alpha_N$, the other methylene segments
(\(\alpha_C\), \(\beta_N\) and \(\beta_C\)) between diamine and carbonyl show a gradual increase in the chemical shift and peaks associated to them become narrower upon heating. The peaks assigned to \(\alpha_C\) and \(\alpha_N\) show the gradual appearance of a shoulder upon heating. For an example, at 145.0 °C \(\alpha_N\) carbon shows an asymmetric peak at 40.9 ppm and with a shoulder at 39.5 ppm. On heating to 211.5 °C the shoulder changes into a well resolved peak at 39.5 ppm. This new signal is assigned to the non-crystalline conformation of the \(\alpha_N\) carbon [14], originating from the introduction of gauche conformer within the aliphatic diamine segment of the polymer chain. On further heating, the \(\alpha_C\) carbon signal becomes asymmetric at 183.1 °C, that could be deconvoluted into a peak at 37.0 ppm and a shoulder at 36.0 ppm. The shoulder develops into well resolved peak at 211.5 °C. Similar to the \(\alpha_N\) gauche conformer, the signal at 36.0 ppm is assigned to the non-crystalline gauche conformers of the \(\alpha_C\) signal. The systematic introduction of gauche conformers in the aliphatic segments suggests enhanced mobility, represented by sharpening of the peak. This mobility is likely to cause the translational motion of the gauche conformer leading to the crank-shaft motion as suggested by Tashiro et al [10]. It is to be recognized that the shoulder in the \(\alpha_N\) peak is observed prior to \(\alpha_C\), this suggests that the hydrogen bonding of NH weakens prior to CO, a result in accordance with Tashiro et al and our earlier reported data. What follows is our study in the conformational changes of PA46 and its influence in the dissolution process in the presence of water and water-ion. For the purpose in-situ \(^1\)H MAS measurements are performed.

### 3.3.3 Dissolution of PA46 in water and ionic solution of monovalent salt LiI

Recently there have been several publications depicting dissolution of PA46 and polyamides in general [4,15]. These studies highlighted crystallographic and conformational changes during the dissolution process of the synthetic aliphatic polyamides in water. To recall, in the presence of 8M LiI amorphous PA46 can be obtained at room temperature. The amorphous state is perceived due to the shielding of hydrogen bonding of amide motifs in PA46. The phenomenon of
shielding and de-shielding process has been addressed in detail in our recent publication [3].

In this chapter we aim to follow the dissolution of PA46 by monitoring in-situ conformational changes of the polyamide combined with the hydrogen bonding efficiency of water in its pure state, and in the presence of salt such as LiI. To follow the changes $^1$H MAS NMR at elevated temperatures has been used. To recall, the sample PA46 with water and water-ion is encapsulated in the sealed glass capillaries.

The glass capillary having 30% (w/w) of PA46 is sealed with water and heated in the NMR probe from room temperature till the dissolution occurs. Subsequently, to follow the crystallization process the solution is cooled from the dissolution temperature to room temperature. In the whole process, no loss of water occurs from the sealed sample tube. The same heating and cooling cycle is repeated for PA46 and water-LiI. The results obtained for heating and cooling cycles of PA46 in water are shown in Figure 3.2.

Figure 3.2: Time resolved $^1$H MAS NMR measurements following dissolution of PA46 in water. PA46 with water was sealed in glass capillaries prior to the experiments. The sealed capillaries were placed in a 4 mm MAS rotor. All experiments were performed at 11.75 T (500.1 MHz for $^1$H) using a spinning frequency of 5.0 kHz. The dash line in Figure on the left refers to the spectra shown on the right at the specific temperature. In the spectra on the right, M and B represent mobile and bulk water, where T in the spectra at 60 °C corresponds to water molecules trapped in the crystalline domains of PA46.
For PA46 immersed in water, Figure 3.2 depicts water proton chemical shift at 4.6 ppm, 38.0 °C. The water proton chemical shift indicates the hydrogen bonding efficiency between the water molecules. With increasing temperature the water proton chemical shift gradually shifts to lower values. The shift to lower values indicates the weakening of the hydrogen bonding efficiency between water molecules [3]. Upon heating to ~130 °C water vapor pressure of ~4 bar is built up and a new signal (3.2 ppm) next to the signal of bulk water (3.4 ppm) is observed (see the NMR spectra on right side at 130.0 °C during heating cycle). The new proton signal at 3.2 ppm indicates the presence of some water molecules in a different chemical environment having weaker hydrogen bonding efficiency than water molecules in the bulk state – thus the appearance of mobile water. The comparison with Figure 2.3a suggests that the difference in chemical environment of some water molecules arises due to the presence of PA46 i.e. possible molecular interaction of water molecules with the polyamide. On heating further, along with the increase in the intensity of the chemical shift of mobile water molecules at the expense of bound water molecules, the appearance of PA46 methylene segment protons also occurs. This indicates gain in mobility of polymer proton due to interaction of water molecules, especially in amorphous domain of the polymer.

On heating further till ~152 °C, continuous drift in the chemical shift of the bulk water and mobile water proton to lower values is observed. However, the signal of the bulk water tends to decrease in intensity, whereas the intensity of the signal attributed to the mobile water increases. (See right side NMR spectra at 150.0 °C during heating cycle). This suggests an increase in the number of the mobile water molecules at the expense of the bound water molecules. Around ~152 °C, along with the increase in the mobile water signal, the appearance of five new sharp proton signals is observed with relatively high intensity is observed. These five new proton signals can be assigned to PA46 dissolved in water (for assignment see Figure 3.1a), indicating the dissolution of the polymer in superheated water. The enhanced exchange process from the bulk to the mobile water, combined with the appearance of the sharp PA46 chemical shift peaks with maximum intensity, suggest that the dissolution is triggered because of the
increasing number of mobile water molecules. To recall, Figure 3.1b shows that in the vicinity of 152.0 °C PA46 also shows presence of gauche conformers between the amide motifs that lead to high chain mobility along the c-axis. In PA46, motion of the gauche conformers is likely to influence the hydrogen bonding efficiency between the amide motifs. In the PA46/water system at 152.0 °C the combined effect of reduced hydrogen bonding efficiency between the amide motifs and the enhanced water mobility is likely to be the cause for the sudden collapse of the PA46 crystalline lattice leading to the dissolution process. On heating beyond 152.0 °C the chemical shifts corresponding to PA46 and water molecules are retained. This unique experiment clearly suggests that water is a good solvent for PA46 at the elevated temperatures and leads to the formation of single crystals having tight folds as shown earlier [4].

To follow the crystallization process of PA46, the solution is cooled to room temperature and the proton spectra are recorded while cooling. Figure 3.2 show that while cooling, around 130.0 °C, a sudden disappearance of the proton chemical shifts associated to PA46 takes place. The sudden disappearance of the chemical shift is indicative of PA46 crystallization that causes drop in the mobility with the formation of rigid conformers. The NMR spectra at 130.0 °C, on cooling, are depicted on the right side of Figure 3.2. The increase in the population of bulk water molecules (3.4 ppm), and decrease in the population of mobile (3.2 ppm) water molecules is evident with changes in the peak intensity. The lower chemical shift (3.2 ppm) at 130.0 °C is associated with the mobile water molecules having restricted mobility, where the restriction arises due to possible interactions of water molecules with PA46. The higher chemical shift (3.4 ppm at 130.0 °C) of water is related to water molecules residing in the bulk state. Upon cooling to 60.0 °C, the proton chemical shift related to polymer backbone disappears completely. Two proton chemical shifts of water molecules at 60.0 °C, corresponding to bulk water (4.3 ppm) and trapped (T) water molecules (4.1 ppm) are evident. The latter is associated to trapped water, because the peak is relatively broad and intensity is significantly lower than bulk water. The observed spectra at 60.0 °C is in accordance with our earlier findings where we also associated the chemical shift at
higher values (5.0 ppm) to the trapped (bound) water, though the position is slightly different because in the earlier work experiments were performed at 20.0 °C and the unbound water was removed by evaporation at 100.0 °C [4]. The presence of bound water in bio or synthetic hydrogen bonded polymers is reported in literature [16]. In the water crystallized polyamides, bound water proton was previously reported at the chemical shift of 5.0 ppm and further strengthened with Fourier Transform Infra-Red Spectroscopy (FTIR), where the bound water in the vicinity of the PA46 amide motif arises as a new 1395 cm⁻¹ band [4]. The NMR study reported in this chapter complements structural changes observed using the time resolved WAXD. These studies demonstrated the dissolution process of PA46 just below the Brill transition temperature and also the crystallization process on cooling from the solution. Thermal transitions during the dissolution and crystallization processes have been supplemented by the thermal analysis studies reported earlier [3].

The earlier studies performed on polyamides while heating from room temperature to melt, by us and several other groups conclusively demonstrated that prior to the Brill transition temperature methylene sequences between the NH motifs gain higher mobility compared to that in the CO motifs [10]. The cause for this distinction in the mobility gained on heating is attributed to the higher constraint in the methylene units between the NH groups compared to the CO groups. These findings were supported by spectroscopy techniques ranging from FTIR, Raman and NMR. However, in the presence of water no such distinction in the mobility of the methylene segments between the amine and carbonyl groups could be made. The ¹H NMR spectra show that all methylene sequence gain mobility at the same time. The cause for this simultaneous gain in mobility of the methylene units can be attributed to fast diffusion of water molecules in polyamides that perturbs hydrogen bonding between the neighboring amide motifs independent of the NH or CO groups.

To understand the influence of water-ion interaction and ionic concentration on dissolution and crystallization of polyamides, in-situ ¹H MAS NMR measurements are performed on PA46 with LiI ions in water. Once ions are
incorporated in water, the hydrogen bonding efficiency of water molecules is influenced (Figure 2.3b). The change in the hydrogen bonding efficiency of water molecules in the presence of ions will have influence on the dissolution process of polyamides. What follows is our study on the dissolution process of polyamide in the presence of LiI salts.

Figure 3.3: Time resolved $^1$H MAS NMR measurements following dissolution of PA46 in monovalent salts, (a) 1M LiI, and (b) 8M LiI. The polymer and ionic solution were sealed in glass capillaries prior to the experiments. The sealed capillaries were placed in a 4 mm MAS rotor. All experiments were performed at 11.75 T (500.1 MHz for $^1$H) using a spinning frequency of 5.0 kHz.

Figures 3.3b and 3.3c depict changes in the chemical shift of water and PA46 (30% w/w) during heating and cooling in the presence of 1M and 8M LiI aqueous solution sealed in the glass capillary. At room temperature the 1M and 8M LiI aqueous solution shows water proton chemical shift at 4.5 ppm and 4.1 ppm, respectively. The difference in the chemical shift with the increasing ion concentration suggests weakening of the hydrogen bonding efficiency between the water molecules with increasing ionic concentration. On increasing temperature the water proton chemical shift moves to lower values that are indicative of the temperature induced weakening of the hydrogen bonding efficiency between the water molecules.
For 1M LiI, at ~140 °C, the mobile water proton signal is observed at the chemical shift of 3.3 ppm, which shifts to lower values with increasing temperature. At ~145 °C proton chemical shift of the PA46 appears. The appearance of five distinct peaks are associated with proton of NH and four methylene segment protons $\alpha_N$, $\alpha_c$, $\beta_N$ and $\beta_c$ at 6.8 ppm, 2.9 ppm, 2.0 ppm, 1.4 ppm and 1.3 ppm, respectively. The appearance of the new chemical shifts suggests dissolution of PA46 around 145.0 °C in the presence of 1M LiI solution. The observed dissolution temperature is lower than the temperature observed without salt, Figure 3.2.

On increasing the salt concentration to 8M LiI aqueous solution, dissolution of the polyamide is observed even below the boiling point of water at ~95 °C, as apparent from the appearance of five sharp peaks belonging to the protons of NH and the four methylene units $\alpha_N$, $\alpha_c$, $\beta_N$ and $\beta_c$ at 7.1 ppm, 3.0 ppm, 2.1 ppm, 1.4 ppm and 1.3 ppm respectively. The difference in the chemical shift positions is attributed to the observed dissolution temperature and shielding of the amide motifs with the ions.

The comparison with Figure 3.2, clearly show that compared to the pure water the dissolution temperature lowers by 10.0 °C and 60.0 °C in the presence of 1M and 8M LiI salt in water. It is remarkable to notice that in the presence of 8M LiI solution dissolution occurs even below the boiling point of the pure water. The distinct difference in the dissolution temperature in the presence of the ions reveals that the hydrogen bonding between the water molecules is strongly perturbed in the presence of LiI (Figure 3.3a, 3.3b) causing higher diffusion of water molecules to PA46 at lower temperatures. The reduced hydrogen bonding efficiency between the water molecules in the presence of salt and polymer is evident from the decrease in the chemical shift of water proton at room temperature and at elevated temperatures. In contrast to water (Figure 3.2) and 1M LiI solution (Figure 3.3a), in the presence of 8M LiI solution (Figure 3.3b), only one $^1H$ chemical shift is observed. In Figure 3.3b, the presence of only one chemical shift prior to dissolution, at 3.7 ppm, is attributed to the high water mobility even at lower temperatures. The higher water mobility causes ease in interaction of water molecules with the hydrogen bonding motifs of polyamides thus suppressing the
dissolution temperature. On cooling from the dissolved state of the polyamide in the ionic solution noticeable changes are observed during crystallization process, revealing the importance of ionic concentration (Figure 3.3b).

To recall, in 1M LiI aqueous solution, with the crystallization of PA46 at 120.0 °C the chemical shifts associated with the methylene units of the polymer disappear, and a bound water proton signal at 3.1 ppm, 115.0 °C, is observed (Figure 3.3a). Compared to the 1M LiI, the results obtained on cooling of PA46 from solution in the presence of 8M LiI are remarkable (Figure 3.3b). On cooling even to 40.0 °C high proton mobility associated with polyamides is retained. The presence of high mobility suggests absence of crystallization even at these low temperatures. Considering that the low temperatures are employed during heating and cooling cycles, combined with the absence of any new chemical shift, degradation of the polyamide is fully excluded. The absence of degradation has been further confirmed by GPC study performed on PA46 samples prior and after the experiments. The GPC results are summarized in Table 3.2. Within the experimental errors no noticeable changes in the molecular weight or molecular weight distribution are observed.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Crystallization medium</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (g/mol)</th>
<th>M&lt;sub&gt;w&lt;/sub&gt; (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA46 As obtained</td>
<td>27660</td>
<td>80500</td>
<td>2.91</td>
<td></td>
</tr>
<tr>
<td>PA46 H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>27300</td>
<td>78500</td>
<td>2.87</td>
<td></td>
</tr>
<tr>
<td>PA46 1M LiI</td>
<td>27500</td>
<td>80000</td>
<td>2.90</td>
<td></td>
</tr>
<tr>
<td>PA46 8M LiI</td>
<td>28290</td>
<td>81500</td>
<td>2.88</td>
<td></td>
</tr>
<tr>
<td>PA46 1M CaI&lt;sub&gt;2&lt;/sub&gt;</td>
<td>25800</td>
<td>75500</td>
<td>2.92</td>
<td></td>
</tr>
<tr>
<td>PA46 6M CaI&lt;sub&gt;2&lt;/sub&gt;</td>
<td>27500</td>
<td>80500</td>
<td>2.92</td>
<td></td>
</tr>
</tbody>
</table>

The observations made by NMR studies on the dissolution of PA46 in the presence of ions have been further strengthened by WAXD studies. Dissolution of PA46 in 8M LiI aqueous solution is followed by time-resolved WAXD measurements in closed glass capillary having ~30 %w/w of the polymer in the solution. These studies also confirm considerable suppression of crystallization in PA46 at room temperature (also see the appendix B.3.1).
3.3.4 Dissolution of PA46 in the ionic solution of divalent cation CaI$_2$ salt

Dissolution process of the polyamide, PA46, in the presence of divalent cation is depicted in Figure 3.4. For the study, low 1M and high 6M salt concentrations have been used. At the low salt concentration partial shielding of the hydrogen bonding is expected, whereas at the high salt concentration the hydrogen bonding motifs of PA46 are likely to be completely shielded resulting into amorphous PA46 at room temperature. Such a possibility has been explored in the presence of LiI in our earlier publication [3] (also see appendix B.3.1). Under the same experimental conditions, in the presence of 1M (Figure 3.4a) as well as 6M (Figure 3.4b) CaI$_2$, the proton of water shows decrease in the chemical shift to lower ppm compared to the bulk water, 4.7 ppm. The shift to the lower values suggests depopulation of hydrogen bonding between the water molecules resulting into the decrease in the hydrogen bonding efficiency in the presence of the divalent cation. As anticipated, higher shift to the lower values is observed in the presence of 6M CaI$_2$, 4.2 ppm, compared to the 1M CaI$_2$, 4.4 ppm. In this respect, even at 38.0 °C, unlike MgCl$_2$ (Figure 2.3c) CaI$_2$ acts as a chaotropic salt.

![Figure 3.4](image_url)

Figure 3.4: Time resolved $^1$H MAS NMR spectra showing dissolution of PA46 in the presence of (a) 1M CaI$_2$, and (b) 6M CaI$_2$ solution. The experiments have been performed to follow dissolution and crystallization process during heating and cooling cycle.
Similar to the monovalent ions, Figure 3.3, the proton chemical shift decreases to lower values on heating. The decrease confirms additional depopulation of hydrogen bonding on heating. In the vicinity of 140.0 °C, five new sharp peaks appear. For 1M CaI₂ the position of the new peaks is similar to that observed for LiI, Figure 3.3. The appearance of the peaks is indicative of the dissolution process that arises with the enhancement in chain mobility due to the random coil conformation that the chains can adopt. Though, unlike in the presence of 1M LiI or pure water, no splitting of the proton water peak prior to the dissolution process is observed, which may be attributed to (a) the divalent larger cation compared to the small monovalent cation, (b) the presence of two fold greater molar concentration of the anion in CaI₂ compared to the LiI. The chaotropic nature of the I⁻, further adds to the depopulation of the hydrogen bonding between the water molecules and the resultant increase in water mobility. Similar changes are also observed in the presence of 6M CaI₂, though at the lower temperatures. The decrease in the dissolution temperature is attributed to the enhancement in water mobility at higher salt concentration, as apparent from the chemical shift. However, prior to the dissolution, compared to the 1M CaI₂ solution distinct differences arises in the 6M CaI₂ solution.

Figure 3.4b shows that prior to the appearance of the chemical shifts related to the protons of methylene units $\alpha_N$ and $\alpha_C$, at temperatures lower than 15.0 °C, sharp proton peaks associated with the proton of NH and methylene units $\beta_N$ and $\beta_C$ are observed. The appearance of these peaks at considerably low temperatures (115.0 °C), and their complete absence in Figure 3.4a, suggest that in the presence of CaI₂ intersheet hydrogen bonding weakens to an extent that higher mobility in the amide motifs combined with the methylene units ($\beta_N$ and $\beta_C$) is perceived prior to the adoption of the random coil conformation. On heating further, by 15.0 °C, the random coil state is obtained. One of the possibilities of the establishment of higher mobility in the proton of amide motifs could be attributed to the strong interaction of the divalent cation with the carbonyl group. On heating, such a possibility may arise due to weakening of the hydrogen bonding between chains in the crystalline lattice. The decrease in the hydrogen bonding between the chains in
the intrasheet becomes apparent with the decrease in the Bragg’s spacing of the 100 diffraction peak, on heating. These findings suggest strong interaction of Ca$^{2+}$ with the amide motifs leading to the unique dissolution process compared to Li$^+$ salts. We will come back to above subject at the end of this chapter.

On cooling, the 1M CaI$_2$ solution shows simple disappearance of the five sharp peaks, which is indicative of the suppression in the mobility of the protons in the polymer chain that arises with crystallization. Similar to Figure 3.3b no differences in the water proton mobility at room temperature are observed. However, on cooling the 6M concentration of CaI$_2$, mobility of the $\alpha_C$ and the $\alpha_L$ protons disappear initially, whereas the $\beta_C$ and $\beta_N$ together with the proton of NH retain mobility. On cooling further, the remaining mobility of the protons is further lost. This may be attributed to the crystallization process that weakens the binding of the calcium ions with the amide motifs. To have further insight on the mechanism involved WAXD studies have been performed.

![Figure 3.5](image)

**Figure 3.5:** WAXD pattern of PA46 in the presence of 6M CaI$_2$ at elevated temperatures (a) 25.0 °C, (b) 140.0 °C, (c) 150.0 °C (dissolved state) and (d) 40.0 °C (upon cooling from the dissolved state). At room temperature intersheet and interchain diffraction ring of triclinic packing can be observed, while prior to dissolution a single diffraction ring indicates pseudo-hexagonal phase of PA46. Upon cooling from the dissolved state, at 40.0 °C an amorphous halo indicates amorphous of PA46.

Figure 3.5 shows WAXD pattern of PA46 in the presence of 6M CaI$_2$. Two diffraction peaks associated with the interchain and intersheet Bragg distance are
observed at the start of the experiments [6]. On heating while the 100 diffraction peak moves to lower d-spacing, the 110/010 diffraction peak shows normal thermal expansion. The contraction of the interchain distance in the hydrogen bonding sheet arises due to weakening of the hydrogen bonding between the amide motifs, as stated earlier. Around 100 °C, the two peaks merge into one suggestive of the crystallographic transformation from triclinic to pseudo-hexagonal phase. The observed Brill transition in the presence of CaI₂, at 100.0 °C is much lower than anticipated for these polymers in the absence of salts (also see appendix B.3.1). Figure 3.5b depicts single diffraction peak above the Brill transition temperature. On heating, beyond 140.0 °C, dissolution occurs. The X-ray diffraction recorded after dissolution is shown in Figure 3.5c. On cooling to room temperature no crystallization peak could be detected, Figure 3.5d. At first instance, conclusions drawn from Figure 3.5d may appear in contradiction with the NMR data reported in Figure 3.4b. The contradiction may be resolved by considering that NMR probes changes in the local length scale and does not require large correlation lengths. Thus the formation of small local crystalline domains that cannot be seen by WAXD can be anticipated. Such a possibility is confirmed on heating the samples to 100.0 °C in the solid state NMR where melting occurs at 100.0 °C only. What follows is the experimental observation.

Figure 3.6a shows compiled NMR data of PA46 crystallized from solution in the presence of 8M LiI and 6M CaI₂ at 20.0 °C. In accordance with the Figure 3.3b, the proton NMR spectra shows high proton mobility arising due to random coil conformation that chains are likely to adopt in the amorphous state. These findings are in accordance with our recent publication where shielding of hydrogen bonding has been used to obtain uniaxially drawn fibers above the glass transition temperature of the amorphous PA46, 20.0 °C [3]. The hydrogen bonding was restored and the oriented structure was fixed with removal of salt by heated water. In the Figure 3.4b, PA46 in the presence of 6M CaI₂ spectra at 20.0 °C shows the absence of the proton mobility in PA46.
The NMR results in combination with WAXD, suggests presence of small crystalline domains having the near absence of long range order that limits the appearance of diffraction peaks. Detailed room temperature FTIR study on PA46 in the presence of 8M LiI and 6M CaI\textsubscript{2} is investigated. This study suggests that the cation stays within vicinity of amide motifs of PA46 (see appendix B.3.2). On heating the sample to 100 °C, Figure 3.6b and 3.6c, in the NMR probe, the appearance of the mobile protons is evident, confirms the melting of the small crystalline domains. The low broad melting temperature, ranging between 60-100 °C, compared to 295 °C in the absence of salt, further confirms the presence of small crystalline domains. The high melting temperature of crystals is restored on removal of salt by heated water.

### 3.4 Conclusions

The study conclusively demonstrates the influence in the hydrogen bonding efficiency of the water molecules in the presence of monovalent and divalent cationic salts and its implications in dissolution of aliphatic polyamides. As
anticipated hydrogen bonding of water molecules tends to decrease with increasing temperature. In the presence of polyamide PA46, on heating two different mobilities in the water molecules are observed. The higher mobility is associated with the water molecules in vicinity of the polyamide and the lower mobility to the bulk water. The population of water molecules in bulk decreases with increasing temperature. The enhanced water mobility facilitates the dissolution process of polyamide at temperatures even 100.0 °C below the melting point. On cooling, crystallization from the solution is observed along with the appearance of a chemical shift associated with the bound water molecules to the polyamide. In the presence of salts, LiI and CaI$_2$, decrease in the chemical shift of the water molecules is observed even at room temperature. The decrease suggests suppression in the hydrogen bonding efficiency between the water molecules. The suppression facilitates the dissolution of the polyamide even at lower temperatures. It is shown that in the presence of 8M LiI solution, on cooling crystallization of the aliphatic polyamide can be fully suppressed. In the presence of 6M CaI$_2$ dissolution of PA46 is observed around 140.0 °C compared to 185.0 °C in the presence of pure water. Prior to dissolution enhanced mobility in the amide motifs and methylene units ($\beta_3$ and $\gamma_3$) between the amide groups is registered by $^1$H NMR. The results suggest the binding of divalent calcium ions to PA46 hydrogen bonding motifs. On complete dissolution the polymer chains adopt random coil conformation, which on cooling tend to crystallize forming small crystalline domains that tend to melt at temperature as low as 100.0 °C. These conclusions have been drawn from the combined study performed by using WAXD, $^1$H NMR, FTIR and DSC. These studies that can be extended to hydrogen bonding materials in general support our earlier findings on synthetic polyamides and conclusively demonstrate that the dissolution process of the polymer is the physical phenomenon that takes place with the changes in the hydrogen bonding efficiency of the solvent and the solute.
References


5 General polyamide (PA) nomenclature features numbers that represent the numbers of carbon atoms present in the monomers. A single number x represents a di-functional monomer with x carbon atoms, while two successive numbers xy indicate the number of carbon atoms in the mono-functional diamine and diacid or diacyl monomers respectively.


10 Tashiro, K.; Yoshioka, Y. *Polymer* 2004, 45, 6349–6355.


12 Ando, I.; Asakura, T. In *Solid state NMR of polymers, Studies in Physical and Theoretical Chemistry*, 1998, Chapter 12.; Vol. 84


Chapter 4

A study on the oxalamide based model compounds

Abstract

In this chapter, the influence of hydrogen bonding efficiency on the self assembling process of two oxalamide motifs based model compounds, having polar (Diethyl 4,5,14,15-tetraoxo-3,6,13,16-tetraazaotadecane-1,18-dioate (\(\text{Di} \text{ala oxa (CH}_2)_6 \text{oxa Di} \text{ala}\)) and non polar (\(N',N^2\)-bis (3-methoxypropyl) 2,11-dioxo-3,10-diaza-1,12-dodecanamide (Meo oxa (CH}_2)_6 \text{oxa Meo}\)) end groups are discussed. The model compounds are crystallized from their melt state and superheated state of water, where the latter is used as a solvent with the aim to make defect free crystals. Temperature dependent changes in the model compounds are examined using DSC and X-ray diffraction techniques. Irrespective of the crystallization history, both model compounds show two phase transformations, solid to solid, prior to melting. Solid state NMR and FTIR spectroscopy are employed to follow conformational changes prior and during the phase transformations. The low temperature crystal-crystal phase transformation is induced with conformational changes at the end group, whereas the high temperature phase transition arises with the induction of gauche conformers, in the aliphatic units between the oxalamide motifs. In the model compounds, crystallized from the superheated state of water, the conformational and the crystallographic changes associated with the phase transformations are found to be more pronounced, confirming our earlier studies that water is a good solvent for hydrogen bonded aliphatic amides facilitating formation of defect free crystals. In the model compound having the polar end group, during the low temperature phase transformation, the transition is induced with gain in mobility of the carbonyl end group whereas the origin of high temperature phase transition, the induction of gauche conformers remains the same. With the high temperature phase transition the crystal packing, of both oxalamides, changes from triclinic to conformational disordered (pseudo) hexagonal phase.
4.1 Introduction

Hydrogen bond formation is donor-acceptor interaction between an electron rich and an electron poor atom, with the specific involvement of hydrogen atoms [1]. In synthetic aliphatic or aromatic hydrogen bonded polymers, such as polyamides or amide based model compounds, formation of inter or intra molecular hydrogen bonding between the amide motifs determines the physical properties, performance and eventual applications. The self-assembling process of macromolecules is driven by the secondary interactions where the simultaneous formation of hydrogen-bonded sheet and their stacking results in triclinic or monoclinic unit cell at room temperature [2]. The development of this unique crystal structure lead to anisotropy in the strength of the secondary interactions within the hydrogen bonding planes and between the planes, where the latter is dominated by weak van der Waals interaction. The hydrogen bonding strength within the plane can be influenced by the density of hydrogen bonding motifs, which can be tailored by varying the number and distance between them. Among several possibilities available where the hydrogen bonding can be influenced by tuning the number of amide motifs, in oxalamide two amide motifs are linked to each other in opposite direction (Figure 4.1). Since these oxalamides could be obtained from natural resources such as oxalic acid, a derivative of sugar, they provide a possibility to develop bio-based macromolecules.

Figure 4.1: Chemical structure of oxalamide motif.

Comparison of structural features of amide and oxalamide motifs is discussed by Casanovas and coworker using ab initio quantum mechanical and density functional calculations [3].Thus in comparison with the amide motifs, in oxalamides the linkage of the two amide motifs in the opposite direction provides strong intermolecular interaction within the hydrogen bonding planes. Moreover, in oxalamides the formation of two intramolecular C₃ interactions are predicted due to
presence of the two amide motifs next each other. The interaction potential of oxalamide motifs as a viscosity modifier for heptylcyclohexanecarboxylic acid has been further demonstrated by Zinic et al [4]. Concentration and temperature dependent self-assembling of chiral bisoxalamide model compound in heptylcyclohexanecarboxylic acid is observed with formation of smectic B and nematic liquid crystalline phases. This suggests supra-molecular assembling characteristic of oxalamide motifs due to intermolecular interaction. These features are prime importance in the polymers where presence of inter or intra molecular interaction determine the properties of the polymers.

Recently oxalamide motifs based aliphatic hydrogen bonded polymers are successfully synthesized, as a promising engineering polymeric materials [5-8]. Shalaby et al synthesized the polyoxalamide designated them as nylon 2,2, having chemical structure as \((\text{NH-CO-CO-NH-(CH}_2\text{)}_n\text{)}\), where \(n\) indicates the number of methylene segment included in aliphatic units. The polyoxalamide (nylon 2,2) show high melting temperature (~400 °C) and are thermally unstable close to the melting temperature [9], which limits application of the polymer. Gaymans et al synthesized nylon 4,2, having melting temperature in the range of 388 °C- 392 °C with 70 % crystallinity. Later Chatani et al reported nylon 6,2 having triclinic packing with similar crystal structure as the \(\alpha\) form of PA66 [8]. Puiggali et al synthesized polyoxalamides having long methylene segments, nylon 9,2 or nylon 12,2 [6,7]. WAXD study of nylon 12,2 reveals polymorphic structure, consisting \(\alpha\) and \(\beta\) forms with progressive stacking of hydrogen bonded sheets. The differences in \(\alpha\) and \(\beta\) polymorphs were attributed to changes in the \(c\)-axis value where, chain axis shifts between the consecutive sheets.

Beside high crystallinity, good solvent resistance and expected excellent fiber forming properties of the polyoxalamides, commercial applicability is limited due to their high melting temperature and thermal degradation close to melting temperature [10]. The good solvent characteristics of water for aliphatic polyamide, recently explored in our group and discussed in Chapter 3, opens a new possibility of self-assembling process without thermal degradation [11-14]. Earlier studies on model compounds, \(N,N'-1,4\text{-butanediyl-bis(6-hydroxy-hexanamide)}\) (BDHA) and
N,N'-1,2-ethanediyl-bis(6-hydroxy-hexanamide) (EDHA), where water was used as a solvent have revealed enhanced hydrogen bonding efficiencies and denser molecular packing [15,16]. Thus one of the possible ways to process polyoxalamide or facilitate the self-assembling process without degradation can be superheated water. This subject has not been addressed in this thesis.

In this chapter we aim to investigate self-assembling characteristics of water molecules for oxalamide based model compounds. For comparison the melt crystallized sample of the compounds will be also investigated. Two model compounds, having six methylene groups between the two oxalamide motifs and having polar and non-polar end groups (Figure 4.2), are synthesized. Changes in the molecular conformation and its implication on crystal structure of the model compounds is investigated using variable temperature solid state NMR, FTIR spectroscopy and X-ray diffraction.

4.2 Materials and synthesis section

4.2.1 Materials

All chemicals used in synthesis of the model compounds were obtained from Sigma-Aldrich and used as received. The synthesis of model compounds was carried out in two steps as described elsewhere [17].

4.2.2 Synthesis procedure

4.2.2.1 Synthesis of Diethyl 2,2'-(hexane-1,6-diylbis(azanediyl))bis(2-oxoacetate)\(\left(OXA_6\right)\)

In the first stage, synthesis of the Diethyl 2,2'-(hexane-1,6-diylbis(azanediyl))bis(2-oxoacetate)\(\left(OXA_6\right)\) was performed by mixing 1,6-diaminohexane and diethyl oxalate in chloroform and the resultant solution was then mixed and stirred at room temperature for 16 hours. The solvent and excess of diethyl oxalate were removed by filtering the product, and further purification was done by dissolving in chloroform followed by precipitation in methanol. The synthesized product, OXA\(_6\), was used as the starting material for the two model
compounds, \( \beta \text{ala oxa (CH}_2\text{)}_6 \text{oxa } \beta \text{ala} \) and \( \text{Meo oxa(CH}_2\text{)}_6 \text{oxa Meo} \) described below. Details on the synthesis of these model compounds are disclosed in a recent publication [18] where the authors used these compounds to make segmented block copolymers having hard (oxalamides) and soft polyether (polytetrahydrofuran) blocks.

4.2.2.2 Synthesis of Diethyl 4,5,14,15-tetraoxo-3,6,13,16-tetraazaoctadecane-1,18-dioate (\( \beta \text{ala oxa (CH}_2\text{)}_6 \text{oxa } \beta \text{ala} \))

Triethyl amine, \( \beta \)-alanine ethyl ester hydrochloride and OXA\(_6\) were dissolved in CHCl\(_3\). Subsequently the mixture was heated at reflux temperature for 16 hour. The solvent and excess of triethyl amine were removed by filtering the product. The filtrate was washed one time with ethanol, two times with CHCl\(_3\) and two times with diethyl ether and dried at 60 °C in vacuum.

4.2.2.3 Synthesis of \( N^1,N^2\)-bis (3-methoxypropyl) 2,11-dioxo-3,10-diaza-1,12-dodecanamide (\( \text{Meo oxa(CH}_2\text{)}_6 \text{oxa Meo} \))

3-Methoxypropylamine and OXA\(_6\) were placed in a round bottom flask. The mixture was gradually heated to 120 °C under nitrogen. After 1 h the temperature is increased to 180 °C and then the pressure is slowly reduced to ~ 20 mbar. The ethanol distilling off during that period was collected in a cold trap, cooled with liquid nitrogen. Subsequently the pressure was further reduced to below 1 mbar in the following 1.5 hours. The reaction mixture was then cooled to room temperature under vacuum. The product was dissolved in chloroform and subsequently precipitated in diethyl ether. The product was filtered and dried at 60 °C under reduced pressure.
Melt crystallized samples of the model compounds were obtained by cooling from melt state at 10 °C/min to 20 °C. Water crystallized samples were prepared using especially designed high pressure cell described elsewhere [12], where powder sample sealed with water in glass capillary was dissolved at 150 °C and subsequently cooled to 20 °C. Excess water was removed by drying the samples at 60 °C under vacuum for 12 hour, prior to their use.

4.2.3 Experimental section

4.2.3.1 Differential Scanning Calorimetry (DSC)

Phase transformations in melt and water crystallized samples of as synthesized βala oxa (CH$_2$)$_6$ oxa βala, and Meo oxa(CH$_2$)$_6$ oxa Meo were studied under nitrogen atmosphere by DSC using TA Q1000 instrument. Heating and cooling rates of all samples were 5 °C/min. The samples were held for 3 min under isothermal condition at the limiting temperatures. All samples were heated from -90 °C till their respective melting temperature and cooled to -90 °C.

4.2.3.2 Fourier Transform Infra-Red spectroscopy (FTIR)

Conformational changes in βala oxa (CH$_2$)$_6$ oxa βala and Meo oxa(CH$_2$)$_6$ oxa Meo crystallized from melt and water were studied by FTIR spectroscopy. The samples were placed on a zinc selenium disk and spectra were recorded on a FTS670IR spectrometer equipped with a microscope with a resolution of 4 cm$^{-1}$ in
the transmission mode. The samples were exposed to heating cycle from 20 °C to temperature below the melting point. Subsequently the samples were cooled to 20 °C. The chosen heating and cooling rates were 5 °C/min. The spectrum recorded at an interval of 10 °C, during the heating and the cooling cycles, was averaged over 100 spectra. The recording was initiated after leaving the sample for 3 min under the isothermal condition. Linkam TMS94 hotstage was used to follow the heating and cooling cycles.

4.2.3.3 Wide Angle X-ray Diffraction (WAXD)

WAXD was performed on melt (MC) and water crystallized (WC) model compounds and diffraction spectra were recorded in transmission mode, using a Bruker AXS HISTAR area detector installed on a P4 diffractometer, using graphite monochromatic CuKα radiation (λ = 0.154 nm) and a 0.5 mm collimator. The data were collected at elevated temperature. The sample temperature was controlled by a linkam TMS94 hotstage. The samples were heated from room to the melting temperature at 5 °C/min and diffraction spectra were recorded after every 10 °C. Similar to FTIR studies, the samples were left under isothermal condition for 3 minutes prior to recording of the diffraction patterns. The 2D data were subsequently background corrected and transformed into 1D profiles via integration.

Material studio software (Accelrys Software Inc.) was employed to calculate the crystallographic parameters. A Pawley refinement method was used to model the experimental WAXD data. The protocol used during modeling the WAXD pattern described below. The integrated patterns were subjected to Materials studio simulations program (Accelrys Software Inc.). After doing the background substation, indexing on the selected set of peaks is performed using a TEROR 90 program. In this trial and error based program primary solution for unit cell was searched from cubic to triclinic. The search ends as the Figure of Merit (FOM) criteria was fulfilled. The proposed unit cell was analyzed using a Pawley refinement iterative method for determination of lattice parameters. When the simulated data fits with the best possible values, a refinement is terminated and the refined lattice parameters were selected.
4.2.3.4 Solid State Nuclear Magnetic Resonance (NMR)

Variable-temperature (VT) $^{13}$C($^1$H) magic angle spinning/cross-polarization (CP/MAS) NMR experiments were carried out on a Bruker ASX-500 spectrometer using a double resonance probe for rotors with 4.0 mm outside diameter. These experiments used 10.0 kHz MAS and a 4 μs $\pi/2$ pulse for $^1$H. All VT $^{13}$C($^1$H) CP/MAS NMR spectra were recorded using a CP contact time of 3.0 ms and TTPM decoupling 35 during acquisition. The temperature was controlled using a Bruker temperature control unit in the range from 30 to 210 °C. The VT $^{13}$C($^1$H) CP/MAS NMR spectra were recorded under isothermal conditions at intervals of 10 °C, employing a heating rate of 2 °C/min between temperatures. Reported temperatures are corrected for friction induced heating due to spinning using 207 Pb MAS NMR of Pb(NO$_3$)$_2$ as a NMR thermometer [19].

The 2D $^1$H-$^1$H Double-Quantum Single-Quantum (DQ-SQ) correlation experiments were recorded on a Bruker AVANCE-III 850 spectrometer ($\nu_L = 850.27$ MHz for $^1$H) using a double-resonance probe for rotors with 2.5 mm outside diameter. Experiments were performed under rotor-synchronized conditions using a spinning frequency of 30 KHz. The BaBa sequence was used for excitation and reconversion of DQ coherences [20,21]. All 2D spectra were recorded using two rotor periods (67.2 μs) of BaBa DQ recoupling. Chemical shifts for $^1$H and $^{13}$C are reported in ppm relative to TMS using solid adamantane as an external reference [22,23].
4.3 Results and discussion

4.3.1 Phase transformation in melt and water crystallized oxalamide motif model compounds

![DSC thermograms](image)

Figure 4.3: DSC thermograms (A) heating and (B) cooling of melt crystallized (a) β-ala oxa (CH₂)₆ oxa β-ala and (b) Meo oxa(CH₂)₆ oxa Meo model compounds. (C) and (D) are the heating and cooling runs of water crystallized oxalamides, respectively. In β-ala oxa (CH₂)₆ oxa β-ala and Meo oxa(CH₂)₆ oxa Meo, before melting two endothermic peaks are observed. The appearance of two peaks, prior to melting, may be attributed to phase transitions. The comparison of the melt and water crystallized samples show similarities in the phase transformations, with the exception that T_H2 peak moves to higher temperatures, closer to the melting point.

Figures 4.3A and 4.3B show DSC thermogram of melt crystallized oxalamide motif based model compounds [a) βala oxa (CH₂)₆ oxa βala and b) Meo oxa (CH₂)₆ oxa Meo] during heating and cooling cycle respectively. On heating, in βala oxa (CH₂)₆ oxa βala, three endothermic transitions at temperatures 59.3 °C, 146.5 °C and 200.2 °C are observed. The enthalpies involved at the transition temperatures are summarized in Table 4.1. Considering the small amount of heat
involved during the endothermic transitions at 59.3 °C and 146.5 °C, the phase transitions can be associated with changes in crystal lattice. The third transition at 200.2 °C is attributed to melting of crystals. Upon cooling from the melt state (205 °C), two exothermic peaks at 194.3 °C and ~6.9 °C are observed. The phase transition at 194.3 °C is crystallization from the melt, whereas the phase transition at 6.9 °C, requires larger supercooling of ~50 °C, indicative of higher entropic barrier to attain the equilibrium state [24].

Table 4.1: Summary of phase transition temperatures and enthalpy involved during the transition of \( \text{fla} \text{la oxa (CH}_2\text{)}_6 \text{oxa fla} \text{la} \) and \( \text{Meo oxa (CH}_2\text{)}_6 \text{oxa Meo} \)

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<td>A</td>
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<td>34.4</td>
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Similarly, for \( \text{Meo oxa (CH}_2\text{)}_6 \text{oxa Meo} \), three exothermic peaks are observed during the heating cycle at temperatures 53.8 °C, 191.4 °C and 212.4 °C. Similar to the transitions observed for \( \text{fla} \text{la oxa (CH}_2\text{)}_6 \text{oxa fla} \text{la} \), the first two transitions at 53.8 °C and 185.9 °C can be attributed to the changes in the crystalline lattice. Whereas, the third transition at 212.4 °C is associated with melting of the model compound. Upon cooling from melt (215.0°C), three exothermic peaks become evident at temperatures 210.4 °C, 186.80 °C and 43.8 °C. Considering the exothermic and endothermic nature of the crystal-crystal phase transformations, and the involvement of similar enthalpy, during cooling and heating cycles, respectively these transformations can be assigned to the first order crystal to crystal transitions.

In case of model compounds crystallized from water, no significant difference are observed as can been seen in Figure 4.3C and 4.3D. To follow the molecular origin
of phase transitions conformational changes have been followed using solid state NMR and FTIR spectroscopy, whereas the crystallographic changes have been monitored by WAXD.

4.3.2 Influence of temperature on the conformation of \( \beta \text{ala oxa (CH}_2\text{)}_6 \)
\( \text{oxa } \beta \text{ala} \) compound

![Figure 4.4: \(^{13}\text{C} \{^1\text{H}\} \text{CP/MAS NMR spectra of } \beta \text{ala oxa (CH}_2\text{)}_6 \text{oxa } \beta \text{ala} \text{ at } 30 \degree \text{C (a), (b), and 60 } \degree \text{C (c), (d) and 150 } \degree \text{C (e), (f) crystallized from melt (a), (c) (e) and water (b), (d) (f)respectively. The numbers at peak positions correspond to carbons labeled for the model compounds presented in (g). Dotted lines compare changes in the chemical shift of the samples crystallized from water or melt at 30 } \degree \text{C and 150 } \degree \text{C.}

At room temperature significant differences in the conformation of melt and water crystallized \( \beta \text{ala oxa (CH}_2\text{)}_6 \text{oxa } \beta \text{ala} \) are observed. Figures 4.4a and 4.4b depicts \(^{13}\text{C} \) solid state NMR spectra of \( \beta \text{ala oxa (CH}_2\text{)}_6 \text{oxa } \beta \text{ala} \) crystallized from melt and water respectively. In the melt crystallized \( \beta \text{ala oxa (CH}_2\text{)}_6 \text{oxa } \beta \text{ala} \) relatively sharp and well resolved peaks are observed. Whereas, in the water crystallized model compounds relatively broad peaks are observed. The sharp peak is representative of enhanced mobility in the melt crystallized samples compared to...
the restricted mobility in the water crystallized samples. The chemical shift values of the individual carbons are summarized in Table 4.2.

Table 4.2: Changes in $^{13}$C chemical shift values of $\text{bala oxa (CH}_2\text{)}_6 \text{ oxa bala}$ crystallized from melt and water at elevated temperature

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<td>34.0</td>
<td>37.9</td>
<td>59.8</td>
<td>14.7</td>
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</tbody>
</table>

From the comparison between Figures 4.4a and 4.4b it is apparent that considerable differences exist in the chemical environment of the oxalamide motifs, where the origin of these differences is attributed to the crystallization conditions. Important to notice is that unlike the $^{13}$C peaks of the oxalamide motifs and the neighboring CH$_2$ units, the $^{13}$C peak position of the CH$_3$ end group remains independent of the crystallization conditions. Moreover, the $^{13}$C peak of the CH$_2$ unit in the middle of the molecule, number 1, remains independent of the crystallization conditions. Comparison between the melt and the water crystallized samples show very small shift in the CH$_2$ peak of carbon number 2. However, dramatic differences are observed in remainder of the Carbon peaks associated with the hydrogen bonding oxalamide motifs ($^{13}$C peak positions of 3, 4, 5) and carbonyl group outside the oxalamide motif (7).

From here it is apparent that the hydrogen bonding is strongly influenced by the crystallization conditions. In the sample crystallized from superheated state of water a possibility of the presence of water molecules within the lattice cannot be excluded, thus the involvement of water molecules and their strong interaction with the hydrogen bonding motifs may influence the chemical shifts. Such a possibility can simply explain the remarkable differences in the peak positioning of the $^{13}$C.
oxalamides, crystallized from melt state or in the presence of water. To check such a possibility 2D $^1\text{H}-^1\text{H}$ double quantum-single-quantum (DQ-SQ) correlation spectroscopy have been performed on the water and melt crystallized samples and depicted in Figure 4.5.

**Figure 4.5**: Room temperature 2D rotor-synchronized $^1\text{H}-^1\text{H}$ DQ-SQ correlation spectra of (a) melt (b) water $\beta$ala oxa $(\text{CH}_2)_6$ oxa $\beta$ala recorded at 20.0 °C.

Within the available resolution limit of the 850 MHz spectrometer, no considerable differences can be observed in the $^1\text{H}$ spectra of the melt and the water crystallized samples. The absence of any water molecules, within the experimental resolution limit, excludes the influence of water molecules on the hydrogen bonding efficiency of the oxalamides. Thus we attribute differences in the spectra of the water and the melt crystallized samples to ease in packing of the macromolecules facilitated by the presence of water, where the latter acts as plasticizer in the structuring process. To have further insight into the conformational differences, the samples are heated under controlled conditions within the spectrometer.

Figure 4.4c and 4.4d shows comparison between the spectra at 60 °C of the water and the melt crystallized sample. It is evident that while the melt crystallized sample hardly shows any changes, the $^{13}\text{C}$ spectra of the water crystallized sample changes significantly. It is to be noted that the remarkable sudden difference sets in above 50 °C only, Figure 4.6 and Figure 4.7. The sudden click in the conformational transformation at 60 °C is associated with the abrupt change in
hydrogen bonding efficiency of the carbonyl groups numbered 7 and 4. At 60 °C, the same positioning of the $^{13}$C peaks of the carbonyl groups in the samples crystallized from melt and water clearly indicate changes in the hydrogen bonding efficiency. The observed changes influences the chemical shift of CH$_2$ units (number 5, 8 and 6) in the vicinity of the oxalamide motifs. It is important to note that the positioning of the methylene units in combination with the carbonyl groups resembles with the melt crystallized sample at 60 °C. However, the difference in the melt and the water crystallized macromolecules persists between the CH$_2$ units numbered 2 and 3 i.e. CH$_3$ units between the oxalamide motifs in the proximity of NH group. The overall changes in the hydrogen bonding motifs, at 60 °C much below the boiling point of water, further strengthens the absence of water molecules within the crystalline lattice. The differences in the positioning of the CH$_2$ units, numbered 2 and 3, between the melt and the water crystallized samples prevails till 130 °C (Figure 4.6). At these higher temperatures the CH$_3$ numbered 1 also gains mobility and shows sudden shift to left. The simultaneous changes in the CH$_2$ groups of 1, 2 and 3 are associated with the enhanced thermal mobility that tend to release the conformational constraints build within the lattice of the water crystallized sample. At 150 °C no differences between the melt and the water crystallized samples are observed (Figure 4.4e and 4.4f).
Figure 4.6: Variable temperature $^{13}$C CP/MAS spectra of melt crystallized $\beta$ala oxa ($CH_2)_6$ oxa $\beta$ala, showing the changes in the conformations of carbon atoms.
Figure 4.7: Variable temperature $^{13}$C CP MAS spectra of water crystallized $\beta$ala-oxa (CH$_2$)$_6$oxa-$\beta$ala, showing the changes in the conformations of carbon atoms.
On heating further around 160 °C, with the intervention of thermodynamic transition $T_{H2}$, conformational changes in both melt and water crystallized samples are reported. Important to note is that the thermodynamic transition $T_{H1}$ which is in the vicinity of 60 °C causes conformational changes in the water crystallized sample but not in the melt crystallized sample, for comparison see Figure 4.6 and Figure 4.7. These findings further strengthen the role of water molecules in the self-assembling process of the hydrogen bonded macromolecules. This result is in agreement with the earlier studies performed in our group [25,26].

The NMR studies are further complemented by the FTIR studies performed on these oxalamides. Figures 4.8a and 4.8b summarizes FTIR spectra recorded on the melt and water crystallized samples. Unlike the NMR spectra the FTIR spectra of the starting material looks similar. No differences in the positioning of the vibrational modes are observed. However, the water crystallized sample shows broader peaks in the region of 1000 – 1400 cm$^{-1}$ compared to the melt crystallized sample. The broad peak in FTIR suggests broader distribution in the vibrational modes. With the onset of the transition $T_{H1}$ in the vicinity of 60 °C, changes are observed in the spectral region of 1000-1400 cm$^{-1}$. To be more specific the vibrational modes associated with the carbonyl group outside the oxalamide motifs show sudden broadening of the peak. These findings are in accordance with the changes registered by the NMR spectra in the water crystallized sample. The vibrational modes are summarized in Table 4.3. Changes in the region of 800 cm$^{-1}$ in both melt and water crystallized samples are also registered. These are also attributed to the conformational changes of the free carbonyl group.
Figure 4.8: Variable temperature changes in the vibration modes of (a) melt and (b) water crystallized \( \text{ala oxa (CH}_2 \text{)oxa oxa} \).

With the onset of the transition \( T_{\text{H2}} \), remarkable changes are observed in the methylene vibrational modes next to the NH group of the oxalamide motifs. These changes arising due to enhanced mobility of the methylene units between the oxalamide groups are in agreement with the NMR studies reported above on both melt and water crystallized samples.
Table 4.3: Vibrations mode of assignment of ȕala oxa (CH$_2$)$_6$ oxa ȕala crystallized from melt and water [26,27,28].

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To follow the crystallographic changes with the phase transformations WAXD studies have been performed in the water and the melt crystallized samples. From Figure 4.9 it is apparent that the water crystallized sample shows greater number of diffraction peaks compared to the melt crystallized sample.

![Diffraction pattern of \( \text{\textalpha} \text{ala oxa} (\text{CH}_2)_6 \text{oxa \textalpha} \text{ala} \) crystallized from (a) melt and (b) water.](image)

Figure 4.9: Diffraction pattern of \( \text{\textalpha} \text{ala oxa} (\text{CH}_2)_6 \text{oxa \textalpha} \text{ala} \) crystallized from (a) melt and (b) water.

The well resolved diffraction pattern of the water crystallized sample further confirms that water act as a good solvent for oxalamides facilitating the self-assembling process. The recorded diffraction pattern of the water crystallized sample is used for determination of the unit cell and crystallographic planes. The method adopted for calculation of the unit cell is described in the earlier work of Harings and Vaidya and have been applied here [26,29]. Figure 4.10 depicts the comparison between the calculated and the simulated patterns. Good agreement between the calculated and the simulated patterns is observed, suggestive of the triclinic unit cell having dimensions \( a = 0.43 \) nm, \( b = 0.87 \) nm, \( c = 2.78 \) nm, \( \alpha = 76.63^\circ \), \( \beta = 85.15^\circ \) and \( \gamma = 49.78^\circ \). The calculated and simulated \( d \)-values with the corresponding miller indices are summarized in Table 4.4.
Figure 4.10: Experimental (black) and TREOR 90 simulated (red) WAXD pattern of water crystallized $\beta$ala oxa $(CH_2)_6 oxa \beta$ala. The green line in bottom shows the difference in the experimental and simulated pattern.

Table 4.4: Diffraction signals of water crystallized $\beta$ala oxa $(CH_2)_6 oxa \beta$ala, having triclinic unit cell at 30 °C.

<table>
<thead>
<tr>
<th>Bravais-Miller indices</th>
<th>Water crystallized at 30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>h k l</td>
<td>$d_{obs}$</td>
</tr>
<tr>
<td>0 0 1</td>
<td>2.682</td>
</tr>
<tr>
<td>0 0 2</td>
<td>1.349</td>
</tr>
<tr>
<td>0 1 1</td>
<td>0.596</td>
</tr>
<tr>
<td>0 1 0</td>
<td>0.644</td>
</tr>
<tr>
<td>1 0 1</td>
<td>0.345</td>
</tr>
<tr>
<td>1 0 0</td>
<td>0.352</td>
</tr>
<tr>
<td>1 1 0</td>
<td>0.457</td>
</tr>
<tr>
<td>1 1 1</td>
<td>0.455</td>
</tr>
</tbody>
</table>

To follow the observed phase transformations WAXD studies have been performed at different temperatures, while heating the samples (both melt and water crystallized) from 30 °C onwards. Figure 4.11 and 4.12 shows the changes in the crystal structure of $\beta$ala oxa $(CH_2)_6 oxa \beta$ala crystallized from melt and water respectively. With the onset of the $T_{1B1}$ phase transformation the water crystallized sample shows sudden change in the $hko$ and $h00$ diffraction peaks, whereas the $002$ diffraction peaks remain unaltered. The observed changes are in accordance with the conformational changes observed in the hydrogen bonding efficiency of the oxalamide motifs and carbonyl group outside the oxalamide.
Figure 4.11: Crystallographic changes during variable temperature WAXD measurements in melt crystallized \( \beta \)ala oxa (CH\(_2\)\(_6\) oxo \( \beta \)ala)

Figure 4.12: Crystallographic changes during variable temperature WAXD measurements in water crystallized \( \beta \)ala oxa (CH\(_2\)\(_6\) oxo \( \beta \)ala)
In contrast to the water crystallized sample no changes in the diffraction pattern of the melt crystallized sample are observed. The observations on the melt crystallized sample are in accordance with the NMR results where no changes in the conformation of the melt crystallized sample are observed. The subtle changes in the FTIR are not sufficient to cause crystallographic transformation.

The T$_{1D}$ phase transition that arises with the enhanced thermal mobility of the methylene units, between the oxalamides, results into the simultaneous disappearance and appearance of several diffraction peaks, suggestive of crystallographic phase transformation from triclinic to conformational disorder (CONDIS), or columnar hexagonal, phase prior to melting [30]. Small shift in the 002 diffraction peak from 2.64 nm to 2.54 nm in water crystallized $\beta$ala oxa (CH$_2$)$_6$ oxa $\beta$ala is observed during increase in temperature from 150 °C to 190 °C (Figure 4.13). This confirms change in the crystallographic phase transformation.

![Figure 4.13: Changes in the 001 and 002 diffraction signal during heating cycle of water crystallized $\beta$ala oxa (CH$_2$)$_6$ oxa $\beta$ala. The symbols ▲ and △ represents 001 and 002 diffraction peak d-value of melt crystallized $\beta$ala oxa (CH$_2$)$_6$ oxa $\beta$ala respectively.](image)

The sudden contraction along the c-axis can be attributed to the introduction of gauche conformers together with the weakening of the hydrogen bonding. A result in accordance with our NMR studies and earlier studies performed by Harings et al on amide based model compounds.
The introduction of defects, suppressed hydrogen bonding and maintained \( c \)-axis are indicative of the columnar hexagonal phase that the model compound is likely to adopt prior to melting [31].

4.3.3 Influence of temperature on the conformation of Meo oxa (CH\(_2\))\(_6\) oxa Meo compound

![Figure 4.14: \( ^{13}C \) CP/MAS NMR spectra of Meo oxa (CH\(_2\))\(_6\) oxa Meo at 30 °C (a), (b); 100 °C (c), (d); 130 °C (e), (f); and 140 °C (g), (h). Spectra (a), (c), (e),(g) represent the material crystallized from melt, and (b), (d), (f), (h) are the spectra crystallized from water. The numbers at peak positions correspond to carbons labeled for the model compounds presented in the schematics on top. Dotted lines are drawn to follow changes in the chemical shift of the samples crystallized from water or melt in the range of 30 °C to 150 °C.]

In analogy with the \( \beta \)ala oxa (CH\(_2\))\(_6\) oxa \( \beta \)ala, the origin of phase transformations in the Meo oxa (CH\(_2\))\(_6\) oxa Meo model compound (Figure 4.3) has been also investigated. Unlike \( \beta \)ala oxa (CH\(_2\))\(_6\) oxa \( \beta \)ala, the Meo oxa (CH\(_2\))\(_6\) oxa Meo model compound constitutes of methoxy propyl end group which is relatively apolar compare to the \( \beta \)-alanine end group. Figures 4.14a and 4.14b depict \( ^{13}C \) solid state NMR spectra of Meo oxa (CH\(_2\))\(_6\) oxa Meo crystallized from melt and water
respectively. At 30 °C, similar to βala oxa (CH₂)₆ oxa βala, considerable
differences in conformation of melt and water crystallized Meo oxa (CH₂)₆ oxa Meo
are evident.

Table 4.5: $^{13}$C chemical shifts of Meo oxa (CH₂)₆ oxa Meo crystallized from melt and water at
different temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>4</th>
<th>2</th>
<th>3</th>
<th>1</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30°C</td>
<td>160.5</td>
<td>30.9</td>
<td>43.1</td>
<td>27.3</td>
<td>37.3</td>
<td>30.5</td>
<td>69.2</td>
<td>58.7</td>
</tr>
<tr>
<td>100°C</td>
<td>160.5</td>
<td>30.5</td>
<td>43.2</td>
<td>30.5</td>
<td>38.7</td>
<td>30.5</td>
<td>71.9</td>
<td>58.6</td>
</tr>
<tr>
<td>130°C</td>
<td>160.7</td>
<td>30.4</td>
<td>43.1</td>
<td>30.4</td>
<td>38.7</td>
<td>30.4</td>
<td>72.0</td>
<td>58.5</td>
</tr>
<tr>
<td>180°C</td>
<td>161.0</td>
<td>30.8</td>
<td>41.8</td>
<td>28.8</td>
<td>41.8</td>
<td>30.0</td>
<td>72.0</td>
<td>58.3</td>
</tr>
<tr>
<td>WC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30°C</td>
<td>160.4</td>
<td>32.6</td>
<td>40.4</td>
<td>30.1</td>
<td>37.2</td>
<td>30.8</td>
<td>71.5</td>
<td>59.2/58.8</td>
</tr>
<tr>
<td>100°C</td>
<td>160.5</td>
<td>30.7</td>
<td>40.2</td>
<td>29.7</td>
<td>38.1</td>
<td>32.3</td>
<td>71.8</td>
<td>58.4</td>
</tr>
<tr>
<td>130°C</td>
<td>160.4</td>
<td>32.3</td>
<td>40.4</td>
<td>30.1</td>
<td>38.6</td>
<td>30.6</td>
<td>71.9</td>
<td>58.4</td>
</tr>
<tr>
<td>180°C</td>
<td>161.0</td>
<td>30.8</td>
<td>41.8</td>
<td>29.4</td>
<td>38.7</td>
<td>30.3</td>
<td>71.9</td>
<td>58.4</td>
</tr>
</tbody>
</table>

In the $^{13}$C spectra of the melt crystallized Meo oxa (CH₂)₆ oxa Meo relatively
narrow and well resolved peaks are observed. Whereas, in the water crystallized
model compounds peaks are relatively broad. The broad peaks represent restricted
molecular mobility which is suggestive of the restricted conformation that the water
crystallized model compound adopts. Chemical shifts of the individual carbons at
different temperatures are summarized in Table 4.5. At 30 °C, differences in the
chemical shifts of the water and the melt crystallized samples indicate different
chemical environment that the hydrogen bonding motifs tend to adopt. In the water
crystallized sample the CH₃ peak of carbon number 8 splits into two peaks. The
peak splitting is likely to arise due to different conformations that the CH₃ unit
residing on the crystal surface can adopt. The other carbon peaks that show
differences in peak positioning are 4, 7, 3, 5, 6, 2, 1. These remarkable differences
may arise due to the presence of water molecules within the crystal structure or
facilitation of chain packing that the water molecules provide. To preclude the
possibility of water molecules within the lattice $^1$H NMR studies have been
performed. Figure 4.15 shows 2D $^1$H−$^1$H double quantum-single-quantum (DQ-
SQ) correlation spectroscopy performed on the melt and the water crystallized
samples.
To our surprise, unlike ȫala oxa (CH$_2$)$_6$ oxa ȫala in the Meo oxa (CH$_2$)$_6$ oxa Meo compound traces of water molecules within the crystalline lattice in the water crystallized samples are observed. Further in the melt crystallized sample unusual peaks in the vicinity of 6-8 ppm are recorded. These foreign molecules within the crystal lattice shadow the clean study. However, it is worthwhile to see some remarkable changes that the presence of water molecules provides in the hydrogen bonding efficiency and the associated conformation.

Independent of the crystallization conditions, NMR spectra of the melt and the water crystallized samples show conformational changes with the onset of the thermodynamic phase transformation. From Figure 4.16, the origin of the phase transformation $T_H$ can be speculated. On increasing temperature from 30 to 40 °C peaks associated with the CH$_2$ units (5,7) outside the oxalamide motifs, closer to the methylene end group gain mobility and shift to higher ppm. On heating further, from 40 to 50 °C, with the completion of the shift the peak associated with CH$_2$ unit (1) at the center of the compound vanishes. Enhanced intensity of the peak 2 and its narrowing in width at 50 °C combined with similar chemical environment that the CH$_2$ units 1 and 2 possess, it is very much likelihood that the peak 1 merges with 2. It is to be noted that the peak position of 6 also similar to 2, which could be easily explained by the similar chemical environment that the CH$_2$ units 1,2,6 will adopt on gaining mobility.
Figure 4.16: Variable temperature $^{13}$C CP/MAS spectra of melt crystallized Meo-oxa-CH$_2$-oxa-Meo, showing the changes in the conformations of carbon atoms.
No changes in the chemical shift of the CH₃ end group (8) and carbonyl group (4) within the oxalamide are observed. With the onset of the transition T_{H2} above 170 °C further conformational changes are observed and differences in the chemical environment of CH₂ groups 6, 2, 1 are realized. These changes in the CH₂ groups can be only explained by considering crystallographic changes that the material similar to βala oxα (CH₂)₆ oxα βala is likely to adopt.

![Figure 4.17: Variable temperature changes in the vibration modes of melt crystallized Meo oxα (CH₂)₆ oxα Meo.](image)

These findings have been further strengthened by FTIR, where changes in the vicinity of 700-1400 cm⁻¹ are observed, especially associated with CH₂ units and C-O-C vibrational modes of methoxy propyl end group (Figure 4.17). Table 4.6 illustrates the band assignment of vibrational modes and temperature dependent changes associated with these vibrational frequencies.
Table 4.6: Vibrations mode of assignment of Meo oxa (CH$_2$)$_6$ oxa Meo crystallized from melt and water

<table>
<thead>
<tr>
<th>Band assignment</th>
<th>30°C</th>
<th>70°C</th>
<th>110°C</th>
<th>170°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH stretch vibration (hydrogen bonded)</td>
<td>3293</td>
<td>3299</td>
<td>3299</td>
<td>3297</td>
</tr>
<tr>
<td>Amide II overtone band</td>
<td>3062</td>
<td>3051</td>
<td>3062</td>
<td>3048</td>
</tr>
<tr>
<td>CH$_2$ antisym. stretch vibration in constrain envir.</td>
<td>2974</td>
<td>2976</td>
<td>2976</td>
<td>2980</td>
</tr>
<tr>
<td>CH$_2$ antisym. stretch vibration</td>
<td>2948</td>
<td>2926</td>
<td>2948/2926</td>
<td>2954/2946</td>
</tr>
<tr>
<td>Amide II: C-N stretching and CNH bending in plane vib.</td>
<td>1471</td>
<td>1466</td>
<td>1466</td>
<td>1465</td>
</tr>
<tr>
<td>CH$_2$ scissoring next to NH scissoring band in constr.</td>
<td>1388</td>
<td>1392</td>
<td>1392</td>
<td>1386</td>
</tr>
<tr>
<td>CH$_2$ scissoring next to NH in trans-conformations</td>
<td>1056</td>
<td>1028</td>
<td>1033</td>
<td>1030</td>
</tr>
<tr>
<td>R-O-CH$_3$ stretching vibration</td>
<td>1303</td>
<td>1301</td>
<td>1305</td>
<td>1301</td>
</tr>
<tr>
<td>C-O-C stretch</td>
<td>1008</td>
<td>1012</td>
<td>1008</td>
<td>1008</td>
</tr>
<tr>
<td>Amide IV band</td>
<td>942</td>
<td>942</td>
<td>942</td>
<td>942</td>
</tr>
<tr>
<td>Crystaline CH$_2$ rocking/lower CH$_2$ in gauche confo.</td>
<td>732</td>
<td>730</td>
<td>730</td>
<td>721</td>
</tr>
</tbody>
</table>

*Absent*
Figure 4.18: Variable temperature $^{13}$C CP/MAS spectra of water crystallized Meo oxa ($\text{CH}_2$)$_6$ oxa Meo. Changes in the conformations of carbon atoms are illustrated with dotted line.
The presence of water molecules within the crystal lattice of the water crystallized MeO-oxa (CH₂)₆ oxa MeO sample opens new possibilities in the understanding of the influence of water traces on hydrogen bonding efficiency. To have insight on such a possibility temperature dependent solid state NMR studies have been performed, Figure 4.18.

The comparison of spectra at 30 °C in Figure 4.14 shows different chemical environment of nearly all CH₂ units except 5, whereas the CO group within the oxalamide motif sharpens in the water crystallized sample. The influence of water molecules on chain conformation becomes further evident when the conformational changes are observed in the vicinity of the boiling point of water. Around 100 °C, the peak position of CH₂ unit (5) next to the NH on the end group side shifts to higher ppm. The CH₂ unit 7 near to the end group also shifts to higher ppm values. These changes in the chemical shift are similar to that observed in the melt crystallized sample at 50 °C, Figure 4.16. As anticipated, with increasing temperature from 30 to 100 °C sharpening of the remainder peaks occur. Considering these changes in the sample near 100 °C the presence of water in bulk state is expected.

The remainder traces of water molecules are likely to be expelled at higher temperatures with the gain in mobility of the methylene (CH₂) units in the model compound. Such a situation is realized at 140 °C, where the comparison of the melt and the water crystallized samples become equivalent. This comparison is illustrated in Figure 4.14g and 4.14h, and changes with temperature are documented in Figure 4.18. The high temperature transformation $T_{H2}$ is similar to the melt crystallized sample. The temperature dependent NMR study is further complimented with FTIR investigation.

Similar to NMR studies of water crystallized MeO-oxa (CH₂)₆ oxa MeO, at 130 °C, sudden changes in the vibrational modes in the range of 700-1400 cm⁻¹ are observed. As discussed in the FTIR analysis of melt crystallized MeO-oxa (CH₂)₆ oxa MeO, these changes are associated with the CH₂ units and C-O-C vibrational modes of the methoxy propyl end group appears close to $T_{H1}$ phase transition temperature (Figure 4.19). Whereas in water crystallized MeO-oxa (CH₂)₆ oxa MeO,
the changes in the vibrational modes of methoxy propyl are observed around 130 °C. This is suggestive removal of water molecules from the lattice of the Meo oxa (CH₂)₆ oxa Meo and reconfirms the NMR observations of water crystallized Meo oxa (CH₂)₆ oxa Meo (Figure 4.18). The temperature dependent changes in vibrational modes are summarized in Table 4.6.

With the onset of the transition Tₓ, around 170 °C drastic changes are observed in the methylene vibrational modes next to the NH group of the oxalamide motifs. These changes are arising due to enhanced mobility of the methylene units between the oxalamide groups are in agreement with the NMR studies reported above on both melt and water crystallized samples.

4.4 Conclusions

With In this study we demonstrated the influence of water on the self assembling process of two oxalamide based model compounds having polar (Diethyl 4,5,14,15-tetraoxo-3,6,13,16-tetraazaoctadecane-1,18-dioate (flala oxa
(\(CH_2\)\(_6\) oxa \(\beta\)ala ) and non polar (\(N_1,\)\(N_2\)-bis (3-methoxypropyl) 2,11-dioxo-3,10-
diaza-1,12-dodecanamide (Meo oxa (\(CH_2\)\(_6\) oxa Meo) end groups.

The model compound, \(\beta\)ala oxa (\(CH_2\)\(_6\) oxa \(\beta\)ala, crystallized from superheated state of water reveals triclinic packing at room temperature. The temperature dependent structural analysis of the melt and the water crystallized \(\beta\)ala oxa (\(CH_2\)\(_6\) oxa \(\beta\)ala showed that two crystal-crystal phase transitions occur prior to melting of the polymer. In the water crystallized \(\beta\)ala oxa (\(CH_2\)\(_6\) oxa \(\beta\)ala, traces of bound water are not identified, suggesting role of water molecules as a plasticizer. The low temperature phase transformation arises with gain in mobility within end groups. In \(\beta\)ala oxa (\(CH_2\)\(_6\) oxa \(\beta\)ala, model compound, having the polar end group, mobility of the carbonyl group in the proximity of the methylene group had the strong influence in the initiation of mobility at chain ends. No crystallographic changes were observed during the phase transition. At the high temperature phase transformation, with the induction of gauche conformers, reduction in the chain length is observed. The simultaneous disappearance of several diffraction peaks suggest triclinic to conformational disorder (CONDIS), or columnar hexagonal, phase prior to melting.

In analogy with the model compound \(\beta\)ala oxa (\(CH_2\)\(_6\) oxa \(\beta\)ala, melt and the water crystallized Meo oxa (\(CH_2\)\(_6\) oxa Meo also showed two phase transitions prior to melting, where the low temperature phase transformation involved mobility of the end group without any crystallographic changes. However, along with the observed phase transformations, the presence of water molecules within the lattice was also recorded. The presence of water molecules in the crystal lattice influenced the appearance of the first phase transition in the motif. Temperature dependent molecular conformational studies of the water crystallized Meo oxa (\(CH_2\)\(_6\) oxa Meo showed changes in the conformation of carbon associated with the end group after removal of water molecules from the crystal lattice. These conclusions were drawn by the combined study performed using DSC, WAXD, \(^{13}\)C NMR, \(^1\)H-\(^1\)H NMR co-relation spectroscopy and FTIR spectroscopy.

The structural studies of the model compounds crystallized from the superheated state of the water demonstrated better crystal packing. These findings were in
agreement with our earlier results where good solvent characteristics of water for synthetic polyamides were demonstrated.

References

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30 Wunderlich, B.; Möller M.; Wiedemann, H., G.; Molecular Crystals and Liquid Crystals, 1986, 140, 211-218.
Chapter 5

Influence of methylene segment length on crystal packing, chain dynamics, and thermal properties of poly(amide-aramid)s

Abstract

In this chapter we report synthesis and structural characterization of poly(amide-aramid) polymers. The polymers are synthesized from p-phenylene diamine and aliphatic dichlorides, having varying aliphatic segments from 3 to 8. Molecular weight, determined using solution NMR spectroscopy and Gel Permeation Chromatography (GPC), of the synthesised polymers is 10 kg/mol, approximately. When the number of methylene segments reaches eight, the poly(amide-aramid)s exhibit melting prior to thermal degradation. In the polymers having methylene segments 3, 4 or 6, the polymer degrades prior to melting. All synthesised poly(amide-aramid)s show solubility in the polymerisation medium. Conformational and structural changes in poly(amide-aramid)s, with increasing methylene units, are characterized using solid-state NMR, FTIR spectroscopy, X-ray diffraction combined with molecular modelling. The studies reveal molecular changes in the conformation of aromatic and aliphatic units of the polymer, eventually influencing the crystal packing. Specifically, the presence of longer methylene segments provides an additional degree of freedom originating from increased chain flexibility at elevated temperature that eventually results in melting of the polymer.
5.1 Introduction

Hydrogen-bonded polymers based on aromatic and/or aliphatic motifs are widely used in engineering applications because of their excellent combination of properties. Examples are aromatic polyamides (aramids) such as Twaron® from Teijin Aramid or Kevlar® from DuPont (Figure 5.1) and are known for their high strength, high modulus and thermal stability. Aliphatic polyamides (PA), such as PA46, are known for their favourable combination of mechanical and melt processing properties (Figure 5.1)[1, 2]. The good mechanical and thermal properties of aliphatic and the aromatic polymers originate from their structural organization induced by strong inter-molecular hydrogen bonds, which govern chain packing and melting behaviour of these hydrogen bonded polymers. For example, the presence of flexible methylene segments between successive amide motifs in aliphatic polyamides, results in polymers having melting temperatures in the range of 200 -320 °C [3].

![Chemical structure of aromatic polyamide (PPTA) and aliphatic polyamide (polyamide 46).](image)

In aramids such as PPTA (Figure 5.1), the presence of a stiff aromatic backbone leads to thermal degradation prior to melting. Therefore, processing of the polymer in uniaxial direction is performed in the lyotropic liquid crystalline phase, where the chosen solvent is H₂SO₄. The solution spun polymer results in the formation of extended chain crystals having modulus and strength greater than 100 GPa and 2.3 GPa, respectively [4,5]. However, the usage of H₂SO₄ in the spinning process of PPTA is disadvantageous from an environmental and economical view point. Thus, there is a great interest in the development of polymeric materials having properties equivalent to aramids and ease in processibility, similar to
aliphatic polyamides. This objective can be achieved by combining rigidity and flexibility provided by aromatic and aliphatic moieties, respectively. However, the introduction of flexible aliphatic moieties causes considerable reduction in the mechanical properties. The synthesised polymer provides a new class of material between the high performing PPTA and aliphatic polyamides.

In the past, several efforts have been made directed to the synthesis of such aromatic-aliphatic polymers or copolymers. Using model compound based system, Gaymans and coworkers demonstrated variation in the melting temperature and its dependence on aromatic and aliphatic units [6]. It was concluded that the presence of aromatic units in the aliphatic polyamides improves chain stiffness and results in higher melting temperature. Morgan and coworkers reported low temperature synthesis of acid chloride - amine polycondensation reaction where hexamethylphosphoramide/N methyl-pyrrolidone (HMPA/NMP) was used as a polymerisation medium [7]. Later Takayanagi and coworkers[8] modified the synthesis route described by Morgan et al. [7] and reported synthesis of segmented block-co-polyamide having varying aromatic segments combined with PA6 and PA66 units. Krigbaum and coworkers synthesized fully aromatic block copolyamides by using the phosphorylation reaction route [9]. The phase behavior of these block copolymers in solution with dimethylacetamide (DMAc) was investigated in the presence of Lithium chloride salt (3 wt%) [10]. Recently, Picken and coworkers demonstrated the synthesis of lyotropic rigid-coil poly(amide-block-aramide)s, where segmented block co-polymers were prepared using PPTA and PA66 in NMP/CaCl₂ [11-13]. Westerhof in his PhD thesis reported the role of CaCl₂ during polymerization of PPTA [14]. The presence of CaCl₂ in NMP is essential to avoid precipitation of the polymer during polymerization. This route helps to obtain high molar mass PPTA. Moreover, it was demonstrated that the anion (Cl⁻) has a preferential interaction with the amide motifs of PPTA, whereas the cation (Ca²⁺) tends to form an aggregate around the amide motif.

Apart from the synthesis of PPTA and rigid-coil polymers, the structure, molecular organization and morphology of these polymers have been extensively
investigated using Wide Angle X-ray Diffraction (WAXD) [15-18], Electron Diffraction (ED)[18], Nuclear Magnetic Resonance (NMR) [19-23], Raman and Fourier Transform Infra Red (FTIR) spectroscopy [24]. Though considerable efforts have been made in the synthesis of aromatic-aliphatic polyamides, detailed investigation on the influence of methylene segments on conformational and structural aspects of the polyamides is not discussed in the literature.

In this chapter, we present controlled synthesis of polymers from p-phenylene diamine (PPD) and aliphatic dichlorides, where the number of CH$_2$ groups is varied from 3 to 8, in a one step process. Unlike the earlier studies where incorporation of the methylene units was done randomly, the adopted polymerisation route provides an alternate distribution of methylene segments between the aromatic motifs, thus allowing systematic study to unravel the structure and conformation. A detailed structural characterization is performed to reveal the origin of melting temperature and influence of methylene segments on crystal packing and chain conformation. For that purpose solid-state NMR and FTIR spectroscopy combined with WAXD have been performed. Interpretation of WAXD data has been carried out using the Cerius$^2$ software [25].

5.2 Materials section

Terephthaloyl dichloride (TDC), having 99 % purity was obtained from Teijin Aramid and was used as received. Triethylamine (Et$_3$N) was received from Fluka. Prior to polymerisation, Et$_3$N was dried over activated 0.400 nm molecular sieves. A dried mixture of ~10.6 %(w/w) of N-Methyl-2-pyrrolidone (NMP)/CaCl$_2$ received from Teijin Aramid, having water content less than ~150 ppm (determined by Karl-Fischer titration), was used as the polymerisation medium. To maintain the low water content, the mixture was stored in a nitrogen rich environment. p-Phenylene diamine (PPD), Glutaryl chloride, Suberoyl chloride, Adipoyl chloride and Sebacoyl chloride were obtained from Sigma-Aldrich and used as received.
5.3 Experimental section

5.3.1 General procedure for polymer synthesis

In a 60 ml inhouse made glass reactor, equipped with mechanical stirrer, diamine (40.0 mmol, 1 eq) was added. To the diamine, 40 mL solvent (CaCl$_2$/NMP, 10.6 wt%) was poured under nitrogen flow (1 ml/min) and the mixture was stirred till complete dissolution of diamine was achieved (~30 min). After mixing, dry Et$_3$N (8.10 g, 80 mmol, 1 eq) was added to the reaction mixture and stirred till complete dissolution of Et$_3$N at room temperature. During the mixing process, the reaction mixture was cooled with an ice bath. To the cooled mixture, di-acid chloride (40.0 mmol, 1 eq) was added. After an hour of reaction under strong mechanical stirring condition, the reaction mixture was coagulated in water. The coagulant was filtered with a Büchnerfilter. On washing the coagulant with water and acetone, yellowish white polymer powder was obtained. The powder was dried overnight in vacuo at 80 °C for 24 hours.

5.3.2 DSC and TGA analysis

The thermal stability of the poly (amide-aramid)s was determined using TGA, TA Instruments Q500. For measurement, standard sampling procedure was followed. 5 mg of the polymer was heated at 10 °C/min from 20 °C to 700 °C in a nitrogen atmosphere. Thermal transitions in Poly (amide-aramid)s were investigated using TA Instruments DSC Q1000. The samples were subjected to heating and cooling cycles between 20 °C to the respective melting temperature of the polymers, at a rate of 10 °C/min. The samples were left under isothermal conditions at the limiting temperatures for 5 min. The cycles were repeated three times to determine melting and crystallization temperatures of the synthesized polymers.

5.3.3 Solution state Nuclear Magnetic Resonance (solution state-NMR)

$^1$H-NMR spectra were recorded at a Bruker Avance III 400 MHz NMR spectrometer. Peaks are denoted as singlet (s), doublet (d), triplet (t), quartet (q),
multiplet (m) and broadened peaks are noted as (br). $^1$H chemical shifts were expressed relative to the residual $\text{D}_2\text{SO}_4$ solvent peak set to 10.2 ppm.

### 5.3.4 Solution Viscometry and Gel Permeation Chromatography

Relative viscosity measurements were performed using an Ubbelohde viscometer with 96% $\text{H}_2\text{SO}_4$ as standard. For Gel Permeation Chromatography (GPC), the polymers were dissolved in 1,1,1,3,3,3-hexafluoropropanol (HFIP). The sample for GPC measurement was prepared by dissolving 3.0 mg of the polymer in 1ml of the solvent. The detector of the GPC apparatus was calibrated with PMMA standards.

### 5.3.5 Solid-state NMR

Solid-state $^{13}$C{$^1$H} cross-polarization/magic-angle spinning (CP/MAS) NMR experiments and the corresponding variable-temperature (VT) experiments were performed on a Bruker ASX 500 spectrometer (500.11 MHz for $^1$H and 125.77 MHz for $^{13}$C) using a double-resonance probe for rotors with 4.0 mm outside diameter and a MAS spinning frequency of 10.0 kHz. All $^{13}$C{$^1$H} CP/MAS NMR employed a 4 $\mu$s $\pi/2$ pulse for $^1$H excitation followed by a CP contact time of 3.0 ms and two phase pulse modulated (TPPM) decoupling during acquisition [26,27]. For the VT $^{13}$C{$^1$H} CP/MAS NMR experiments, the temperature was controlled using a Bruker temperature control unit in the range from 30 to 200 °C and the spectra were recorded under isothermal conditions at intervals of 10 °C, employing a heating rate of 2 °C/min between temperatures. Reported temperatures are corrected for friction induced heating caused by MAS using $^{207}$Pb MAS NMR of Pb(NO$_3$)$_2$ as a NMR thermometer[28]. The 2D $^1$H-$^1$H Double-Quantum Single-Quantum (DQ-SQ) correlation experiments were recorded on a Bruker AVANCE-III 850 spectrometer ($\nu_L = 850.27$ MHz for $^1$H) using a double-resonance probe for rotors with 2.5 mm outside diameter. Experiments were performed under rotor-synchronized conditions using a spinning frequency of 30 KHz. The BaBa sequence was used for excitation and reconversion of DQ coherences [29,30]. All 2D spectra were recorded using two rotor periods (67.2 $\mu$s) of BaBa DQ recoupling.
Chemical shifts for $^1$H and $^{13}$C are reported in ppm relative to TMS using solid adamantane as an external reference [31,32].

**5.3.6 Wide Angle X-ray Diffraction (WAXD)**

For the present investigation X-ray diffraction (XRD) measurements were carried out using a Bruker D8 Advance diffractometer in 0/20 geometry, equipped with parallel beam optics, point detector (scintillation counter) and auto changer. The optics consists of a primary 60 mm Göbel mirror (a parabolic Ni/C multilayer device) providing Cu-Kα radiation (Kα$_1$/Kα$_2$ doublet, Kα wavelength = 0.154 nm), and 0.12° Soller slits. The measurements were carried out in reflection mode.

Crystal structure model building was carried out using the Cerius$^2$ software package [25] employing the Compass force field. For purposes of comparison simulated XRD data were calculated using the Cerius$^2$ diffraction module. The Lorentz and polarization factors are included in the calculated reflection intensities. The crystallite sizes and temperature factors were chosen to match the observed diffraction patterns.

Variable temperature WAXD measurements were performed in transmission mode, on a Bruker AXS HI-STAR area detector, installed with P4 Diffractometer, using graphite-monochromated Cu Kα radiation ($\lambda = 0.154$ nm) and a 0.5 mm collimator. The data was collected on both dried and annealed PPTA and poly (amide-aramide)s polymers. For WAXD measurements, the polymer powder was sealed in a glass capillary (Lindemann capillary of 1.0 mm diameter), where the sample was heated at a rate of 10 °C/min, from 40 °C to 330 °C using a Linkam TMS94 hotstage. Successively, the values of the temperatures reported are corrected using standard calibrating materials for Linkam hotstage. Details on calibration are reported elsewhere [42]. The 2D data were corrected for detector non-uniformity and spatial distortion. Subsequently background subtraction was performed and the 2D data were transformed into a 1D profile via integration.
5.4 Results and discussion

5.4.1 Synthesis and dissolution of poly (amide-aramid)s (PmMPA)

Poly(amide-aramid)s are synthesized using \textit{para}-phenylene diamine (\textit{p}-PPD) and aliphatic dichlorides. Figure 5.2 depicts synthesis scheme of the poly(amide-aramid), where “\textit{m}” represents the number of methylene segments. For simplification, here onwards, poly(amide-aramid)s will be presented as PmMPA where \textit{m} represents the number of methylene segments (Figure 5.3). During polymerisation, triethylamine (Et$_3$N) is used as acid (HCl) scavenger. The presence of Et$_3$N traps the acid and increases molar mass of the polymer. The physical characteristics of the synthesized poly(amide-aramid)s are summarized in Table 1 (see appendix C.5.1).

Figure 5.2: Aramide and amide monomers used for synthesis of poly(amide-aramid).

Table 5.1: Summary of melting and dissolution behavior and molar mass of poly(amide-aramid)s.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molar mass</th>
<th>( \eta _\text{in} )</th>
<th>Dissolution in solvent</th>
<th>( T_m(\degree\text{C}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMR (g/mol)</td>
<td>GPC (g/mol)</td>
<td>(dL/g)</td>
<td>NMP/CaCl$_2$</td>
</tr>
<tr>
<td>PPTA</td>
<td>15000</td>
<td>-</td>
<td>6.48</td>
<td>No</td>
</tr>
<tr>
<td>P3MPA</td>
<td>10750</td>
<td>9500</td>
<td>1.18</td>
<td>Yes</td>
</tr>
<tr>
<td>P4MPA</td>
<td>12850</td>
<td>11300</td>
<td>1.09</td>
<td>Yes</td>
</tr>
<tr>
<td>P6MPA</td>
<td>11260</td>
<td>13400</td>
<td>1.25</td>
<td>Yes</td>
</tr>
<tr>
<td>P8MPA</td>
<td>12570</td>
<td>14300</td>
<td>1.15</td>
<td>Yes</td>
</tr>
</tbody>
</table>

* using H$_2$SO$_4$ as solvent and 0.25 mg/l of polymer concentration. \( ^b \) not observed
Figure 5.3: Chemical structures of the poly(amide-aramid)s named according to PmMPA, where \( m \) is the number of methylene segments between the amide groups. The \(^{13}\)C assignment, used for interpretation of the NMR data, is also presented with the structure of the polymer.

The synthesized polymers are characterized using \(^1\)H NMR, and molecular weights are determined by integration of the end-group signals relative to the proton signal intensities of the polymer backbone (see appendix C.5.2). GPC analyses of the polymers are performed in hexafluoroisopropanol (HFIP). Table 5.1 depict, molar mass determined from \(^1\)H NMR analysis and GPC, the data obtained from the two different techniques are in good agreement. For all synthesized polymers, molecular weights are in proximity of 10,000 g/mol. Relative to PPTA, the intrinsic viscosity decreases with the incorporation of methylene units. The decrease in relative viscosity is in accordance with the reduction in chain stiffness [33].

The solubility of the poly(amide-aramid)s has been further investigated in 100% \( \text{H}_2\text{SO}_4 \) and in NMP/\( \text{CaCl}_2 \) (10 w/w%) solution. Poly(amide-aramid)s show a maximum solubility in \( \text{H}_2\text{SO}_4 \) at ~35 (w/w%) and ~20 (w/w%) of NMP/\( \text{CaCl}_2 \). It is to be noted that in \( \text{H}_2\text{SO}_4 \) the polymer dissolves at room temperature, whereas in NMP/\( \text{CaCl}_2 \) dissolution occurs at ~110 °C. On cooling the solution, the polymer stays in dissolved state. Since no birefringence is observed between the cross-polarized optical microscopy, it is anticipated that none of the poly(amide-aramid)s exhibit lyotropic liquid crystalline behavior in either \( \text{H}_2\text{SO}_4 \) or NMP/\( \text{CaCl}_2 \). The
reason for the good solubility in $\text{H}_2\text{SO}_4$ and NMP/CaCl$_2$ is attributed to the presence of flexible aliphatic chain segments that can promote dissolution.

The thermo gravimetric analysis showed that poly(amide-aramid)s are thermally stable up to 400 °C. As anticipated, the synthesized PPTA did not show any melting. Degradation of PPTA is observed above 545 °C [34]. However, the theoretical melting temperature of PPTA was reported by Tadokoro et al, in the vicinity of ~530 °C. Similar to PPTA, no melting temperature is evident in poly(amide-aramid)s having six or less methylene units. In the case of P8MPA a melting peak is observed at ~343 °C. Figure 5.4 illustrates the DSC thermogram of melt crystallized P8MPA during the second heating and cooling cycle.

Figure 5.4: DSC thermogram of melt crystallized P8MPA during heating and cooling cycles. The asterix (*) shows the cold crystallization peak or the superimposed melting and crystallization behavior during the 2nd heating cycle.

The melt crystallized P8MPA sample shows an endothermic peak at 343 °C which can be attributed to melting of the polymer. However, prior to melting an additional small peak is observed, which most likely originates from partial melting followed by crystallization of the polymer or melting of some low molar mass component. The presence of small endotherm prior to the main melting peak is known in aliphatic polyamides and is associated with reorganization process in the amorphous component [35]. On cooling from the melt state, crystallization of P8MPA is observed at 323 °C. Considering that the small peak also appears during
crystallization, the small peak during melting is likely to arise from the presence of a low molar mass component. The manifestation of the melting temperature in P8MPA suggests a higher thermal motion of the polymer backbone at elevated temperatures compared to PPTA or poly(amide-aramid)s having methylene segment shorter than 8. The appearance of a melting temperature in P8MPA can be attributed to temperature induced mobility within the methylene segments at elevated temperature [36]. What follows is the solid state NMR study, at room temperature, to characterize conformational changes in poly(amide-aramid)s with the increasing number of methylene segments.

5.4.2 Molecular packing, chain conformations, and chain mobility in poly(amide-aramid)s

The $^{13}$C($^1$H) CP/MAS NMR spectra of poly(amide-aramid)s are depicted in Figure 5.5, where the peak assignment is performed according to the scheme shown in Figure 5.3. For comparison, Figure 5.5 also includes a $^{13}$C($^1$H) CP/MAS NMR spectrum of PPTA. The spectrum is included for identification of the structural changes caused by the incorporation of methylene segments with increasing length. In PPTA, the carbonyl ($^{13}$C=O) resonates at the chemical shift of 166.5 ppm. This is a very low $^{13}$C chemical shift value for an amide moiety and indicates the strong intermolecular hydrogen bonding of the carbonyl groups, confirming the rigid polymer backbone in PPTA [37]. Furthermore, the $^{13}$C($^1$H) CP/MAS NMR spectra in Figure 5.5 and Table 5.2 illustrate that an increasing number of methylene groups between the amide motifs (see Figure 5.3) leads to a gradual increase of the $^{13}$C chemical shift value and narrowing of the resonance assigned to the carbonyl group. For example, the carbonyl in P3MPA resonates at 171.6 ppm, which increases to 172.3 ppm for P8MPA. This shows that an increasing number of methylene groups leads to a decreased magnetic shielding of the carbonyl group, i.e., the methylene groups act as a spacer between the hydrogen-bonded amide motifs, offering an increase in conformational freedom for the polymer chains.
Figure 5.5. Selected regions of the $^{13}$C($^1$H) CP/MAS NMR spectra recorded at 11.75 T (500 MHz for $^1$H) for (a) P8MPA, (b) P4MPA, (c) P3MPA, (d) PPTA, and (e) calculated $^{13}$C chemical shifts for PPTA (see text). Details about all polymers can be found in Table 1 and the assignment used in (a-c) is given in Figure 5.3. All spectra employed a spinning frequency of 10.0 kHz and a CP time of 3.0 ms. All $^{13}$C signal between 42-60 ppm are spinning side bands from the aromatic groups, indicated as asterisk (*). The synthesized polymers were used after drying at 80 °C for 24 hours.

Table 5.2. $^{13}$C chemical shifts determined for the poly(amide-aramid)s (see Table 5.2). The nomenclature and assignment schemes given in Figure 5.3 have been used.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>CO</th>
<th>Aₙ</th>
<th>Bₙ</th>
<th>γ_C</th>
<th>9C</th>
<th>9E</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPTA</td>
<td>166.7</td>
<td>137.5/Y</td>
<td>127.7/X</td>
<td>134.2/ne</td>
<td>123.3/ne</td>
<td></td>
</tr>
<tr>
<td>P1,3MPA</td>
<td>171.6</td>
<td>133.1</td>
<td>123.3</td>
<td>36.8</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>P1,4MPA</td>
<td>172.3</td>
<td>133.9</td>
<td>123.6</td>
<td>36.8</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>P1,8MPA</td>
<td>172.3</td>
<td>133.9</td>
<td>123.6</td>
<td>37.6</td>
<td>31.8</td>
<td>29.7</td>
</tr>
</tbody>
</table>

Aₙ and A represents the aromatic carbons between the carbonyl group of PPTA (Figure 5.3).

The region from 110 to 150 ppm includes the $^{13}$C resonances corresponding to aromatic carbons of PPTA and the poly(amide-aramid)s. For PPTA, five different $^{13}$C signals are observed (Figure 5.5). A fully symmetric configuration of the two different aromatic moieties in PPTA, where one phenylene group is centered between NH and the other between CO groups, would lead to only four $^{13}$C resonances. These observations compare well with a detailed NMR study of PPTA in dilute solutions and in the solid state performed at ambient and elevated conditions.
temperatures reported by English [38]. Although these NMR studies were performed more than 25 years ago, the current data for PPTA recorded at a higher magnetic field strength (11.75 T vs. 7.05 T) and MAS frequency (10.0 kHz vs. 4.3 kHz) compares well, including the number of observable $^{13}$C signals and their spectral resolution. These observations point towards highly ordered crystal packing in PPTA. To assign the $^{13}$C resonances to the specific carbon sites in PPTA we have performed ab initio geometry optimization and subsequent NMR chemical shift calculations of an isolated PPTA fragment. The optimized PPTA fragment has similar dihedral angles as found in the reported crystal structure [16,17] and only deviate ~2-3° for the CO-centered phenylene ring. Further details about these calculations are given in the appendix C.5.3. On this basis the calculated spectrum shown in Figure 5.5e is obtained, which shows good agreement with the experimental spectrum in Figure 5.5d. The small differences between calculated and experimental $^{13}$C chemical shifts are most likely a result of several packing effects, including ring currents effects and conformational constraints in the solid state, which are not accounted for in the gas-phase calculations. However, clear differences between the two phenylene moieties in PPTA can be observed. For example, the $^{13}$C resonances from the NH-centered phenylene ring ($A_N$, $B_N$, and $C_N$) are high-field shifted compared to the corresponding resonances ($A_C$, $B_C$, and $C_C$) of the CO-centered phenylene ring (see Figure 5.5e). The origin of this shift is caused by the unequal electronic density distribution of the CO- and NH-centered phenylene rings, due to the fact that CO and NH act as electronic acceptor and donor, respectively. It is noteworthy to mention that the NH groups do not affect the $^{13}$C chemical shifts of the NH-centered phenylene ring significantly, whereas the CO groups do. This is evident from the calculated spectrum in Figure 5.5e where a large splitting between the positions of $B_C$ and $C_C$ of ~6 ppm is observed. For $B_N$ and $C_N$ this splitting is only ~1 ppm, making them overlapping and indistinguishable in the experimental spectrum, Figure 5.5d. Based on these results it is apparent that only minor differences for the $^{13}$C chemical shifts in the aromatic region are to be expected for the PmMPAs samples, since all CO-centered
phenylene rings are replaced by extended methylene segments and therefore only 
NH-centered phenylene rings are remaining in these polymers.

For all other poly(amide-aramid)s shown in Figure 5.5 only four aromatic 
$^{13}$C resonances are observed: two narrow signals which are flanked by two broad 
signals. The reduced number of $^{13}$C resonances compared to PPTA is expected as 
discussed above. In principle, the solid-state packing in a crystal of the aromatic 
moieties in the PmMPAs can result in three $^{13}$C signals, where one is associated 
with the quaternary carbons in para position ($A_N$) and two with the proton bearing 
carbons on each side of the phenylene ring ($B_N$ and $C_N$, see Figure 5.5e). However, 
according to the calculations presented above, the $^{13}$C chemical shift for the $B_N$ and 
$C_N$ carbons were rather insensitive to the amide conformation. Thus, taking into 
account the large difference in linewidths between the narrow and broad $^{13}$C 
resonances in Figure 5.5a-c, the four resonances can be assigned to signals that 
arise from the crystalline and the amorphous domains of the samples, respectively. 
This illustrates that all PmMPA samples are semi-crystalline having similar 
crystallinity. We note that an exact determination of these fractions requires the 
application of single-pulse $^{13}$C MAS NMR recorded with long recycle delays to 
allow for full spin relaxation (five times the longest $T_1$ for $^{13}$C). Another feature 
observed for the $^{13}$C{$_1$H} CP/MAS NMR spectra in Figure 5.5 is that the linewidth 
of the aromatic signals decreases with the increasing number of methylene 
segments. This observation is in agreement with those made above for the carbonyl 
groups and it demonstrates that the extended methylene segments in the PmMPA 
samples leads to dynamically averaged phenylene groups as a result of the 
increased conformational freedom of the polymer chains.

The spectral range from 10 to 50 ppm is where the methylene units between 
the amine or carbonyl groups of the poly(amide-aramid)s resonate. The observed 
signals have a systematic appearance as a result of the increasing number of 
methylene groups. For P3MPA, two $^{13}$C carbon signals are observed at a chemical 
shift of 36.8 ppm and 23.5 ppm. These can be assigned to the methylene groups 
directly bound to the carbonyl groups and methylene groups in the chain. The 
resonance located at 23.5 ppm also includes a shoulder at its high-field side at 22.9
ppm characteristic of methylene groups that are in gauche conformation, i.e., the signal at 23.5 ppm can be assigned to the C₆ methylene unit in trans conformation. The trans and gauche conformers are related to crystalline and amorphous region of the sample, respectively, since a C₆ methylene unit in gauche conformation does allow for a planar hydrogen-bonding geometry of the amide group in P₃MPA[39-42]. The ratio between trans and gauche conformers is similar to the ratio that can be derived from the resonances of the phenylene groups (see above). For the remaining PₙMPAs, P₄MPA and P₈MPA, the assignment of $^{13}\text{C}$ resonances to gauche conformers is not feasible due to either spectral overlap or fast exchange between the two conformers. Thus, for these samples the crystallinity can only be judged on the basis of the signals from the phenylene groups.

To determine the dynamical behavior of the phenylene groups in the methylene-extended poly(amide-aramid)s we have recorded variable-temperature (VT) $^{13}\text{C}$ [$^{1}\text{H}$] CP/MAS NMR experiments for melt crystallized P₈MPA as shown in Figure 5.6. From these spectra the dynamics of the phenylene rings in P₈MPA can be directly followed. This relies on the fact that a decrease in signal intensity for the protonated $\beta_{N}$ resonance is observed, reaching a minimum at ~100 °C, followed by an increase in intensity at higher temperatures [43, 44]. Such an intensity behavior as a function of temperature is characteristic of $^{13}\text{C}$ moieties that undergo mobility on the time scale of the NMR experiment, i.e., a loss of signal occurs when the frequency of the associated motion is matched by the frequency of either (i) the involved $^{1}\text{H}$-$^{13}\text{C}$ dipole-dipole couplings, (ii) the proton decoupling field, or (iii) the magic-angle spinning [45]. In the current experiments these frequencies fall in the range 10-60 kHz, illustrating that motion of the phenylene groups in the crystalline domains of melt crystallized P₈MPA reaches this frequency scale at 100 °C approximately. The amorphous fraction, located at ~120 ppm as a broad shoulder to the crystalline resonance, decreases rapidly with increasing temperature and is hardly visible above a temperature of ~150 °C. Previous studies of the phenylene dynamics in crystalline PPTA using static $^{2}\text{H}$ solid-state NMR methods have shown that the underlying dynamics is quite heterogeneous [19,46]. The heterogeneity comes as a result of two different types
of phenylene motions: a rigid and a second undergoing 180° flips, where both motions include small-angle excursions [47,48]. Such complex dynamics has also been reported recently on the basis of \(^1\)H-\(^{13}\)C dipole-dipole couplings and \(^{13}\)C chemical shift anisotropy (CSA) NMR experiments for studies of molecular dynamics in shape-persistent poly-phenylene dendrimers, polycarbonate, and disc-shaped aromatic molecules forming discotic liquid crystals [49,50,51,52]. The first type of phenylene motion has been assigned to the interior of the crystallites and the second to the crystallite surfaces, which illustrates that the difference in molecular order can induce the two types of motions. For the current sample, P8MPA, the observations made above for the crystalline and amorphous regions suggest that these phases include similar phenylene dynamics as in PPTA. Thus, in the amorphous regions of P8MPA where limited order is expected, the phenylene rings undergo 180° flips, while the crystalline regions with higher order include phenylene rings that perform small-angle excursion, reaching the kHz regime at \(~100\) °C. Both types of motions are consistent with the \(^{13}\)C intensity behavior observed in Figure 5.6. The increasing phenylene dynamics at higher temperatures influence both the carbonyl and the methylene groups and it leads to a decrease in the intensity of signal at higher temperatures as expected. This is most pronounced for the carbonyl resonance, which also displays a shift towards higher ppm values, while only minor changes in position and intensity for the methylene groups are observed. The most significant changes for the methylene groups are related to those present in the amorphous phase (see Figure 5.6). These appear as a broad signal with a faster decay than those from the crystalline fraction in agreement with the conclusions drawn from the phenylene rings. Similar to the \(^{13}\)C\(^{1}\)H CP/MAS measurements presented above, the effect of varying aliphatic segment lengths on the molecular packing, chain mobility, and hydrogen bonding of poly(amide-aramid)s has been investigated by 2D \(^1\)H-\(^1\)H double quantum-single-quantum (DQ-SQ) correlation spectroscopy (Figure 5.7). For PPTA two broad resonances are observed. These can be assigned to the hydrogen-bonded amine protons (\(~9.8\) ppm) and to the protons associated with the phenylene rings (\(~7.0\) ppm). A clear and
intense DQ cross signal between these two resonances located at ~16.8 ppm confirms that the structure of PPTA is indeed quite rigid.

Figure 5.6. Selected regions of VT $\^{13}$C [$^1$H] CP/MAS spectra for melt crystallized P8MPA recorded at 11.75 T (500 MHz for $^1$H). Dashed lines indicate $^{13}$C resonances related to the amorphous (A) fraction of the sample, whereas the grey highlighted areas are signals influenced by chain dynamics in the crystalline (Cr) phase. The assignment below the spectra follows that given in Figure 5.3 and the asterisk indicates a spinning side band. The polymer P8MPA used for the measurement was crystallized from the melt state (353 °C).

Figure 5.7. 2D rotor-synchronized $^1$H-$^1$H DQ-SQ correlation spectra of (a) PPTA, (b) P3MPA, (c) P4MPA, and (d) P8MPA recorded at 20.0 T ($\omega_0 = 850.27$ MHz for $^1$H) using a MAS frequency of 30 KHz and two rotor periods of BaBa recoupling [49,52]. The labels NH, Ar, and Me refer proton resonances that can be assigned to amide, aromatic, and methylene segments, respectively. The synthesized polymers were used after drying at 80 °C for 24 hours.
For the other samples P3MPA, P4MPA, and P8MPA, the introduction of methylene segments results in additional signals and correlations as indicated in Figure 5.7. These are related to both DQ cross and auto correlations between the different chemical groups of the PmMPA polymers. For the amine groups a DQ signal at 10-11 ppm characteristic of methylene segments built into the polymer backbone is observed. Likewise, the phenylene groups display a DQ cross peak to the methylene groups at 8-9 ppm. The DQ auto correlation signals located at the diagonal suggest well-defined interactions between the aliphatic/aliphatic and aromatic/aromatic moieties. However, the most striking feature of Figure 5.7 is the substantial decrease in $^1$H linewidth with increasing number of methylene segments, leading to quite well resolved resonances for P8MPA. This particular sample also includes residual water molecules (likely to be adsorbed during the coagulation process after polymerization) in its structure as also observed recently in a water-crystallized sample of polyamide 46 [50]. The decrease in $^1$H linewidth can in principle have different origin: (i) high crystallinity or (ii) increased molecular dynamics as a result of polymer chain flexibility [51,52]. The latter leads to efficient averaging of the homonuclear $^1$H-$^1$H dipolar couplings between the different groups consistent with the results discussed above.

This further leads to weakening of the hydrogen bonding which in the 2D $^1$H-$^1$H DQ-SQ is observed as a shift of the amine resonance to lower frequencies. The changes in the conformation of PmMPA and complete band assignment are presented in the appendix C.5.4. What follows is the influence of the methylene segments on crystal structure of the polymers, where the experimental data are interpreted through modeling using Cerius2 software.

5.4.3 Crystal structure and modeling

The composition of the PmMPA polymers is such that they share the aliphatic dicarboxylic acid monomer with polyamides n, m+2 (m=3, 4 or 8) and the aromatic diamine monomer with PPTA. It is therefore anticipated that the crystal structures of the PmMPA polymers will be related to the crystal structures of the
polyamides mentioned and/or that of PPTA. Let us first briefly summarize the reported crystal structures of polyamides.

The crystal structures of polyamides can be subdivided into three basic schemes depending on the methylene content of the repeat units and in particular on the torsion angles involving amide groups. In the first scheme the structure consists of hydrogen-bonded sheets made up of fully extended all-trans polymer chains. Such sheets are energetically favorable when NH and CO groups of adjacent polymer chains face each other so that hydrogen bonds with favorable geometry can be formed (donor-acceptor distance close to 0.280 nm, N-H - O angles close to 180°). The sheet packing can be either progressively sheared (α form) or alternatingly sheared (β form). An example of the former structure is that of PA66, first reported by Bunn and Garner in 1947 [53]. The latter structure was reported for polyamides 2N, 2(N+1), e.g. by Gaymans et al. [6] and Jones et al.[54].

The second scheme corresponds to a pseudohexagonal structure, called the γ phase. In this structure the amide groups are tilted about 60° out of the methylene carbon plane, which leads to a characteristic shortening of the repeat unit compared to a fully extended molecular conformation. This structure is observed in aliphatic polyamides based on odd diamine or odd dicarboxylic acid monomers [55].

Recent reports show that several even-odd or odd-even polyamides turn out to crystallize in a third structural scheme. In this scheme the amide groups of the odd monomer rotate about 30° in opposite directions from the plane formed by the methylene carbon atoms, leading to a structure somewhat similar to the α phase, i.e. with lower lattice symmetry than the γ phase, but with hydrogen bonds in two different directions [56,57].
5.4.3.1 Analysis of XRD patterns

Figure 5.8 shows the reflection mode XRD patterns of PPTA, P3MPA, P4MPA and P8MPA after drying the samples at 80 °C for 24 hours. Figure 5.9 shows the same samples after annealing at 300 °C for 30 minutes. These measurements show that the annealing hardly influences the crystal structures of the PPTA and P3MPA samples. However, for the P4MPA and P8MPA samples, i.e. with increased methylene segment length, the annealing leads to peak sharpening and for P8MPA even to the development of diffraction peaks at about 6 °(2θ) and 25 °(2θ) (note that a hint of these diffraction peaks is already present before annealing). This indicates that with increasing methylene segment length heat treatment leads to increased structural perfection. This observation is in agreement with the NMR results pointing to an increase in molecular mobility with increasing methylene segment length. In the following we will focus attention on the XRD patterns of the annealed samples.
Figure 5.8. XRD patterns of PPTA (black), P3MPA (green), P4MPA (red) and P8MPA (blue) after drying at 80 °C for 24 hours.
Figure 5.9. XRD patterns of PPTA (black), P3MPA (green), P4MPA (red), P8MPA (blue) after heat treatment at 300 °C for 30 minutes, together with the XRD pattern of a commercial PA46 sample (orange). The dashed line is drawn through the maximum of the intersheet diffraction peak of P4MPA to guide the eye.
In the XRD pattern of PPTA the intersheet 200 diffraction peak and the 110 diffraction peak overlap. The tops of the peaks, however, are clearly separated (Figure 5.9). The XRD pattern of the P3MPA polymer resembles that of PPTA, but the tops of the 200 and 110 diffraction peaks are no longer resolved, they seem to have merged into one single asymmetric peak, which is clearly composed of multiple reflections peaks. Hence as a result of substituting terephthalic acid by the dicarboxylic acid with 3 methylene groups the crystal lattice changes from the pseudo orthorhombic PPTA lattice to a lattice that has a more hexagonal character. An interesting question is if the resulting structure is sheet-like or not. We will return to this point in the sequel.

The low angle diffraction peak that is present in the XRD pattern of P3MPA has a spacing of 1.240 nm, which is close to the length of the P3MPA repeat unit consisting of the diacid monomer linked to the diamine monomer. In PPTA a similar low angle diffraction peak is absent (or of low intensity) due to the pseudotranslational symmetry of the PPTA unit cell, more specifically due to the similarity of the aromatic diamine and diacid. This similarity no longer exists in P3MPA, since the aromatic diacid is substituted by the aliphatic diacid and hence the pseudotranslational symmetry is broken, mainly because the length of the c-axis projection of the aliphatic diacid differs from that of the aromatic diamine.

The XRD patterns of the P4MPA and P8MPA polymers displayed in Figure 5.9 show the familiar two strong diffraction peaks that are often observed in the XRD patterns of both aliphatic and aromatic polyamides, characteristic of a sheet-like crystal structure. The right-hand member of the pair of diffraction peaks is located at about 23° (2θ), its position showing little variability. The associated d-spacing corresponds to the distance between hydrogen-bonded sheets. For the P4MPA and P8MPA polymers this intersheet distance is 0.399 and 0.395 nm respectively, which is very close to that of PPTA (0.392 nm) and somewhat larger than that of PA46 (0.384 nm). This indicates that in the P4MPA and P8MPA polymers the diamine phenyl rings are rotated out of the planes of the hydrogen bonded sheets, as is typical for PPTA and PPTA-like structures (see Figure 5.12). From Figure 5.9 it is clear that the position, and hence the d-spacing, of the left-
The hand member of the two strongest diffraction peaks of the various polymers shows larger variability than the right-hand member. Although the left-hand diffraction peak gives information on the interchain distance in the hydrogen bonded sheets, its $d$-spacing is also influenced by the structural details of the projection unit cell (e.g. the reciprocal angle $\gamma$, centering, etc.) and hence by the details of the packing of the hydrogen-bonded sheets. Clearly this packing shows more variation than the intersheet distance, which explains the larger variability of the left-hand diffraction peak. Figure 5.9 shows that the $d$-spacing of the left-hand side diffraction peak for P4MPA and P8MPA is larger than that of the other polymers, with a value of 0.470 nm for P8MPA, compared to 0.434 nm for PPTA. We will set up a structural model for the P4MPA polymer that will incorporate the observed structural information.

The XRD pattern of P4MPA does not show a low angle diffraction peak, similar to the XRD patterns of PPTA and PA46, but unlike those of the P3MPA and P8MPA polymers. This is due to the fact that the $c$-axis projection of the 4-methylene dicarboxylic acid is closer in length to that of the aromatic diamine than the 3-methylene and 8-methylene dicarboxylic acids.

### 5.4.3.2 Model building

Caution should be exercised in deriving structural models for the PmMPA polymers based on powder XRD patterns with relatively broad peaks, since the XRD patterns do not yield enough information to uniquely determine their crystal structures. However, since hydrogen bonding plays a key role in the polymers investigated, the polymers will probably be composed of hydrogen-bonded sheets similar to the hydrogen-bonded sheets in PPTA or polyamides. Such sheets are in fact structural building blocks that show relatively little structural variability. The task then is to find out how these sheets pack together into crystal structures. For this purpose a combination of force field based energy minimization and diffraction pattern matching is used. In this procedure a suitable starting model is adapted until the simulated XRD pattern matches the observed XRD pattern. The accuracy of the resulting models and the precision of e.g. their unit cell parameters will be lower than in e.g. fiber XRD studies.
Ricart et al. investigated the hydrogen bond geometry of even-odd and odd-even polyamides [58]. They pointed out that polyamides derived from odd diamine or odd dicarboxylic acid monomers cannot adopt a conventional sheet structure when molecular chains have an all-trans conformation. This is illustrated in Figure 5.10, which shows potential unfavorable hydrogen bonding geometry in PA65 reproduced from the report by Ricart et al. The authors presented a new polyamide structure characterized by hydrogen bonding in two different directions. In this scheme the amide groups of the odd monomer rotate about 30° in opposite directions from the plane formed by the methylene carbon atoms. The P3MPA polymer provides another test case for unconventional hydrogen bonding schemes, due to the presence of the same odd diacid as in PA65. Clearly the XRD pattern of P3MPA is markedly different from that of P4MPA and P8MPA, with their even-numbered diacid monomers. However, since the XRD pattern of P3MPA resembles that of PPTA, as can be verified in Figure 5.9, a similar hydrogen bonding scheme as that proposed for PA65 is unlikely.

Figure 5.10. Unfavorable hydrogen bond geometry between odd diamide units of PA65 when molecular chains have an all trans conformation (reproduced from Ricart et al., 2006) [58].

In view of the similarity of the XRD pattern of P3MPA and PPTA, we will set up a structural model for P3MPA starting from the structure of PPTA. The crystal structure of PPTA has been extensively discussed by Northolt et al. and Haraguchi et al. [16,17]. Furthermore, single crystal diffraction studies of PPTA were reported by Jackson et al. and Liu et al. [15,18]. The crystal structure discussed by Haraguchi et al. was observed in PPTA film spun from isotropic or
anisotropic solutions. This structure is known as modification II. After a heat
treatment modification II transforms into the Northolt structure, which is known as
modification I. The schematic of crystalline polymorphs reported for PPTA is
illustrated in Figure 5.11. The Northolt and Haraguchi structures have a pseudo-
orthorhombic lattice with two chains per unit cell and similar cell dimensions.
However, the positions of the polymer chains differ in modifications I and II, as
shown in Figure 5.11.

Figure 5.11. PPTA crystal structures as reported in the literature; A: Modification I and B:
Modification II.

For the type I polymorphs different monoclinic space groups were proposed
by Northolt (Pn and P21/n), Tadokoro (P21/n), and Liu et al. (Pc) [16,18]. Figure
5.12 presents a view of the Pn crystal structure of Northolt. The centre chain has a
c-axis shift of 0.064 nm compared to the structure with the higher space group
symmetry P21/n. Lowering the symmetry of the Pn structure to space group P1
followed by energy minimization produces a structure with cell parameters 0.765
nm, 0.514 nm, 1.298 nm, 90°, 90°, 90°. This structure is very close to the Pn
structure reported by Northolt, which was based on fiber XRD data (experimental
unit cell parameters 0.787 nm, 0.518 nm, 1.290 nm, γ = 90°). This indicates that the
Pn structure is very close to a minimum energy structure using the Compass force
field. At the same time it shows that the Compass force field is well suited to model
this type of structures.
A model for the crystal structure of P3MPA was built using the Cerius² software, starting from Northolt’s Pn structure. The terephthalic acid (TPA) monomer was replaced by a diacid monomer with three methylene groups to model the P3MPA structure. The polymer chain axis was assumed to be all-trans, leading to an extended chain structure. The P3MPA model structure was energy-minimized using the Compass force field. Note that the odd number of methylene groups leads to a structure where the carbonyl groups of each aliphatic diacid monomer point in the same direction, unlike the carbonyl groups of the aromatic diacid in PPTA, which point in opposite directions. This also implies that P3MPA has four monomers in its c-axis repeat unit, whereas PPTA has only 2 monomers in its c-axis repeat unit. Figure 5.12 displays the final model structure of P3MPA, together with the structure of PPTA. The unit cell parameters are listed in Table 5.3.

Simulation of the powder XRD pattern using Cerius² on the basis of the energy-minimized P3MPA model produces the XRD pattern shown in Figure 5.13. The simulated XRD pattern matches the experimental pattern very well, thus lending support to the P3MPA structural model. The low angle peak observed at 2θ = 7.16° (d = 1.230 nm) is indexed as 002. This peak is reproduced well in the simulated pattern. In the observed XRD pattern the left-hand side of the asymmetric main peak shows some extra intensity that may be due to amorphous material or to a type-II like polymorph. A similar asymmetry is observed in PPTA (Figure 5.9).

In the model the central polymer chain is staggered, just like in the Pn structure of PPTA. The size of the c-axis shift in the model is larger: 0.250 nm versus 0.064 nm. Without this c-axis shift the symmetry would be described by the monoclinic space group P111 (Pc in short notation), hence the symmetry is pseudo monoclinic. Due to the stagger the symmetry reduces to the triclinic space group P1.

The c-axis projection of the P3MPA model is very similar to that of PPTA, as is evident from Figure 5.12. The model is sheet-like, but the inter sheet distance is expanded and the intra sheet distance has decreased, compared to PPTA. The decrease in intra sheet distance allows a hydrogen bond length that is very similar to that in PPTA: 0.290 nm versus 0.300 nm for PPTA. The hydrogen-bonded sheet structure is shown in Figure 5.14. Clearly the hydrogen bond angles are less
favorable than in PPTA or in aliphatic polyamides like PA 46. The sheet structure resembles that of the $\gamma$-structure of e.g. PA77, the main difference being that the P3MPA polymer chains are extended.

**Figure 5.12.** Left-hand side: PPTA crystal structure according to Northolt (modification I), showing two unit cells. Right-hand side: model of the P3MPA structure, showing 1 unit cell. Color coding is as follows, red: oxygen atoms, blue: nitrogen, grey: carbon, white: hydrogen, yellow dashed lines: hydrogen bonds.
Figure 5.13. XRD pattern of the P3MPA polymer: (i) observed (upper diagram), (ii) calculated based on the P3MPA model (lower diagram).

Table 5.3. Symmetry and unit cell parameters of PnMPA structural models and of PPTA [16].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Symmetry</th>
<th>Unit cell parameters</th>
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<td></td>
<td></td>
<td>$a$ (nm) $b$ (nm) $c$ (nm) $\alpha$ ($^\circ$) $\beta$ ($^\circ$) $\gamma$ ($^\circ$)</td>
</tr>
<tr>
<td>PPTA (modification I)</td>
<td>P1$n$</td>
<td>0.787 0.518 1.290 90</td>
</tr>
<tr>
<td>P3MPA</td>
<td>P1 (pseudo P1a1)</td>
<td>0.850 0.470 2.480 90 85 90</td>
</tr>
<tr>
<td>P4MPA</td>
<td></td>
<td>0.540 0.700 2.800 38.5 77 63.5</td>
</tr>
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The XRD pattern of P4MPA, displayed in Figure 5.9, is similar to that of aliphatic polyamide PA46, although the $d$-spacings of the two strong diffraction peaks are somewhat larger for P4MPA as compared to those of PA46. In view of this similarity we will use a polyamide-like structure as starting model for the P4MPA crystal structure. Figure 5.15 displays a schematic view of the two possible sheet structures for PA46, as reported by Gaymans et al. [6]: a progressively sheared intra sheet structure ($\alpha$ form) and an alternatingly sheared sheet structure ($\beta$ form). In the $\beta$ form the diamine monomers are not adjacent to diacid monomers, whereas in the $\alpha$ form diamine monomers and diacid monomers are placed side-by-side. For P4MPA the $\beta$ form seems much less likely, since it would require the
side-by-side packing of aliphatic diacid monomers and aromatic diamine monomers side-by-side.

Moreover this is unlikely in view of the length difference between the aromatic and aliphatic monomers. Taking the above considerations into account the P4MPA structure was modeled starting from the classic \( \alpha \) structure of PA66, reported by Bunn and Garner in 1947 [53]. In this structure the diacid and diamine monomers were replaced by a diacid monomer with four methylene groups and the aromatic diamine respectively. The model was energy minimized, and the unit cell parameters were adapted to match the diffraction pattern. The resulting sheet structure is shown in Figure 5.16 and its simulated XRD pattern in Figure 5.17.

The calculated XRD pattern shows a good match with the observed XRD pattern. Note that the low angle region is reproduced correctly, i.e. the low angle peak is absent. In the P4MPA model hydrogen bonds are along the \( a \) direction following the Bunn and Garner choice of unit cell axes, therefore the indexing of the XRD pattern follows the familiar polyamide indexing. The hydrogen bond
length in the model is 0.320 nm. To have further insight into the structural changes with temperature time resolved XRD studies are performed on P8MPA.

Figure 5.16. Hydrogen-bonded sheet of P4MPA. Color code: see Figure 5.12.
5.4.3.3 Time resolved changes in the crystal structure of P8MPA

A pronounced influence of the methylene segment on the crystal packing is observed in the P8MPA (Figure 5.9). Two strong diffraction peaks at 23° and 18° (2θ) are observed along with the 002 diffraction peak at 6° (2θ). The presence of the two strong diffraction peaks indicates sheet like packing of P8MPA similar to that of polyamides. Upon heating the P8MPA, melting and crystallization
temperature becomes evident at 343 °C and 329 °C respectively (see Figure 5.4). A variable temperature $^{13}$C CP/MAS solid state NMR study of P8MPA showed that the phenylene ring within the amorphous component changes its conformation and transforms into a more ordered phase (Figure 5.6). At 100 °C, with the introduction of mobility in the phenylene ring the amorphous component starts to transform into the ordered phase. At 160 °C, complete disappearance of peaks associated with the amorphous component becomes evident. To investigate the implication temperature of crystallographic structure, variable temperature WAXD was employed.

![Figure 5.18: WAXD powder diffraction of P8MPA as a function of heating cycle. Annealed P8MPA (300 °C for 30 minutes) was used for the experiment.](image)

Figure 5.18, depicts crystallographic changes in P8MPA as a function of temperature. In Figure 5.18, the 002 diffraction peak at room temperature is absent. The absence of 002 peak can be attributed to the adopted measurement mode of the WAXD technique. To recall, Figure 5.9 shows the presence of 002 diffraction peak. The data presented in Figure 5.9 are obtained in reflection mode, whereas the data depicted in Figure 5.18 are obtained in the transmission mode. Besides this, the appearance of 002 diffraction peak depends upon the thermal history of the sample. For example, in Figure 5.18 the 002 diffraction peak becomes evident at ~170 °C. Within vicinity of this temperature, in the variable temperature $^{13}$C CP/MAS NMR
measurements, the phenylene ring within the amorphous phase transforms into the crystalline phase. Furthermore, the appearance of the 002 diffraction peak can be also associated with the alignment of the phenylene ring within the crystal plane. Thus in Figure 5.18, the origin of the 002 diffraction signal can be correlated with the transformation of the amorphous component of the phenylene ring in the crystalline state combined with the re-organization of the phenylene ring in the unit cell. Upon heating above ~150 °C, the intensity of the 002 diffraction peak increases significantly. On heating from 25°C to 328 °C, the diffraction peak at 23° (corresponding to distance between the hydrogen bonding sheets) shifts to lower angles reflecting decrease in the van der Waals interaction, whereas the peak around 18° moves to higher angles suggesting contraction in the Bragg’s spacing between the hydrogen bonding chains. These changes that are similar to aliphatic polyamides, suggest possible weakening in the hydrogen bonding efficiency of the amide motifs with increasing temperature. However, at 135 °C appearance of new diffraction peak at 41° and its splitting at 310 °C cannot be explained at this stage. Further insight can be obtained with combined WAXD and molecular modeling.

The structural changes observed around 170 °C are likely to arise with the transformation of amorphous phenyl rings into crystalline state, as depicted by time resolved 13C CP/MAS NMR shown in section 5.4.2.

5.5 Conclusions

Using the known PPTA synthesis, poly (amide-aramid)s having molar mass (>10 kg/mol) with varying methylene segments are synthesized. The poly (amide-aramid)s, up to 20 wt%, are found to be soluble in their polymerization medium (NMP/CaCl2). Changes in the crystal structure and the conformation of poly (amide-aramid)s with varying methylene segments have been investigated by solid state NMR and WAXD. The introduction of methylene units provides flexibility to the polymer backbone leading to melting of the polymer prior to degradation. The phenomenon becomes evident in the polymer having eight methylene units, P8MPA. Modeling studies conclusively demonstrate the influence of odd or even methylene units in the crystallographic packing of chains. For example the polymer
P3MPA, the presence of odd dicarboxylic acid monomer leads to an expansion of inter sheet distance and a contraction of the intra sheet distance as compared to PPTA. As a result of these changes the lattice acquires a more hexagonal character. Due to the intra sheet contraction the hydrogen bond length in P3MPA is very similar to that of both aliphatic and aromatic polyamides, despite the presence of odd monomer.

For the P4MPA and P8MPA polymers the intersheet distance is 0.399 and 0.395 nm respectively, which is close to that of PPTA (0.392 nm). The diffraction data indicate that the crystal structure is related to the \( \alpha \) form of polyamide. An adapted \( \alpha \) form structure was presented for P4MPA that fits well with the WAXD data.

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Chapter 6

Concluding remarks

Crystallization or self assembling process of synthetic as well as biopolymers, is strongly influenced by the secondary interactions such as hydrogen bonding. In this thesis, chemistry is utilized to manipulate the chemical and physical aspects of the hydrogen bonded materials by instigating the structural modifications in hydrogen bonded motifs. The concepts shown are related to the addition of Hofmeister ions in water which result in either enhancement or perturbation of hydrogen bonding efficiency between the water molecules. These changes can significantly influence physical properties of water at room as well as elevated temperature. Thus the molecular origin of these interactions between the water molecules in the presence of Hofmeister ions is a subject of scientific and technological interest.

From the studies performed in this thesis it is evident that in the presence of monovalent salts such as lithium or sodium halides, decrease in the overall hydrogen bonding efficiency of water molecules occurs. Unlike the monovalent salts, in the presence of divalent magnesium halide salts the hydrogen bonding efficiency of water molecules increases. The study also demonstrated that the hydrogen bonding efficiency generally decreases with increasing ionic radii of the tested ions. The molecular dynamic (MD) simulations supported this phenomenon where water molecules could cluster around smaller ions and minimize the loss in hydrogen bonding efficiency which however was not possible in the case of larger ions.

These structural changes in water molecules have strong implications in dissolution and crystallization phenomenon of polyamides. To have molecular insight in the dissolution process, structural changes in aliphatic polyamides as a function of temperature, in the presence of water-ions are investigated by time resolved dynamic NMR. On increasing temperature, with the decrease in the
hydrogen bonding efficiency of water molecules with or without ions two different mobilities of water molecules, in the presence of polyamide PA46 are observed. It was also observed that the population of water molecules in bulk decreases with increasing temperature. The enhanced water mobility effectively facilitates the dissolution process, around 100°C below the melting point of PA46. On cooling, with the crystallization of PA46 sudden shift from mobile to bulk water is observed.

In the presence of (8M) LiI solution, the suppression of hydrogen bonding efficiency in water molecules causes the dissolution of PA46 at even lower temperatures (approximately 130 °C below the melting point). Additionally, the crystallization of aliphatic polyamide could be fully suppressed. While in the presence of (6M) CaI$_2$ solution not only the dissolution occurred at lower temperatures (approximately 145 °C below the melting point of PA46) but also strong binding characteristic of Ca$^{2+}$ with amide motifs on crystallization is observed. Both these studies conclusively demonstrate that the dissolution of polyamides is a physical phenomenon which results from weakening of the hydrogen bonding efficiency of the solvent as well as the solute. Thus the good solvent characteristics of water for polyamides, opens a new possibility of self-assembling process, for synthetic as well as biopolymers, without degradation.

Further self-assembling characteristics of two oxalamide based model compounds having polar (Diethyl 4,5,14,15-tetraoxo-3,6,13,16-tetraazaoctadecane-1,18-dioate ($\bar{\alpha}$ala oxal $\bar{\alpha}$ala oxal $\bar{\alpha}$ala) and non-polar ($N^2,N^2$-bis (3-methoxypropyl) 2,11-dioxo-3,10-diaza-1,12-dodecanamide(Meo oxal $\bar{\alpha}$ala oxal $\bar{\alpha}$ala) end groups is investigated in the presence of water. The temperature dependent structural analysis of the melt and the water crystallized $\bar{\alpha}$ala oxal $\bar{\alpha}$ala oxal $\bar{\alpha}$ala depicted two crystal-crystal phase transitions prior to melting. The low temperature phase transformation was attributed to the gain in the mobility of the end groups, whereas the high temperature phase transformation arose from the induction of gauche conformers in the methylene units causing reduction along the c-axis of the unit cell. Similarly, the melt and the water crystallized Meo oxal $\bar{\alpha}$ala oxal $\bar{\alpha}$ala Meo also showed two phase transitions prior to melting. However, along with the observed phase transformations, the presence of water molecules within the
lattice was also recorded for water crystallized Meo oxa (CH$_2$)$_6$ oxa Meo. Removal of these water molecules from crystal lattice showed changes in the conformation of carbon associated with the end group. Additionally, structural studies of these model compounds crystallized from the superheated state of water demonstrated better crystal packing.

Modifying molecular rigidity between the hydrogen bonding motifs could be another way to influence the hydrogen bonding efficiency in the polyamides. This was investigated by varying methylene unit lengths (3, 4, 6 and 8) and their effect on thermal properties of poly(amide-aramid). The introduction of methylene units provided flexibility to the polymer backbone which not only led to the melting of poly(amide-aramid) before degradation but also promoted dissolution in the polymerization medium. The melting temperature phenomenon was, however, observed only in the polymer having eight methylene units, P8MPA. The wide angle x-ray diffraction (WAXD), crystallographic modeling and solid state nuclear magnetic resonance (NMR) studies conclusively demonstrated changes in crystal packing and conformation of the poly(amide-aramid) with varying methylene units. The studies reported in this work are of generic nature that should be applicable to hydrogen bonded materials in general where the interplay between water, ions, molecular flexibility will have implications in structural organization at different physical parameters such as pressure, temperature, concentration.
Appendix A

A.2.1: Influence of monovalent ion hydrogen bonding efficiency of water molecules probed with ATR-FTIR

In complimentary to $^1$H MAS NMR measurement, influence of lithium and sodium halide salts on the hydrogen bonding efficiency of water molecules is further investigated using ATR-FTIR spectroscopy at room temperature. Water in its liquid state shows three major bands. Two bands observed in the region of 3500-3200 cm$^{-1}$ are attributed to -OH anti-symmetric and symmetric stretching vibration modes of water molecules. Another band associated with the –OH vibration can be observed close to ~1640 cm$^{-1}$. This band corresponds to the bending mode of hydrogen bonded water molecules. The wavenumber of these three bands determine the hydrogen bonding efficiency between water molecules.

Figure A.2.1: The influence of monovalent cation and anion on the hydrogen bonding efficiency of water molecules probed with ATR-FTIR spectroscopy. (a) -OH anti-symmetric, (b) –OH symmetric stretch, and (c) -OH bending modes.

Figures A.2.1a, A.2.1b and A.2.1c illustrate changes in the wavenumber of the OH asymmetric and OH symmetric stretching vibration modes, and –OH bending mode of water molecules with and without ions at different ionic concentrations. Peak positions of the -OH anti-symmetric and –OH symmetric vibrations are deconvoluted from the FTIR spectra and are plotted as function of ionic strength. The asymmetric peak at ~3353cm$^{-1}$ is associated with the anti-symmetric –OH stretching, whereas the shoulder at ~3245cm$^{-1}$ is assigned to the
symmetric stretching vibration mode of -OH group. The bending vibration of –OH groups are observed at ~1640 cm\(^{-1}\).

Using ATR-FTIR Kazarian \textit{et al} have studied the effect of temperature on the hydrogen bonding efficiency of water molecules in the superheated state of water. As a function of temperature, changes observed in the -OH anti-symmetric (increase in the wave number), the –OH symmetric (decrease in the wave number), and -OH bending (decrease in the wave number) vibration modes are attributed to decrease in the hydrogen bonding efficiency between the water molecules. The cause for the decrease in the hydrogen bonding efficiency is linked with the gain in mobility of the water molecules, due to weakening of the intermolecular hydrogen bonding \cite{1}.

Our findings on changes in the vibration modes with increasing ionic concentration, at room temperature, are in accordance with the observations made by Kazarian \textit{et al} on increasing temperature. In this respect the decrease in the hydrogen bonding efficiency with the increasing ionic concentration is in equivalence with the increasing temperature. The changes observed not only depend on the ionic concentration but also show strong dependence on the ionic radii.

For an example, 1M LiCl shows increase in the –OH anti-symmetric vibration to 3360 cm\(^{-1}\) compare to 3350 cm\(^{-1}\) of pure water. With the increasing concentration of LiCl from 1M to 7M, the vibration wavenumber increases further to 3370 cm\(^{-1}\). The effect becomes more pronounced on increasing the anionic radii. For an example for 1M salt concentration, the –OH anti-symmetric vibration at 3360 cm\(^{-1}\) in LiCl moves to 3370 cm\(^{-1}\) in LiI. The difference in the shift of the vibration bands, with the increasing anionic radii, is attributed to enhanced perturbation of the hydrogen bonding between water molecules.

In the presence of sodium halide salts, that represents the case of larger cations relative to lithium, even more pronounced effects are observed. In the presence of 3M NaCl, the –OH anti-symmetric vibration moves to the wavenumber of 3375 cm\(^{-1}\) compare to 3368 cm\(^{-1}\) observed in the 3M LiCl solution. The enhanced shift in the wavenumber shows decrease in the hydrogen bonding
efficiency of water molecules in the presence of larger ionic radii. These results are in accordance with the data reported in Figure 2.2b, reinstating that larger ions function as chaotropes perturbing the hydrogen bonding efficiency of water molecules. What follows is the influence of divalent cation on the hydrogen bonding efficiency between water molecules.

A.2.2: Influence of divalent cations and monovalent anions on the hydrogen bonding efficiency of water molecules probed with ATR-FTIR

Figure A.2.2: The influence of divalent cations and anions on the hydrogen bonding efficiency of water molecules probed by ATR-FTIR. (a) -OH anti-symmetric stretch, (b) –OH symmetric stretch, and (c) -OH bending vibration modes.

In the presence of magnesium and calcium halide salts, the influence of divalent ions on the hydrogen bonding efficiency is investigated using ATR-FTIR. In the presence of magnesium halide salt (especially MgCl\textsubscript{2}), compare to pure water, the \textsuperscript{1}H NMR shows increase in chemical shift. Similar trends are observed in the ATR-FTIR study though in comparison with the \textsuperscript{1}H NMR the results are not pronounced. For example, the –OH anti-symmetric vibration band at 3354 cm\textsuperscript{-1} in pure water shifts to 3338 cm\textsuperscript{-1} in the presence of 6M MgCl\textsubscript{2}. These findings further confirm the kosmotropic nature of Mg\textsuperscript{2+} ion.

In the presence of calcium halide salts, shift in the anti-symmetric –OH vibration mode to higher values is evident. In the presence of 1M CaCl\textsubscript{2} the anti-symmetric -OH anti vibration moves to 3368 cm\textsuperscript{-1}, whereas the 6M CaCl\textsubscript{2} increase
to 3380 cm⁻¹. With the increasing ionic radii of anions, more perturbation in the hydrogen bonding efficiency gets evident. For an example, the –OH anti symmetric vibration at 3368 cm⁻¹ moves to 3380 cm⁻¹ in the presence of 1M CaI₂. Thus at room temperature, unlike Mg²⁺, Ca²⁺ ions show chaotropic nature (structure breaker) of water molecules.
Appendix B

B.3.1: Influence of water on crystallographic packing and Brill transition temperature

In many synthetic polyamides, on heating from room temperature, two main transitions are observed – Brill transition and melting temperature. While the Brill transition arises due to changes in the crystallographic packing from triclinic/monoclinic to pseudo-hexagonal phase without any involvement of heat, melting from solid to liquid phase is the well-known first order phase transition. Inspite of the Brill transition to be the crystallographic transformation and melting to be the thermodynamic transition, both are reversible that appear on cooling from melt. In polyamides where the Brill transition arises prior to melting, its appearance on heating strongly depends on the thermal history involved during crystallization.

The origin of Brill transition in the polyamides is correlated with the unique crystallographic packing that arises with the formation of the anisotropic distribution of the secondary interactions along the \( a \) and \( b \) axes. The presence of hydrogen bonding sheets along the \( ac \) plane and weak van der Waals interactions between them cause unique changes in thermal expansion on heating. For example, on heating, as the intermolecular hydrogen bonding weakens contraction occurs causing decrease in the intermolecular distance within the hydrogen bonding sheets (interchain/intrasheet). The thermal motion, causing the decrease between interchain/intrasheet, along the \( c \)-axis shows strong dependence on the chain segments residing in the amorphous region, that links the adjacent/non-adjacent re-entry of the chain segments. On the contrary to the contraction between the chains within the hydrogen bonding planes, the intermolecular interaction between the chains linked by van der Waals interaction (interchain/intersheet) decreases with increasing temperature – causing normal expansion process. The two prime diffraction peaks, interchain/intrasheet and interchain/intersheet, tend to merge at the Brill transition temperature. It is also well documented in literature that the position of Brill transition temperature in polyamides depends on the crystallization conditions. For an example, PA46 when crystallized from solution shows higher
Brill transition temperature (205 °C) compared to that crystallized from melt (in the vicinity of 180 °C). The difference in the Brill transition temperature is associated with the stronger hydrogen bonding in the solution crystallized sample compared to the melt crystallized sample. The former arises because of the presence of hydrogen bonding amide motifs aligned opposite to each other in the (interchain/intrasheet) hydrogen bonding planes. Such an alignment becomes apparent with the positioning of the two strong diffraction peaks, interchain/intrasheet and interchain/intersheet, at the maximum distance, at room temperature. The influence of crystallization condition on the appearance of the Brill transition temperature is well depicted in Figure B.3.1 below, where single crystals are sedimented from the water solution through a Büchner funnel to form a mat. The data is adopted from an earlier publication from our group [2].

**Figure B.3.1:** Simultaneous SAXS/WAXD recorded on heating of PA46 single crystal mat from 50 °C to 250 °C and cooling from 250 °C to 50 °C; both at 10 °C/min. It is to be realized that these samples were not heated above their melting temperature. PA46 was crystallized from water and crystals were sedimented to form mat. Excess water was removed by drying process in vacuum oven, around 50 °C, for overnight.
This single crystal mat is allowed to dry under ambient conditions before performing simultaneous SAX/WAXD on the samples. Figure B.3.1 elucidates the heating/cooling run of the dried sedimented crystal mats on a Linkam hotstage. X-ray diffraction patterns are recorded while heating/cooling the crystal mats between 50 and 250 °C at a rate of 10 °C/min. Figure B.3.1a shows WAXD patterns of the solution grown crystals. The starting values for the interchain/intrasheet and interchain/intersheet distances at 0.44 and 0.37 nm respectively are comparable to the crystals grown from other solvents. The Brill transition from the monoclinic to the pseudo-hexagonal phase is observed around 205 °C. On cooling from 250 °C, i.e. below the melting temperature of 295 °C, crystals in the pseudo-hexagonal phase transform into the monoclinic phase around 120 °C (Figure B.3.1 b). At 50 °C, comparison with the starting material shows remarkable difference in the interchain and intersheet distances, whereas the SAXS peak position and its intensity remains unaltered.

Quantitative changes in the interchain and intersheet distances on heating and cooling are summarized in Figure B.3.1e. On heating, the expected increase in the \((010)/(110)\) intersheet distance of the single crystal mats can be explained by the thermal expansion of the lattice, whereas the decrease in the \((100)\) interchain distance is due to the motion of the methylene units between the amide groups. The motion in the methylene unit next to the amide group will weaken the hydrogen bonding and will cause some translational motion along the c-axis. If the intermolecular chains on the hydrogen bonded plane are adjacently re-entrant, the translational motion between the adjacent chains is likely to be in the opposite direction, thus maintaining the lamellar thickness although perturbing the interchain and intersheet packing. On cooling from a temperature below the melting temperature, the expected contraction in the intersheet distance decreases. The strength of the hydrogen bonding between the interchain amide groups increases due to a decrease in the motion of the methylene units. This causes an increase in the intersheet distance with respect to the original distance. A complete recovery of the unit cell to the dimensions prior to heating will not be feasible since on cooling the strengthening of the hydrogen bonds between the chains prevent their...
translation back to their original positions. The Brill transition temperature will depend on the extent to which the interchain and intersheet distances are recovered on cooling. The large interchain and small intersheet distance, and the corresponding high Brill transition temperature of the water crystallized sample, suggest that the solution crystallized sample is the thermodynamically stable crystal. Figure B.3.1d shows the simultaneously recorded SAXS patterns. Note that the lamellar thickness of 6 nm hardly changes on heating/cooling the sample to/from 250 °C, see Figures B.3.1d, B.3.1e, and B.3.1f, despite the changes in the interchain and intersheet distances. This thickness of 6 nm corresponds well with the lamellar thickness reported by Atkins et al. where the long period consists of four chemical repeat units along the chain, i.e., $4 \times 1.47 \text{ nm} = 5.88 \text{ nm}$. These findings, together with those of Atkins et al., strongly suggest that the PA46 crystals grown from water are made up of tight folds and adjacent entangled chains similar to the β-bends in proteins. This in only feasible if an amide group is incorporated in the fold, rather than aliphatic segments, as shown in Figure B.3.2 (adapted from Atkins et al., Figure 11).

Figure B.3.2: A representation of a PA46 chain-folded sheet where the amide group is incorporated in the fold, adapted from Atkins et al.

Considering the correlation between the lamellar thickness of 6 nm and the anticipated theoretical value of 5.88 nm, the possibility of loose folding can be
overruled. Having an amide group on the surface of the crystal has implications for the adsorption of water on the crystal surface and the mobility of the amide protons. The model in Figure B.3.2 should exhibit two different proton mobilities associated to the amide groups; a free amide group residing on the fold surface and the amorphous component, and the hydrogen bonded amide group within the crystal. What follows are the changes in the intersheet and interchain distances of PA46 during dissolution process.

Figure B.3.3: Simultaneous SAXS/WAXD collected on heating 30wt% PA4,6 in water from 50 °C to 200 °C and cooling from 200 °C to 50 °C; both at 10 °C/min. A contribution form the glass capillary, water, and amorphous component have been subtracted from each diffraction pattern. The amorphous component, modeled with a Gaussian distribution which was allowed to vary with temperature so as to allow for thermal expansion, as well as the water component has been subtracted. Every second data file is plotted for clarity.

Figure B.3.3 shows the simultaneously recorded SAXS/WAXD data obtained on heating 30wt% of PA46 crystallized from formic acid, in water in a
sealed vessel from 50 to 200 °C at 10 °C/min. As shown in Figure B.3.3 a, on heating, prior to the merging of the (100) interchain and (010)/(110) intersheet reflections, the polymer becomes amorphous, i.e. the interchain and intersheet reflections disappear or merge into a halo around 180 °C. The normal melting point for PA46 is expected to be at ~295 °C, this shows the dissolution of PA46 in superheated water 100 °C below the melting point. With the onset of dissolution, i.e. the last few frames at about 8 °C prior to dissolution, the interchain and intersheet reflections deviate from each other and decrease in intensity. This is most likely due to the water molecules, which are highly mobile due to the elevated temperatures, penetrating the crystal lattice and breaking the hydrogen bonds between the amide groups. This causes the interchain distance to increase, and consequently the intersheet distance to decrease. The simultaneously recorded SAXS data shown in Figure B.3.3d show a well defined halo corresponding to a d-spacing of 9.5 nm at 50 °C. On heating, up to 150 °C, the lamellar thickness hardly changes. Above 150 °C the lamellar thickness increases with a broadening of the halo and finally disappears completely at 180 °C. On cooling the polymer/water solution from 200 °C as shown in Figure B.3.3b, crystallization occurs directly in the triclinic phase with the appearance of two reflections corresponding to the (100) interchain and (010)/(110) intersheet reflections respectively. The simultaneously recorded SAXS data shown in Figure B.3.3e show the appearance of a sharp halo on crystallization at much lower angles than before dissolution corresponding to a lamellar thickness of ~13 nm, i.e. considerably larger than the value of 9.5 nm prior to dissolution. The considerable increase in lamellar thickness suggests that a considerable amount of water resides within the amorphous and/or crystalline component of the lamellae. As we have already commented, water easily adheres to the amorphous component of polyamides; PA46 can contain up to 7.5 wt% water in the amorphous phase at low crystallinity. The increase in lamellar thickness may also be due to a change in crystallinity. However, the WAXD data does not suggest that a large change in crystallinity has occurred. On cooling to 50 °C, almost no shift in the lamellar thickness is observed.
We have demonstrated that PA46 can be dissolved in superheated water at ~200 °C by encapsulating the polymer with water in a closed vessel and heating the vessel to 200 °C, which is well below the melting point of PA46 (~295 °C). The process shown in Figure B.3.3 proceeds under pressure, i.e. as water enters the superheated state, pressure increases. As discussed in chapters 2 and 3 of this thesis, water in the presence of ions can further suppress the dissolution temperature and amorphous polyamide at room temperature can be obtained. What follows are the *in-situ* changes in the crystallographic structure of PA46 in the presence of monovalent and divalent ions and its implication on the appearance of Brill transition.

B.3.2: Influence of monovalent and divalent ions on crystallographic packing and Brill transition temperature

From the section above it is apparent that the differences in the WAXD between the starting material and the thermally treated material, in combination with no changes in SAXS, are indicative of considerable deviation in the molecular packing within the lattice, Figure B.3.1. The observed differences in the chain packing have implications on the Brill transition temperature. Thus the positioning of the Brill transition temperature and the crystallographic packing is likely to alter with the interaction of ions, and will have the potential to provide insight on the structural organization of chains in crystalline lattice.

Figure B.3.3a shows changes in the interchain and intersheet distances while heating PA46 in the presence of divalent Ca$^{2+}$ ion (6M CaI$_2$). It is apparent that the interchain distance contracts significantly by 0.02 nm, while heating the sample from 25 °C to 80 °C only. In the same temperature range the intersheet distance expands by 0.1nm. Above 80 °C, the interchain distance remains constant while the intersheet distance continues to increase till the two diffraction peaks merge into one at 105 °C. Thus the temperature, 105 °C, at which the two diffraction peaks merge is the Brill transition temperature of PA46 in the presence of the divalent ion. Beyond this temperature a single diffraction peak is observed and the crystalline
PA46 adopts the pseudo-hexagonal packing till it disappears due to melting of crystals around 150 °C.

![Graph](image)

**Figure B.3.3:** Changes in the intersheet and interchain spacing of PA46 as a function of temperature in the presence of (a) 6M CaI\(_2\) and (b) 8M LiI.

Figure B.3.1b shows changes in the intersheet and interchain distances of PA46 in the presence of 8M LiI while heating. Above 130 °C, prior to the appearance of the Brill transition dissolution of PA46 occurs. In this respect the dissolution process of PA46 in the presence of LiI is different than CaI\(_2\), but has similarities with dissolution in the presence of pure water. Just prior to the dissolution, contraction in the interchain (100) distance and expansion in the intersheet distance, similar to the dissolution process in pure water, are observed.

Table B.3.1 summarizes melting or dissolution temperatures of PA46, Brill transition temperature, and the intersheet, interchain distances in the presence of divalent and monovalent ions at room temperature.

From Table B.3.1, it is apparent that the intersheet distance between the hydrogen bonding planes increases with the addition of the divalent ions. Comparison with the monovalent ions indicates that the intersheet distance expands on addition of the Ca\(^{2+}\) ions, whereas in the presence of Li\(^+\) ions no significant differences with the pure water are observed. The similarities in the physical characteristics of PA46 in the presence of 8M LiI ionic solution and pure water are attributed to the smaller ionic size of Li\(^+\). Significant differences in the positioning of the Brill transition temperature and melting of the polymer PA46 suggest
intercalation of ions in the crystal lattice influencing hydrogen bonding, Figure B.3.3a.

Table B.3.1: Physical characteristics of PA46 in the presence of ionic solutions at 20 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent (mol/l)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$T_d$ ($^\circ$C)</th>
<th>$T_B$ ($^\circ$C)</th>
<th>$d$-spacing (nm) at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA46</td>
<td>-</td>
<td>295</td>
<td>205</td>
<td>0.44</td>
<td>0.37</td>
</tr>
<tr>
<td>PA46</td>
<td>H$_2$O</td>
<td>180</td>
<td>-</td>
<td>0.44</td>
<td>0.37</td>
</tr>
<tr>
<td>PA46</td>
<td>8M LiI</td>
<td>145</td>
<td>-</td>
<td>0.44</td>
<td>-0.37</td>
</tr>
<tr>
<td>PA46</td>
<td>6M CaI$_2$</td>
<td>145</td>
<td>105</td>
<td>-0.42</td>
<td>-0.38</td>
</tr>
</tbody>
</table>

* water crystallized PA46, $T_m$ melting temperature, $T_d$ dissolution temperature, $T_B$ Brill transition temperature

B.3.3: Conformation of PA46 in the presence of ionic solution probed with ATR-FTIR:

Figure B.3.4 depicts the ATR-FTIR spectra of aqueous PA46 in the presence of different ionic solutions (8M LiI and 6M CaI$_2$). The spectrum of water crystallized (WC) PA46 is used as reference. The samples are prepared with the concentration of salt, where complete shielding of the amide motifs of PA46 can be achieved. Significant differences in the positioning and peak shapes in the vibration of N-H stretching, Amide I (hydrogen bonded C=O stretch), Amide II (C-N stretch and C-N-H bending in plane vibration), Amide III (C-N stretch and N-H deformation) and CH$_2$ scissoring bands are observed in the samples crystallized from different ionic solutions at different concentrations. The changes in the bands are summarized in table B.3.2. The mentioned vibration bands represent the hydrogen bonding efficiency of the polyamide.
Figure B.3.4: Illustrates the ATR-FTIR spectra of the aqueous polyamide solution (PA46) prepared in different ionic solutions at different concentrations.

Table B.3.2: Assignments of the ATR-FTIR spectra of polyamide without and with different ions

<table>
<thead>
<tr>
<th>Polymer</th>
<th>N-H stretching</th>
<th>Amide I</th>
<th>Amide II</th>
<th>CH₂ Scissoring</th>
<th>Amide III</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA46 WC</td>
<td>3295</td>
<td>3094</td>
<td>1630</td>
<td>1535</td>
<td>1417</td>
</tr>
<tr>
<td>PA46-8MLiI</td>
<td>3290</td>
<td>3106</td>
<td>1620</td>
<td>1543</td>
<td>1413(²)</td>
</tr>
<tr>
<td>PA46-6MCAI²</td>
<td>3283</td>
<td>3097</td>
<td>1623</td>
<td>1547</td>
<td>1201</td>
</tr>
</tbody>
</table>

² represents first overtone of amide II. ² CH₂ scissoring band in crystalline state conformations. ³ very low absorbance, broad peak.

The N-H stretching of polyamide can be observed in the region of wavenumbers 3500-3100 cm⁻¹. For PA46 crystallized from the superheated state of water, the N-H stretching vibration is observed at 3295 cm⁻¹. In the sample crystallized from 8MLiI and 6MCAI² the N-H stretching vibrations are observed at 3290 cm⁻¹ and 3283 cm⁻¹ respectively. Vibrational frequencies in the range of 1650-1620 cm⁻¹ belongs to the amide I band i.e. the carbonyl stretching of the amide motifs. Frequency in the range of 1560-1530 cm⁻¹ originates from amide II, i.e. N-H in plane bend and C-N out of plane stretching with overtone of this signal in the range of 3100-3070 cm⁻¹. Wavenumbers of amide I and amide II signal accounts for the hydrogen bonding efficiency in the polyamide. Amide I (1630 cm⁻¹) and amide II (1535 cm⁻¹) frequencies observed in the case of water crystallized PA46 will be considered as reference for the comparison of polyamides crystallized from the...
ionic solutions, both monovalent and divalent. From Table B.3.2, in the presence of 8M LiI and 6M CaI$_2$ significant changes in the amide I and the amide II vibration modes are evident. The differences in the positioning of bands in the presence of ionic solutions compared to the pure water arises due to variation in hydrogen bonding efficiency. Another band that corresponds to the crystalline state of polyamide is CH$_2$ scissoring band. This band is observed at ~1417 cm$^{-1}$, depicted in Figure B.3.4 for the water crystallized sample. In the presence of 8M LiI and 6M CaI$_2$ the band disappears completely. The absence of the CH$_2$ scissoring band in the polyamides crystallized from the monovalent and divalent ionic solutions indicate the adoption of random coil conformation of polymer chain – thus amorphous polymer at room temperature.

The Amide III vibrations (C-N stretch and C-N-H bend in plane, coupled to carbon) show changes in the N-H group of the amide motifs that are strongly influenced in the presence of ions. The positioning of the vibrational bands in the presence of 8M LiI (1199 cm$^{-1}$) and 6M CaI$_2$ (1201 cm$^{-1}$) suggests that the ions, especially cations, interact with the amide motif of polyamides. This data further compliments $^1$H MAS NMR, where, the amorphous state of PA46 is obtained after dissolution in ionic solutions (Figure 3.3b and 3.4b). The presence of small crystallites at room temperature cannot be ruled out. This is evident from a small endotherm observed at low melting temperature on heating the PA46 crystallized from 6M CaI$_2$.

![Figure B.3.5: DSC traces of PA46 crystallized from 6M CaI$_2$. The sample was prepared by dissolving PA46 in 6M CaI$_2$ solution. Prior to the DSC run the sample was dried at 60°C for 12hrs to improve the baseline.](image-url)
Appendix C

C.5.1: Synthesis of PmMPA

Poly(propylene-phenyleneamide) (P3MPA)
Polymer P3MPA was synthesized from \( p \)-phenylenediamine (4.32g, 39.8 mmol) and glutaryl chloride (7.00 g, 41.4 mmol) following the general procedure described above in 40 ml CaCl\(_2\)/NMP (10.6 wt%). P3MPA was isolated as a dark green powder (6.84 g, 80%). \(^1\)H-NMR (D\(_2\)SO\(_4\)) \( \delta \): 7.07 (br, 4H ArH), 2.43 (br, 2H O=C-C\(_2\)H\(_2\)), 1.81 (br, 2H, O=C-C\(_2\)H\(_2\)).

Poly(butylene-phenyleneamide) (P4MPA)
Polymer P4MPA was synthesized from \( p \)-phenylenediamine (4.43 g, 40.9 mmol) and adipoyl chloride (7.73 g, 42.1 mmol) following the general procedure described above in 40 ml LiCl/DMAc (8.0 wt%), but no HCl scavenger was used. P4MPA was isolated as a yellow powder (8.13 g, 81%). \(^1\)H-NMR (D\(_2\)SO\(_4\)) \( \delta \): 7.34 (d, 4H, ArH), 7.19 (d, 2H, NH\(_2\)-ArH), 2.67 (br 2H, O=C-C\(_2\)H\(_2\)), 2.43 (br 2H, O=COH-C\(_2\)H\(_2\)), 1.74 (br, 2H O=C-CH\(_2\)-CH\(_2\)), 1.74 (br, 2H O=COH-CH\(_2\)-CH\(_2\)).

Poly(octylene-phenyleneamide) (P8MPA)
Polymer P8MPA was synthesized from \( p \)-phenylenediamine (3.39 g, 31.3 mmol) and sebacoyl chloride (7.90 g, 33.0 mmol) following the general procedure described above in 40 ml CaCl\(_2\)/NMP (10.6 wt%). P8MPA was isolated as a white powder (8.99 g, 72%). \(^1\)H-NMR (D\(_2\)SO\(_4\)) \( \delta \): 7.31 (br, 4H, ArH), 7.17 (d, 2H, NH\(_2\)-ArH), 2.56 (br 2H, O=C-CH\(_2\)), 1.55 (br, 2H, O=C-CH\(_2\)-CH\(_2\)), 1.17 (br, 2H, O=C-CH\(_2\)-CH\(_2\)-CH\(_2\)), 1.03 (br, 2H O=C-CH\(_2\)-CH\(_2\)-CH\(_2\)).
C.5.2: Chemical Structure determination of P6MPA

The chemical structure of synthesized Poly (amide-aramid)s is illustrated in the Figure C.5.1. Using 2D-NMR, the structure could be confirmed and molar masses of the polymers could be determined by revealing the position of the end groups within the $^1H$ spectrum. The details of the number average molar masses as determined by using $^1H$-NMR spectroscopy and the inherent viscosities of the polymers are presented in the Table C.5.1. $^1H$-NMR spectra of the polymer confirmed that the synthesized of Poly (amide-aramid)s are mainly end capped with PPD end groups and relatively less with carboxylic acid end group. The $^1H_1/^1H_2$ proton of aromatic block in the polymer (P6MPA) is verified by the singlet found for the phenyl ring with chemical shift around 7 ppm. However, within the 2D COSY also a cross-peak between 2 aromatic doublets is found at 7.11 and 6.85 ppm (annotated as 2’, 1’), these 2 doublets are derived from the PPD end group. The aliphatic part between the carbonyl motifs could be confirmed by the COSY cross peaks between $^1H_3/^1H_8$, $^1H_4/^1H_7$ and $^1H_4/^1H_7$, $^1H_5/^1H_6$ with the chemical shift at 2.3 ppm, 1.3 ppm and 1.3 ppm, 0.9 ppm, respectively. Peak broadening due to viscosity and anisotropy hampered observation of the multiplicity of these peaks.
Their position and integral, however, is in accordance with the expectation: less de-shielding due to presence of the carbonyl for the middle 2 methylene moieties; equal intensities for the PPD and 3 internal methylene units.

For the carboxylic acid end groups a set of cross peaks annotated as 3',4', 4',5', 7',6' and 8',7' were observed at (2.04, 1.14), (1.14, 0.78), (1.23, 0.87) and (2.31, 1.23) ppm, respectively (see Figure C.5.1). Similar experiments are performed on all the polymers and their structures could be confirmed. NMR measurement shows high purity (more than 99 w/w%) of synthesized poly(amide-aramid) with some traces of polymerization solvent NMP and ethanol as observed from the $^1$H spectra. However, in case of P3MPA, a trace of a cyclic oligomer of PPD and glutaric acid is observed with minor concentration (<0.1 w/w%). These cyclic oligomers are expected to be similar as previously reported in the synthesis polyethyleneterephthalate [3]. Using the area under the aromatic and carboxylic acid end group peaks, the molar mass of the polymers was determined and compared with PPTA. All synthesized poly(amide-aramid)s have number average molar mass (M_n) of around 10 kg/mol. This value suggests that the polymer chain consist of 90-120 monomeric units. The molar mass and molar mass distribution of poly (amide-aramide) is also determined using Gel Permeation Chromatography (GPC) using hexafluoropropanal (HFIP) as a solvent. The molar mass data obtained using NMR and GPC are similar as can be seen in Table C.5.1 along with relative concentration of amine and carboxylic acid end groups.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molar mass</th>
<th>End groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMR (g/mol)</td>
<td>GPC (g/mol)</td>
</tr>
<tr>
<td>PPTA</td>
<td>15000$^a$</td>
<td>No</td>
</tr>
<tr>
<td>P3MPA</td>
<td>10750</td>
<td>9500</td>
</tr>
<tr>
<td>P4MPA</td>
<td>12850</td>
<td>11300</td>
</tr>
<tr>
<td>P6MPA</td>
<td>11260</td>
<td>13400</td>
</tr>
<tr>
<td>P8MPA</td>
<td>12570</td>
<td>14300</td>
</tr>
</tbody>
</table>

$^a$ the molar mass of PPTA determined base on relative viscosity measurements.
C.5.3: Geometry optimization and NMR chemical shift calculations

All calculations were performed with Gaussian03 program package (Cite: Frisch, M. J. Gaussian 03 Revision D. 02; Gaussian, Inc.: Wallingford, CT, 2004). The isolated PPTA fragment was fully optimized at the B97-D/6-311G** level of theory using Grimme dispersion correction (S. Grimme, J. Comp. Chem., 27 (2006) 1787-99). The optimized structure was further proceeded for NMR chemical shifts calculations via B97-D/6-311G**.

C.5.4: FTIR band assignment of PmMPA and methylene units conformation

Conformational changes in the Poly(amide-block-aramid)s were studied using ATR-FTIR spectroscopy, using a Varian 670IR spectrometer. All spectra were measured in the range of 4000 cm⁻¹ to 650 cm⁻¹ at the resolution of 4 cm⁻¹ in Attenuated Total Reflection (ATR) mode. For the purpose the SLIDE-ON ATR selenium crystal was used. The ATR-FTIR spectra of Poly (amide-aramide)s are depicted in Figure C.5.2 and detailed of the vibrational band assignments are summarized in Table C.5.2.

![Figure C.5.2: FTIR spectra of poly(amide-aramid)s having varying length of methylene units after drying the synthesized samples at 80 °C for 24 hours.](image-url)
Vibrational modes close to ~3300 cm\(^{-1}\) corresponds to the N-H stretching vibration of PPTA and poly(amide-aramid)s polymers. To specify, N-H stretching vibration for PPTA are observed at 3318 cm\(^{-1}\) with relatively broad peak associated with localized N-H stretching interactions originating from two different units in monomer.

In case of the poly(amide-aramid)s, the wavenumber positions decreases with increasing the length of methylene segment. For example, P3MPA and P8MPA have N-H stretching vibrations at 3303 cm\(^{-1}\) and 3294 cm\(^{-1}\) respectively. Decrease in the N-H stretching vibration is indicative of decrease in intermolecular hydrogen bonding efficiency. The higher wavenumber value of the PPTA for N-H stretching vibration at 3318 cm\(^{-1}\) compared to the poly(amide-aramid)s further confirms the presence of strong intermolecular hydrogen bonding as suggested by the \(^{13}\)C CP/MAS NMR (Figure 5.4e). However, the presence of broad peak is associated with ATR-FTIR mode measurements and sample preparation.

The presence of methylene segment in poly(amide-aramid)s are observed with appearance of CH\(_2\) anti-symmetric and symmetric stretching bands in the region of 3000-2800 cm\(^{-1}\). Intensity of symmetric and anti-symmetric bands increases systematically whereas the wavenumber value reduces with increasing the length of the methylene segment. The other most important vibrational frequencies which defines the structure of the hydrogen bonding efficiency in polyamides are Amide I (C=O stretching) and Amide II (C-N stretch and C-N-H in-plane bending). These vibrational bands can be observed in the vibrational frequency range of 1700-1400 cm\(^{-1}\). For PPTA, amide I and amide II vibrations are observed at 1642 cm\(^{-1}\) and 1541 cm\(^{-1}\) respectively. For poly(amide-aramid)s, amide I wavenumber position decreases and amide II wavenumber value increases to higher number compared to the PPTA wavenumbers. Furthermore a shift in amide III band towards lower wavenumber is also observed. These changes in the vibrational frequencies suggest presence of strong intermolecular hydrogen bonding in poly(amide-aramid)s. The FTIR data complements solid state NMR findings discussed in the section 5.4.2.
### Table C.5.2: Infrared band assignment of Poly (amide-aramid)s [4]

<table>
<thead>
<tr>
<th>Type of vibration</th>
<th>PPTA</th>
<th>FM3PA</th>
<th>FM4PA</th>
<th>FM6PA</th>
<th>FM8PA</th>
<th>FM9PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N-H) stretch</td>
<td>s 3318</td>
<td>s 3303</td>
<td>s 3294</td>
<td>s 3297</td>
<td>s 3294</td>
<td></td>
</tr>
<tr>
<td>ring (C-H) stretch</td>
<td>w 3050</td>
<td>W 3051</td>
<td>w 3055</td>
<td>w 3055</td>
<td>w 3051</td>
<td></td>
</tr>
<tr>
<td>anti-sym (CH2) stretch</td>
<td>A</td>
<td>A</td>
<td>W 2943</td>
<td>S 2943</td>
<td>s 2934</td>
<td>s 2928</td>
</tr>
<tr>
<td>sym (CH2) stretch</td>
<td>A</td>
<td>A</td>
<td>vw 2875</td>
<td>s 2841</td>
<td>s 2858</td>
<td>s 2853</td>
</tr>
<tr>
<td>amide I</td>
<td>s 1642</td>
<td>S 1653</td>
<td>s 1653</td>
<td>s 1653</td>
<td>s 1657</td>
<td></td>
</tr>
<tr>
<td>ring (C=O) stretch</td>
<td>w 1604</td>
<td>w 1608</td>
<td>w 1618</td>
<td>W 1618</td>
<td>w 1608</td>
<td></td>
</tr>
<tr>
<td>Amide II</td>
<td>s 1541</td>
<td>s 1552</td>
<td>s 1548</td>
<td>s 1543</td>
<td>s 1548</td>
<td></td>
</tr>
<tr>
<td>(C-H) in-plane bending</td>
<td>w 1508</td>
<td>s 1512</td>
<td>s 1512</td>
<td>s 1512</td>
<td>s 1512</td>
<td></td>
</tr>
<tr>
<td>(C-H) scissoring in gauche conformation</td>
<td>w 1478</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>ring (C=H) in-plane bending</td>
<td>s 1401</td>
<td>s 1401</td>
<td>s 1401</td>
<td>s 1401</td>
<td>s 1401</td>
<td></td>
</tr>
<tr>
<td>ring (C=C) stretch</td>
<td>x 1309</td>
<td>x 1301</td>
<td>x 1301</td>
<td>s 1301</td>
<td>s 1301</td>
<td></td>
</tr>
<tr>
<td>Amide III</td>
<td>m 1253</td>
<td>m 1249</td>
<td>m 1249</td>
<td>m 1235</td>
<td>m 1235</td>
<td></td>
</tr>
<tr>
<td>in plane ring (CH) bend</td>
<td>w 1179</td>
<td>w 1179</td>
<td>w 1176</td>
<td>w 1176</td>
<td>w 1176</td>
<td></td>
</tr>
<tr>
<td>in plane (CH=CH) bond</td>
<td>s 1109</td>
<td>s 1131</td>
<td>m 1117</td>
<td>m 1117</td>
<td>m 1117</td>
<td></td>
</tr>
<tr>
<td>(CC=O) sym. stretch</td>
<td>A</td>
<td>w 952</td>
<td>w 955</td>
<td>w 955</td>
<td>w 955</td>
<td></td>
</tr>
<tr>
<td>ring (C-H) out of plane bending</td>
<td>m 891</td>
<td>m 899</td>
<td>m 899</td>
<td></td>
<td>A</td>
<td></td>
</tr>
</tbody>
</table>

- **I** = intensity, **Freq.** = frequency, **s** = strong, **w** = weak, **m** = medium, **A** = absent, **sh** = shoulder, **vw** = very weak, **a** = ring between amine group, **b** = ring/methylene segment between carbonyl group

### References

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Though, many have not been mentioned, none are forgotten.
List of Publications

Patent Applications


Peer Reviewed Publications

- Understanding the effect of a polar and non-polar end group on crystallization of strongly hydrogen bonded oxalamide motif based model compounds: Part 1 (Molecular conformation study). Y. S. Deshmukh; M. R. Hansen; R. Graf; E. Klop; R. Broos; S. Rastogi; under preparation, 2012.
- Hydrogen bonding in highly concentrated salt solutions: The case of LiI. N. Illanes; Y. S. Deshmukh; C. Allolio; S. Rastogi; M. R. Hansen; D. Sebastiani; under preparation, 2012.
- Beyond the first solvation shell - a first principles perspective on ion specific effects in aqueous hydrogen bonding networks. C. Allolio; Y. S. Deshmukh; S. Rastogi; M. R. Hansen; D. Sebastiani; under preparation, 2012.
- Influence of methylene segment length on crystal packing, chain dynamics, and thermal properties of poly(amide-arahid)s. Y. S. Deshmukh; C. H. R. M. Wilsens;
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R. Verhoef; Dmytro Dudenko; M.R. Hansen; R. Graf; E. Klop; S. Rastogi; Submitted, 2012.


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Yogesh Sheshrao Deshmukh was born in Akola (India) on 10th August 1981. After finishing Diploma of Engineering (Major: Plastics & Polymer Engineering) from Government Polytechnic Amravati, India in August 2000, he completed Bachelors of Engineering (Major: Polymer Engineering) from Maharashtra Institute of Technology (University of Pune), India in August 2003. The following three years, he worked in Complex Fluids and Polymer Engineering Group (CFPE) at National Chemical Laboratory Pune, India. In August 2006, he got scholarship from TU Eindhoven to pursue Master of Science degree in Chemical Engineering (Major: Polymers and Composites) from Eindhoven University of Technology, Netherlands and he finished the program in June 2008. He completed his Master’s research project on “Shielding and de-shielding of amide motifs of polyamides using Hofmeister ions” in the group “Laboratory of Polymer Technology” under the supervision of Prof. Sanjay Rastogi.

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