Solid-state modification of polyamide-6,6

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Solid-state Modification of Polyamide-6,6

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Chapter 1

Introduction

Abstract

This introduction presents a general background on polyamides (PA), their different synthetic routes and their properties, especially concerning PA-6,6. A brief overview of the solid-state polymerization technique (SSP) is given. The SSP reaction mechanism, the reaction parameters affecting the rate of SSP and its advantages over other conventional synthetic methods are discussed. Various modification processes to obtain copolyamides and their advantages are included as well. The new concept of solid-state modification (SSM) is introduced, which is significantly different compared to conventional melt modification methods. The aim and the outline of the thesis are also given at the end of this chapter.

1.1 General Introduction

Polyamides (PAs), the fully linear aliphatic types commercially known as nylons, are an essential class of condensation polymers.[1,2] Nylon was the first ever commercial thermoplastic, introduced as a nylon-bristled toothbrush in 1938.[3] PAs, being semi-crystalline materials, display a number of useful properties, such as high heat distortion temperatures, good mechanical properties up to high temperatures, good chemical resistance and stable electrical insulation properties.[4] Polyamide-6 (PA-6) and polyamide-6,6 (PA-6,6) are the most used representatives of this class. Wallace Carothers[1,5] invented polyamide-6,6 (PA-6,6) and within a few years his pioneering work concerning the development of polymeric materials led to the commercialization of PA-6,6 as the first synthetic fiber. Thanks to continuous research and development, PA-6,6 now constitutes

36% of the total polyamide market.[6] PAs have amide (–CO-NH-) containing repeating units that exhibit a form of ‘physical cross-linking’ in the polymer crystal through hydrogen bonding between the amide linkages. The hydrogen bond is unquestionably essential in explaining the structure and the chain conformation within the polymer crystals of the PAs.

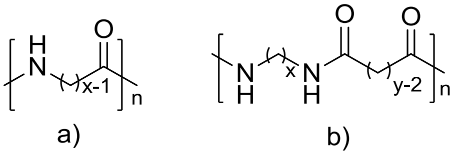

Figure 1.1 General structures of linear aliphatic polyamides a) polyamide-x; b) polyamide-x,y.

Polyamides, depending upon the type of repeating units as shown in Figure 1.1, can be synthesized by a condensation reaction between a) amino acids to yield polyamide-x type polymers or between b) diamines and diacids, to yield polyamide-x,y type polyamides as shown in Figure 1.2. Various melt and solution condensation routes have been studied in literature to prepare PA-6,6.[7-9] In view of the easier and cheaper work up processes melt polymerizations are strongly preferred over solution-based processes. However, if the reactants are sensitive to higher temperatures or if the polymer degrades before the melting temperature is reached, it is most preferred to apply the interfacial polycondensation technique[10-13] using a dicarboxylic acid chloride and diamines in a presence of a strong base. The synthesis of PA-6,6 has been studied extensively and many reviews have appeared in literature describing its currently applied industrial manufacturing processes.[14] Ring opening polymerization (ROP)[15] is mostly used to convert cyclic lactams to polyamides-x (Figure 1.3). This reaction begins with a hydrolytic ring opening of a lactam which can be catalyzed by an acid or a base, by an amino acid or by an amine carboxylate, e.g. nylon-6,6 salt. This ring-opened lactam initiates the ROP of ε-caprolactam, which is responsible for the first molecular weight build up. When the lactam concentration becomes relatively low, further molecular weight build up takes place by polycondensation reactions between carboxylic acid and amine end groups under the elimination of water.

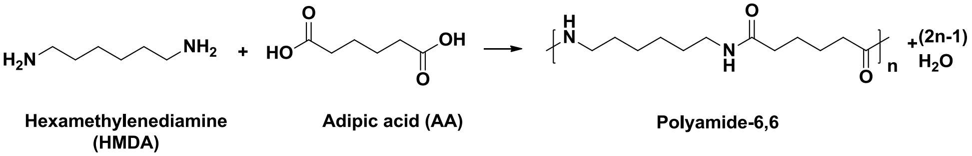

Figure 1.2 PA-6,6 synthesis reaction scheme.

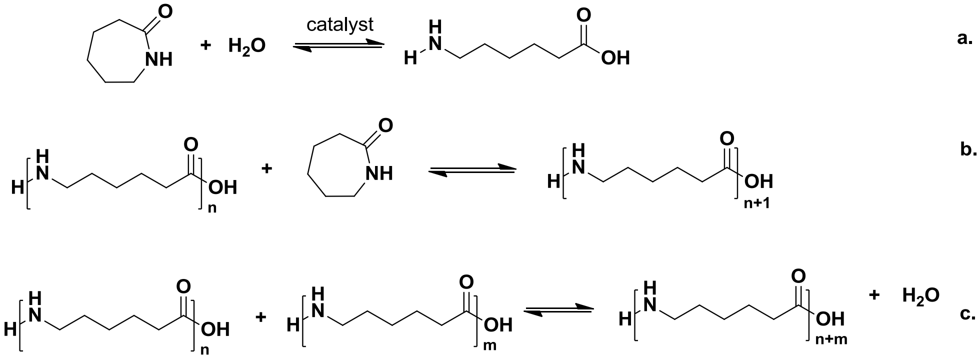

Figure 1.3 Hydrolytic ring opening polymerization of *ε*-caprolactam for the synthesis of Polyamide-6: a) hydrolytic ring opening of *ε*-caprolactam (CL), b) addition reaction of *ε*-caprolactam to a growing chain, the CL ROP and c) polycondensation reaction between the end groups.

Block co-polyamides were synthesized by interfacial condensation[16,17] or solution methods and it was found that the sequence distribution of the aromatic copolyamides is affected by the type of solvents, *viz*. polar or apolar. Nakata et al.[18] synthesized HMDA-containing semi-aromatic copolyamides by using the regular condensation method and found that the solubility of the polymer depends on the sequential regularity of the copolyamides.

1.2 Solid-state polymerization (SSP)

Although different polymerization methods are available for PA synthesis, there are always molecular weight limitations for the melt or solution methods mentioned above. As the molecular weight (or the degree of polymerization, DP) increases, the viscosity also increases and this result in limitations of the heat and mass transfer during the reaction. Lower molecular weight polyamides (M_n < 25 kg/mol) may be suitable for textile and fiber applications, whereas for blow-molding and injection-molding applications a significantly higher molecular weight (M_n > 25 kg/mol) is required.[19,20] Solid-state polymerization (SSP) is a well-established method, known since 1930 and widely used in industry, to increase the molecular weight of polycondensates, *viz*. polyesters and polyamides, via post-condensation.[21,21-23] First, a relatively low molecular weight semi-crystalline prepolymer is prepared, which is pelletized and subsequently subjected for 8-24 hours to a higher temperature between T_g and T_m, typically between 160 and 200 °C, depending on the melting temperature of the polymer concerned. This treatment is performed in a solid-state polymerization (SSP) reactor under an inert gas flow to achieve post condensation and, thus, molecular weight enhancement. The inert gas flow facilitates the removal of the condensation water from the polymer pellets.

1.3 Properties of PAs

Polyamide-6,6 is a tough and rigid material. It has a relatively high use temperature (up to about 260 °C) and is used in the manufacturing of products ranging from automotive gears to hairbrush handles. Molded PA-6,6 is used to make skate wheels, motorcycle crank cases, bearings, tractor hood extensions, skis for snowmobiles, lawnmower blades, etc. Since polyamides and most other condensation polymers contain polar groups such as amide- or ester-linkages which allow for hydrogen bonding in the case of polyamides and polar interactions in the case of polyesters, such materials are stronger, more rigid and tougher compared to most vinyl polymers. In addition, PAs do not need lubricants to improve their performance and therefore they can be used to produce mechanical bearings and gears that do not need periodic lubrication. Several polyamides have been invented to date and they vary in their degrees of crystallinity, melting temperature and properties depending on the number of flexible methylene groups present in the diamine and the diacid monomer residues. In general, in fiber applications the polymers exhibit a higher crystallinity than in thermoplastic applications due to the highly ordered structure in the drawn fibers.

The key properties of PA-6,6 are:

- High strength, rigidity and hardness.
- High dimensional stability, even at high temperature.
- High abrasion resistance.

However PAs are hygroscopic materials, meaning that, depending on the amide density along the chains, they may absorb significant amounts of water. Their mechanical properties are significantly affected by the water content, especially their flexibility and toughness, which both are enhanced upon moisture absorption, and their maximum tensile strength and stiffness, which both are reduced in humid environments. At standard atmospheric conditions of 23 °C and 50% relative humidity, the equilibrium water content of PA-6,6 is approximately 6.0 wt%.

1.4 Modification of PA-6,6

In order to improve the properties of PA-6,6 different approaches have been described in literature. These improvements all imply a modification, which can be done: a) chemically, i.e. by changing the backbone of PA-6,6 by either copolymerization or by a transamidation reaction with PA-6,6 using other polyamides, b) by blending PA-6,6 with other suitable polymers, or c) by the addition of another component which might not be miscible but which is compatible with the PA-6,6 matrix, an illustrative example being the toughening of PA-6,6 using reactive elastomers. In the following paragraphs several important approaches are discussed in more detail.

1.4.1 Blending approach

Research efforts have been focused largely on improving the properties of PA-6,6, as it is a notch-sensitive and poorly flame resistant material.[24-26] The limiting oxygen index (LOI) is the minimum concentration of oxygen, expressed as a percentage, that will support combustion of a polymer and the LOI of PA-6,6 is around 22-24%. The improvement of these bulk properties can be achieved by copolymerization.[27-29] Another effective approach is to blend PA-6,6 with another polyamide or with a polyester which has better mechanical, barrier and flame retardant properties.[30,31] GE Plastics succeeded in blending poly(phenylene oxide) (PPO), a more thermally resistant engineering plastic, with PA-6,6. The resulting successful commercial products are used in automotive applications,[32] where mechanical strength and chemical resistance are required.[33,34] The compatibility between PPO and the polyamide was e.g. improved by anhydride modification of PPO in the first step, followed by reactive compatibilization with PA-6,6.[35] During melt blending the amine end groups of the PA react with the anhydride groups attached to the PPO, thereby forming a compatibilizing block or graft copolymer.

Alternatively, PA-6,6 can be blended with poly(meta-xylylene adipamide) (MXD6) to improve the barrier properties, leading to a material which is successfully applied in laminates and packaging applications.[36] Furthermore, PA-6,6/polypropylene (PP) blends are targeted for reduced water absorption properties.[37]

1.4.2 Interchange reactions

In 1976, Miller[38] studied the interchange reactions in mixtures N-ethyl caproamide and N-hexylacetamide containing small concentrations of hexylamine and caproic acid, as schematically presented in Figure 1.4. The names of the interchange reactions are related to the initiating functional group. For example, acidolysis (equation 1) is the exchange reaction in which a carboxylic acid group attacks the amide bond and aminolysis (equation 2) is an amine-initiated reaction, whereas amidolysis is initiated by an amide group. Kotliar et al.[39] investigated the rate-determining step of these interchange reactions and found that the apparent lower rates of interchange for polyester melts compared to polyamides is undoubtedly a reflection of the extremely low water content of polyesters, which is a must in view of their equilibrium constant of the order of unity. The much higher equilibrium constant of polyamides (more than 100 times higher) allows the presence of measurable amounts of water in the system at the end of the synthesis, which under trans-reaction conditions can generate relatively high numbers of reactive amine and carboxylic acid end groups by hydrolysis. These newly generated end groups accelerate the interchange reactions.

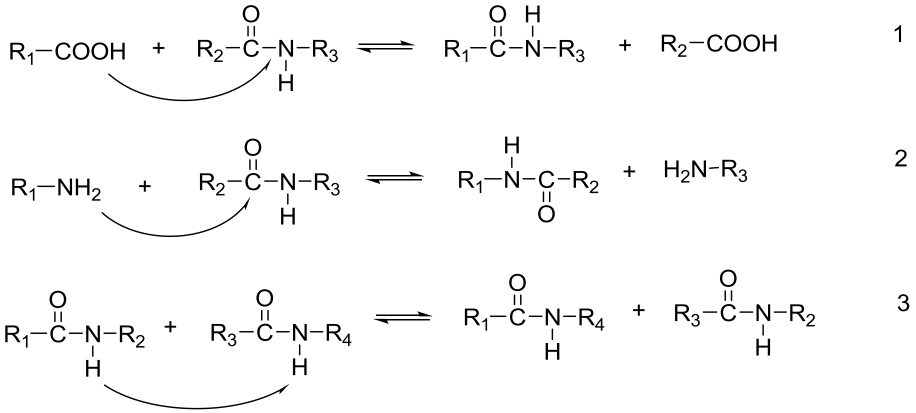

Figure 1.4 Interchange reactions of polyamides: (1) acidolysis, (2) aminolysis, (3)amidolysis[40]

1.5 Interchange reactions during SSP

Interchange or exchange or trans-reactions do occur during SSP reactions.[41,42] SSP is a subcase of bulk polymerization, as no solvents are used, applied to obtain high molecular weight material which might be difficult or impossible by a solution or a melt process. The latter kinetically reduces the mobility of the active end groups due to the increased viscosity. SSP entails heating a polymer or a mixture of monomers in the solid state to a temperature just below the melting temperature of the crystalline fraction of the material, yet high enough to initiate and propagate the interchange reactions in the mobile amorphous phase. SSP can also be performed by microwave heating or electron beam irradiation,[43-45] but conventional heating is mostly preferred to have more controlled reaction kinetics. As the polymerization takes place in the solid state and, consequently, all issues associated with the high temperature of melt processing and degradation as well as with the usage of solvents are avoided, SSP can be considered to be a ‘*green´* route.[46,47] An overview of the conditions applied during SSP of polyamides and polyesters is given in Table 1.1.

Table 1.1 Comparison between PET and PA6/PA-6,6 SSP Processes[48]

		Polyamide	
	PET	**PA-6**	**PA-6,6**
SSP temperature (°C)	200–240	140–200	140 – 200
SSP time (h)	10–26	6–24	6–24
Number-average MW	16,000–38,000	18,000–36,000	18,000–36,000
O_2 sensitive	>180 °C	>60 °C	>60 °C
Crystallization during SSP	Yes	No	No
Thermal pretreatment	Yes	No	No
Moisture (inlet)	<0.2 %	14 %	<1 .0 %

1.6 SSP Mechanisms

The SSP reaction is referred to as a ‘physico-chemical process’ as it involves the physical diffusion of monomer into and of condensation product out of the polymer and, in addition, it involves the chemical reactions of labile linkages and/or end groups. The SSP reaction is explained as '*a crystal-growth model'*. According to this model there are two main factors that play a role: 1) chemical constitution of the monomer and 2) its crystal lattice. There are some morphological factors expected to exert an influence on the SSP behavior, which are the following specifically explain the SSP reaction, where all monomers are in the crystalline state.[49]

The spatial arrangement of active groups of the monomer in the crystal lattice (in SSP), the distance at which they are separated, and their relative orientation. Molecular mobility is vastly more restricted in the solid state compared to that in the melt or solution, and so for at least the initiation of polymerization, the molecules must be "within reach" of each other. Once polymerization is initiated, the same factors may then influence the reaction rates and conceivably also the structure (morphology) of the resulting polymer. "Texture" of the monomer, as related to the size of the crystals, number and type of lattice defects, and the presence of impurities.

These factors may together exert their influence through related mechanisms or arise from common causes. For example, crystal edges and defects may in some cases inhibit the propagation of polymerization through physical separation of the polymerizing units, while in other cases they may act as "active centers" for initiation. Impurities may act by creating lattice defects that subsequently affect the polymerization, they may act as a physical diluent to impede polymerization, or may serve to increase molecular mobility and aid in polymerization.

The morphology of the semi-crystalline PA-6,6 based copolyamides can be described as a three phase model i.e. crystalline, rigid amorphous (which are in the proximity of the crystalline to amorphous phase transition region, with restricted mobility) and mobile amorphous phase. Unlike the SSP reaction mechanism as explained earlier, the solid-state modification (SSM, explained in section 1.8) reactions occur in the mobile amorphous phase[50] (as schematically shown in Figure 1.5) where the chain mobility is high and where any condensate formed is removed from the amorphous phase by passing through an inert gas or by maintaining reduced pressure during the SSP process.

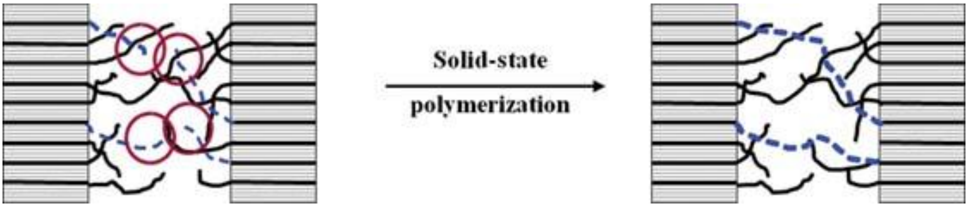

Figure 1.5 The scheme of the SSP reaction, predominantly occurring in the mobile amorphous phase of the polymer.

1.7 Factors affecting the SSP rate

As it involves both chemical and physical aspects, SSP represents a complex reaction process and one can identify several possible rate-determining steps. The most important four factors are given below and some more details are presented in Table 1.2:

- The intrinsic kinetics of the chemical reaction
- The diffusion of the reactive end groups
- The diffusion of the condensate inside the solid reacting mass (interior diffusion)

The diffusion of the condensate from the reacting mass surface to the inert gas (surface diffusion)

Table 1.2 Dependence of the most important variables on the controlling mechanism of SSP, when by-product is not a limiting factor.

Parameters ---->	**Reaction temperatures**		**Particle size**	**Prepolymer MW & crystallinity**	**Catalyst concentration**
Controlling mechanism	**Lower temperatures**	**Higher temperatures**			
1. Chemical reaction	Yes (strong influence)	Yes (weak influence)	No	No	Yes
2. End group diffusion	Yes (weak influence)	Yes (strong influence)	No	Yes	No
3. Interior by-product diffusion	Yes (weak influence)	Yes (strong influence)	Yes (strong influence)	Yes	N.A.

1.8 Solid-state polymer modification (SSM)

As described earlier, there is detailed literature available and extensive research has been done on SSP by both academia and industry. Though the concept of SSP is known since 1921, surprisingly the research on this topic is still very active. This can be observed from the number of scientific papers published until 2012, as shown in Figure 1.6. These publications are mainly focused on the solid-state post condensation (SSPc) reaction.

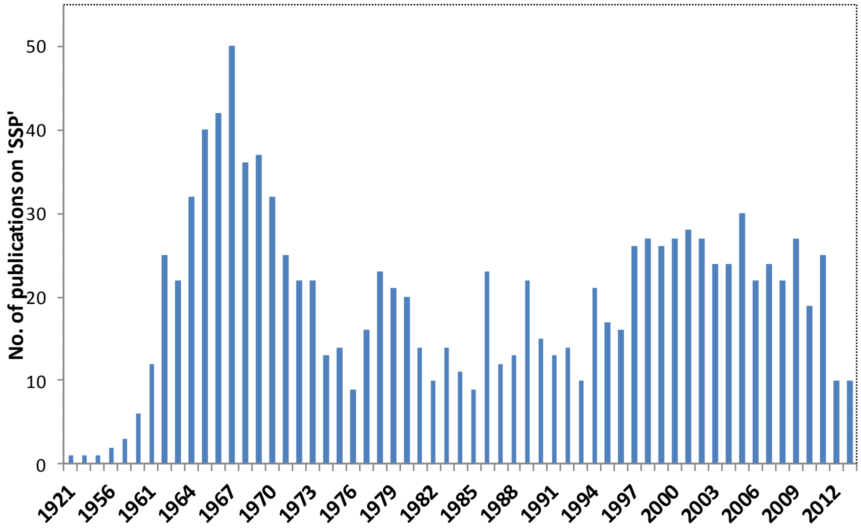

Figure 1. 6 History of number of publications (patents and journals) on SSP (Data obtained from Scifinder scholar search engine, 2012).

To the best of our knowledge, Jansen et al.[51-53] for the first time studied the solid-state modification (SSM) of semi-crystalline polyesters by incorporating T_g-enhancing comonomers into the polymer main chains in the solid state. Jansen et al. applied the SSP process for the chemical modification of a condensation polymer, *viz.* poly(butylene terephthalate) (PBT), and succeeded in the non-random incorporation of significant amounts of Dianol (2,2-Bis[4-(2-hydroxyethoxy)phenyl]propane, commercially known as Dianol 220®) comonomer into PBT without completely losing the crystallinity of the resulting block-like copolyester, since the reaction was constrained to the mobile fraction of the amorphous phase, leaving long crystallizable sequences of pure PBT intact. The chemical microstructure analyzed by ^{13}C NMR spectroscopy showed that the copolyesters synthesized via SSP are more blocky in nature, having a degree of randomness (R) value lower than unity, compared to compositionally similar copolyesters prepared via the melt polymerization (MP) route, which proved to have an overall random chemical structure with R values of around unity.

1.9 Aim and outline of the thesis

There is lot of research on going to reduce the moisture absorption of polyamides along with enhancing or retaining their thermal properties, *viz*. glass transition and melting and crystallization temperatures, which make them even more suitable for e.g. the automotive market where dimensional stability is crucial. The best way to realize such a modification is via solid-state modification as this process modifies only the amorphous phase, leaving the crystalline phase untouched. The advantage of this concept is that relatively long homo PA-6,6 sequences are retained, which exhibit better crystallization properties than random copolyamides. The main objective of this thesis is to modify PA-6,6 with a T_g-enhancing aromatic comonomer salt (equimolar xylylene diamine/adipic acid salt, MxAd) in the solid state to yield a block-like copolyamide with homo PA-6,6 as well as copolyamide blocks. The resulting SSM product is targeted to have retained the major part of its crystallizability compared to that of pure PA-6,6, while the physical, mechanical and thermal properties should be enhanced with respect to PA-6,6. Since the conventional melt route is not suitable to prepare such copolyamides, but rather yields random copolyamides with reduced crystallinity and properties, the SSP process is the preferred route to achieve this goal. To the best of our knowledge, this is the first time that the solid-state modification is explored for PA-6,6.[54]

In **Chapter 2**, the chemistry and the analytical monitoring of the incorporation of the comonomer salts, *viz. para*- and *meta*-xylylenediamine (PXDA and MXDA, respectively), into the PA-6,6 backbone is studied. The SSM was performed at 200 and 230 °C for 24 hours. The occurrence of transamidation reactions was confirmed by size exclusion chromatography (SEC) with UV detection (275 nm), which showed the presence of aromatic moieties in the final SSP product, whereas the starting PA-6,6 is virtually UV-inactive. The occurrence of the transamidation reactions was also proven by ^{1}H NMR spectroscopy. Herewith the concept of this thesis was proven.

Chapter 3 describes the influence of the concentration of the comonomer salt (MxAd), ranging from approx. 2.5 to 20 mol%, on the SSM reaction rate. In order to understand whether either aminolysis by (excess of) diamine or acidolysis by (excess of) dicarboxylic acid is the predominant step in the reaction mechanism a 20 mol% excess diamine or dicarboxylic acid was mixed with equimolar MxAd salt into the $(PA66_{80}MxAd_{20})_{Feed}$ and the SSM reaction kinetics was investigated. Also an attempt was made to prove whether the protonated amine or the deprotonated carboxylate ion in the comonomer salt is the active species initiating the attack on the amide bond during the SSM transamidation reaction. This was proven by reacting PA-6,6 with individual model compounds containing either protonated primary amines connected to an aromatic ring or containing deprotonated carboxylate species. The difference in the chemical microstructure of the $(PA66_{80}MxAd_{20})_{Feed}$ copolyamides synthesized via SSM and MP with comparable molar ratios PA-6,6/MxAd were determined using quantitative ^{13}C NMR sequential analysis.

Chapter 4 focuses on the thermal properties, *viz.* the melting and crystallization temperatures of the copolyamides, and these parameters are used to support the chemical microstructure determined in the previous chapter and to investigate the amorphous phase of the copolyamides in which the chemical modification occurs during SSM. The structural development during the SSM reaction of one specific copolyamide, *viz.* $(PA66_{80}MxAd_{20})_{SSM,Feed}$, was analyzed by studying the heating and cooling traces in DSC for samples taken at different SSM residence times. This chapter also discusses the differences in crystallinity of the SSM and MP samples by comparing heats of melting of SSM and MP samples with similar overall compositions.

In **Chapter 5**, the crystal structures of the copolyamides are studied by wide-angle x-ray diffraction (WAXD). The morphological changes of the copolyamides during stepwise heating to well above its T_g was studied by solid-state ^{13}C NMR on the copolyamide $(PA66_{80}MxAd_{20})_{Feed}$ prepared via SSM and MP. This affords additional supporting data to prove that the aromatic moiety is incorporated into the amorphous phase of PA-6,6 by applying SSM. In order to study the differences between transamidation performed during melt mixing compared to the transamidation process occurring during SSM, homopolymers of PA-6,6 and poly(*meta*-xylylene adipate) (MXD6) (80 and 20 mol%, respectively), having high molecular weights ($M_{n,SEC}$ approximately 35 KDa for both homopolymers) were melt mixed in a twin screw co-rotating lab extruder with L/D = 25. The chemical microstructure, crystallization behavior and the moisture absorption of the copolyamides obtained via SSM, MP and melt mixing were studied in water for 24 hours and compared.

Having understood most aspects of the fascinating SSM process, applied to modify PA-6,6 and to obtain blocky copolyamides with improved thermal and structural properties, an industrial scale-up step was attempted and the outlook is described in **Chapter 6** as a technology assessment.

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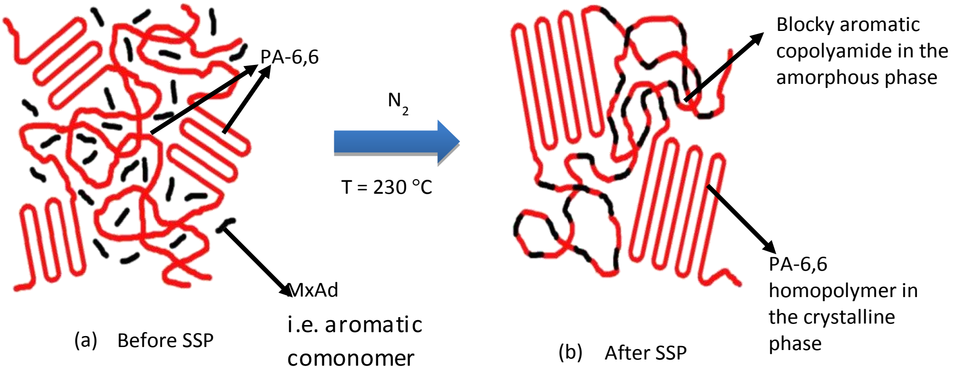
Chapter 2

Polyamide-6,6-based blocky copolyamides obtained by solid-state modification (SSM)



Abstract

In this chapter copolyamides based on poly(amide-6,6) (PA-6,6) were prepared by solid-state copolymer modification (SSM). Para- and meta-xylylenediamine (PXDA, MXDA resp.) were successfully incorporated into the aliphatic PA-6,6 backbone at 200 and 230 °C under an inert gas flow. The 'salts' of adipic acid and PXDA or MXDA were mixed in solution with PA-6,6 and after evaporation of the solvent the salts were built into the main chain of PA-6,6 by transamidation reactions. In the initial stage of the copolymerization below the melting temperature of PA-6,6 a decrease of the molecular weight was observed due to chain scission, followed by a built-up of the molecular weight and incorporation of the comonomer by post-condensation during the next stage. When sufficient time was used for the solid-state copolymerization the starting PA-6,6 molecular weight was regained. The incorporation of the 'salts' into the PA-6,6 main chain was confirmed by size exclusion chromatography (SEC) with UV detection, which showed the presence of aromatic moieties in the final SSM product. The occurrence of the transamidation reaction was also proven by ^{1}H-NMR spectroscopy. Since the transamidation was limited to the amorphous phase, this SSM modification resulted in a non-random overall structure of the PA copolymer as shown by the degree of randomness obtained by using ^{13}C NMR spectroscopy. The thermal properties of the SSM products were compared with melt-synthesized copolyamides of similar chemical composition. The higher melting and higher crystallization temperatures of the solid-state modified copolyamides confirmed the non-random, block-like chemical microstructure.

2.1 Introduction

Since Carother's invention[1] polyamides are well known and used in many applications because of the high dimensional stability under dry conditions, good mechanical and thermal properties, and excellent solvent resistance. Also polyamide copolymers have gained attention, since additional properties can be introduced while retaining the advantageous properties.

Solid-state polymerization (SSP), in which the polymerization is performed below the melting temperature but above the glass transition temperature, was specially developed to increase the molecular weight and viscosity of condensation polymers, such as (co)polyesters and (co)polyamides, after an initial melt polymerization. During the SSP process between T_g and T_m the residual reactive end groups of polyamides and polyesters present in the amorphous phase have enough mobility to react and the condensation products, normally water in the case of polyamides and water or a diol in the case of polyesters, are removed from the system by an inert gas stream or by applying vacuum. A number of studies were reported in literature on SSM methods, SSM reactor-design and SSP kinetics for both polyesters[2] and polyamides.[2-12] In most cases, these studies focused on solid-state post-condensation (SSPc). Only a few studies reported on copolymerization reactions by using solid-state polymerization.

Copolymers of polyamides can be obtained by either copolycondensation or ring-opening copolymerization in the melt, in solution or by using phase transfer methods, but these synthesis routes usually yield random copolymers. Groeninckx and coworkers[13-18] studied the modification of polyamides by transamidation reactions in the melt. When these reactions were carried out in a single-phase system, fully random copolyamides were obtained and it was very difficult to control the chemical microstructure and/or limit randomization. Especially for higher comonomer contents, random copolymers usually lose their ability to crystallize, which is a major disadvantage of such copolymers.

To the best of our knowledge, Jansen et al.[19,20] applied for the first time the SSM process for the chemical modification of a condensation polymer, *viz.* poly(butylene terephthalate) (PBT). The SSM modification resulted in an non-random incorporation of significant amounts of comonomer (e.g. 2,2-bis[4-(2-hydroxyethoxy)phenyl]propane, bis(2-hydroxyethyl)terephthalate and 2,2’-biphenyldimethanol) into PBT without completely losing the crystallinity of the resulting block-like copolyester. This is due to the fact that the reaction was constrained only to the mobile fraction of the amorphous phase, leaving long crystallizable sequences of pure PBT in the main chain.

To the best of our knowledge, SSM copolymerization has not yet been applied for polyamides. A difference with the mentioned PBT SSM modification is that commercial polyamides usually do not contain a polymerization catalyst. Titanates were used as a transesterification catalyst in polyesters (*viz.* PET, PBT) and they are not fully removed from the end product. So, mostly the commercial PBT contains titanate-based catalyst. On the other hand, the PA-6,6 used in our study contains no catalyst. In this paper, we describe the incorporation of semi-aromatic 'nylon salts' from p- or m-xylylenediamine and adipic acid (PxAd resp. MxAd) into the amorphous phase of poly(amide-6,6) (PA-6,6) via the solid state using a process very similar to the one described above for the PBT SSM modification. The main objective of this chapter is to demonstrate that this SSM modification indeed results in a less random chemical microstructure than a modification in the melt with a similar comonomer composition, and that the SSM product exhibits better thermal properties than that of the corresponding melt copolymerization product. In addition, for a fixed amount of salt the 'kinetics' of the incorporation of the 'nylon salt' at different temperatures was studied for a constant SSM reaction time. The aromatic comonomer incorporation was monitored by using UV detection coupled to size exclusion chromatography (SEC) and by using ^{1}H NMR spectroscopy. In the subsequent chapters a more detailed analysis of the crystalline nature of the blocky reaction products obtained after SSM in comparison with that of the more random copolyamides obtained from the melt route will be presented.

2.2 Experimental Section

2.2.1 Materials

Poly(amide-6,6) (PA-6,6, Ultramid® A-27) pellets (M_n = 38 kg/mol, M_w = 72 kg/mol) were supplied by BASF SE, Ludwigshafen, Germany. Adipic acid (AA) as well as para- and meta-xylylenediamine (PXDA resp. MXDA) were purchased from Sigma Aldrich. Ethanol (99%) required for the preparation of the diamine/diacid salt was also purchased from Aldrich. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, 99%), obtained from Biosolve (Valkenswaard, the

Netherlands), was used for solution mixing of PA-6,6 with the diamine/adipic acid salt. For NMR measurements deuterated trifluoroacetic acid (TFA-d, 99.5% deuterated) was obtained from Cambridge Isotope Laboratories, Inc., USA.

2.2.2 Solution preparation of the SSM reaction mixture

PA-6,6 pellets were ground into powder by a Retsch type ZM 100 mill in a cryogenic way. This powder was dried in a vacuum oven at 70 °C for 48 h. Then, 80 mol % of PA-6,6 and 20 mol% of comonomer salt were dissolved in 10-15 mL of HFIP at a temperature of approximately 50 °C. All the reaction mixtures were prepared in this way unless otherwise mentioned and no transamidation catalyst was present in or added to the starting material. After complete dissolution, the temperature was raised to 65 °C and HFIP was removed by drying under vacuum. The solid mixture lump was dried in an oven for 24 h and was then cooled in liquid nitrogen and ground into powder using an analytical laboratory mill (Waring, type 32BL80), after which the powder was filtered using a sieve to get a more or less uniform particle size of 100 µm or smaller. This powder was subsequently dried in a vacuum oven for a period of 48 h prior to the SSM reaction.

2.2.3 Solid-state modification (SSM)

The experimental setup for SSM consisted of a glass reactor, equipped with a fluidizing purge gas tube. A salt mixture of KNO_3 (53 wt %), $NaNO_2$ (40 wt %), and $NaNO_3$ (7 wt %) was used as the heating medium for the reactor.[26] The reactor consisted of a glass tube (inner diameter ~ 2.4 cm) and a sintered glass-filter plate at the bottom. A small heat exchange glass coil (inner diameter ~ 5 mm) surrounded the reactor (Figure 2.1). An argon gas flow was heated by passing through this heated coil before entering the inner glass tube at the bottom just below the glass filter plate. The gas flow was controlled by a flow meter. The SSM reaction temperature was measured with a thermocouple inserted into the PA-6,6/nylon salt mixture.

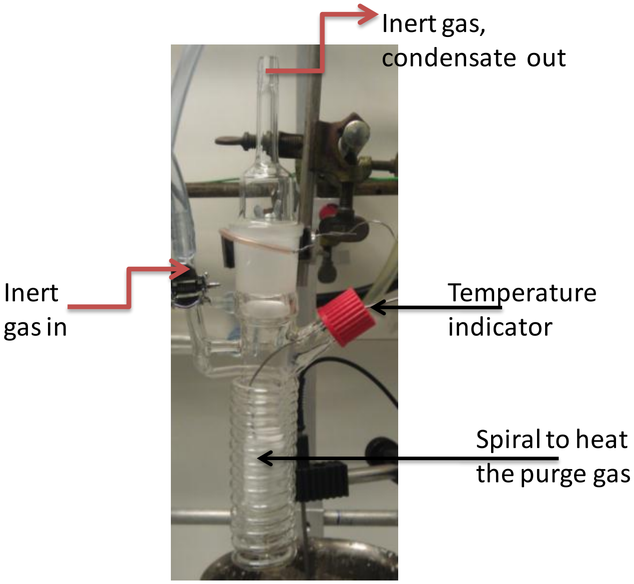


Figure 2.1 Laboratory-scale SSM reactor.

2.2.4 Preparation of comonomer salt

The preparation of 'comonomer salts' involved mixing the diamine (p-xylylenediamine or m-xylylenediamine) with adipic acid in equimolar proportions, by mixing equivalent amounts of ethanol solutions of both components (see Scheme 2.1, where Ar = CH_2-phenyl-CH_2). The nylon salts, *viz*. MxAd (m-xylylenediamine::adipic acid salt), PxAd (p-xylylenediamine:adipic acid salt), were precipitated out of ethanol in an equimolar composition once they were formed. The salts were filtered, vacuum dried at a temperature of approximately 50 °C for 4 h and their equimolarity was checked and confirmed by ^{1}H NMR spectroscopy.

$$HOOC\text{-}(CH_2)_4\text{-}COOH + H_2N\text{- }Ar\text{ - }NH_2 \longrightarrow {}^{-}OOC\text{-}(CH_2)_4\text{-}COO^{-}\ .\ {}^{+}H_3N\text{- }Ar\text{ - }NH_3^{+} \qquad (1)$$

Scheme 2.1 Synthesis of aromatic comonomer salt.

2.2.5 Melt polymerization (MP)

The melt copolymerization was carried out after dissolving in total 200 g of $(HMDA{:}AA)_{80}$ and $(MxAd)_{20}$ in 200 g of water (x,y denotes the mol% of the salt as per feed compositions) placed into a 1.2 L pressure reactor. The reactor was heated to 210 °C at 15 bar for 15 minutes, and the temperature was raised in steps of 20 °C. Then the temperature inside the reactor was subsequently raised to 220 °C and kept isothermal at that temperature for ca. 55 minutes under 15 bar pressure while removing water and forming a PA-6,6 prepolymer. Then, the temperature and pressure were reduced to 267 °C and 1 bar for 30 minutes, and after removal of the water the melt polycondensation reaction was carried out at 271 °C for 10 min with removal of condensation water, after which the copolyamide $(PA66_{80}MxAd_{20})_{MP,\ Feed}$ was granulated in an underwater granulation system. The number-average molecular weight (M_{n},$_{SEC}$) of $(PA66_{80}MxAd_{20})_{MP,\ Feed}$ copolyamide is 31 kg/mol.

2.2.6 Characterization

2.2.6.1 Size exclusion chromatography (SEC)

SEC was used to determine the average molecular weight and molecular weight distribution (M_{w}/M_{n}) of the polymer samples. For the PA-6,6 and SSM reaction samples, SEC in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was performed on a system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (35 °C), and ultraviolet (UV) detectors operating at a wavelength of 275 nm (these detectors are in series respectively), a Waters 2707 auto sampler, and a PSS PFG guard column followed by 2 PFG-linear-XL (7 µm, 8 × 300 mm) columns in series at 40 °C. HFIP with potassium trifluoroacetate (3 g/L) was used as eluent at a flow rate of 0.8 mL/min. The molecular weights were calculated against poly(methyl methacrylate) standards (Polymer Laboratories, M_{p} = 580 Da up to $M_{p} = 7.1 \times 10^{6}$ Da). Before the SEC analysis was performed, the samples were filtered through a 0.2 µm PTFE filter (13 mm, PP housing, Alltech). It has to be mentioned that some of the reaction samples that are branched/cross-linked might contain some gel particles. As the gel particles were filtered out before the SEC measurements, the data obtained may not be a true representation of the sample, and for these specific samples the M_n and M_w values as well as the PDI may be underestimated.

2.2.6.2 NMR Spectroscopy

NMR spectra were recorded on a Varian Mercury Vx (400 MHz) spectrometer at 25 °C. The solvent used was deuterated trifluoroacetic acid (TFA-*d*) and ^{1}H NMR spectra were referenced internally using the signal of residual solvent protons. Sequential analysis of the copolyamides was probed in ^{13}C NMR using HFIP:$CDCl_3$ in a 3:1 vol.%/vol.% ratio. The ^{13}C NMR spectra (5 mm probe, 400 MHz) were recorded overnight at room temperature with an acquisition time of ca. 1.5 s and a delay time (d1) of ca. 10 s in the NOE-decoupling mode.

2.2.6.3 Differential Scanning Calorimetry (DSC)

The melting (T_m) and crystallization (T_c) temperature and enthalpy were measured by a TA Instruments Q100 Differential Scanning Calorimeter (DSC) equipped with an auto sampler and a refrigerated cooling system (RCS). The DSC cell was purged with a nitrogen flow of 50 mL/min. The temperature was calibrated using the onset of melting for indium. The enthalpy was calibrated with the heat of fusion of indium. For the copolyamides prepared via SSM or MP, samples having a weight of 4-6 mg were prepared in crimped hemetic pans. All samples were measured in the temperature range from -40 to 290 °C using heating and cooling rates of 10 °C/min (unless specified), respectively, and having isothermal periods of 5 min at 0 and 290 °C respectively.

2.3 RESULTS AND DISCUSSION

2.3.1 Recipe

For the reactions 80 mol% of PA-6,6 and 20 mol% of the salt was dissolved in HFIP without any catalyst and the reaction mixture was prepared as explained in the experimental section on **Solution preparation of the SSM reaction mixture**. The mol percentage is calculated as the number of moles of the salt with respect to the total number of moles of the repeating groups in PA-6,6 plus the total number of moles of salt, either PxAd or MxAd, present in the mixture. This solution mixing is done prior to the SSM reaction to ensure optimum homogenization of the mixture and to maximize the chance that the salt is dissolved into the amorphous phase of PA-6,6. It is unlikely that the salt is incorporated into the PA-6,6 crystals, which are formed during the slow evaporation of the HFIP. The SSM modification reaction is expected to occur exclusively in the amorphous phase at the chosen reaction temperature, leaving the crystalline phase unaffected. This also limits the maximum amount of comonomer incorporation into the backbone by SSM.

2.3.2 Modification of PA-6,6 with p-xylylenediamine (PXDA)

The reaction of PA-6,6 (80 mol%) with the equimolar nylon salt based on p-xylylenediamine (PXDA) and adipic acid (AA) (20 mol%) (denoted as ($PA66_{80}PxAd_{20}$) was performed at 200 °C for 24 h under 1 L/min argon gas purge. Samples were taken at different intervals of the reaction and were analyzed with SEC (RI and UV detection). The SEC chromatograms of the starting materials, *viz*. PA-6,6 and PxAd salt as well as those of pure PXDA and pure AA, are presented in Figure 2.2. With the RI detector, the PA-6,6 polymer (elution time ca. 21 min) and the salt components (*viz.* PXDA or protonated PXDA at ca. 26.8 min and adipic acid or deprotonated AA at ca. 28.6 min) are clearly observed (see Figure 2.2a). Aliphatic PA-6,6 does not give a strong UV signal (see Figure 2.2b), so only the PxAd components (PXDA or its protonated form at ca. 25.6 min, respectively ca. 26.2 min, and adipic acid or its deprotonated form at ca. 27.4 min) give a signal in the UV detection chromatogram (see Figure 2.2b).

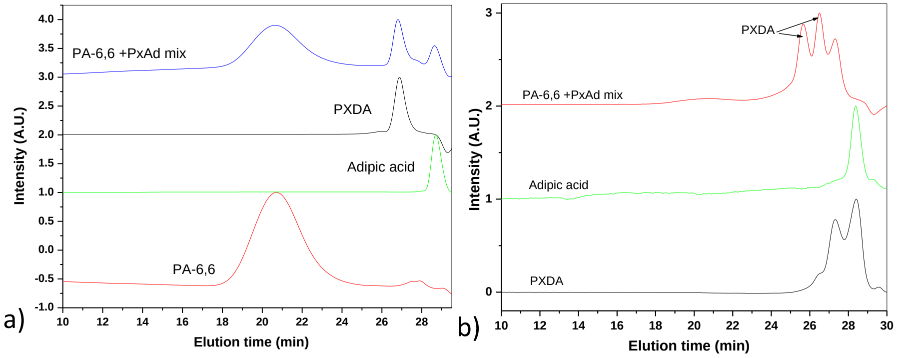


Figure 2.2 SEC chromatograms of SSM reaction starting materials, i.e. mixtures of PA-6,6 and PxAd salt, and pure PA-6,6 and salt components PXDA and AA: a) RI detection and b) UV detection.

The SSM reaction at 200 °C monitored by the SEC RI detector, as shown in Figure 2.3a, reveals that the peak of the PXDA comonomer around 26 min slowly starts to disappear as the reaction proceeds. After 2 h of SSM reaction time the intensity of this peak has clearly decreased and after approximately 8 h the peak is no longer visible. The broad polyamide-6,6 peak, recorded for the non-modified Ultramid® A-27 starting material, is found around 18 min with a peak maximum around an elution time of 20-21 min. The molecular weight reduced initially, which is visible from the slight shift of the peak maximum from ca. 20-21 min for the initial, non-modified PA-6,6 (left peak of bottom chromatogram) to a slightly higher elution time for the sample taken after 2 h of SSM reaction time. The shift, which is extremely small, is attributed to transamidation reactions occurring between the PA-6,6 main chain and the nylon salt components, causing chain scission resulting in an increase of the number of free carboxylic acid and amine end groups. These newly formed end groups at a later stage can be post-condensed to higher molecular weight copolyamide, which is illustrated by the slight shift of the peak maximum recorded after 2 h back to a lower elution time recorded after 8 and 24 h of SSM. During this post-condensation the condensation product (water) is removed from the reaction mixture by the continuous inert gas stream flushing through the reactor.

The UV detection chromatogram, shown in Figure 2.3b, shows a similar trend for the disappearance of PXDA comonomer or its protonated form and AA or its deprotonated form (PXDA ca. 25.6 min, adipic acid ca. 27.4 min). Please note that in the physical mixture of PA-6,6 and the PxAd salt, so before any reaction took place, no UV absorption is visible in the low elution region corresponding to the polymer. This is as expected, since the fully aliphatic PA chain has no or a negligible UV absorption. With increasing SSM reaction time the intensity of the PXDA peak is decreasing, but the polymer, eluting around 17-23 min, starts to become UV active (around ~ 275 nm), confirming the incorporation of the aromatic and UV-active PXDA monomer. Since the original PA-6,6 curve is not visible in the chromatograms with UV detection, no shift of the high molecular weight peak to higher residence times is visible, but for longer SSM times the shift to lower retention times can be seen. The observation that the initial molecular weight can be regained after a first break-down of the chains is a strong indication that not only the PXDA, but also the adipic acid residues become incorporated into the PA-6,6 main chain, which agrees with the disappearance of the peak of the deprotonated AA peak around 27.4 min. If this would not be the case, the non-equivalence of functional groups would prevent the restoration of the initial molecular weight. The observed trend in the number-average molecular weight (M_n) development as a function of SSM reaction time, *viz.* an initial decrease due to chain scission followed by an increase due to post-condensation (see Figure 2.4), is typical for a SSM process involving transreactions between polymers and low molecular weight compounds.[19] It has to be mentioned that the decrease in M_n during SSM at 200 °C is very limited and that the transreactions proceed in a slow way. The PDI of this reaction system overall shows an increasing trend, as seen in Figure 2.4, as during post-condensation some chains gain a lot in weight, whereas some low molecular weight chains remain present.

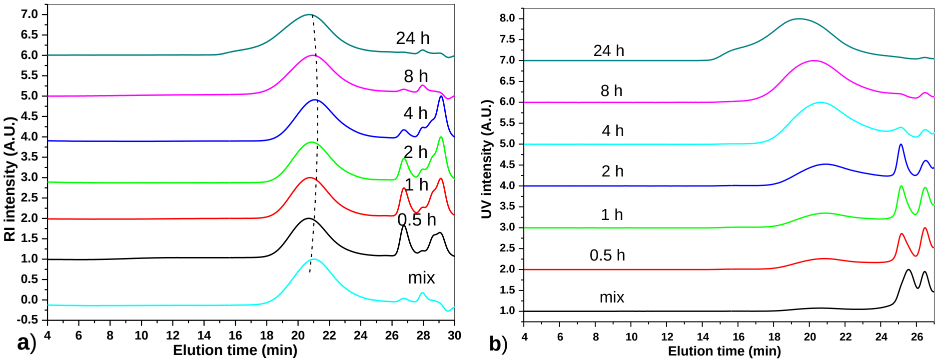


Figure 2.3 SEC chromatograms of SSM reaction products obtained by modification of (PA66$_{80}$PxAd$_{20}$)$_{Feed}$ at 200 °C: a) RI detection and b) UV detection.

It should be mentioned that in view of the exclusion of the crystalline part of the PA-6,6 from the transreactions one cannot expect the theoretical PDI value of 2, since in this case after SSM no Flory[21] distribution is obtained. In addition, at this reaction temperature after the occurrence of transamidation reactions, some gel-formation is observed, most probably initiated by the reaction between two amine end groups with release of ammonia. The resulting secondary amine group causes branching or even cross-linking (see Scheme 2.2), which is also confirmed by the development of a tail at lower elution times of ca. 14-16 min in the UV detection chromatogram of the SSM product (Figure 2.3b). Since the non-soluble part of the SSM product is filtered out before performing SEC, the reported molecular weights and PDIs are underestimated. It also has to be mentioned that after 2 h of SSM the post-condensation reaction dominates the chain scission reaction.

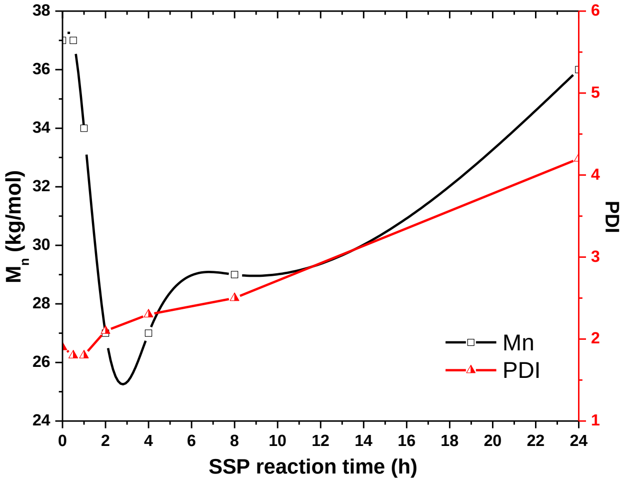
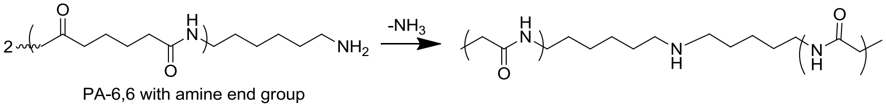


Figure 2.4 Number-average molecular weight (M_n) and PDI (from SEC) for the SSM product $(PA66_{80}PxAd_{20})_{Feed}$ as a function of SSM reaction time at 200 °C.



Scheme 2.2 Origin of cross-linking of PA-6,6 by amine end group reaction, causing higher molecular weight branched PA or even in insoluble gel formation. The secondary amine can react with a carboxylic acid-terminated PA chain.

The same SSM reaction was done at 230 °C for 24 h under a 1 L/min inert gas stream. At this higher temperature, the reaction rate of the chain scission of the PA-6,6 main chain by the PxAd salt was significantly faster than at 200 °C, and a significantly lower number-average molecular weight (M_n) was obtained during the first part of the transreaction processes (see Figure 2.4 compared to Figure 2.6). Also during the second part of the SSM process a much higher molecular weight was obtained due to a more efficient post-condensation at this higher temperature. Whereas at 200 °C chain scission appears to be the dominant process until an SSM reaction time of 2 h, at 230 °C the post-condensation already dominates after 1 h.

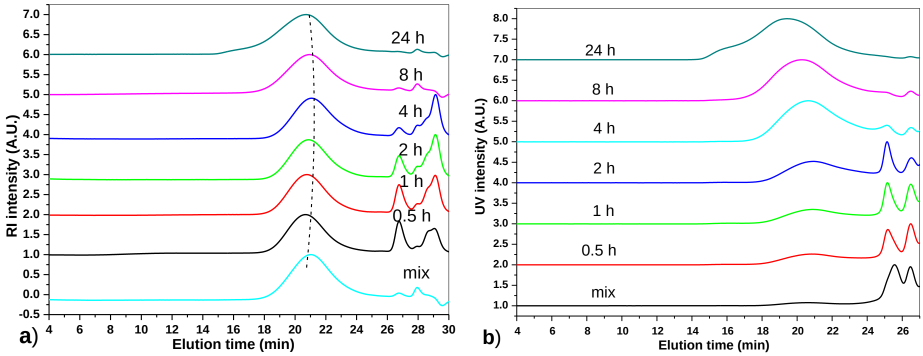


Figure 2.5 SEC chromatograms of SSM reaction products obtained from the sample $(PA66_{80}PxAd_{20})_{SSM,Feed}$ upon reaction at 230 °C: a) RI detection and b) UV detection.

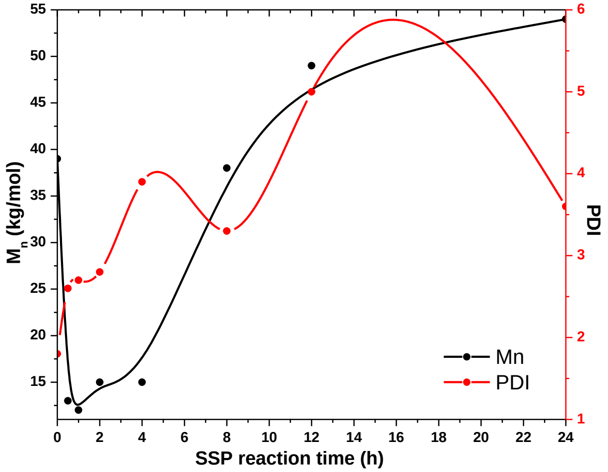


Figure 2.6 Number-average molecular weight (M_n) and PDI as a function of SSM reaction time at 230 °C for $(PA66_{80}PxAd_{20})_{Feed}$.

The development of the PDI as a function of time points to a significant degree of branching for longer SSM times, especially at 230 °C. Branching and even some cross-linking was evidenced by the presence of some HFIP-insoluble polymer material. These gel particles are filtered out before the sample is examined by SEC, which may explain the remarkable development of PDI with increasing SSM time. The kinetics of the trans-amidation at 230 °C is much faster than that at 200 °C (Please compare Figures 2.4 and 2.6).

2.3.3 Modification of PA-6,6 with m-xylylenediamine (MXDA)

The PA-6,6-based copolyamide resulting from the incorporation of PxAd might have a crystal structure in which both the 6,6 and PXDA,6 repeat units might fit in view of their very similar distances (1.72 nm) between the hydrogen bonding motives (c-axis of the unit cell of the crystal). So, after melting co-crystallization might be possible in the corresponding SSM products given the rather similar distance between the nitrogens in PXDA and 1,6-hexamethylenediamine, the major difference being the presence of the phenyl group in PXDA (In **Chapter 5** we will come back to this issue and by performing a careful XRD analysis it will be shown that such a co-crystallization indeed takes place for PA-6,6/PxAd copolyamides). Therefore, it is interesting to investigate the modification of PA-6,6 with both MxAd and PxAd, since MXDA,6 units are not *a priori* expected to fit into the crystal lattice of PA-6,6 (For PA-6,6/MxAd copolyamides in **Chapter 5** it will be shown that the MxAd units indeed are predominantly present in the amorphous phase of the copolyamide). Here, a similar modification of PA-6,6 was done with the equimolar nylon salt of m-xylylenediamine and adipic acid (MxAd), also at 200 (see Figure 2.7) and 230 °C (see Figure 2.8) for 24 h under 1 L/min inert gas stream. Samples taken at different time intervals were analyzed by SEC (RI and UV detection). The molecular weight trend (M_n) is similar to that of the PA-6,6 SSM modification with the equimolar PxAd salt, although the reactivity of the MxAd salt was found to be lower. This is obvious on comparing Figures 2.5 and 2.8b at the same temperature. The higher the rate of transreactions, the faster is the chain scission resulting in a lower molecular weight.

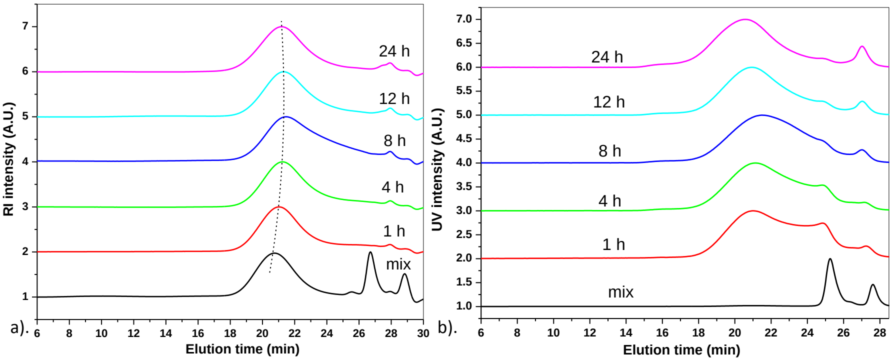


Figure 2.7 SEC chromatograms of SSM reaction products obtained from the sample $(PA66_{80}MxAd_{20})_{Feed}$ at 200 °C: a) RI detection and b) UV detection.

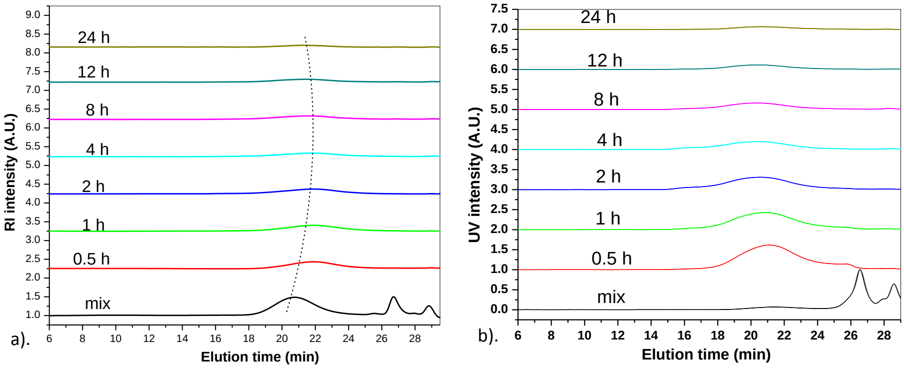


Figure 2.8 SEC chromatograms of SSM reaction products obtained from the sample $(PA66_{80}MxAd_{20})_{Feed}$ at 230 °C: a) RI detection and b) UV detection. (The chromatogram peaks appear flatter after normalization.)

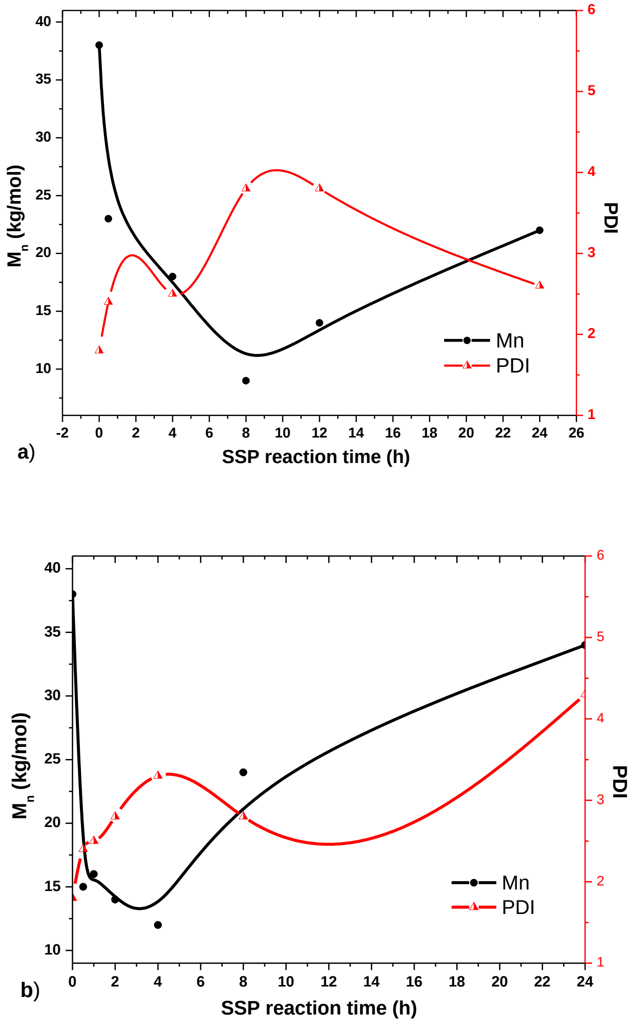


Figure 2.9 (PA66$_{80}$MxAd$_{20}$)$_{Feed}$: Molecular weight (M_n) and PDI as a function of SSM reaction time at reaction temperatures of: a) 200 °C and b) 230 °C.

The incorporation of the aromatic MXDA comonomer into the high molecular weight PA-6,6 was confirmed by SEC, both by RI detection, showing the disappearance of the MXDA peak around 25-28 min, and by UV detection, showing both the disappearance of the MXDA peak and the incorporation of a UV-active moiety in the high molecular weight fully aliphatic polyamide, which in itself is not or only moderately UV active. The ^{1}H NMR spectra of the neat PA-6,6, the starting material, and the comonomer along with the SSM-modified product are given in Figure 2.10. The benzyl proton (G) of the comonomer is shifted from approximately 3.5-4.0 ppm to approx. 4.5-5.0 ppm after incorporation into the aliphatic PA-6,6 backbone. The amount of comonomer incorporation was calculated, both for the SSM and the corresponding melt copolymerization $(PA66_{80}MxAd_{20})_{Feed}$ product, from the ratio of the intensity of the comonomer signal to that of both PA-6,6 and comonomer in the ^{1}H NMR spectra (NMR spectrum of melt route product not shown here). The MxAd content in the copolyamides was 17.0 mol% for the SSM product and 17.6 mol% for the melt route product, whereas 20 mol% of equimolar MxAd salt was present in the reaction feed in both cases (Note: In the remaining part of this chapter the copolyamide will still be identified as $(PA66_{80}MxAd_{20})_{Feed}$).

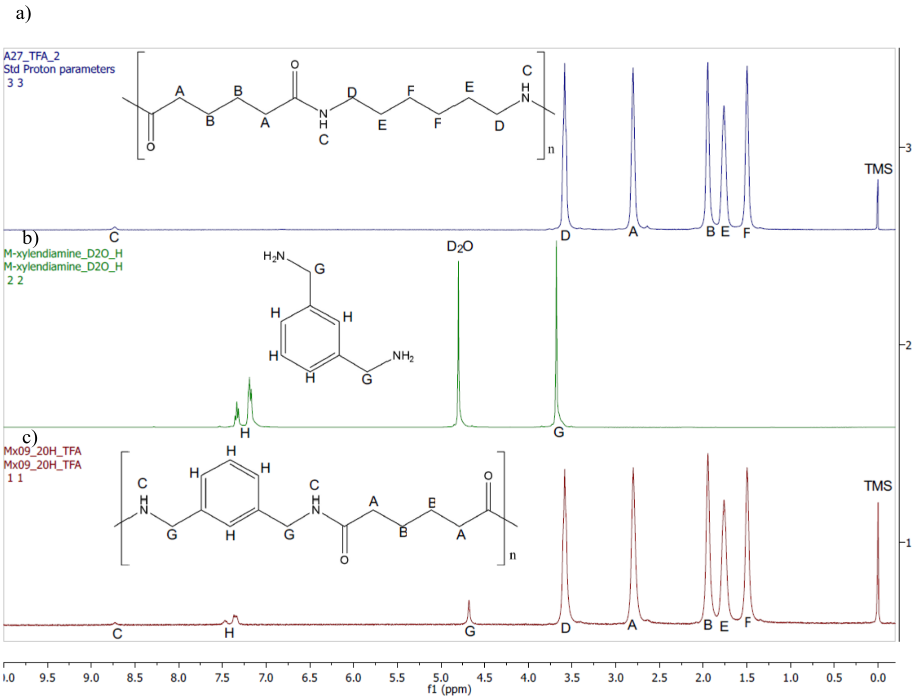


Figure 2.10 ^{1}H NMR spectra of the starting materials and the SSM reaction product of

($PA66_{80}MxAd_{20}$) (top to bottom): a) PA-6,6, b) m-xylylenediamine and c) SSM-modified PA-6,6 with aromatic diamine MXDA.

2.3.4 Chemical microstructure of PA-6,6/MxAd copolyamides and its effect on thermal transitions

The reaction products obtained after the SSM modification and melt copolymerization reactions were analyzed by NMR spectroscopy and DSC in order to determine the relation between the degree of randomness of the copolyamides and the crystallization and melting behavior. For the SSM product one might expect a block-like copolymer structure, since transreactions are expected to occur only in the amorphous phase leaving the crystalline pure PA-6,6 phase intact. On the other hand, the copolyamide prepared via the melt route (MP) is expected to be more random in nature. The microstructures, more specifically the comonomer sequences, of the copolyamides with comparable mol% incorporated MxAd salt either prepared via the melt route (MP) or by SSM were investigated using ^{13}C NMR spectroscopy. Hereto, 10 wt% of the product was dissolved in HFIP and then $CDCl_3$ was added to obtain a 3:1 vol/vol ratio of HFIP: $CDCl_3$. The solvent mixture results in a low viscosity and enables an accurate structural characterization based on ^{13}C-NMR spectra (see Figure 2.11) of poly(amides) as reported by Novitsky et al.[22]

Different dyads present in the copolyamides can be identified by analyzing the different carbonyl carbon peaks occurring in the ^{13}C NMR spectra. The carbonyl carbons positioned between two aliphatic main chain parts (an adipic acid and a hexamethylene diamine) have a different chemical shift compared to the carbonyl carbons in between both an aromatic MXDA or PXDA residue and an aliphatic residue. The influence of an aromatic residue on the shift of carbonyl carbons may be felt even at a position separated from this moiety by six methylene groups in the chain, as illustrated in Figure 2.12, and for the PA-6,6/MxAd copolyamide at least four different carbonyl carbons can be expected. The carbonyl group in the copolyamides surrounded by a high concentration of moieties based on methylene-based diamines is shifted to higher ppm[23-25] values in comparison to carbonyl carbons surrounded by lower numbers of methylene diamine residues.

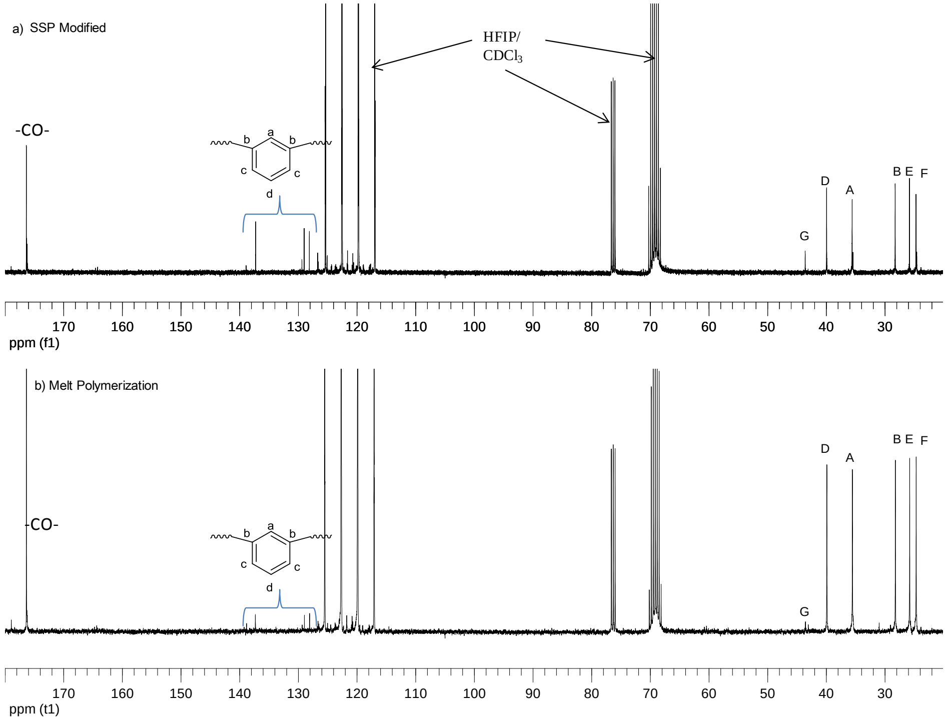
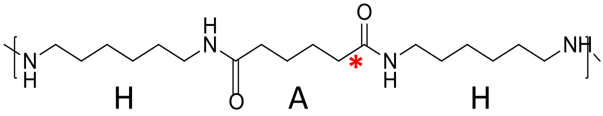
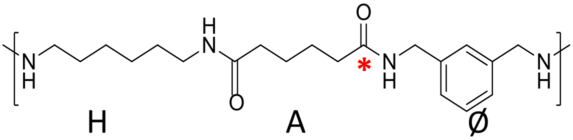


Figure 2.11 ^{13}C NMR spectra of $(PA66)_{80}(MxAd)_{20}$ copolyamide with 20 mol% of MxAd salt in the feed: (a) SSM modification reaction product and (b) same product by melt route. The structure given in Figure 2.10 was used for the peak identification.

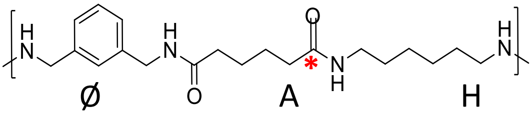
H-A-H (A)
ca.176.4 ppm



H-A-Ø (B)
ca.176.3 ppm



Ø-A-H (C)
ca.176.26 ppm



Ø-A-Ø (D)
ca.176.2 ppm

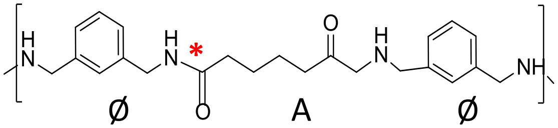


Figure 2.12 Four possible sequences (A, B, C, and D) of dyads in the PA-6,6/MxAd copolyamides represented by their chemical structure. H= hexamethylene diamine, A= adipic acid and Ø = m-xylylene diamine.

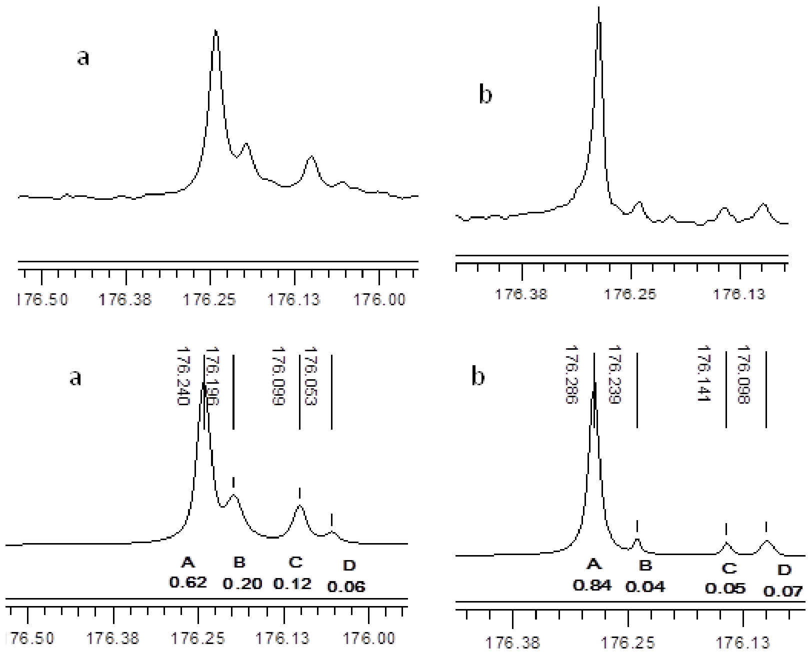


Figure 2.13 ^{13}C NMR spectra of $(PA66)_{80}(MxAd)_{20.}$ As-recorded spectra above and deconvoluted spectra below of the carbonyl dyads in the 176.5-176.0 ppm region with A-D sequences of: (a) melt-route product (MP) and (b) SSM-modified product.

The degree of randomness (R) of the copolyamides can be calculated by using eqs. (2.2) - (2.5), by incorporating the integral values listed under the deconvoluted peaks shown in Figure 2.13. These integral values of the four sequences are normalized to one.

$F_{HA\O,total} = F_{HA\O,HA\O\text{-side}} + F_{HA\O,\O AH\text{ -side}}$ (2.2)

$F_{HAH,total} = (F_{HA\O\ X,total}) / 2 + F_{HAH}$ (2.3)

$\mathrm{F}_{\O A\O,total} = (F_{HA\O,total}) / 2 + F_{\O A\O}$ (2.4)

$\mathrm{R}_{total} = F_{HA\O,total} / 2.(F_{HA\text{-}H,total} * F_{\O\ A\text{-}\O,total})$ (2.5)

F_{i} denotes the molar fraction of each sequence, as shown in Figure 2.13. $F_{\text{HAH,total}}$ and $F_{\text{HAØ,total}}$ denote the total molar fractions of the aliphatic and aromatic (MXD) side respectively.

Table 2.1 Molar fractions of the aliphatic-aliphatic (HAH), aromatic-aromatic (ØAØ), aromatic-aliphatic (ØAH) and aliphatic-aromatic (HAØ) sequences and the calculated degrees of randomness (R) for SSM-modified and melt-polymerized copolyamides as derived from ^{13}C NMR spectra using eqs. (2.2) to (2.5)

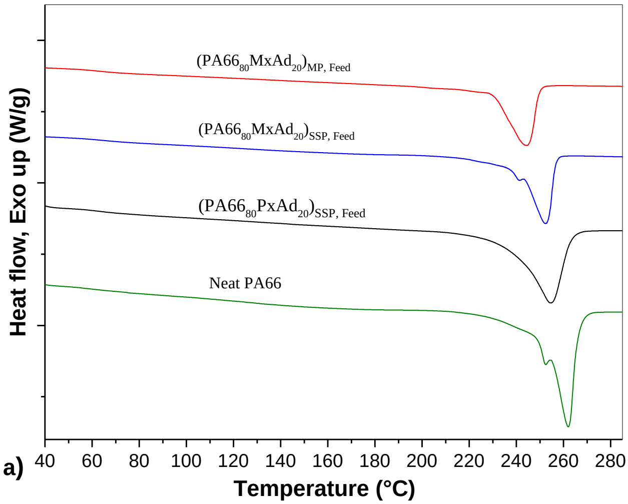
S. No	**$(PA66)_{80}(MxAd)_{20}$ copolyamide synthesized by**	$F_{\text{HAØ,total}}$	$F_{\text{HAH,total}}$	$F_{\text{ØAØ,total}}$	R_{total}
1	Melt route	0.326	0.779	0.221	0.95
2	SSM modification	0.085	0.844	0.113	0.43

From Table 2.1 it is evident that the microstructure of the SSM-modified product is arranged in a more blocky way than that of melt-route product having the same overall chemical composition, since the degree of randomness (R) of the SSM product is far below 1, which is the theoretical R value for a completely random copolymer. The degree of randomness of the melt-polymerized copolyamide is, as expected, very close to unity.

Now we have identified pronounced differences in the chemical microstructure, although the overall composition of the SSM and MP copolyamide is very similar, it is very interesting to compare possible differences in their crystallization and melting behavior as analyzed by DSC. From the second cooling run shown in Figure 2.14b, it is apparent that the onset of the crystallization peak after the SSM modification is not changed with respect to the pure PA-6,6, which strongly indicates that the modification with the MxAd salt happened only in the amorphous phase, leaving long pure PA-6,6 blocks with a good crystallization behavior. The T_g of the SSM-modified PA-6,6 is increased by approximately 11 °C (from ca. 55 to 66 °C, see Figure 2.14a, by the incorporation of 17.0 mol% of MxAd salt. The crystallization temperature as well as the melting temperature obtained during the second heating run of the SSM-modified material are significantly higher than the corresponding temperatures of the melt-modified material containing 17.6 mol% MxAd, and are in fact very close to the T_c and T_m values of pure PA-6,6 (see Table 2.2). This is due to the block-like structure of the SSM copolyamide, which renders relatively long pure PA-6,6 sequences and accordingly a much better crystallizable copolymer than the random copolyamide prepared by the melt route. As such, the approximate retention of the second heating melting temperature of $(PA66_{80}MxAd_{20})_{SSM,Feed}$ copolyamide is symptomatic of a lack of co-crystallization of MXDA-based units with PA-6,6 repeat units. On the contrary, the SSM copolyamides modified by similar amounts of PxAd comonomer exhibited a lower melting temperature than that of PA-6,6 (T_m ca. 254.5 °C, see Table 2.2), pointing to co-crystallization of the repeat units based on the aromatic diamine (PXDA) with six carbon atoms between the amine groups, being exactly the number of C-atoms as in hexamethylenediamine. The introduction of the rigid PxAd residues into the copolyamide crystals was expected to enhance the melting point due to the enhanced chain stiffness. The unexpected lowering of T_m with respect to PA-6,6 is possibly due to a somewhat disturbed packing of the chains in the a- and b-direction of the unit cell of the crystal structure, also resulting in a reduced crystallinity (see corresponding enthalpies of melting in Table 2.2). The $(PA66_{80}PxAd_{20})_{SSM,Feed}$ also resulted a higher crystallization temperature (T_c ca. 233 °C) compared to neat PA-6,6 at a 10 °C/min cooling rate. A detailed analysis of the crystallization behavior as a function of the incorporated mol% of comonomer salt will be presented in the subsequent chapters (**Chapters 4** and **5**).

Table 2.2 Results of DSC analysis obtained from second heating cycles (10 °C/min) of $(PA66_{80}MxAd_{20})_{Feed}$ copolyamides synthesized by melt- and SSM-route

S. No.	Sample	T_g (°C)	T_m(°C)	Δ*H*m, (J/g)	T_c (°C)
1.	PA-6,6 unmodified	~55	262.6	70.8	221.0
2.	SSM (17 mol% MxAd)	62.5	260.5	57.9	220.5
3.	Melt route (17.6 mol% MxAd)	66.3	244.4	43.3	198.6
4.	SSM (18 mol% PxAd)	62.5	254.5	65.3	233.1



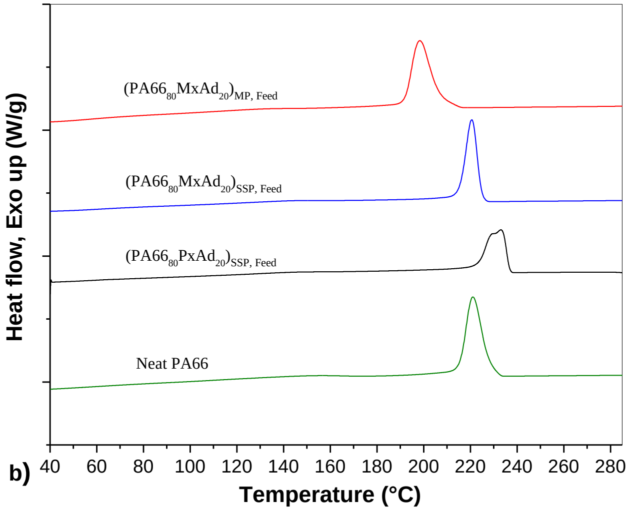


Figure 2.14 The DSC thermograms of unmodified PA-6,6 and SSM-, MP-copolyamides, (PA66$_{80}$ P/MxAd$_{20}$)$_{Feed}$: a) second melting run and b) second cooling run (stacked vertically for clarity).

2.4 Conclusions

For the first time for polyamides, a solid-state modification of the amorphous phase of a polyamide was performed below the melting temperature. Semi-aromatic para- and meta-xylylenediamine:adipic acid 'nylon salts' were incorporated into the main chain of PA-6,6. In a first step, these salts were mixed into the amorphous PA-6,6 phase by a solution-evaporation process using the common solvent HFIP. After the SSM treatment SEC in combination with UV detection confirmed the presence of the aromatic moiety in the aliphatic PA-6,6 main chain. Since the PA-6,6 chain segments present in the crystals during the solid-state polymerization (SSM) process do not participate in the transamidation reactions, the SSM modification reaction results in relatively long blocks of pure PA-6,6 segments and blocks of copolyamide segments. As expected, the kinetics of the transamidation is much faster at 230 than at 200 °C and the SSM-modified copolyamide initially shows a significant molecular weight reduction by chain scission by transamidation with the incorporated salt, followed by a restoration of the molecular weight to a value close to the starting value after 8-12 h of reaction time. At higher reaction temperatures branching and cross-linking reactions, resulting in gel formation, are observed after 8 h of reaction. The degree of randomness (R) of the SSM reaction product proved to be around 0.4, whereas for a melt-polymerized copolymer with a similar composition an R value of ca. 0.95 was obtained, which is very close to the theoretical value of 1 for a fully random copolymer. The more blocky microstructure of the SSM product, exhibiting longer PA-6,6 sequences, is also reflected in a more favorable crystallization behavior of this copolyamide from the melt, showing higher melting and crystallization temperatures in comparison to a melt-synthesized copolyamide with similar composition. In fact, the melting and the crystallization temperatures of the SSM product containing approximately 17 mol% of MxAd salt are very close to the corresponding values of pure PA-6,6, whereas a melt-polymerized copolyamide containing 17.6 mol% MxAd exhibits significantly lower values for both transitions. Moreover, the T_g was raised by the incorporation of the semi-aromatic salt into the PA-6,6.

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Chapter 3

Solid-state modification of PA-6,6 with a semi-aromatic salt (MxAd): The influence of the salt concentration on the reaction rate and chemical microstructure

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Abstract

The reaction kinetics of the solid-state modification (SSM) of polyamide-6,6 with the equimolar aromatic comonomer salt of meta-xylylenediamine and adipic acid (MxAd) was studied at 230 °C for different PA-6,6/comonomer-salt mol/mol ratios. It was observed that the SSM transamidation reaction rate was higher for higher comonomer-salt concentrations, resulting in a lower intermediate molecular weight (M_n*) as monitored by SEC. The influence of an excess diamine or diacid in the salt on the SSM-reaction rate was studied and was found to be insignificant. Statistical calculations based on* ^{13}C *NMR spectroscopic analysis were used to analyze the chemical microstructure of the obtained copolymers synthesized via SSM. For comparison, the microstructure of a copolyamide exhibiting a similar chemical composition but prepared via a melt polymerization route (MP) was also analyzed. The analysis revealed that the copolyamides synthesized via SSM have a more blocky structure with degrees of randomness (R) lower than one, whereas the melt-polymerized copolyamides possess R-values of one, typical for a fully random microstructure.*

3.1 Introduction

PA-6,6 and PA-6 are among the most widely used step-growth polymers for various applications. They are well known and used in many applications because of the high dimensional stability under dry conditions, their good mechanical and thermal properties, and their excellent solvent resistance. PA-6,6 itself comprises approx. 36% of the total polyamide market.[1] Lower molecular weight polyamides are quite suitable for textile and fiber applications, whereas for blow-molding and injection-molding applications a somewhat higher molecular weight is preferred.[2,3] Solid-state polymerization (SSP) is a traditional method, known since 1930 and widely used in industry, to increase the molecular weight of polycondensates, *viz*. polyesters and polyamides, via post-condensation.[4-6] The primary industrial process for polyamide-6,6 (PA-6,6) production involves a first solution polymerization step starting from an aqueous PA-6,6 salt solution, removal of the water from the reactor and a final polymerization step in the melt state (250–270 °C).[7] The high temperatures combined with long residence times might lead to thermal degradation and undesirable side reactions, such as dimerization of hexamethylene diamine residues to the corresponding diamine structures. These trifunctional structures may lead to branching or the formation of a three-dimensional network, resulting in gel formation which might impair the end product quality.[8,9] Apart from this, the melt process involves many unit operational difficulties due to the increase in the melt viscosity during the polycondensation reaction required to reach a minimum number-average molecular weight of 15-25 kg/mol. Especially achieving higher number-average molecular weights (M_n) of ca. 30-45 kg/mol by only melt polymerization is a challenge and implies relatively long residence times in the melt, with possible degradation reactions as a consequence. Therefore, in order to achieve higher molecular weight products an SSP reaction could be a suitable method.[10,11] SSP has many advantages over melt or solution (co)polymerizations. As SSP reactions are carried out at relatively low temperatures[12] (as a rule of thumb 10-20 °C below the melting temperature T_m of the polymer, whereas melt polymerizations are usually performed at least 20 °C above T_m), undesired side products are limited and predominantly linear polyamides are formed. Furthermore, usually the products prepared via SSP have a higher thermal stability than the (co)polyamides prepared entirely via the melt polymerization route (MP).[13] Numerous studies were reported in literature on SSP[5,6,14-18] as well as various mechanisms[20,21] and an extensive review was published by Papaspyrides and coworkers.[21] Most of these studies predominantly focus on solid-state post-condensation (SSPc), while reports on chemical modifications of step-growth polymers in the solid state by e.g. transreactions are scarce. On the other hand, transreactions in the melt of polyamides were discussed more extensively. Puglisi et al.[14] illustrated the amide-amide exchange reactions between carboxylic acid-terminated PA-6,6 and PA-6,10 in the melt and found that these melt-mixing reactions for different compositions mostly result in random copolyamides. Only for equimolar compositions and upon applying a longer heating time segmented, blocky copolyamides were obtained.[14] The degrees of randomness and the interchange reactions were determined by matrix-assisted laser desorption ionization−time-of-flight (MALDI−TOF) mass spectroscopy. Groeninckx and co-workers[22-25] studied interchange reactions between amide groups by melt mixing two homopolymers, *viz.* polyamide-4,6 and polyamide-6,I, in an extruder and applied a statistical method to calculate both the degree of transamidation and the sequence length of the blocks of the resulting copolymers by using ^{13}C NMR spectroscopy.[26-28]

Such transreactions could also be performed in the solid state with the advantages described above. To the best of our knowledge, the first time an SSP-like process was applied for the chemical modification of a step-growth polymer was the solid-state transesterification of poly(butylene terephthalate) (PBT) with a T_g-enhancing diol, as reported by Jansen et al.[29-32] This concept resulted in a non-random incorporation of significant amounts of comonomer into PBT, without completely losing the crystallinity of the resulting block-like copolyester. In our earlier paper,[33] we reported for the first time the application of this elegant concept for the chemical solid-state modification (SSM) of a polyamide. PA-6,6-based semi-aromatic, blocky copolyamides were prepared by forcing transamidation chemistry between PA-6,6 and aromatic comonomer salts, i.e. para- and meta-xylylenediamine/ adipic acid (PxAd, MxAd resp.), in the solid state. The blocky structure, consisting of relatively long homo PA-6,6 blocks and copolyamide blocks, was confirmed by a detailed ^{13}C NMR analysis from which a degree of randomness of around 0.4-0.5 could be deduced, which is far below the degree of randomness of a random copolymer, being unity. The explanation for the generation of block copolymers is that the relatively long homo PA-6,6 sequences present in the crystals during the SSM do not participate in the transamidation reactions, which only occur in the amorphous phase exhibiting sufficient mobility. The progress of the reaction was followed by using size exclusion chromatography (SEC) with RI and UV detectors.

As we reported earlier, the SSM-reaction was exclusively studied with a feed mol ratio PA-6,6/MxAd salt of 80/20 ($((PA66_{80}MxAd_{20})_{Feed})$) using an equimolar MxAd comonomer salt. In the current study, the possible influence of a deviation from the equimolar ratio of the components of the MxAd salt on the reaction rate and chemical microstructure is studied. This is highly relevant, since it might reveal whether either the diamine or the diacid is the active species in the SSM chemistry. Therefore, a 20 mol% excess diamine or diacid was mixed together with equimolar MxAd salt into the $(PA66_{80}MxAd_{20})_{Feed}$. The results are compared with the equimolar comonomer salt in the system $(PA66_{80}MxAd_{20})_{Feed}$. Moreover, the effect of different comonomer salt (MxAd) concentrations in the feed (varying from ca. 2.5 to 20 mol% with respect to the number of moles of PA-6,6 repeat units present) on SSM-reaction speed was studied. All SSM reactions reported in this work were carried out at 230 °C for 24 h and the kinetics of the reactions as a function of MxAd salt concentration and/or diamine/dicarboxylic acid excess in the salt were followed by measuring $M_{n,SEC}$ at different reaction time intervals. The chemical microstructure of the SSM copolyamides was deduced from the ^{13}C NMR carbonyl group signals, by carefully determining the dyad sequence concentrations in the copolyamides from which the corresponding degrees of randomness were calculated. The degrees of randomness of copolyamides obtained via MP with a similar overall chemical composition are also discussed and compared with the corresponding values for the SPM products. In **Chapter 4**, a detailed analysis of the influence of the comonomer content on the thermal properties of these copolyamides, either synthesized via SSM or via MP, will be presented. This chapter will focus on the chemical microstructures of the SSM and MP copolyamides.

3.2 Experimental Section

3.2.1 Materials

Poly(amide-6,6) (PA-6,6, Ultramid® A-27) pellets (M_n = 38 kg/mol, M_w = 72 kg/mol) were supplied by BASF SE, Ludwigshafen, Germany. Adipic acid (AA) as well as meta-xylylenediamine (MXDA) were purchased from Sigma Aldrich. Ethanol (99%) required for the preparation of the diamine/diacid salt was also purchased from Aldrich. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, 99%), obtained from Biosolve (Valkenswaard, the Netherlands), was used for solution mixing of PA-6,6 with the diamine/adipic acid salt. For NMR measurements deuterated trifluoroacetic acid (TFA-d, 99.5% deuterated) was obtained from Cambridge Isotope Laboratories, Inc., USA. All chemicals and solvents were used as received.

3.2.2 Preparation of comonomer salt

The preparation of 'comonomer salts' involved mixing the diamine (p-xylylenediamine or m-xylylenediamine) with adipic acid in equimolar proportions, by mixing equivalent amounts of ethanol solutions of both components (see Scheme 3.1, where Ar = CH_2-phenyl-CH_2). The nylon salts, viz. MxAd (m-xylylene adipic acid salt), precipitated out of ethanol in an equimolar composition once they were formed. The salts were filtered, vacuum dried at a temperature of approximately 50 °C for 4 h and their equimolarity was checked and confirmed by ^1H NMR spectroscopy.

$$HOOC\text{-}(CH_2)_4\text{-}COOH + H_2N\text{- Ar - }NH_2 \longrightarrow {}^{-}OOC\text{-}(CH_2)_4\text{-}COO^{-}\ .\ {}^{+}H_3N\text{- Ar - }NH_3^{+} \tag{3.1}$$

Scheme 3.1 Synthesis of aromatic comonomer salt.

3.2.3 Solution preparation of the SSM reaction mixture

PA-6,6 pellets were ground into powder by a Retsch type ZM 100 mill in a cryogenic way. This powder was dried in a vacuum oven at 70 °C for 48 h. Then, 80 mol% of PA-6,6 and 20 mol% of comonomer salt were dissolved in 10-15 mL of HFIP at a temperature of approximately 50 °C. All the reaction mixtures were prepared in this way unless otherwise mentioned and no transamidation catalyst was present in or added to the starting material. After complete dissolution, the temperature was raised to 65 °C and HFIP was removed by drying under vacuum. The solid mixture lump was dried in an oven for 24 h and was then cooled in liquid nitrogen and ground into powder using an analytical laboratory mill (Waring, type 32BL80), after which the powder was filtered using a sieve to get a more or less uniform particle size of 100 µm or smaller. This powder was subsequently dried in a vacuum oven for a period of 48 h prior to the SSM reaction.

3.2.4 Solid-state modification (SSM)

The experimental setup for SSM consisted of a glass reactor, equipped with a fluidizing purge gas tube. A salt mixture of KNO_3 (53 wt %), $NaNO_2$ (40 wt %), and $NaNO_3$ (7 wt %) was used as the heating medium for the reactor.[39] The reactor consisted of a glass tube (inner diameter ~ 2.4 cm) and a sintered glass-filter plate at the bottom. A small heat exchange glass coil (inner diameter ~ 5 mm) surrounded the reactor. An argon gas flow was heated by passing through this heated coil before entering the inner glass tube at the bottom just below the glass filter plate. The gas flow was controlled by a flow meter. The SSM reaction temperature was measured with a thermocouple inserted into the PA-6,6/nylon salt mixture.

3.2.5 Melt polymerization (MP)

The melt copolymerization was carried out after dissolving in total 200 g of different salt mixtures of $(HMDA:AA)_x$ and $(MxAd)_y$ in 200 g of water (x,y denotes the mol% of the salt as per feed compositions) placed into a 1.2 L pressure reactor. The reactor was heated to 210 °C at 15 bar for 15 minutes, and the temperature was raised in steps of 20 °C. Then the temperature inside the reactor was subsequently raised to 220 °C and kept isothermal at that temperature for ca. 55 minutes under 15 bar pressure while removing water. Then, the temperature and pressure were reduced to 267 °C at 1 bar for 30 minutes, and the melt polycondensation reaction was carried out at 271 °C for 10 min after which the copolyamide $(PA66_xMxAd_y)_{MP,\ Feed}$ was granulated in an underwater granulation system. The molecular weight ($M_{n,\mathrm{SEC}}$) of these MP copolyamides is in the range of 25-35 Kg/mol.

3.2.6 Characterization

3.2.6.1 Size exclusion chromatography (SEC)

SEC was used to determine the average molecular weight and molecular weight distribution ($M_\mathrm{w}/M_\mathrm{n}$) of the polymer samples. For the PA-6,6 and SSM reaction samples, SEC in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was performed on a system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (35 °C), ultraviolet (UV) detectors operating at a wavelength of 275 nm (these detectors are in series respectively), a Waters 2707 auto sampler, and a PSS PFG guard column followed by 2 PFG-linear-XL (7 µm, 8 × 300 mm) columns in series at 40 °C. HFIP with potassium trifluoroacetate (3 g/L) was used as eluent at a flow rate of 0.8 mL/min. The molecular weights were calculated against poly(methyl methacrylate) standards (Polymer Laboratories, M_p = 580 Da up to $M_\mathrm{p} = 7.1 \times 10^6$ Da). Before the SEC analysis was performed, the samples were filtered through a 0.2 µm PTFE filter (13 mm, PP housing, Alltech). It has to be mentioned that some of the reaction samples that are branched/cross-linked might contain some gel particles. As these gel particles were filtered out before the SEC measurements, the data obtained may not be e a true representation of the sample, and for these specific samples the M_n and M_w values as well as the PDI may be underestimated.

3.2.6.2 NMR Spectroscopy

NMR spectra were recorded on a Varian Mercury Vx (400 MHz) spectrometer at 25 °C. The solvent used was deuterated trifluoroacetic acid (TFA-*d*) and ^{1}H NMR spectra were referenced internally using the signal of residual solvent protons. Sequence analysis of the copoly(amides) was probed in ^{13}C NMR using HFIP/$CDCl_3$ in a 3/1 vol./vol. ratio.[36] The ^{13}C NMR spectra (5 mm probe, 400 MHz) were recorded overnight at room temperature with an acquisition time of ca. 1.5 s and a delay time (d1) of ca. 10 s in the NOE-decoupling mode.

3.2.6.3 Differential Scanning Calorimetry (DSC)

The enthalpy of melting and the degree of crystallinity were measured by a TA Instruments Q100 Differential Scanning Calorimeter (DSC) equipped with an auto sampler and a refrigerated cooling system (RCS). The DSC cell was purged with a nitrogen flow of 50 mL/min. The temperature was calibrated using the onset of melting for indium. The enthalpy was calibrated with the heat of fusion of indium. For the $(PA66_xMxAd_y)_{SSM}$ and $(PA66xMxAdy)_{MP}$ copolymers, samples having a weight of 4–6 mg were prepared in crimped hermetic pans. All samples were measured in the temperature range from -40 to 290 °C using heating and cooling rates of 10 °C/min (unless specified differently), and applying isothermal periods of 5 min at respectively 0 and 290 °C. The degrees of crystallinity (X_c) of PA-6,6 and its copolyamides were calculated from the heat of fusion (ΔH_m) of the second heating run using the following relation:

$$X_c = \{\Delta H_m/\Delta H_{0m})\} \times 100\%$$

where ΔH_{0m} is the heat of fusion for 100% crystalline PA-6,6, which was taken as 188 J/g.[34]

3.3 Results and Discussion

3.3.1 Influence of excess diamine or excess dicarboxylic acid on SSM modification

This study was aimed to investigate whether the excess of one of the salt components has any effect on the kinetics of the transamidation reaction, e.g. by compensating for possible losses of one of the salt components during SSM under a continuous inert gas flow, applied to facilitate removal of condensation products from the reaction mixture. This might also reveal whether either aminolysis by (excess of) diamine or acidolysis by (excess of) dicarboxylic acid is the predominant step in the reaction mechanism. The SSM experiments were performed in exactly the same way as described **Chapter 2**, in which the concept of the solid-state modification of PA-6,6 was presented for the first time.[33] The excess of the counter part of the salt (either dicarboxylic acid or diamine) was added during the solution mixing in addition to the equimolar MxAd salt. The final composition of the mixture had 20 mol% excess of either dicarboxylic acid or diamine, so the mol ratio added diamine/dicarboxylic acid is either 60/40 or 40/60. The reaction was performed with 80 mol% of PA-6,6 and 20 mol% of MxAd salt with molar meta-xylylenediamine (MXDA)/adipic acid (AA) ratios of 12/8 or 8/12. The effect of the diacid/diamine ratio in the added MxAd salt on the kinetics was studied at 230 °C for 24 h and the molecular weight distribution of the samples was monitored by SEC at different time intervals. The 8 h reaction sample was used for the ^{1}H NMR analysis.

The number-average molecular weight (M_n) trend of the SSM reaction of PA-6,6/MxAd mixtures with excess of diamine or dicarboxylic acid in the salt is plotted as a function of reaction time in Figures 3.1a and 3.1b. It can be observed that neither the excess diamine nor the excess dicarboxylic acid in the salt resulted in any significant change in the kinetics of the transamidation reaction, since there is no significant change in the number-average molecular weight (M_n) development as a function of time upon addition of such an excess. The observed minor differences in the M_n development between reactions with equimolar salt or with salt with one of the components present in excess is most probably due to the

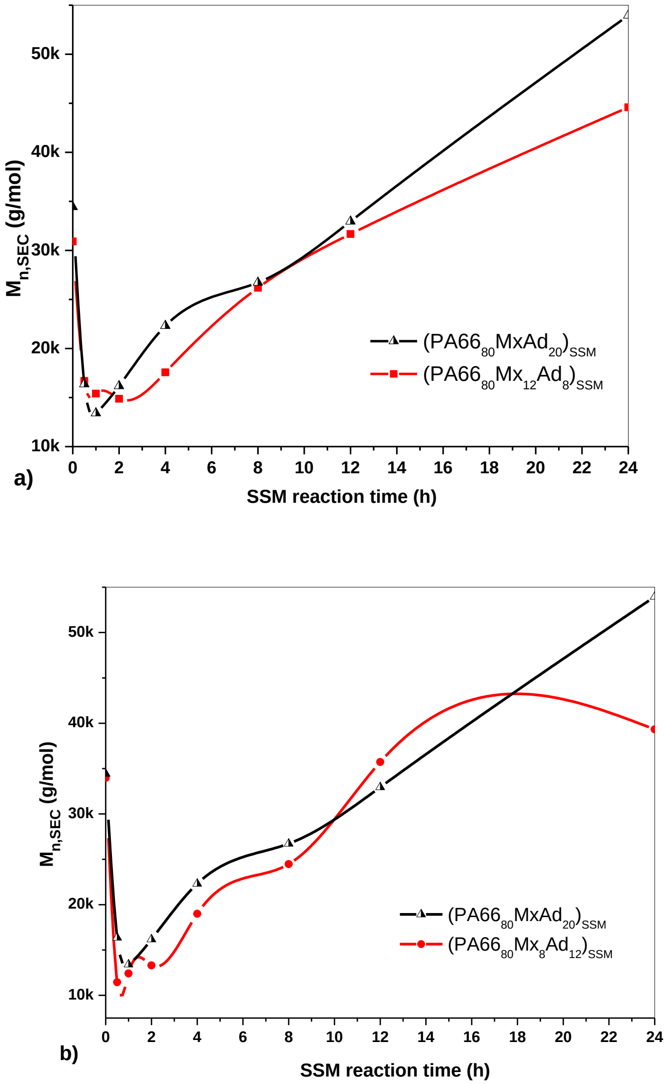

Figure 3.1 Number-average molecular weight (M_n) determined by SEC as a function of SSM reaction time for the incorporation of MxAd salt into PA-6,6: a) with excess diamine $(PA66)_{80}(Mx_{12}Ad_8)$ and b) with excess dicarboxylic acid $(PA66)_{80}(Mx_8Ad_{12})$ in the salt (Both are compared with the system $(PA66_{80}MxAd_{20})_{SSM,\ Feed}$ with equimolar MxAd salt) (--▲--).

standard deviation of the SEC measurement itself. Even the plots for excess diamine (Figure 3.1a) and for excess dicarboxylic acid (Figure 3.1b) show a very similar M_n development versus SSM reaction time. These observations make it unlikely that either the diamine or the dicarboxylic acid themselves are the active species during SSM, causing the initial chain scission.

3.3.2 SSM reaction mechanism: Aminolysis or Acidolysis?

It was shown in Section 3.3.1 that the SSM reaction rate is not affected by using an excess of either the diamine or the dicarboxylic acid species in the PA-6,6/MxAd reaction mixture, but the question remains whether the SSM transamidation reaction is initiated by the protonated amine ($-NH_3^+$) (i.e. aminolysis) or by the deprotonated carboxylate ($-COO^-$) (i.e. acidolysis) present in the comonomer salt (MxAd). To study which species is most probably responsible for the initiation of the transamidation reaction, causing the initial chain scission after which the molecular weight is reconstructed by condensation reactions, PA-6,6 was reacted with individual model compounds containing either protonated primary amine or deprotonated carboxylate species. To avoid the degradation or the evaporation of the model compounds during this study, the non-functional groups are selected in such a way that the melting temperature of the compound is equal to or above 230 °C. The SSM reaction was first carried out with PA-6,6 and 20 mol% of methyl amine hydrochloride (MAH) in the feed composition ($(\mathrm{PA66_{80}MAH_{20}})_{\mathrm{SSM,Feed}}$) as two steps. The first step was at a lower temperature (ca. 180 °C for 3 hours) to avoid the volatility of the compound, while the second step was performed at 230 °C for 5 h and the reaction was monitored by SEC. It is evident from the SEC chromatograms, given in Figure 3.2, that the molecular weight of the starting PA-6,6 decreases, as evidenced by the increasing elution time from ca. 22 min to ca. 26 min after 3 h of SSM reaction time at 180 °C. The model amine compound (i.e. MAH) peak intensity decreased from elution time of ca. 28 min after first step and after almost disappeared after 1 h of SSM reaction at 230 °C as seen in Figure 3.2.

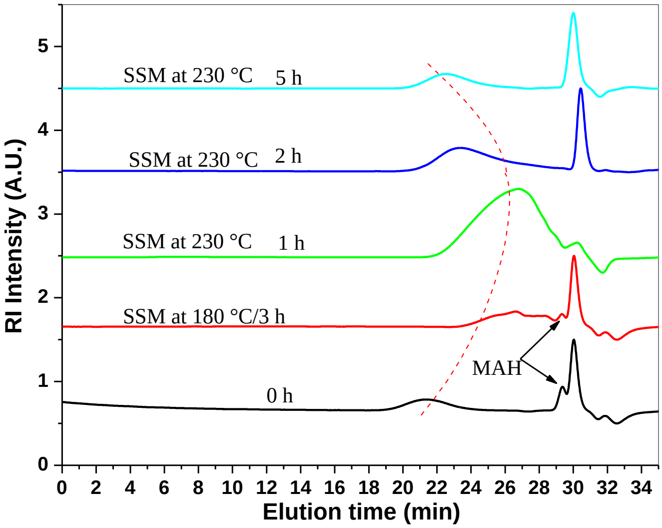

Figure 3.2 SEC chromatogram (RI detector) of a SSM model reaction of PA-6,6 with methyl amine hydrochloride in the composition $(PA66_{80}MAH_{20})_{SSM}$ at 230 °C.

After 5 h of the SSM reaction at 230 °C, the molecular weight started to increase due to post-condensation. As discussed in **Chapter 2**, this is a typical trend observed during transamidation reactions. So, we can conclude that the SSM transamidation reaction is an aminolysis process as it is initiated by a protonated amine (NH_3^+).

To check whether acidolysis, in addition to the confirmed aminolysis, also plays a role in the SSM transamidation reaction, SSM was performed at 230 °C during 8 h using a mixture of PA-6,6 and 20 mol% of sodium benzoate salt (SB) ($(PA66_{80}SB_{20})_{SSM,Feed}$). As SB is an aromatic compound, the SSM could be followed by UV and RI detectors in SEC. As can be seen in Figure 3.3a, the PA-6,6 elution time of 22 min only marginally changes during the SSM model reaction. Also, the monomer signal of the sodium benzoate salt (SB) is present throughout the entire reaction time. In fact, instead of a decrease (observed for the protonated amine, see Figure 3.2) a slight increase in molecular weight was observed, indication that post-condensation occurred. This proves that the SSM transreaction does

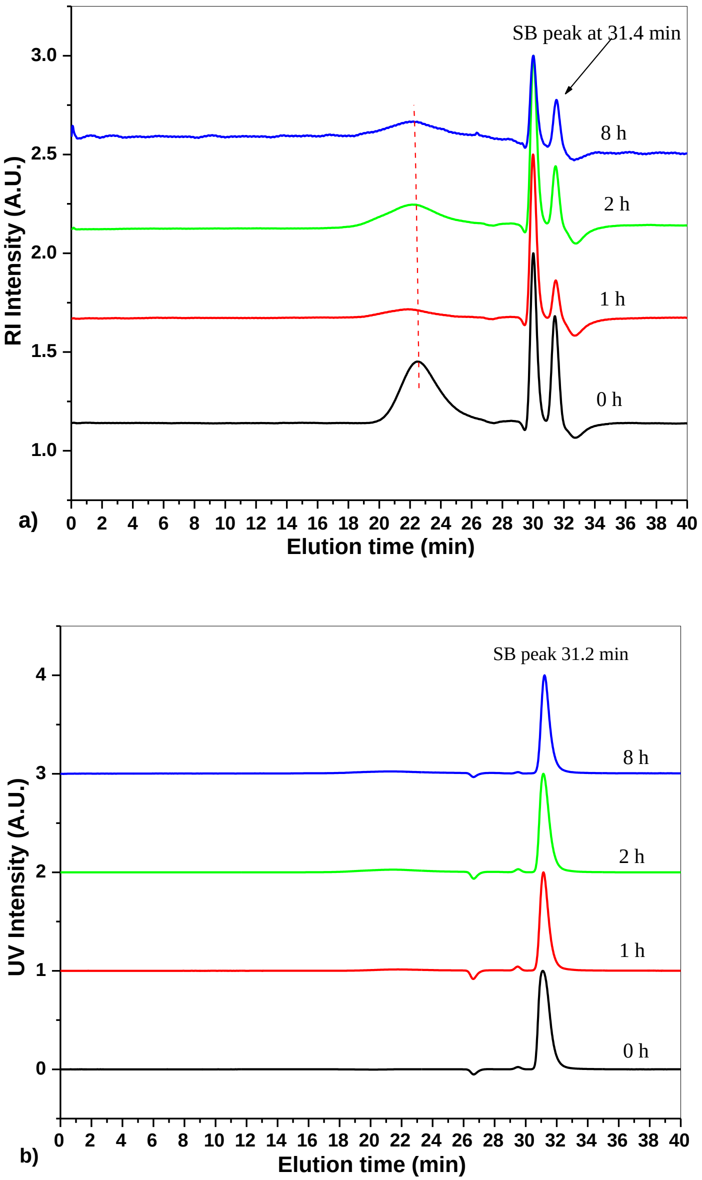

Figure 3.3 SEC chromatogram of a SSM model reaction of PA-6,6 with sodium benzoate (SB) in the composition $(PA66_{80}SB_{20})_{SSM}$ at 230 °C: a) RI detector and b) UV detector.

not occur via the acidolysis pathway. This is supported by the SEC chromatogram measured by the UV detector at 275 nm (see Figure 3.3b). PA-6,6, being a fully aliphatic structure, does not lead to UV absorption. From the UV chromatogram in Figure 3.3b, it becomes clear that no UV active moiety (i.e. SB) is incorporated into the PA-6,6 sample during the SSM reaction. This proves that the SSM reaction is not initiated by a carboxylate species and, thus, does not proceed via acidolysis.

3.3.3 Solid-state modification of PA-6,6 with different amounts of MxAd salt

($PA66_xMxAd_y$) copolyamides were synthesized via solid-state modification (SSM) and melt polymerization (MP) using different PA66/MxAd salt molar ratios. For the SSM reactions initially x mol% of PA-6,6 and y mol% of the comonomer salt was prepared as the reaction feed mixture as mentioned in Section 3.2.3. The amount of the comonomer salt (MxAd) was varied from 2.5 to 20 mol%. This mol percentage is calculated as the number of mols of the salt with respect to the total number of mols of repeat units present in the added PA-6,6 and the total number of mols of MxAd salt present in the mixture. The solution mixing is done prior to the SSP reaction to ensure optimum homogenization of the mixture and to maximize the chance that the salt is dissolved into the amorphous phase of PA-6,6. It is unlikely that the salt is incorporated into the PA-6,6 crystals, which are formed during the evaporation of the HFIP. The solid-state modification reaction is expected to occur exclusively in the mobile amorphous phase at the chosen reaction temperature,[33] which is significantly above T_g but still below T_m of the PA-6,6 crystals leaving the crystalline phase unaffected during this modification. This also limits the maximum amount of comonomer incorporation into the backbone by this SSM treatment. In this chapter, a maximum of 20 mol% of comonomer salt was incorporated into PA-6,6.

3.3.4 The percentage transamidation as determined from ^1H NMR spectroscopy

The incorporation of the aromatic MXDA comonomer into the high molecular PA-6,6 was confirmed by SEC, both by RI and UV detection as discussed earlier in **Chapter 2**[33]. SEC analysis on the samples collected after various reaction times showed the disappearance of the MXDA peak and the incorporation of a UV-active moiety in the high molecular weight fully aliphatic polyamide, which in itself is not or only moderately UV active. The ^{1}H NMR spectra of the neat MxAd salt, the unreacted PA-6,6/MxAd comonomer salt mixture (i.e. SSM reaction time 0 h) along with the SSM-modified product after an SSM reaction time of 8 h ($PA66_{80}MxAd_{20}$), are given in Figure 3.4. The benzyl proton (G) of the comonomer salt is shifted from ~4.5 ppm to ~4.7 ppm after incorporation into the aliphatic PA-6,6 backbone. The amount of comonomer incorporation was calculated from the ratio of the intensity of the comonomer signal (H) to the total intensity of both PA-6,6 and comonomer in the ^{1}H NMR spectra.

The molar compositions of the ($PA66_xMxAd_y$) copolymers were calculated using eqs. 3.1a, 3.1b and 3.1c, by incorporating the ^{1}H NMR peak integrals of the aromatic moiety in the 7-8 ppm region (see Figure 3.4).

$$F_{\mathrm{MXDA}} = \mathrm{H} / (\mathrm{D} + \mathrm{H}) \qquad (3.1a)$$

$$F_{\mathrm{MxAd}} = 2^* F_{\mathrm{MDA}} \qquad (3.1b)$$

$$F_{\mathrm{PA66,total}} = 1- F_{\mathrm{MxAd}} \qquad (3.1c)$$

In equations. 3.1a-3.1c, F_{MXDA} and F_{MxAd} denote the mol fractions of m-xylylenediamine (MXDA) and MxAd salt, respectively. The mol fraction of MxAd residues in the copolyamide is twice the mole fraction of MDA monomer residues (with respect to all monomer residues present in the entire copolyamide), as the MxAd salt contains equimolar amounts of MXDA and AA. Integral H denotes the aromatic phenyl protons and (D+H) represents the total amount of copolymer content.

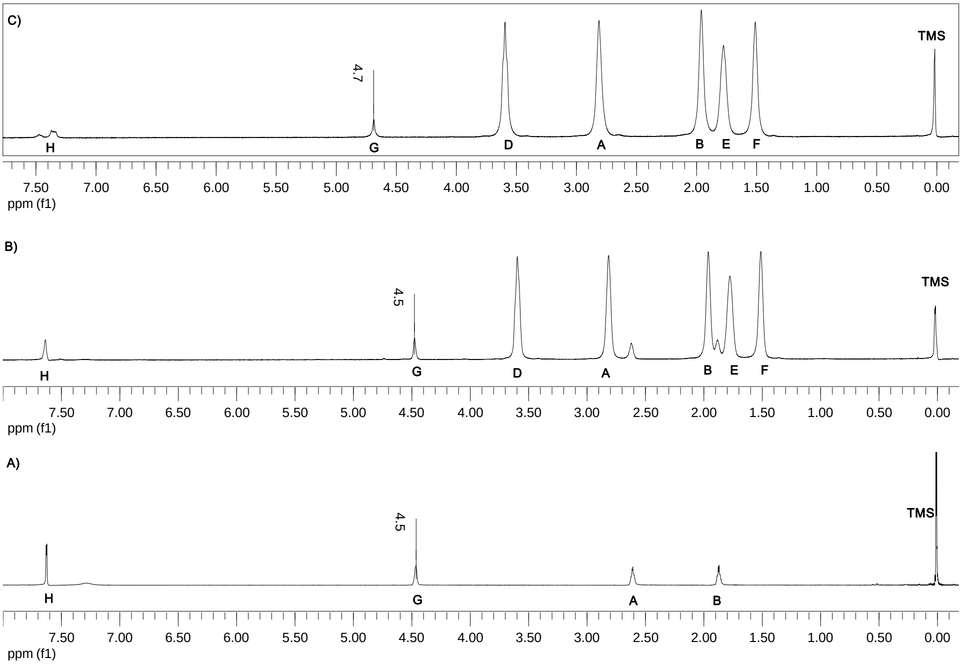

Figure 3.4 ^{1}H NMR spectra of the starting materials and the SSM reaction product of (PA66$_{80}$MxAd$_{20}$) (top to bottom): a) MxAd salt, b) non-transamidated PA-6,6/MxAd mix (0 h of SSM reaction) and c) solid-state modified PA-6,6 with MxAd salt (SSM reaction time 8 h).

Table 3.1 Overview of all (PA66$_x$MxAd$_y$)$_{SSM}$ samples synthesized by SSM for 24 h at 230 °C

Composition feed		**Composition after SSM***		**SEC**	
***PA66*, feed (mol%)**	***MxAd*, feed (mol%)**	***PA66*, total (mol%)**	***MxAd*, total (mol%)**	**M_n (kg/mol)**	**PDI**
Pure PA66		100.0	0.0	38	2.1
100.0	0.0	100.0	0.0	42	2.7
97.5	2.5	97.5	2.5**	48	4.7

Composition feed		Composition after SSM*		SEC	
$PA66_{, feed}$ (mol%)	$MxAd_{, feed}$ (mol%)	$PA66_{, total}$ (mol%)	$MxAd_{, total}$ (mol%)	M_n (kg/mol)	PDI
95.0	5.0	95.0	5.0	53	5.1
90.0	10.0	89.0	11.0	49	1.8
80.0	20.0	83.0	17.0	54	3.1

*Compositions were obtained by ^{1}H NMR spectroscopy on 8 h sample (as given in Figure 3.7). **Feed value (see further)

3.3.5 Different comonomer mol ratios

With the amount of comonomer salt increasing from 2.5 to 20 mol% the rate of the transamidation reaction increases, as observed by the rate of decline in molecular weight (M_n) during the time interval from 0-2 h (see Figure 3.5a). At very low mol% MxAd salt (*viz*. 2.5), there is no significant transamidation reaction observable in the $M_{n,SEC}$ versus time plot. In this case the solid-state post-condensation (SSPc) reaction of the neat PA-6,6 overrules the chain scission, resulting in a direct increase in molecular weight (M_n) right from the start. The PDI trend (Figure 3.5b) follows a similar pattern as M_n, only slowly increasing from around 1.8 to 3.8 with reaction time. The higher PDI (ca. 3.8) might be due to the branching and cross-linking reactions due to the formation of triamine-functionalities by condensation of two primary amines with the release of ammonia, as explained in the earlier chapters.[33,35] At 5 and 10 mol% of the comonomer salt, the transamidation (resulting in chain scission and a decreasing molecular weight) was clearly observed during the first 2 hours of the SSM reaction.

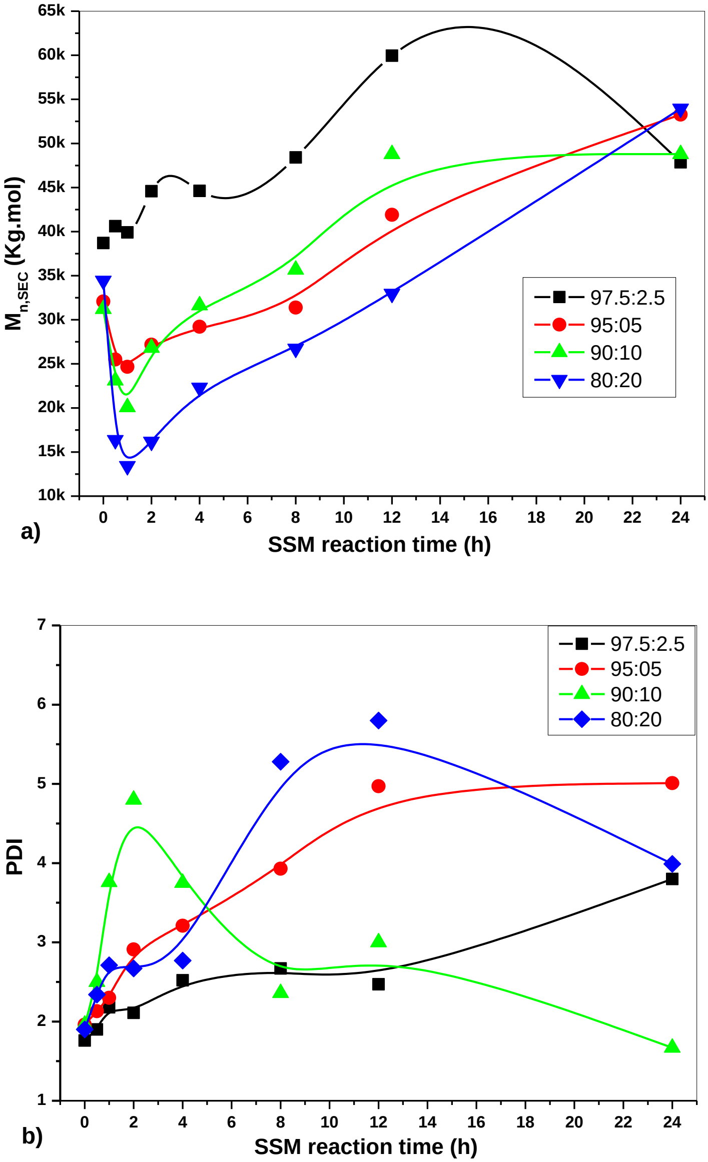

Figure 3.5 SSM of $(PA66_xMxAd_y)_{SSM}$ at 230 °C: a) number-average molecular weight ($M_{n,SEC}$) and b) PDI as a function of SSM reaction time.

Then, the second step of the SSM treatment, i.e. the SSPc reaction, starts with the available free amine and carboxylic acid end groups generated during the chain scission step. The slope of the second part of the reaction, that is the increasing part of the curve, representing the rate of the molecular weight (M_n) build-up, is more or less comparable for the systems containing 5 and 10 mol% of equimolar nylon salt. From Figure 3.5b, it is evident that the PDI of the system containing 5 mol% of MxAd salt is quite steadily increasing during the second part of the SSPc treatment, which seems to be rather controlled at 230 °C. On the other hand, the PDI trend of the system containing 10 mol% of equimolar MxAd salt is quite strange and probably branching/cross-linking occurs immediately after the first transamidation reactions have occurred. Most probably, the decreasing part of the PDI versus SSM time curve observed after several hours is due to filtering out of cross-linked gel particles during the sample preparation for SEC. The solid-state modifications with 20 mol% comonomer salt resulted in very low number-average molecular weights after the transamidation during the first couple of hours (M_n ca.13 kDa, see Figure 3.5a) compared to other SSM reactions discussed here, pointing to much higher rates of the chain scission generating transamidation reaction. For these higher molar percentages of MxAd salt the initial molecular weight (M_n) is restored after 8-12 h of SSM reaction time and almost levels off up to 24 h of reaction. Also in this case the strongly fluctuating PDI trend, observed after 8 h of reaction time might be caused by branching and the uncontrolled formation of gel particles, of which the bigger ones are filtered out during SEC sample preparation. The second part of the SSM reaction, *viz.* the post-condensation, was virtually independent of the mol% of the added MxAd salt, as it is very clear from Figure 3.5 and Table 3.1 that the final molecular weights (M_n) of the soluble parts of all end products are in the range of 50 kg/mol.

3.3.6 ^{1}H NMR Analysis of PA66$_x$MxAd$_y$ copolyamides with different comonomer salt concentrations

The SSM reactions between PA-6,6 and different mol% of the 'nylon' salt MxAd at 230 °C were analyzed by NMR spectroscopy to study the comonomer incorporation and to quantify the extent of transamidation reactions. ^{1}H NMR analysis of all samples obtained after 24 h of SSM reaction was not reliable, since significant and varying amounts of gel particles present in the samples remained undissolved in TFA-d, making a quantitative solution NMR analysis to determine the degree of transamidation impossible. Hence, instead samples obtained after 8 h of SSM were analyzed by solution ^{1}H NMR spectroscopy and these results are reported here. As the transamidation was almost over after 2 h of the SSM reaction, from 8 h onwards the chemical microstructure does not change anymore but merely molecular weight built-up occurs by SSPc. The corresponding NMR spectra are presented in Figure 3.7. The structure of the expected block copolymer product is presented in Figure 3.6, in which the chemical groups are labeled for NMR peak identification.

At lower mol% of the comonomer salt (*viz.* 2.5-10 mol%), the corresponding benzyl and aromatic protons are very weak in intensity. The chemical shift of the benzyl protons (G) to lower field (ca. 4.7 ppm), caused by the incorporation into the main chain of PA-6,6, was clearly observed for all SSM reactions performed with 2.5 mol% to 20 mol% of added salt.

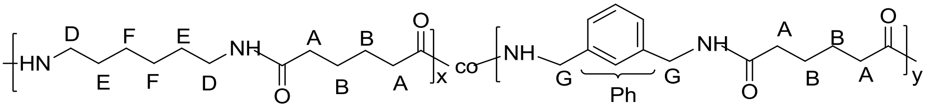

Figure 3.6 Chemical structure of a (PA66$_x$MxAd$_y$) copolymer labeled for NMR peak identification (for all subsequent ^{1}H and ^{13}C NMR spectra).

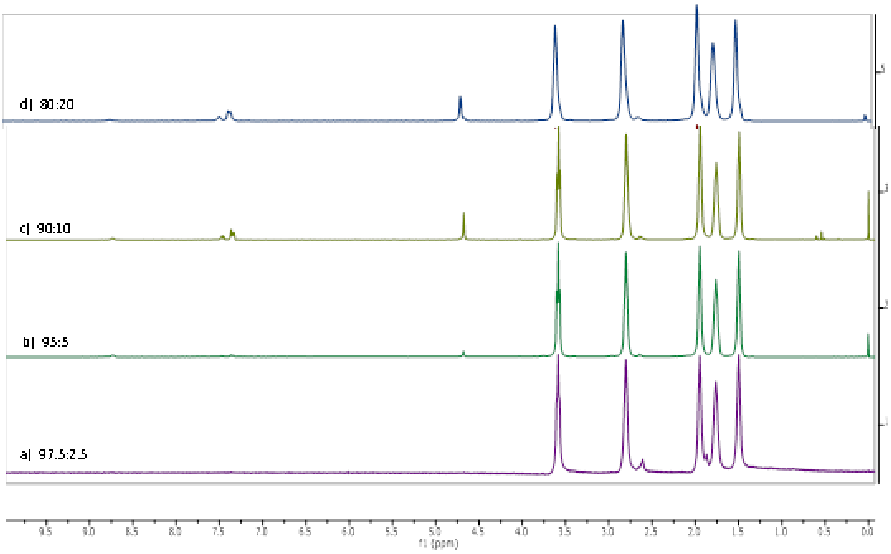

Figure 3.7 The ^{1}H NMR spectra of different feed compositions of the system(PA66$_x$MxAd$_y$) after 8 h of SSM reaction at 230 °C, where the numbers x,y represent the weighed-in PA-6,6/MxAd mol/mol ratios: a) (PA66$_{97.5}$MxAd$_{2.5}$), b) (PA66$_{95}$MxAd$_5$), c) (PA66$_{90}$MxAd$_{10}$) and d) (PA66$_{80}$MxAd$_{20}$).

^{1}H NMR analysis of the SSM products modified with 5, 10 and 20 mol% of comonomer salt resulted in spectra with peak intensities in the aromatic region around 7.5 ppm, as visible in Figures 3.7b, 3.7b and 3.7d. The mol percentages of incorporated diamine comonomer into the PA-6,6 main chains were calculated from the corresponding integration ratios of the aromatic peak intensities to that of the sum of the aromatic and any present repeating unit of PA-6,6 (See also Table 3.1). Unfortunately, for the copolyamide containing 2.5 mol% MxAd in the feed mixture the incorporated amount of aromatic salt is too low for allowing an accurate determination by ^{1}H NMR spectroscopy and in this case the feed value was assumed (see Table 3.1). The final composition of the synthesized (PA66$_x$MxAd$_y$)$_{SSM}$ samples is plotted as a function of the weighed-in feed compositions in Figure 3.8. The experimentally obtained values of the MxAd$_{NMR}$ in the resulting SSM copolyamides are close to the feed values after 8 h of SSM reaction time. It should be mentioned here that the experimental NMR-based values measured after 24 h of SSM reaction, valid for the *soluble* part of the copolyamides, result in a MxAd content of merely ca. 60 % of the feed compositions, which is assumed to be related to the formation of gel particles in the amorphous phase of the SSM product, formed by the earlier-mentioned trifunctional amine-related cross-linking reactions occurring at elevated reaction temperatures.[34] As long as the entire copolyamide, including both the crystalline and the amorphous fraction, is soluble an NMR analysis will deliver the right MxAd fraction corresponding to the weighed-in mol percentage (provided that no monomer is lost by e.g. evaporation). However, the MXDA is only present in the amorphous fraction, which is most probably the phase in which the most significant cross-linking can take place during longer SSM reactions. So, with respect to the entire copolyamide the insoluble fraction is enriched in MxAd, and accordingly the soluble fraction analyzed by NMR has a lower MxAd mol percentage than was weighed-in.

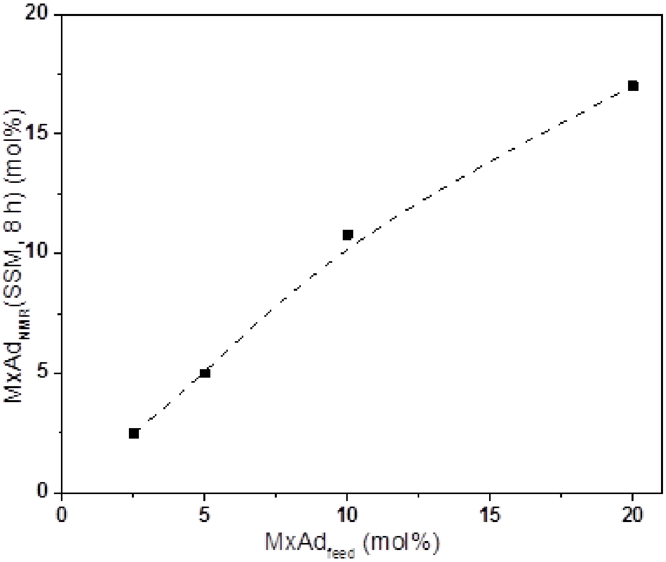

Figure 3.8 The actual molar contents of the comonomer salt after 8 h SSM time at 230 °C, as determined by ^{1}H NMR spectroscopy, as a function of the initially fed MxAd$_{feed}$ mol percentage.

3.3.7 ^{13}C NMR dyad sequence analysis of $(PA66_xMxAd_y)_{SSM}$ and $(PA66_xMxAd_y)_{MP}$ copolyamides

The microstructure of the reaction products obtained after the solid-state modification can be studied by sequence analysis by either ^{1}H or ^{13}C NMR spectroscopy. As there is no clear stereochemistry present in the comonomer (MXDA) that is used in our study, characterizing the different present dyads by quantifying the different carbonyl peaks of the copolyamides in ^{13}C NMR is more appropriate. To compare the chemical microstructure of the SSM-copolyamides with their melt-synthesized counterparts, a few selected copolyamides were synthesized via MP as well. As mentioned earlier, the selective transamidation of the comonomer salt into PA-6,6, and specifically into the amorphous phase of the semi-crystalline homo PA, should yield a different microstructure compared to the incorporation of this salt into homo PA-6,6 via MP, starting from ‘nylon 6,6’ salt and MxAd salt. The ^{13}C NMR spectra of the end products $(PA66_{80}MxAd_{20})_{feed}$ obtained either via SSM (8 h, 230 °C) or by MP, analyzed using a HFIP/d-$CDCl_3$ 70/30 vol/vol solvent mixture[36], are given in Figure 3.9.

As mentioned in Table 3.1 the SSM $(PA66_{80}MxAd_{20})_{feed}$ copolyamide contained 17.0 mol% incorporated MxAd, whereas the MP copolyamide with the same mol% MxAd in the feed contained 17.2 mol% in the final copolyamide. The chemical shifts of the methylene group of MXDA in the ^{1}H NMR spectrum provided clear evidence for its incorporation into the PA-6,6 main chain. Moreover, for the copolyamides the carbonyl group gives dyad sequences in the 170-180 ppm region. The peak intensities for the dyad sequences representative for blocky copolyamides are remarkably different from those of random copolyamides. Different dyads present in the copolyamides can be identified by analyzing the different carbonyl carbon peaks observed in the ^{13}C NMR spectra. The carbonyl carbons positioned between two aliphatic main chain parts (one adipic acid monomer residue and one hexamethylene diamine residue) have a different chemical shift compared to the carbonyl carbons in between both an aromatic MXDA residue and an aliphatic residue.

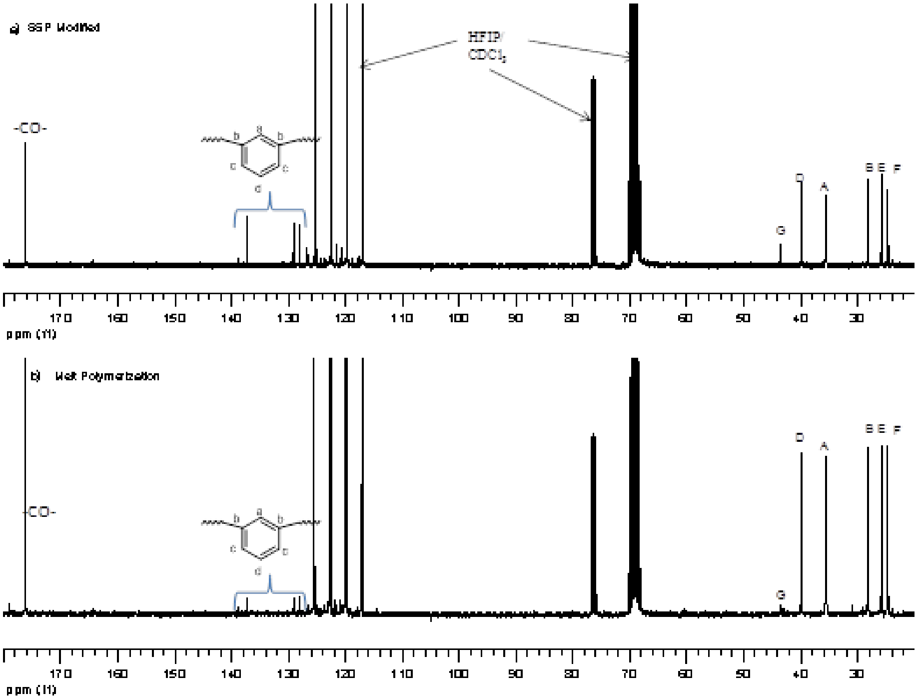

Figure 3.9 ^{13}C NMR spectra of (PA66$_{80}$MxAd$_{20}$) copolyamide with 20 mol% of MxAd salt in the feed: a) SSM reaction product (8 h, 230 °C),and b) same overall composition by melt route. The structure given in Figure 3.6 was used for the peak identification.

The influence of an aromatic residue on the shift of carbonyl carbons may be experienced even at a position separated from this moiety by six methylene groups in the chain, as illustrated in Figure 3.10, and therefore for the PA-6,6/MxAd copolyamide at least four different carbonyl carbon peaks can be expected. In the copolyamides the carbonyl groups surrounded by a high concentration of moieties based on linear aliphatic methylene-based diamines is shifted to higher ppm[27-29] values in comparison to carbonyl carbons surrounded by lower numbers of such methylene diamine residues. Especially for lower comonomer compositions, the dyad sequences were very difficult to analyze by integration, as these dyads are positioned within a spectral range of 0.2-0.3 ppm. In order to resolve such a delicate, very densely populated area of dyads and to correct for overlapping of the peaks, a deconvolution method to estimate the correct integral values of the separate peaks was applied to the carbonyl dyads, assuming Gaussian peak shapes. The integral values of the four peaks were normalized to a total value of one and presented in Table 3.2. Calculation of the degrees of randomness from the integrals of the dyads was carried out. It should be noted that a quantitative analysis of ^{13}C NMR spectra is only possible if the peaks involved have equal relaxation times and Nuclear Overhauser Enhancements (NOE).[37] In the current analysis the dyads were all originating from the quaternary carbon atom of the carbonyl groups and have identical relaxation times. Furthermore, the ^{13}C NMR spectra were recorded in the 'NOE-Decoupled' mode to avoid any coupling that might result in erroneous integral values. The (PA66$_x$MxAd$_y$) copolyamides synthesized either via SSM or MP was also mainly linear (at least for SSM reaction times up to 8 h at 230 °C, see earlier) and therefore it may be assumed that the integral values are nearly quantitative.

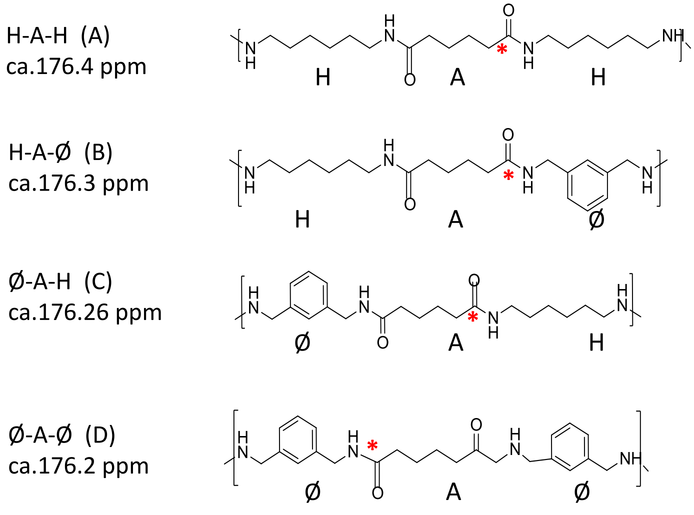

Figure 3.10 Four possible sequences (A, B, C, and D) of dyads in the PA-6,6/MxAd copolyamides from the perspective of the quaternary carbonyl carbon (*), represented by their chemical structures. H= hexamethylene diamine, A= adipic acid and Ø= m-xylylenediamine.

The degrees of randomness (R) of the copolyamides can be calculated by using equations (3.2) - (3.5), by incorporating the integral values listed under the deconvoluted peaks shown in Figure 3.11. These integral values of the four sequences are normalized to one.

$$F_{\text{HAØ,total}} = F_{\text{HAØ,HAØ-side}} + F_{\text{HAØ,ØAH -side}} \qquad (3.2)$$

$$F_{\text{HAH,total}} = (F_{\text{HAØ X,total}}) / 2 + F_{\text{HAH}} \qquad (3.3)$$

$$F_{\text{ØAØ,total}} = (F_{\text{HAØ,total}}) / 2 + F_{\text{ØAØ}} \qquad (3.4)$$

$$R_{\text{total}} = F_{\text{HAØ,total}} / 2.(F_{\text{HA-H,total}} * F_{\text{Ø A-Ø,total}}) \qquad (3.5)$$

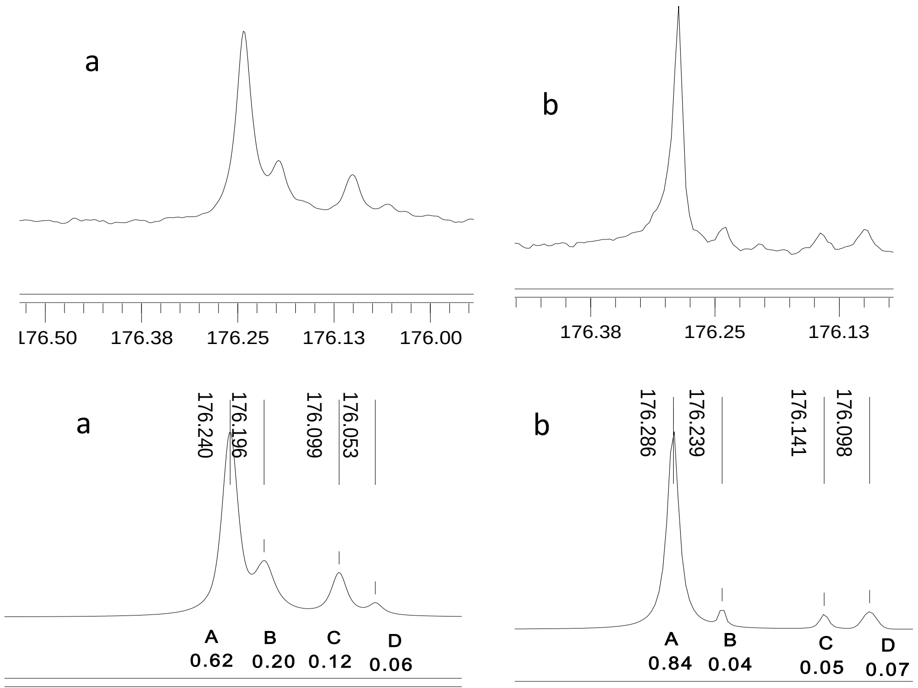

Figure 3.11 ^{13}C NMR spectra of ($PA66_{80}MxAd_{20}$). As-recorded spectra (above) and deconvoluted spectra (below) of the carbonyl dyads in the 176.5-176.0 ppm region with A-

D sequences (see Figure 3.10) of: a) melt-route product (MP) and b) SSM product (after 8 h at 230 °C).

3.3.8 Chemical microstructure of $(PA66_xMxAd_y)_{SSM}$ and $(PA66_xMxAd_y)_{MP}$ and crystallinity

The degrees of randomness, R_{total} , of the SSM-synthesized copolyamides are given in the upper part of Table 3.2. These values are within the error of ± 0.1. The degree of randomness of a SSM-copolyamide containing a lower mol% of MxAd in the feed, *viz.* 10 mol%, was almost equal to one (see Table 3.2), reflecting a highly random incorporation of the low amount of comonomer salt into the excess of the amorphous fraction of the PA-6,6 without forming long homo polyamide-MXD,6 sequences. Increasing the mol% of the comonomer in the feed to 20 mol%, an amount of MxAd salt that is close to full miscibility with the amorphous PA-6,6 phase (see **Chapter 4**) resulted in less random copolyamides and increasing the MxAd mol% further to 30 mol% did not affect the sequence length and a relatively similar degree of randomness of around 0.4 was found (see Figure 3.12), indicating that the transamidation led to mostly blocky copolyamides via SSM. Evidently, copolyamides $(PA66_xMxAd_y)_{SSM}$ with 20-30 mol% of MxAd salt incorporated into PA-6,6 have a non-random, blocky structure and the aromatic comonomer salt incorporation occurred selectively in the amorphous phase as proven by the sequence analysis. One has to realize that in the case of 30 mol% added MxAd salt some phase separation may take place between the amorphous PA-6,6 phase and the salt (see **Chapter 4**), which prevents the entire amount of added salt from transreacting with PA-6,6 and therefore is expected to result in some MXD.6 block formation. On the other hand, as shown in the lower part of Table 3.2 and in Figure 3.12, the melt-polymerized copolyamides of comparable composition exhibited for all investigated mol percentages MxAd salt, even up to 50 mol%, random copolyamide structures with the R_{total} value close to unity, the theoretical R value for completely random copolymers. In one of the investigated systems R was found to slightly exceed unity, which is theoretically impossible. This apparent outlier is most probably caused by errors in the NMR analysis, which for lower mol percentages of MxAd salt (like 10 mol%) may be relatively high.

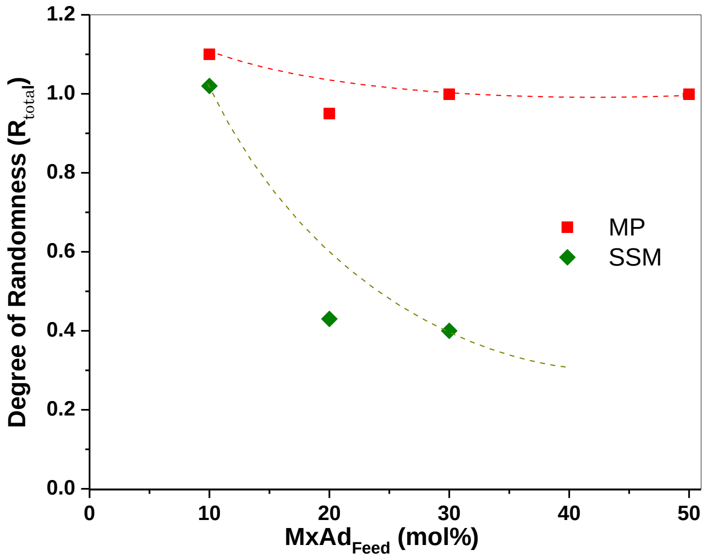

Figure 3.12 Degree of randomnes R_{total} of the copolyamides ($PA66_xMxAd_y$) synthesized via SSM (8 h, 230 ˚C) and MP as a function of incorporated mol% of MxAd.

Table 3.2 Degrees of randomness (R) calculated from ^{13}C NMR spectra for $(PA66_xMxAd_y)_{SSM}$ (8 h, 230 ˚C) and $(PA66_xMxAd_y)_{MP}$

$[(PA66)_x(MxAd)_y]_{feed}$ via SSM	**$F_{HAØ,total}$**	**$F_{HAH,total}$**	**$F_{ØAØ,total}$**	**R_{total}**
$(PA66)_{70}(MxAd)_{30}$	0.17	0.70	0.30	0.40
$(PA66)_{80}(MxAd)_{20}$	0.09	0.84	0.11	0.43
$(PA66)_{90}(MxAd)_{10}$	0.03	0.98	0.02	1.02

$[(PA66)_x(MxAd)_y]_{feed}$ via MP	**$F_{HAØ,total}$**	**$F_{HAH,total}$**	**$F_{ØAØ,total}$**	**R_{total}**
$(PA66)_{50}(MxAd)_{50}$	0.49	0.53	0.46	0.99
$(PA66)_{70}(MxAd)_{30}$	0.41	0.72	0.29	1.01
$(PA66)_{80}(MxAd)_{20}$	0.33	0.80	0.22	0.95
$(PA66)_{90}(MxAd)_{10}$	0.48	0.72	0.28	1.09

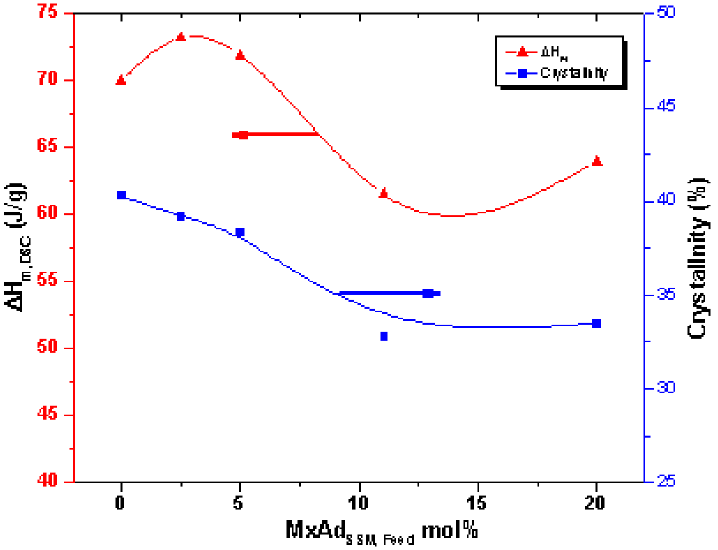

Figure 3.13 Total degree of crystallinity (X_c) and the enthalpy of melting (ΔH_m), from the DSC second heating runs as a function of the MxAd mol% incorporated by SSM (8 h, 230 ˚C).

Having confirmed from the ^{13}C NMR sequence analysis that, contrary to MP copolyamides of similar compositions and irrespective of their overall chemical compositions, all copolyamides synthesized via SSM are non-random, blocky in nature, it is interesting to study the degrees of crystallinity of the SSM copolymers and also to compare these with the corresponding values of the MP systems. To prove that the SSM reaction almost exclusively takes place in the amorphous phase, which is highly mobile at the applied SSM temperatures around 230 ˚C, leaving the PA-6,6 crystalline phase undisturbed, it is important to check whether the degree of crystallinity (X_c) compared to the starting PA-6,6 base-polymer (X_c approximately 40 %) is reduced or not. In Figure 3.13, it can be observed that the degree of crystallinity (X_c) is only slightly decreased due to the incorporation of the aromatic MxAd salt via SSM. The incorporation of 2.5 and 5 mol% of the MxAd into PA-6,6 resulted in a more or less similar crystallinity as the starting PA-6,6 homopolymer (see Figure 3.13, most left data points). An additional small drop in crystallinity of ca. 5% occurred upon enhancing the MxAd comonomer salt content from 5 to 10 mol%, which is not very significant. A further enhancement of the mol% of MxAd salt up to 20 mol% results in more or less the same percentage crystallinity as measured for the 10 mol% sample (ca. 33 %), supporting the SSM-reaction mechanism hypothesis that the crystalline phase of PA-6,6 was left more or less unaffected during the SSM treatment, leaving relatively long PA-6,6 blocks intact which promote the crystallization from the melt. A much more detailed analysis of the thermal properties of the ($PA66_xMxAd_y$) copolyamides synthesized via SSM and MP, will be presented in the succeeding part of this thesis on the solid-state modification of PA-6,6.

3.4 Conclusions

Copolyamides, ($PA66_xMxAd_y$) with different mol% of MxAd, were synthesized via solid-state modification (SSM) and melt polymerization (MP). For obtaining the SSM samples the PA-6,6 homopolymer and the m-xylylenediamine/adipic acid ‘nylon salt’ were premixed in solution, and after evaporation of the solvent the mixture was submitted to a thermal treatment between T_g and T_m of PA-6,6. The progress of the transamidation reaction as revealed by the initial decrease in molecular weight during the chemical incorporation of the aromatic comonomer salt was monitored using SEC. The molecular weight $M_{n,SEC}$ decreases at a higher rate during the first transamidation step when higher mol percentages of MxAd salt were premixed with the PA-6,6 homopolymer. This molecular weight decrease, caused by chain scission, is followed by a built-up of $M_{n,SEC}$ due to post-condensation of the free amine and acid end groups resulting from the first transamidation step. Beyond 8 h, gelation due to branching or cross-linking was observed, leading to large errors in the M_n and PDI values measured by SEC, as the gels were filtered out before SEC sample analysis was performed. The actual incorporated MxAd mol percentages were determined using ^{1}H NMR spectroscopy, and for at least SSM times of 8 h at 230 ˚C were found to be comparable to the weighed-in mol% MxAd salt within experimental error. The SSM reaction mechanism was investigated and it was found that the transamidation or chain scission was initiated by protonated amine species ($-NH_3^+$). It was also observed that neither an excess of diamine nor an excess of dicarboxylic acid in the salt resulted in any significant change in the kinetics of the transamidation reaction with respect to the equimolar salt system, since for both cases no significant change was observed in the number-average molecular weight (M_n) development as a function of time. An in-depth study on the chemical microstructure was performed on the $(PA66_xMxAd_y)_{SSM}$ and $(PA66_xMxAd_y)_{MP}$ samples exhibiting similar overall compositions. The sequence analysis based on solution ^{13}C NMR experiments confirmed that the copolyamides prepared via SSM and containing 20-30 mol% of MxAd salt in the feed exhibited a more blocky structure with overall degrees of randomness R_{total} of ca. 0.4. On the other hand, the melt-polymerized copolyamides having a similar overall composition exhibited R_{total} values around unity, typical for fully random copolymers. The formation of a blocky structure was attributed to the exclusion of the crystalline PA-6,6 parts of the polyamide from transreactions during SSM, whereas during melt copolymerization all PA-6,6 chain parts can participate in the randomization process. The earlier mentioned presumption that during SSM the transamidation reactions selectively occur in the amorphous phase, leaving the homopolymer of crystalline PA-6,6 intact, was further supported by the observation that the $(PA66_xMxAd_y)_{SSM}$ products with up to exhibited only slightly lower degrees of crystallinity and enthalpies of melting as compared to pure PA-6,6, which can only be explained by the presence of long homo PA-6,6 blocks in the SSM products. A much more detailed investigation on the thermal properties and crystal structures of the SSM-based copolyamides as a function of the mol% of incorporated MxAd salt are discussed in the succeeding part of the thesis on the solid-state modification of PA-6,6.

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Chapter 4

The influence of the comonomer content on the thermal properties of copolyamides prepared via solid-state modification and melt polymerization

Abstract

In the previous ***Chapters 2*** *and* ***3****, we showed that the transamidation reaction between an aromatic comonomer salt, i.e. meta-xylylenediamine:adipic acid salt (MxAd), and polyamide-6,6 (PA-6,6) in the solid state resulted in blocky copolyamides with a retained crystallinity, since during the solid-state modification (SSM) the comonomers are preferably located in the amorphous phase of PA-6,6, leaving the crystalline phase unaltered. In this study, the influences of the comonomer salt content on the thermal properties of the copolyamides, viz. the glass transition, melting and crystallization temperatures, are analyzed and compared to copolymers with a similar composition, but prepared via a melt polymerization route (MP). To get more insight into how the chemical microstructure and the morphology develop during the solid-state modification reaction, the thermal properties of a system with 20 wt% MxAd were investigated by using DSC on samples taken at different reaction time intervals and by comparing the first and second heating and cooling cycles. The copolyamides obtained via SSM and via MP have a totally different thermal behavior, in agreement with the differences in the chemical microstructure of the SSM copolyamides as resolved by* ^{13}*C NMR sequential analysis. The blocky structure of the SSM-copolyamides seemed to be retained after melt processing, since after this treatment the high melting and*

crystallization temperatures were almost unchanged, indicating that randomization of the aromatic moieties only occurred to a limited degree.

4.1 Introduction

Polyamide-6,6 (PA-6,6 or Nylon-6,6) is an aliphatic semi-crystalline polyamide that is used in a variety of applications due to its excellent combination of properties like strength, ductility and heat resistance[1]. The main applications for PA-6,6 range from industrial yarns, apparel, electrics & electronics to automotive. PA-6,6 is produced by condensation polymerization. The physical and mechanical properties of the PA-6,6 can be strongly influenced by the crystallinity and the morphology of the final product. It has been reported that the crystallinity,[2,3] lamellar thickness[4-6] and the organization of the lamellar stacks within polyamide end products strongly depend on the used processing method.[7-10] However, there are some specific properties of PA-6,6 such as moisture absorption and brittleness that limit its utilization in some applications. The moisture penetrates preferentially into the amorphous regions and establishes hydrogen bonds with the amide groups, thereby acting as a plasticizer enhancing the toughness but also decreasing the glass transition temperature as well as the strength and stiffness.[1,11] The moisture absorption also negatively affects other mechanical, electrical, optical, and chemical properties, and also leads to a poor dimensional stability.[1]

The solid-state modification (SSM) is a very promising route to prepare step-growth copolymers, largely retaining the crystal structure of the starting material, as it selectively modifies the amorphous phase, leaving the crystalline phase intact.[12,13] Most of the literature on SSM is focused on solid-state post-condensation (SSPc) chemistry and its kinetics. The SSPc review on polyamides and polyesters by Papaspyrides and coworkers described all the various SSPc reaction mechanisms and concomitant reaction kinetics.[14-16] Groeninckx and coworkers investigated copolyamides prepared by melt mixing and studied the degree of transamidation reactions.[17-19] The various factors affecting the efficiency of transamidation or interchange reaction were considered. To the best of our knowledge, no transamidation chemistry has been reported so far for the modification of polyamides in the solid state.

In a previous study[20] (**Chapter 2**), we reported on the interchange reactions occurring between PA-6,6 and para-xylylenediamine:adipic acid (PxAd) and meta-xylylenediamine:adipic acid (MxAd) comonomer salts. The chemical incorporation of the aromatic *meta*-xylylenediamine (MXDA) comonomer into the high molecular weight PA-6,6 by SSM was confirmed by SEC, using both RI and UV detection, as was already discussed in detail (**Chapter 2)**. Size Exclusion Chromatography (SEC) analysis on the samples collected at various reaction times showed the disappearance of the MXDA peak and the incorporation of a UV-active moiety in the high molecular weight, fully aliphatic polyamide, which in itself is not or only moderately UV active. In the work described in **Chapter 3**, the influence of the molar percentage of the incorporated aromatic comonomer salt (MxAd) on the rate of the chemical modification reaction at 230 °C for 24 h was investigated using SEC, again by taking and analyzing samples at different reaction time intervals. The typical decreasing molecular weight trend proved the chain scission generated by transamidation reactions between the salt and PA-6,6 during the first part of the SSM, whereas at a later stage the post-condensation reaction leading to a significant increase in the number-average molecular weight (M_n) after 4 h of the solid-state reaction was the dominant reaction. The molecular weight enhancing effect of the reaction was attributed to the solid-state post-condensation (SSPc) of the free carboxylic acid and amine end-groups generated during the first part of the SSM treatment, the transamidation reaction, and after 12 h of solid-state reaction the starting molecular weight was almost recovered. Also the microstructures of the SSM $(PA66_xMxAd_y)_{SSM}$ and MP $(PA66_xMxAd_y)_{MP}$ copolyamides were studied by using ^{13}C NMR spectroscopy. It was found that the SSM polyamides were blocky in nature, exhibiting degrees of randomness R far below unity ($R_{total,SSM}$ ca. 0.4), whereas the MP copolyamides with similar overall chemical compositions were random in nature ($R_{total,MP}$ ca. 1). These detailed studies were already presented in **Chapter 3**.

The melting and crystallization behavior and the physical changes associated with them are among the most important properties of polymers in general and they are directly related to the chemical nature of the copolyamides. In this present chapter, the effect of the molar concentration of the aromatic diamine salt on the melting and crystallization temperatures of the resulting copolyamides prepared via SSM and MP are investigated. Different feed mol/mol ratios PA-6,6/MxAd comonomer salt or 'Nylon-6,6 salt'/MxAd salt were used to obtain copolyamides via SSM and MP, respectively, having different compositions. As the SSM transamidation occurs only in the amorphous phase of the semi-crystalline polymer, PA-6,6 in this case, an important question concerns the solubility of the comonomer salt in the amorphous phase of the PA-6,6. An attempt was made to check the maximum solubility of the comonomer salt in the PA-6,6 amorphous phase by analyzing the melting temperatures of the unreacted mixtures at different molar feed ratios. The impetus for this study was to correlate the chemical microstructure reported in **Chapter 3** with the thermal properties (viz. melting temperature, crystallization temperature and the degree of crystallinity) of the blocky SSM copolyamides as a function of the molar percentage of comonomer (ca. 5 to 20 mol%) and to compare this relationship with that of copolyamides prepared via melt polymerization (MP) exhibiting a similar overall, but random, chemical composition.

4.2 Experimental Section

4.2.1 Materials

Polyamide-6,6 (PA-6,6, Ultramid® A-27) pellets (M_n = 38 kg/mol, M_w = 72 kg/mol) were supplied by BASF SE, Ludwigshafen, Germany. Adipic acid (AA) as well as *meta*-xylylenediamine (MXDA or Mx) was purchased from Sigma Aldrich. Ethanol (99%), required for the preparation of the diamine/diacid salt, was also purchased from Aldrich. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, 99%), obtained from Biosolve (Valkenswaard, the Netherlands), was used for solution mixing of PA-6,6 with the diamine/adipic acid salt. For the NMR measurements deuterated trifluoroacetic acid (TFA-d, 99.5% deuterated) was obtained from Cambridge Isotope Laboratories, Inc., USA. All chemicals and solvents were used as received, unless stated otherwise.

4.2.2.1 Preparation of comonomer salt

The preparation of the 'comonomer salt' involved mixing the diamine (*m*-xylylene diamine) with adipic acid in equimolar proportions, by mixing equivalent amounts of ethanol solutions of both components (see Scheme 4.1, where Ar = CH_2-phenyl-CH_2). The nylon salts, *viz*. MxAd (*m*-xylylene:adipic acid salt), precipitated out of ethanol in an equimolar composition once they were formed. The salts were filtered, vacuum dried at a temperature of approximately 50 °C for 4 h and their equimolarity was checked and confirmed by ^1H NMR spectroscopy.

$$HOOC\text{-}(CH_2)_4\text{-}COOH + H_2N\text{- Ar - }NH_2 \longrightarrow {}^-OOC\text{-}(CH_2)_4\text{-}COO^- \,.\, {}^+H_3N\text{- Ar - }NH_3^+ \quad (1)$$

Scheme 4.1 Synthesis of aromatic comonomer salt.

4.2.2.2 Solution preparation of the SSM reaction mixture

PA-6,6 pellets were ground to a powder by using a Retsch type ZM 100 mill in a cryogenic way by soaking the pellets in liquid nitrogen while feeding into the grinder. The obtained powder was dried in a vacuum oven at 70 °C for 48 h. Then, 2 grams (80 mol%) of PA-6,6 and 0.5 gram (20 mol%) of comonomer salt were dissolved in 10-15 mL of HFIP at a temperature of approximately 50 °C. All the reaction mixtures were prepared in this way unless mentioned otherwise and no transamidation catalyst was present in or added to the starting material. After complete dissolution of PA-6,6 and the MxAd salt, the temperature was raised to 65 °C and HFIP was removed by drying under vacuum. The resulting solid lump was dried in an oven for 24 h and was then cooled in liquid nitrogen and ground to a powder using an analytical laboratory mill (Waring, type 32BL80), after which the powder was filtered using a sieve to get a more uniform particle size of 100 µm or smaller. This powder was subsequently dried in a vacuum oven for a period of 48 h prior to the SSM reaction.

4.2.2.3 Solid-state modification (SSM)

The experimental setup for SSM consisted of a glass reactor, equipped with a fluidizing purge gas tube. A salt mixture of KNO_3 (53 wt %), $NaNO_2$ (40 wt %), and $NaNO_3$ (7 wt %) was used as the heating medium for the reactor.[26] The reactor consisted of a glass tube (inner diameter ~ 2.4 cm) and a sintered glass-filter plate at the bottom. A small heat exchange glass coil (inner diameter ~ 5 mm) surrounded the reactor. The argon gas flow was heated by passing through this heated coil before entering the inner glass tube at the bottom just below the glass filter plate. The gas flow was controlled by a flow meter. The SSM reaction temperature was measured with a thermocouple inserted into the PA-6,6/ salt mixture. All the SSM reactions were carried out at 230 °C for 20-24 h.

4.2.2.4 Melt polymerization (MP)

The melt copolymerization was carried out after dissolving in total 200 g of different salt mixtures of $(HMDA:AA)_x$ and $(MxAd)_y$ in 200 g of water (x,y denotes the mol% of the salt as per feed compositions) placed into a 1.2 L pressure reactor. The reactor was heated to 210 °C at 15 bar for 15 minutes, and the temperature was raised in steps of 20 °C. Then, the temperature inside the reactor was subsequently raised to 220 °C and kept isothermal at that temperature for ca. 55 minutes under 15 bar pressure while removing water. Subsequently, the temperature and pressure were reduced to 267 °C and 1 bar for 30 minutes, and the melt polycondensation reaction was carried out at 271 °C for 10 min after which the copolyamide $(PA66_xMxAd_y)_{MP,\ Feed}$ was granulated in an underwater granulation system. The number-avarage molecular weight ($M_{n,\mathrm{SEC}}$) of these MP copolyamides is in the range of 20-35 kg/mol.

4.2.2.5 Characterization – Differential Scanning Calorimeter (DSC)

The melting (T_m) and crystallization (T_c) temperatures and enthalpies were measured by a TA Instruments Q100 Differential Scanning Calorimeter (DSC) equipped with an auto-sampler and a refrigerated cooling system (RCS). The DSC cell was purged with a nitrogen flow of 50 mL/min. The temperature was calibrated using the onset of melting for indium. The enthalpy was calibrated with the heat of fusion of indium. For the $(PA66_xMxAd_y)_{SSM}$ and $(PA66xMxAd_y)_{MP}$ copolymers, samples having a weight of 6–8 mg were weighed into crimped hermetic pans. All samples were measured in a temperature range from -40 to 290 °C using heating and cooling rates of 10 °C/min (unless specified differently), and having isothermal periods of 5 min at respectively 0 and 290 °C. The degrees of crystallinity (X_{cr}) of PA-6,6 and its copolyamides were calculated from the heat of fusion (ΔH_m) of the second heating cycle with the following relation:

$$X_c = \{\Delta H_m/\Delta H_{0m})\}\ x100\%$$

where ΔH_{0m} is the heat of fusion for 100% crystalline PA-6,6, which was taken as 188 J.g^{-1}.[31]

The percentage of crystallinity of the PA-6,6 in the SSM reaction feed mixture (0 h sample) was calculated with correction for the present amount of PA-6,6. The enthalpy of melting per g of the mixture was corrected by multiplying this value with the weight fraction of pure PA-6,6 present in the mixture (i.e. PA-6,6 present in the mixture (g)/total weight of PA-6,6/MxAd in the reaction mixture), and then the corrected heat of melting was divided by the ΔH_{0m}.

4.3 Results and Discussion

In **Chapter 2,** the incorporation of the MxAd conomomer salt into PA-6,6 via SSM and MP was described in detail. In **Chapter 3** and the present chapter different PA-6,6/MxAd molar ratios were used to obtain copolyamides of different compositions. The general chemical structure of the copolyamides is represented schematically in Figure 4.1.

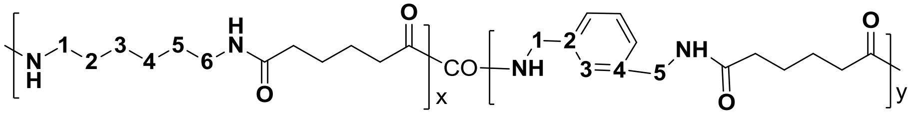
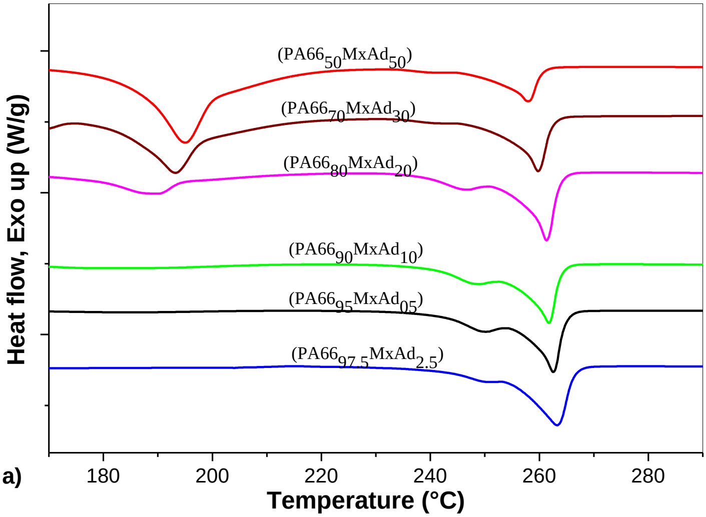


Figure 4.1 Chemical structure of $(PA66_xMxAd_y)_{SSM}$ showing the two different repeat units.

4.3.1 Miscibility study of aromatic diamine salt into PA-6,6 for SSM reactions

As described earlier, the solid-state modification (SSM) of PA-6,6 was done using the semi-aromatic *m*-xylylenediamine:adipic acid salt (MxAd) and different PA-6,6/MxAd salt mol/mol ratios were prepared by solution mixing for this solid-state process. After performing the modification chemistry, the chemical microstructures of the different compositional SSM-copolyamides were studied by using ^{13}C NMR spectroscopy. It is interesting to study the limit of the comonomer salt concentration (mol%) that can readily dissolve in the amorphous phase of the starting PA-6,6 and to verify whether our hypothesis that *the comonomer is homogeneously dissolved into the amorphous phase of the polymer* is correct and, if it is verified, up to which salt concentration it is valid. In literature, an SSP reaction is considered to proceed according to a nucleation-and-growth model.[21] In our studies, it was found that the solution mixing process prior to SSM reactions, enabling the diffusion of the comonomer salt into the amorphous phase, is crucial to enable the transamidation reaction. In the physical PA-6,6/MxAd mixture, the comonomer can act as a solvent by dissolving into the amorphous phase, increasing the mobility and decreasing the T_g of the polymer, but this is usually limited to lower amounts of comonomer. When a certain comonomer concentration is exceeded, phase separation could occur resulting in the homo-polymerization of the comonomer salt upon heating of the system, rather than a transamidation reaction of the salt with PA-6,6. Alternatively, the transamidation reactions could be limited to the interface between the PA-6,6 and the salt domains. In order to determine to which extent the comonomer acts as a diluent or solvent, the as-prepared salt/PA-6,6 mixtures (subjected to 0 h of SSM) were analyzed by DSC (heating/cooling rate of 10 °C/min). The first DSC run of the homogeneously solution-mixed PA-6,6/MxAd composition was expected to resemble the initial sample morphology, revealing whether the MxAd is completely dissolved in the amorphous PA-6,6 fraction or present as a separate phase. The first heating run possibly offers the comonomer additional time to mix homogeneously into the PA-6,6 amorphous phase by thermal diffusion, as it was subjected to a temperature of 290 °C (beyond the melting temperatures of both MxAd and PA-6,6, being approximately 200 and 262 °C, respectively). The second heating run probes the previously molten mixture, having its thermal history erased. In the relatively short periods of time required to record the DSC traces it is expected that only a limited degree of transamidation occurs. Furthermore, it is assumed that sufficient swelling of the amorphous phase by the monomer salt can occur during the heating run.

It is evident from the first heating runs (Figure 4.2a) that the comonomer salt MxAd has completely dissolved into the PA-6,6 after solution mixing of the polyamide with 2.5, 5 and 10 mol% of MxAd, since the MxAd salt generally has a melting endotherm at a T_m of approximately 200 °C and such an endotherm is completely absent in the first heating curves of these physical mixtures. For higher amounts of MxAd salt introduced into PA-6,6, the first DSC heating runs show the presence of MxAd comonomer salt that might have either been partially dissolved or completely phase separated, as can be clearly seen in Figure 4.2a for 20, 30 and 50 mol% of MxAd. The endotherm of the MxAd salt around 200 °C is completely absent in the second heating thermograms, irrespective of the added amount of MxAd salt (Figure 4.2b). The results presented in Figures 4.2a and 4.2b indicate that the comonomer salt is miscible with the amorphous part of the PA-6,6 up to at least 5–10 mol% of MxAd salt in the feed. However, it is also obvious that there is a clear decrease in the polymer's melting temperature with increasing amounts of MxAd. This melting temperature depression can be due to both thermodynamic and kinetic effects. The T_g values of the PA-6,6-rich phases presented below have been obtained from the DSC's first heating traces, and were obtained from the peak values of the first derivatives of the heat flow versus temperature curves. The MxAd comonomer salt acts as a plasticizer for the PA-6,6 polymer, dissolves into the amorphous phase and thus increases the mobility, resulting in a decreased T_g as seen in Figure 4.3. The T_g values for the 2.5–5.0 MxAd mol% mixtures remain roughly the same but they sharply decrease to ca. 52 and 46 °C for 10 and 20 mol% of added MxAd salt, respectively. The T_g of the 30 mol% comonomer mixture is slightly higher than that of the 20 mol% mixture, which is unexpected and which could be due to a more complete phase separation between a PA-6,6 rich phase, containing less MxAd than in the case of the 20 mol% sample, and an MxAd phase. The degrees of crystallinity of the PA-6,6 present in the non-transamidated feed mixtures are given in Figure 4.4. These degrees of crystallinity were obtained by correcting the heats of melting of the physical PA-6,6/MxAd mixtures for the total amount of crystallizable PA-6,6 units present in the PA-6,6/MxAd mixtures (as explained in **Section 4.2.6**). In fact, these values represent the degrees of crystallinity of the PA-6,6 in the PA/salt mixtures that were subjected to the SSM treatment later on. The data in Figure 4.4 show that the crystallinity of the PA-6,6 in the PA/salt mixtures for 2.5-10 mol% of MxAd salt varies between ca. 36 and 41 wt%, which can be considered as being nearly constant in view of the experimental error, whereas the crystallinity of the sample containing 20 mol% MxAd is significantly lower, *viz.* 31 wt%. Obviously too high amounts of MxAd dissolved in the HFIP hinder the crystallization of the present PA-6,6. This means that for the SSM samples containing 2.5, 5 and 10 mol% of MxAd salt in the feed, the amount of PA-6,6 participating in the SSM reactions is quite similar, whereas for the sample containing 20 mol% MxAd in the feed the amount of PA-6,6 excluded from the transamidation reactions because of its presence in the crystals is slightly lower. This finding is important for the discussion concerning the melting temperatures of the SSM samples (*vide infra*). For MxAd contents exceeding 20 mol% (*viz.* 30 to 50 mol%) the degrees of crystallinity decrease concomitantly with the melting temperatures of the as-prepared samples. In the next section, a detailed thermal analysis of the SSM samples of the PA-6,6/MxAd mixtures containing 2.5–20 mol% MxAd will be presented.



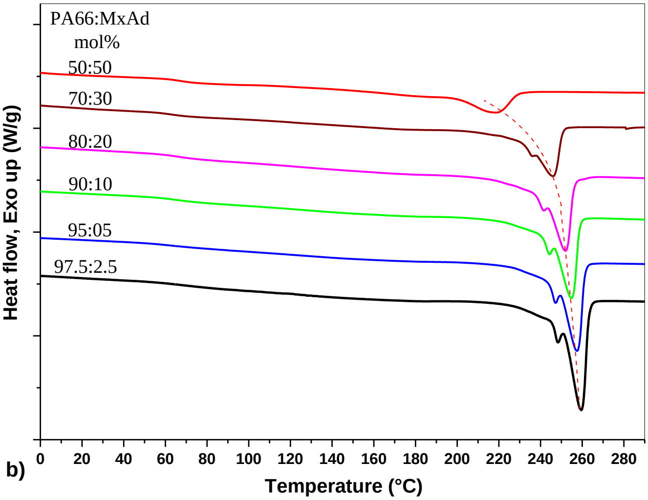


Figure 4.2 DSC traces of non-transamidated ((PA66$_x$MxAd$_y$)$_{SSM,feed}$ mixtures. a) 1st heating and b) 2nd heating traces. (they are stacked vertically for clarity).

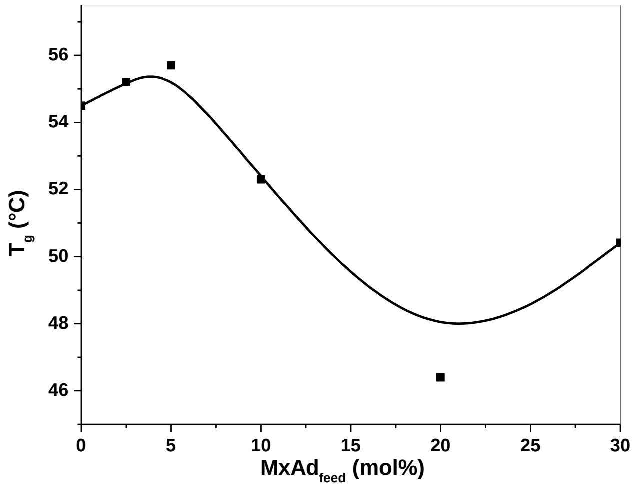


Figure 4.3 Glass transition temperature (T_g) of physical PA-6,6/MxAd mixtures (0 h, non-transamidated) as a function of MxAd mol% in the feed (determined from first heating run).

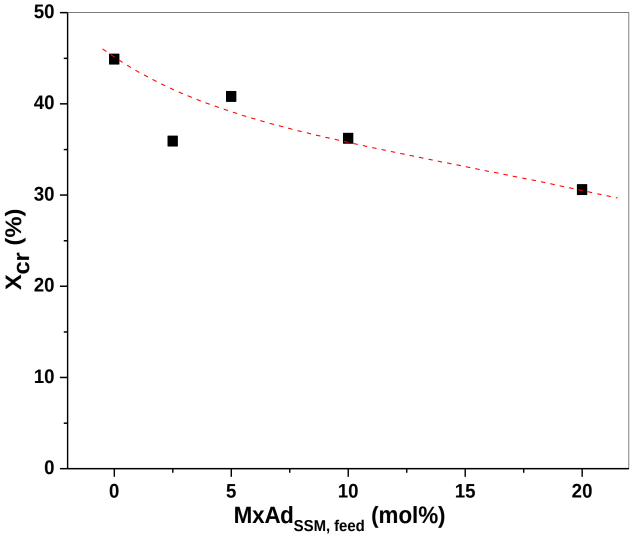
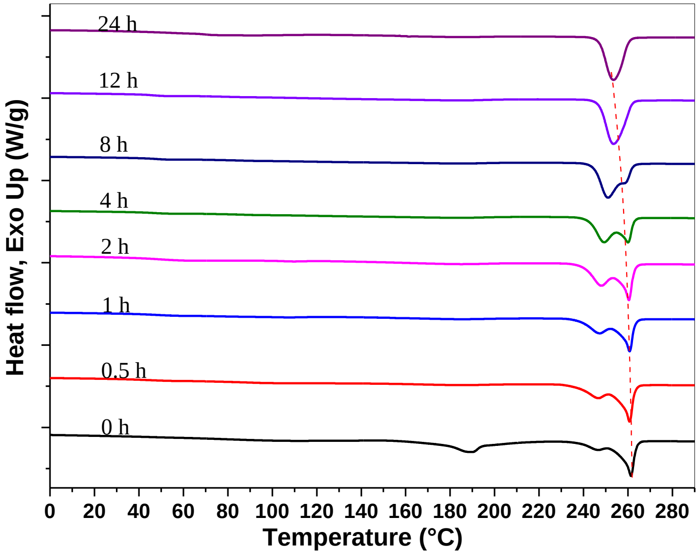


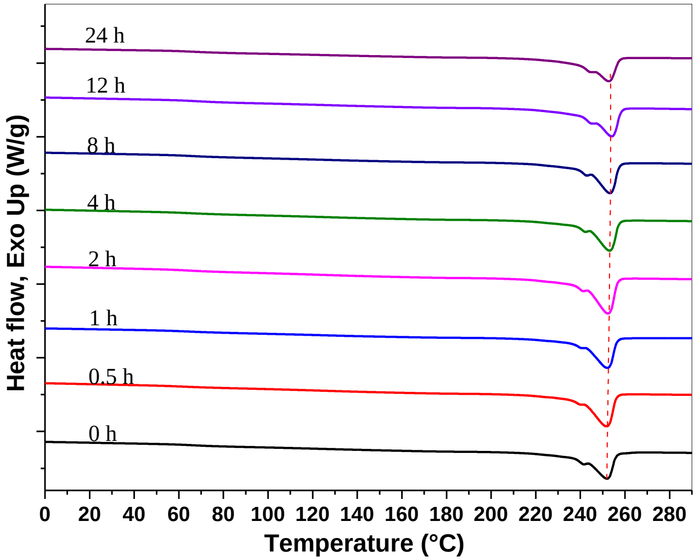
Figure 4.4 Degree of crystallinity of the non-transamidated $(PA66_xMxAd_y)_{SSM,feed}$ mixtures, corrected for the pure crystallizable PA-6,6 present in the mixture, as a function of comonomer salt concentration (MxAd mol%) in the feed.

4.3.2 Monitoring the thermal properties of the copolyamides during SSM

In this section, the changes in the thermal properties during the relatively long SSM-reaction, which according to the foregoing are directly related to the chemical microstructure of the copolyamides, is studied. For this purpose one specific SSM sample composition, *viz*. $(PA66_{80}MxAd_{20})_{feed}$, was selected to be analyzed in detail. The first heating and second heating DSC traces of the SSM reaction product are given as a function of SSM time in Figures 4.5a and 4.5b, respectively. At 20 mol% of MxAd in the feed, the comonomer did not fully act as a solvent to swell the amorphous phase of PA-6,6 as it gives a separate melting endotherm around 190 °C (see Figure 4.5a). However, this endotherm is suppressed after 30 minutes of the SSM reaction, as the transamidation started. As the reaction proceeded the shape and the position of the double melting peaks of the PA-6,6 changed. It is evident that the lower temperature melting endotherm has become equally intense as the higher melting endotherm after 4 h of the SSM reaction (see the first heating traces in Figure 4.5a). The first endothermic peak (lower T), which is attributed to less perfect crystals or thinner lamellae, is followed by a melting peak (higher T) of more perfect crystals or thicker lamellae. In other words, this might also be due to a bimodal distribution of the crystal size as explained later in **Section 4.3.3**. After 8 h of SSM reaction the lower melting peak (ca. 250 °C) increased its area at the expense of the higher melting peak (ca. 262 °C). The reorganization that occurred during the latter part of the SSM reaction resulted in a single melting endotherm after 24 h, representing a crystalline polymer material entirely exhibiting the same degree of crystal perfection or a quite similar lamellar thickness, as evidenced by the first DSC heating cycle. The slight decrease of the first heating melting temperature from ca. 262 to ca. 250 °C during the 24 h of SSM reaction at 230 °C (see bended dashed line in Figure 4.5a) may be due to the gradual dissolution and recrystallization of chain segments, resulting in somewhat thinner lamellae. Such a thinning of the crystalline lamellae and a reduction of T_m during SSM was also observed by Jansen *et al.* for the previously mentioned Dianol/PBT system.[13]


24 h
12 h
8 h
4 h
2 h
1 h
0.5 h
0 h
Heat flow, Exo Up (W/g)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
Temperature (°C)

a)


24 h
12 h
8 h
4 h
2 h
1 h
0.5 h
0 h
Heat flow, Exo Up (W/g)
0
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200
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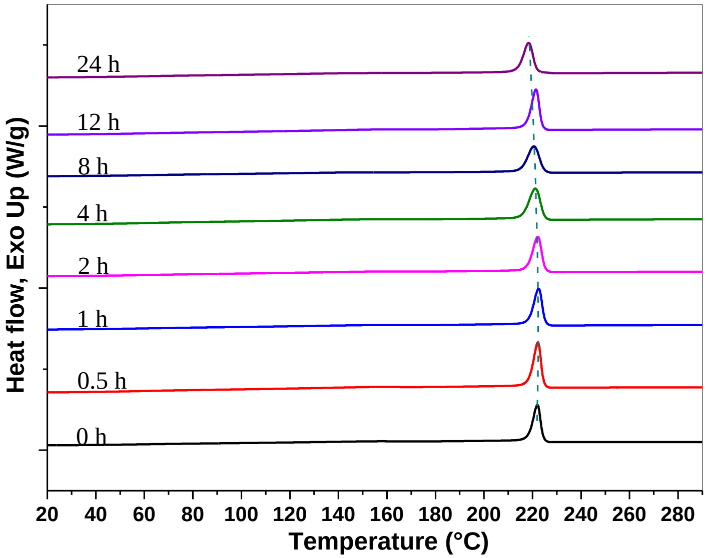
Temperature (°C)

b)



c)

Figure 4.5 DSC curves of the $(PA66_{80}MxAd_{20})_{SSM,feed}$ SSM reaction at 230 °C as a function of reaction time: a) first heating, b) second heating and c) second cooling (The traces are stacked upwards for clarity).

The copolyamides perfectly reorganize themselves during the cooling cycles, irrespective of the SSM reaction time, which becomes evident when examining the second heating traces given in Figure 4.5b. The second heating melting temperatures are almost independent of the transamidation time. This may be related to the fact that the PA-6,6 chains present in the crystals during SSM are not taking part in the chemistry. Two processes can occur simultaneously during the SSM-reaction. One involves the transamidation reaction of the MxAd salt in the swollen amorphous PA-6,6 segments and the other process concerns the crystal reorganization by transformation of non-swollen rigid segments into the crystal phase, making the crystals larger, or by dissolving part of the crystals, making them smaller. Which of these processes dominates depends on the comonomer content and on whether the swelling is significant on the reaction kinetics. Similarly to the second heating melting temperatures, the crystallization temperatures T_c remain rather constant during the entire SSM reaction (see Figure 4.5c), which most probably is again related to the inertness of the

PA-6,6 chain segments present in the crystals during the transamidation process. Nevertheless, the crystallization peak becomes somewhat broader after 4 h of reaction time as more and more comonomer becomes incorporated into the copolyamide blocks, thereby somewhat retarding the crystallization of the blocky copolyamides.

4.3.2 Crystallization behavior of SSM copolyamides vs. their MP counterparts

Different theories exist in literature concerning the crystallization of polymers during solid-state polymerization (SSP) reactions. Some claim that there is a limit to the extent of crystallization, as after a certain period of SSP the chain mobility has decreased due to the increased viscosity.[5] However, other theories argue that there can be a continuous crystallization during SSP and that the crystallization rate is higher at higher reaction temperatures.[3,4,6] During the solid-state modification (SSM) reactions of PA-6,6 yielding copolyamides, the development of the degree of crystallinity may be entirely different compared to the previously mentioned SSP process as there are two processes occurring simultaneously, viz. transamidation and crystallization. The degrees of crystallinity of PA-6,6/MxAd copolyamides with different compositions, prepared by SSM and accordingly exhibiting a block-like structure, were determined from the first and the second DSC heating curves and are plotted as a function of the incorporated mol% of MxAd in Figure 4.6a. For comparison purposes, random PA-6,6/MxAd copolyamides were prepared by melt polymerization and the resulting degrees of crystallinity determined from the second heating DSC run are given as a function of the MxAd content in Figure 4.6b. The incorporation of an aromatic diamine salt with five carbon atoms between the amine groups, deviating from the six carbons between the amines in hexamethylenediamine, certainly affects the regularity and the crystallizability of the copolyamide chains.[1,2]

Figure 4.6a shows that right after the SSM treatment the degrees of crystallinity of the blocky PA-6,6/MxAd copolyamides are very high and do not vary much as a function of the incorporated amount of MxAd salt. The SSM treatment can be regarded as a very efficient annealing procedure, thereby raising the crystallinity to ca. 40-45%.

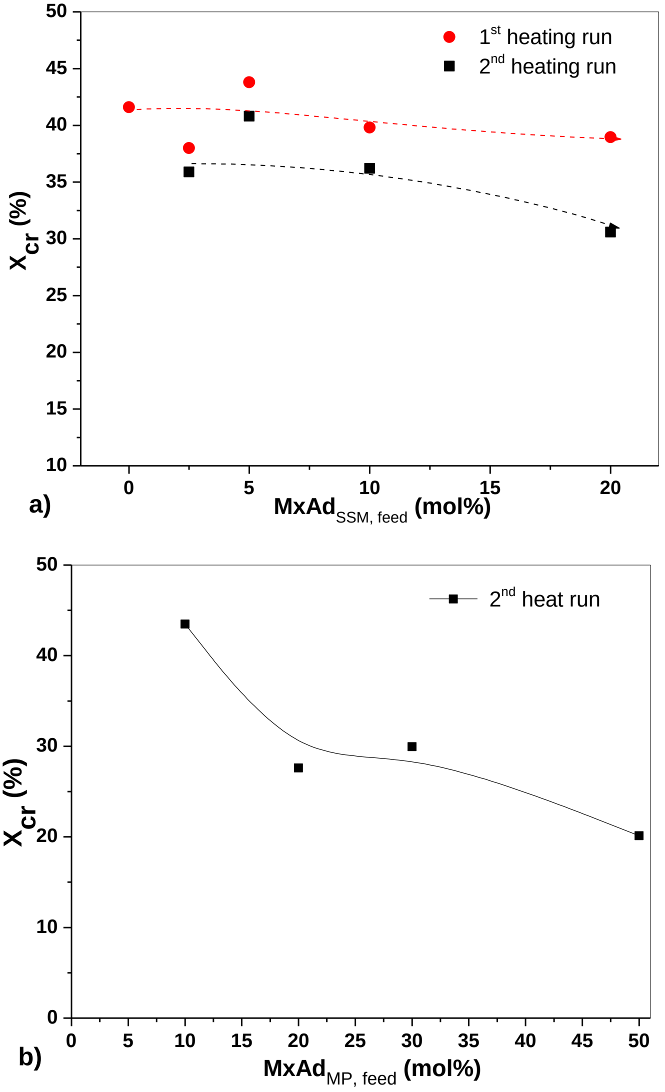


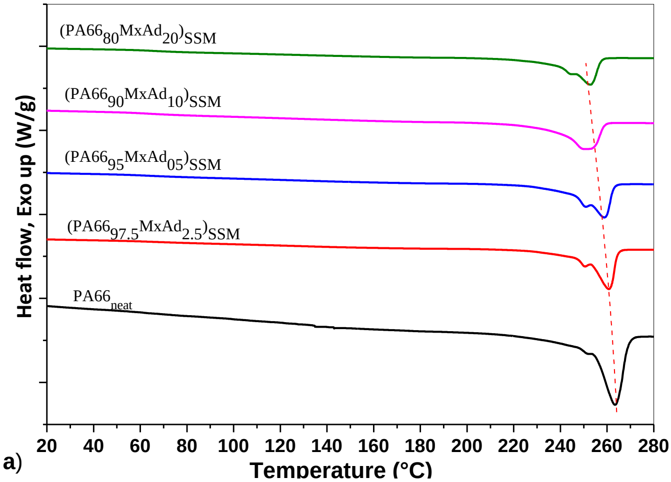
Figure 4.6 Degree of crystallinity, X_{cr} (%), as a function of MxAd content (in mol%) in the copolyamides prepared via a) SSM route and b) MP route.

The second heating runs, recorded on copolyamides crystallized from the melt, exhibit significantly lower crystallinities in the order of 31-38 wt% (see Figure 4.6a). First of all, in this case no annealing took place. Moreover, the relatively rigid copolyamide blocks, containing different amounts of MXDA, hinder the crystallization and the chain folding of the PA-6,6 blocks from the melt, which not only results in lower melting temperatures (see the section on thermal transitions) but also reduces the crystallinity. The crystallinities from the second heating runs of the 2.5 and 5 mol% SSM copolyamides are similar to that of PA-6,6 (~ 38-41%), but they decrease with the increasing molar percentage of incorporated MxAd to values exceeding 5 mol%, in agreement with the decreasing melting temperatures of these copolyamides with increasing MxAd contents and increasing chain stiffness (see Figure 4.9a).

For higher MxAd contents the degree of crystallinity of the blocky SSM copolyamides is slightly higher than that of the MP copolyamides with similar MxAd contents. To illustrate this, the crystallinities of the SSM sample with 20 mol% MxAd in the feed (17.0 mol% incorporated in the copolyamide) and the MP copolyamide with 20 mol% MxAd in the feed (17.2 mol% incorporated in the copolyamide) are compared. The SSM sample has a degree of crystallinity of ca. 32-33 wt%, whereas the corresponding MP copolyamide has a crystallinity of ca. 27-28 wt%. This illustrates the advantage of a block-like structure with relatively long crystallizable PA-6,6 blocks over a fully random copolymer structure with similar MxAd comonomer content and shorter average pure PA-6,6 sequence lengths. The higher crystallinity of the SSM samples implies an MXDA (or Mx) enrichment in the amorphous phase with respect to the MP samples, where the MXDA is diluted by a higher amount of amorphous PA-6,6. This should be reflected in higher glass transitions temperatures for the SSM samples with respect to MP samples with similar overall MxAd contents. This will be discussed in the following section on the thermal transitions.

4.3.3 Thermal analysis of copolyamides prepared by SSM versus MP

The difference in the chemical microstructure between the $(PA66_xMxAd_y)_{SSM}$ and $(PA66_xMxAd_y)_{MP}$ copolyamides having similar overall compositions, i.e. the SSM copolymers being more blocky and the MP copolyamides being random as shown in the previous chapter, is expected to be reflected in the corresponding thermal properties. Therefore, in this section the melting and crystallization temperatures of the copolyamides were studied by DSC. From the previous section on the miscibility of the MxAd salt with PA-6,6 we learned that up to 10 mol% MxAd salt can be homogeneously dissolved in the amorphous phase of PA-6,6 and that the first signs of phase separation of the physical MxAd/PA-6,6 mixtures were observed when adding 20 mol% of MxAd salt to PA-6,6. Therefore, it was decided to focus on the thermal analysis of SSM samples containing up to 20 mol% MxAd in the feed, whereas for the MP samples salt contents up to 50 mol% were studied. The DSC second heating runs recorded for both the SSM and the MP copolyamides are given in Figures 4.7a and 4.7b, respectively. The first cooling curves of both series of copolyamides are given in Figures 4.8a and 4.8b. The different thermal transitions observed in these curves (T_g, T_m *and* T_c), as well as the values of $T_m - T_c$, are given in Table 4.1 for the SSM samples (PA66$_x$MxAd$_y$)$_{SSM}$ and in Table 4. 2 for the MP samples ((PA66$_x$MxAd$_y$)$_{MP}$).



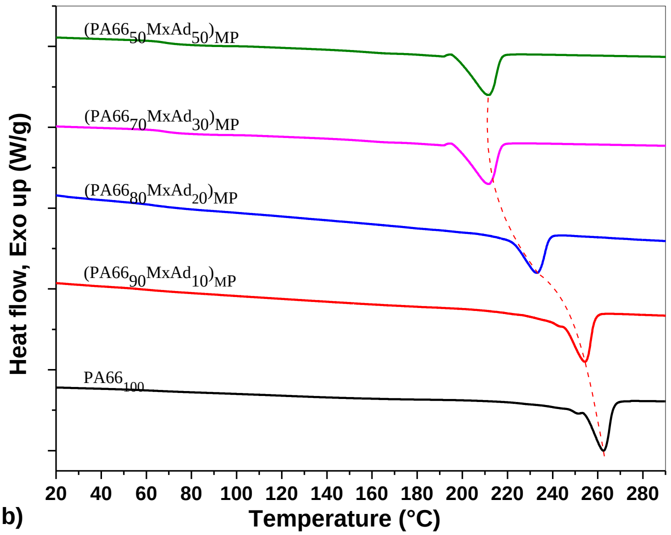
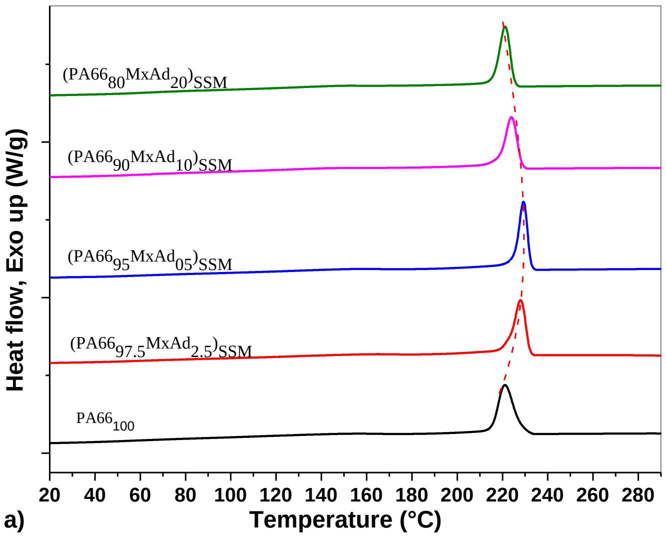


Figure 4.7 DSC second heating runs of the copolyamides prepared via: a) (PA66$_x$MxAd$_y$)$_{SSM}$ at 230 °C/24 h and b) (PA66$_x$MxAd$_y$)$_{MP}$.



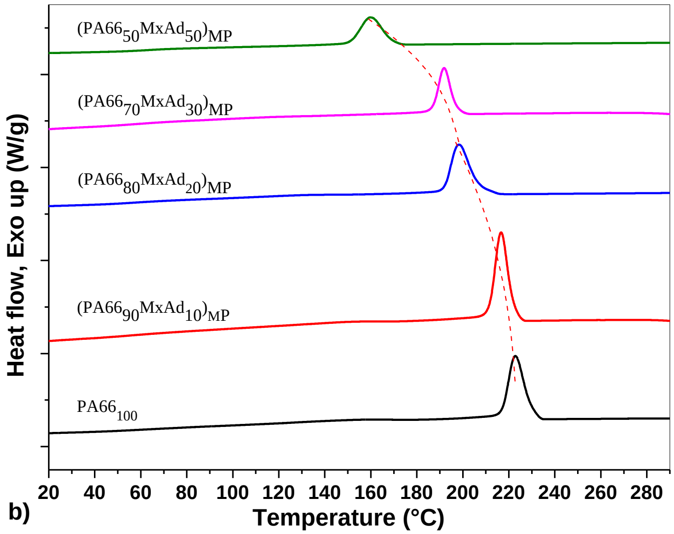


Figure 4.8 DSC cooling traces measured after the first heating of the different copolyamide compositions prepared via: a) (PA66$_x$MxAd$_y$)$_{SSM,feed}$ at 230 °C/24 h and b) (PA66$_x$MxAd$_y$)$_{MP,feed}$.

Table 4.1 Thermal properties of the copolyamides (PA66$_x$MxAd$_y$)$_{SSM}$ at 230 °C for 24 h

Composition feed		**Composition after SSM***		**2nd Heating Run^a**		**1st Cooling Run^a**	
***PA66*$_{, feed}$ (mol%)**	***MxAd*$_{, feed}$ (mol%)**	***PA66*$_{, total}$ (mol%)**	***MxAd*$_{, total}$ (mol%)**	T_g (°C)	T_m (°C)	T_c (°C)	T_m- T_c (°C)^{a,b}
100.0	0.0	100.0	0	55.0	263.3	221.8	41.5
97.5	2.5	97.5	2.5	61.8	260.6	228.0	32.6
95.0	5.0	95.0	5.0	62.4	258.8	230.3	28.5
90.0	10.0	89.0	11.0	63.2	252.2	223.7	28.5
80.0	20.0	83.0	17.0	65.1	252.6	220.4	32.2

`**Table 4.2** Thermal properties of synthesized copolyamides ($(PA66_xMxAd_y)_{MP}$)

Composition feed		**Composition after MP***		**2nd Heating Run[a]**		**Cooling Run 1[b]**	
***PA66*$_{,\text{feed}}$ (mol%)**	***MxAd*$_{,\text{feed}}$ (mol%)**	***PA66*$_{,\text{total}}$ (mol%)**	***MxAd*$_{,\text{total}}$ (mol%)**	**T_g (°C)**	**T_m (°C)**	**T_c (°C)**	**T_m- T_c (°C)[a,b]**
Pure PA66		100.0	0	55.0	262.9	221.8	41.1
90.0	10.0	91.9	8.1	55.9	254.7	216.7	38.0
80.0	20.0	82.8	17.2	61.8	244.7	198.3	46.4
70.0	30.0	71.7	28.3	63.3	232.9	191.8	41.1
50.0	50.0	52.6	47.4	68.3	212.1	159.3	52.8

*Compositions were obtained by ^{1}H NMR spectroscopy

[a] T_g, Tc, and T_m were determined by means of DSC (TQ100) using a heating/cooling rate of 10 °C/min.

[b] The T_m and T_c values shown are the peak values of the melting endotherms and crystallization exotherms respectively.

A careful examination of the second heating endotherms of the SSM-copolyamides with different MxAd comonomer contents given in Figure 4.7a and the corresponding thermal transitions given in Table 4.1 shows that the melting temperature of the copolyamides is only reduced with approximately 10 °C with respect to pure PA-6,6 upon the incorporation of 20 mol% of the MxAd salt. The crystallization temperatures of these copolyamides have been almost completely retained (only a slight reduction from 221.8 to 220.4 ˚C was observed). In fact, the highest T_c value was observed for the copolyamide containing 2.5-5 mol% of MxAd, see Table 4.1. (Note: a similar positive effect on the crystallization temperature upon incorporation of small amounts of nylon salt into a polyamide was previously observed for PA-6 and was attributed to a plasticizing effect, resulting in increased mobility favoring crystallization.[32]) The difference between the melting and crystallization temperatures T_m-T_c, the so-called super cooling required to cause crystallization from the melt, is even smaller for the copolyamides compared to neat PA-6,6, meaning that the copolyamides are readily crystallizable polymers, which is very favorable for injection-molding applications. This reduced super cooling is attributed to the reduced melting temperatures and not to enhanced values of the crystallization temperatures.

For imperfectly co-crystallizing comonomers the thermal transitions of copolyamides and other step-growth copolymers usually occur at reduced temperatures compared to the corresponding homopolymer. The generally accepted explanation for the T_m reduction is the existence of thinner crystal lamellae or smaller crystallites in the copolymers with respect to the pure homopolymer, in our case PA-6,6. This effect is related to the presence of shorter PA-6,6 sequences due to the incorporation of MxAd salt residues into the amorphous PA-6,6 parts, which are turned into the copolyamide blocks of the resulting blocky copolymer. So, the general reduction of the DSC second heating melting temperatures of the SSM copolyamides with respect to the melting temperature of pure PA-6,6 can be explained. The question remains why the T_m is further reduced with increasing amounts of incorporated MxAd salt from 2.5 to 10 mol%, since the initial PA-6,6 degrees of crystallinity of these physical mixtures, before SSM is started, are very comparable in view of the experimental error and the amount of PA-6,6 excluded from the transamidation reactions is therefore very comparable as well (see previous section). We believe that the observed slight reduction of the second heating melting temperatures of the copolyamides from ca. 263 to ca. 252 ˚C with increasing comonomer salt content from 0 to 10 mol% (see Table 4.1 and Figure 4.7a) is related to the presence of increasing amounts of the bulky aromatic groups of the Mx residues in the copolyamide block of the block copolymer during crystallization from the melt after first heating, thereby reducing the mobility of the crystallizable pure PA-6,6 segments and hampering the crystallization. The melting endotherms of the copolyamides containing 2.5 or 5 mol% of MxAd in the feed (see Figure 4.7a) are relatively sharp, whereas the endotherms of the copolyamides containing

10 and 20 mol% MxAd salt in the feed are broader, meaning that the distribution of the size of the crystals is narrower for lower comonomer salt feed contents (2.5-5 mol%) and that a broader size distribution of crystals is obtained at higher amounts of salt in the feed (i.e. 10 and 20 mol%). This may be also related to the limit of the miscibility of the comonomer salt in the amorphous phase. Regarding the double melting peak behavior of PA-6,6, the two higher temperature peaks comprise a double melting endotherm which results from melting of two different forms of the γ-phase.[7,21] The first peak in the double melting endotherm, "γ1," observed at 256 °C, is related to the melting of γ-phase crystallites that are weakly hydrogen bonded. The second peak in the double melting endotherm, "γ2," which occurs at 262 °C, arises from the melting of more strongly hydrogen-bonded γ-phase crystallites.

It should also be noted that the double melting peak behavior of PA-6,6 is retained in all the SSM cases except for the copolyamide containing 10 mol% of MxAd comonomer. The double melting peak phenomenon of polymers (PA-6,6) has already been studied in detail and several explanations are given in literature.[22] Some authors assigned these peaks to different types of spherulites leading to different melting temperatures. Others assigned this double melting peak behavior to the formation of a bimodal distribution of crystals in lamellar thickness formed during cooling from the melt.[23-26] Recently, it was shown that the most likely explanation for the presence of this double melting peak behavior is a reorganization of less perfect crystals into thicker and more perfect crystals.[27,28] Unlike the SSM copolyamides, the MP copolyamides exhibit single melting endotherms (see Figure 4.7b). This may be due to a more perfect crystal formation from the melt as compared to the crystal formation during SSM. This is plausible, as the semi-aromatic MP copolyamide has a uniform and fully randomized chemical microstructure and in the melt state there is no enrichment of the bulky aromatic residues in a specific fraction of the material which might seriously hamper the formation of crystals with a higher degree of perfection, as may be the case for the SSM samples (*vide supra*). It should be mentioned that the recorded melting temperature of neat PA-6,6 of approximately 263 °C is in good agreement with the values mentioned in literature.[29] The glass transition temperatures of the $(PA66_xMxAd_y)_{SSM}$

samples measured by DSC are higher than the T_g of PA-6,6 due to rigid aromatic moiety incorporated into the amorphous phase, and a single T_g is observed.

The melting and crystallization temperatures versus the molar percentage of MxAd salt incorporated into the SSM and the MP samples are given in Figures 4.9a and 4.9b, convincingly showing the advantage of SSM over MP with respect to the resulting thermal transitions. The molecular weight of these copolyamides is at a level where the melting (T_m) and crystallization (T_c) temperatures do not strongly depend on the molecular weight anymore. The melting temperatures as well as the crystallization temperatures of $(PA66_xMxAd_y)_{MP}$ samples are lower than those of the copolyamides with similar overall compositions obtained via SSM. For instance, the T_m of the MP sample containing 17.2 mol% MxAd is ca. 245 ˚C (see Table 4.2), whereas the T_m of the SSM sample containing 17.0 mol% MxAd is approximately 253 ˚C (see Table 4.1), a difference of 8 ˚C. For MxAd contents exceeding 20 mol%, the melting temperatures of the MP samples are even reduced to below 220 °C. This is in full agreement with the more random structure of the copolyamides prepared by the melt route as revealed by the ^{13}C NMR chemical microstructure analysis discussed in **Chapter 3**. For the SSM samples, the Mx residues are concentrated in the blocks forming the amorphous phase during the SSM treatment, whereas in the MP polymers the MXDA units are randomly distributed over the entire copolyamide chain, resulting in longer pure PA-6,6 sequences in the case of the SSM samples and accordingly into thicker crystal lamellae, exhibiting a higher melting temperature than the thinner lamellae generated in the case of the MP copolyamides exhibiting shorter pure PA-6,6 sequences. The longer PA-6,6 blocks present in the SSM samples also result in significantly higher crystallization temperatures, e.g. ca. 220 ˚C for the SSM sample containing 17.0 mol% of MxAd versus ca. 198 ˚C for the MP sample containing 17.2 mol% of MxAd. As mentioned earlier, very important for injection-molding applications is the required super cooling for crystallization from the melt. Let us again compare the two samples containing ca. 17 mol% MxAd. For the SSM sample with $M_{n,SEC}$ = 49 kg/mol, T_m - T_c is ca. 32 ˚C, whereas this is ca. 46 ˚C for the MP sample with $M_{n,SEC}$ = 31 kg/mol. This very convincingly shows the superior crystallization behavior of the block-like SSM samples with respect to the random

MP samples, certainly if one takes into account the lower viscosity (lower M_n) of the MP sample. A lower melt viscosity usually results in lower T_m - T_c values and a faster crystallization from the melt. So, it is obvious that the blocky SSM copolyamides are much more suitable for injection-molding applications than the random MP copolyamides. The melting endotherms of the MP copolyamides are broader compared to those of SSM copolyamides with similar overall compositions. The discussion given above shows that for similar overall compositions the copolyamides obtained via SSM and via MP have a significantly different thermal and crystallization behavior, which is in agreement with the differences in the chemical microstructure. It should be mentioned here that this is not the case for the incorporation of Dianol (2,2-Bis[4-(2-hydroxyethoxy) phenyl]propane, commercially known as Dianol 220®) into poly(butylene terephthalate) (PBT) via SSM.[30,33] In this case, despite the differences in the chemical microstructure, the thermal properties determined by DSC were almost equal for the copolyesters synthesized via SSM and via MP.

Table 4.3 Number-average molecular weights and polydispersity indices of the copolyamide series $(PA66_xMxAd_y)_{MP}$ and $(PA66_xMxAd_y)_{SSM}$

Composition feed		**SEC - SSM copolyamides**		**SEC – MP copolyamides**	
***PA66*, feed (mol%)**	***MxAd*, feed (mol%)**	**M_n (kg/mol)**	**PDI**	**M_n (kg/mol)**	**PDI**
100.0	0.0	38	2.1	--	--
97.5	2.5	42	2.7	--	--
95.0	5.0	48	4.7	--	--
90.0	10.0	53	5.1	33	2.1
80.0	20.0	49	1.8	31	2.1
50.0	50.0	--	--	25	1.9

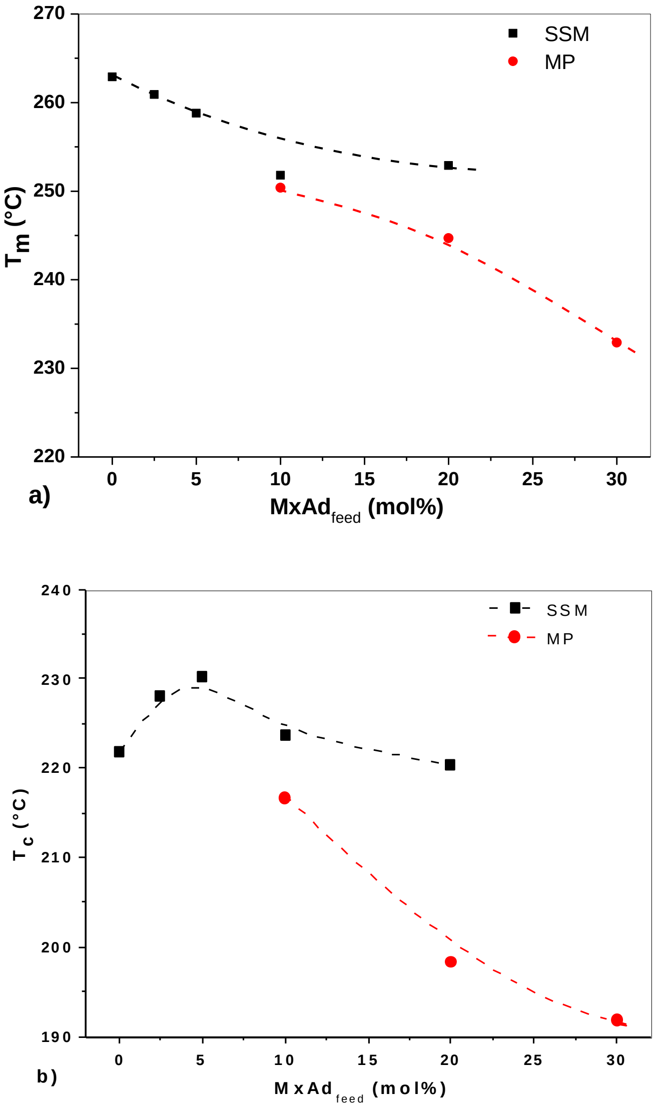


Figure 4.9 Comparison of a) melting temperatures and b) crystallization temperatures of the copolyamide series $(PA66_xMxAd_y)_{SSM,feed}$ at 230 °C/24 h, $(PA66_xMxAd_y)_{MP,feed}$ as a function of comonomer content.

For the SSM as well as for the MP samples, the T_g of the copolyamides clearly increases with increasing comonomer content (see Tables 4.1 and 4.2). The highest T_g value of ca. 68 °C is obtained for the MP sample with 50 mol% of MxAd salt in the feed, resulting in 47.4 mol% MxAd incorporated into the PA-6,6. When comparing the T_g values of the two samples with ca. 17 mol% MxAd incorporated it becomes clear that the T_g of the SSM copolyamide is ca. 3 °C higher than that of the MP copolyamide, namely 65 versus 62 °C. This can be explained by the higher degree of crystallinity (ca. 29.5 %) of the blocky SSM copolyamide, resulting in a higher weight percentage of the T_g-enhancing Mx residues in the amorphous phase of the SSM sample in comparison with the MP sample (of which the degree of crystallinity is ca. 25 %).

4.3.4 Melt processing stability of the blocky SSM copolyamides

The thermodynamic stability and the entropy of the blocky copolyamides synthesized via SSM remains a challenge to control during processing. The crucial question is whether the blocky copolyamide, with all its advantages compared to its random MP counterpart, will retain its blocky structure upon melt processing. PA-6,6, being a semi-crystalline polymer, is mostly processed under shear at 260 – 280 °C with a few minutes of residence time in the melt. In order to mimic these processing conditions, unfortunately *without* the possibility of applying shear, samples of approximately 5-6 mg of the copolyamide prepared via SSM, placed in a hermetic DSC pan and heated at 10 °C/min, were kept at 290 °C for 15 minutes. Then, the melt was cooled to 0 °C at a rate of 10 °C/min, followed by a heating and cooling cycle as shown in Figure 4.10. Note that 290 °C is approximately 30 °C above the melting temperature of PA-6,6. To investigate the thermal stability and the retention of the blockyness (i.e. the PA-6,6 block in the crystalline phase and the semi-aromatic, Mx-containing copolyamide block in the amorphous phase) in the melt, two SSM copolyamides with different compositions were tested and analyzed. The thermal stability studies performed by recording DSC traces are given in Figures 4.10a and 4.10b. The conventional heating and cooling DSC traces are compared with the isothermal melt measurements.

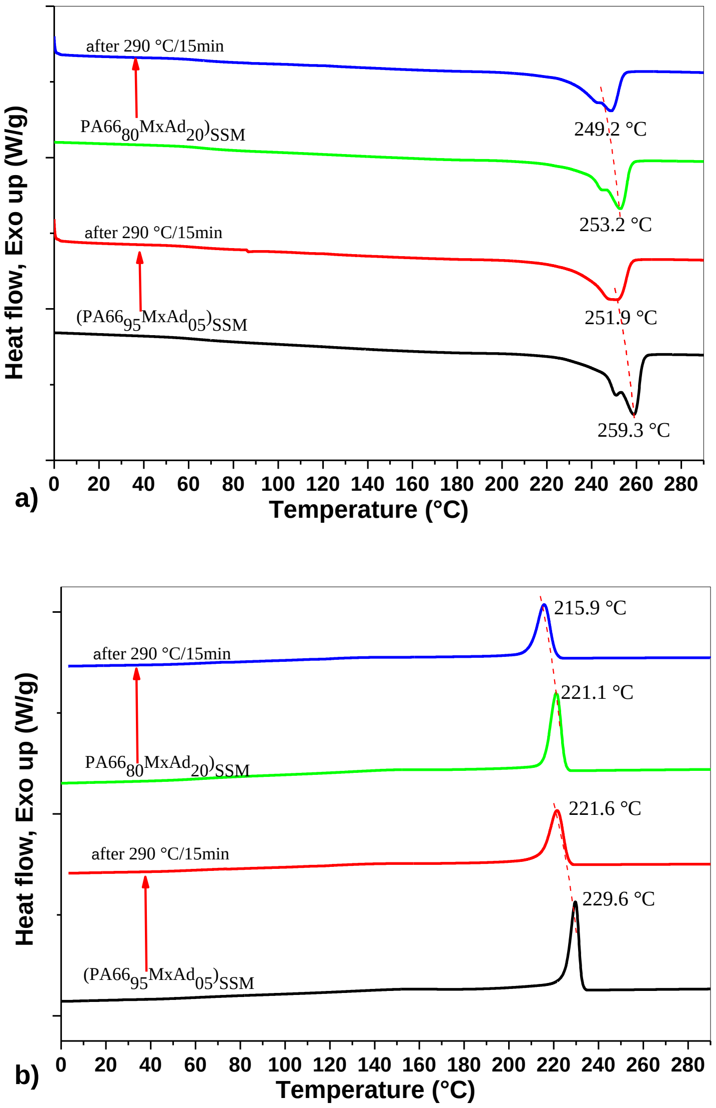


Figure 4.10 Thermal stability of the $(PA66_{95}MxAd_{5})_{SSM,feed}$ and $(PA66_{80}MxAd_{20})_{SSM,feed}$ at 230 °C/24 h subjected to isothermal at 290 °C for 15 min: a) heating and b) cooling runs.

The melting temperatures of the $(PA66_{95}MxAd_{05})_{SSM,feed}$ and $(PA66_{80}MxAd_{20})_{SSM,feed}$ samples did decrease a few degrees after a residence time of 15 min in the melt at 290 °C (see Figure 4.10a), but remained within the same range. If these blocky semi-aromatic copolyamides were not thermodynamically stable, then they might have undergone complete reorganization, redistributing the aromatic content, resulting in more random (or less blocky) copolymers, which would have resulted in significantly lower melting temperatures, most probably very close to the melting temperatures of the completely random copolyamides obtained via MP (being e.g. 245 °C for $(PA66_{80}MxAd_{20})_{MP,feed}$, see Figure 4.9a). The fact that the melting temperatures of both SSM samples remain much higher than the corresponding melting temperatures of the MP samples with comparable overall chemical composition implies that the thermal treatment for 15 min at 290 °C, only results in a partial randomization of the semi-aromatic blocky copolyamide. This is also supported by the largely retained crystallization temperatures of the $(PA66_{80}MxAd_{20})_{SSM,feed}$ and $(PA66_{95}MxAd_{05})_{SSM,feed}$ copolyamides obtained via SSM, as seen in Figure 4.10b, which remain significantly higher than the crystallization temperatures of the corresponding MP samples (being e.g. 197 °C for $(PA66_{80}MxAd_{20})_{MP,feed}$, see Figure 4.9b). So, the blocky microstructures obtained after the SSM treatment seem to be quite robust.

4.4 Conclusions

As described in **Chapter 3** the incorporation of the m-xylylenediamine:adipic acid (MxAd) comonomer salt into PA-6,6 via solid-state modification (SSM) and via melt polymerization (MP) yields copolyamides with block-like and random microstructures, respectively. The current chapter describes the influence of these differences in chemical microstructure on the thermal properties and the crystallization behavior of the SSM and MP copolyamides.

For similar amounts of incorporated amounts of MxAd salt the block-like structure of the SSM copolyamides results in higher melting and higher crystallization temperatures in comparison with the MP counterparts. The relatively long homo-PA-6,6 blocks result in thicker crystalline lamellae with respect to the shorter homo-PA-6,6 sequences present in the random MP copolyamides. The longer PA-6,6 sequences of the SSM copolyamides also facilitate the crystallization from the melt, thereby not only enhancing the crystallization temperature but also the degree of crystallinity. Increasing the mol% of MxAd in the copolyamides decreases the melting temperatures, but for similar amounts of incorporated MxAd salt this effect is less pronounced in the case of the SSM copolyamides. The relatively high crystallization temperature of the SSM copolyamides results in a significantly lower super cooling, required to crystallize the copolyamides from the melt in comparison with MP copolyamides with similar chemical composition. Accordingly, the SSM copolyamides are more suitable for injection-molding applications. The higher degree of PA-6,6 crystallinity of the SSM samples with respect to the MP samples, again comparing similar MxAd contents, results in a higher glass transition temperature of the SSM copolyamide because of its relatively higher content of the rigid MXDA monomer residues in the amorphous phase. Finally, it turned out that the block-like microstructure of the SSM copolyamides, with all its advantages with respect to thermal transitions and crystallizability, is quite robust with respect to melt processing: even after a residence time in the melt for 15 min at 290 ˚C the crystallization and melting temperatures remain significantly higher than those of the corresponding random MP counterparts, suggesting that full randomization of the structure does not occur.

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Chapter 5

Structure-properties relations of MXD6-modified copolyamides based on PA-6,6: SSM vs. melt-blending

Abstract

The solid-state modified (SSM) copolyamides, synthesized using isomeric para- and meta-xylylene diamine comonomer salts (PXDA and MXDA resp.), were studied as a function of comonomer content using room temperature WAXD and their crystal structures were analyzed. The presence of the aromatic (MXDA) moiety in the amorphous phase of the copolyamide was confirmed by performing temperature-variable solid-state ^{13}*C NMR spectroscopy. To assess the advantage of the SSM process, an alternative melt-mixing process was performed by melt-mixing PA-6,6 and polyamide-MXD,6 (MXD6) homopolymers in a lab-scale co-rotating twin-screw mini- extruder. The thermal properties and its chemical microstructure of the transreacted product was analyzed and compared with other copolyamides prepared via SSM and melt-polymerization (MP). Dynamic mechanical thermal analysis (DMTA) of the copolyamides prepared via SSM, MP and the melt-mixing process was performed. An isothermal crystallization evaluation was performed on the SSM copolyamides using fast-scanning calorimetry (FSC). Finally, the moisture absorption of the copolyamides obtained via SSM, MP and via the melt-mixing process was evaluated and compared with the starting PA-6,6 homopolymer.*

5.1 Introduction

Solid-state Polymerization (SSP) is a well-known method to increase the molecular weight of polycondensates.[1-3] On the other hand, solid-state modification (SSM) is a very promising route to prepare step-growth copolymers, largely retaining the crystal structure of the starting homopolymer material, as it selectively modifies the amorphous phase, leaving the crystalline phase intact.[4-5] The SSP review on polyamides and polyesters by Papaspyrides and co-workers described the various reaction kinetics and solid-state postcondensation (SSPc) reaction mechanisms.[6-8] The various factors affecting the efficiency of transamidation or interchange reactions involved in the SSP reactions have been investigated by several research groups.[7-9]

In our research, the comonomer incorporation via the SSP reaction has been adapted which is only limited to the amorphous phase of the polymer, whereas the crystalline phase is left unmodified. In previous chapters, it was shown that the solid-state modification (SSM) can be used to incorporate a comonomer salt into the semi- crystalline polyamide-6,6 (PA-6,6). The main advantage of copolymerization in the solid state compared to the melt copolymerization route is that the comonomer incorporation occurs only in the amorphous phase, whereas the polymer chain segments in the lamellar crystals are not mobile enough to participate in the transamidation reactions and thus the crystalline phase remains unchanged. Therefore, the polymer properties may be enhanced by selective modification of the amorphous phase, while the crystallization behavior is more or less preserved due to the presence of large homopolymer blocks. Thus, the SSM copolyamides resulted in a T_g enhancement and an approximate retention of the melting (T_m) and crystallization (T_c) temperatures as discussed in **Chapter 4**.

We reported on the interchange reactions occurring between PA-6,6 and *para*-xylylenediamine:adipicacid (PxAd) and *meta*-xylylenediamine:adipicacid (MxAd) comonomer salts. The chemical incorporation of the aromatic *meta*- xylylenediamine (MXDA) comonomer into the high molecular weight PA-6,6 by SSM was confirmed by SEC, using both RI and UV detection, as was already discussed in detail (**Chapter 2)**. Size Exclusion Chromatography (SEC) analysis on the samples collected at various reaction times showed the disappearance of the MXDA peak and the incorporation of a UV-active moiety in the high molecular weight, fully aliphatic polyamide, which in itself is not or only moderately UV active.

In **Chapter 3**, the influence of the molar percentage of the incorporated aromatic comonomer salt (MxAd) on the rate of the chemical modification reaction was investigated using SEC, again by taking and analyzing samples at different reaction time intervals. The typical decreasing molecular weight trend evidenced the chain scission generated by transamidation reactions between the salt and PA-6,6 during the first part of the SSM, whereas after 4 h of the solid-state reaction the post-condensation reaction leading to a significant increase in the number- average molecular weight (M_n) was the dominating reaction. The molecular weight enhancing effect of the reaction was attributed to the solid-state post condensation (SSPc) of the free carboxylic acid and amine end- groups generated during the first part of the SSM treatment, the transamidation reaction, and after 12 h of solid - state reaction the starting molecular weight was almost recovered. Also the microstructures of the SSM $(PA66_xMxAd_y)_{SSM}$ and melt-polymerized (MP) $(PA66_xMxAd_y)_{MP}$ copolyamides were studied using ^{13}C NMR spectroscopy. It was found that the SSM polyamides were blocky in nature, exhibiting degrees of randomness R far below unity ($R_{total,SSM}$ ca. 0.4), whereas the MP copolyamides with similar overall chemical compositions were random in nature ($R_{total,MP}$ ca. 1).

The effect of the molar concentration of the aromatic diamine salt on the melting and crystallization temperatures of the resulting copolyamides prepared via SSM and MP was discussed in **Chapter 4**. Different feed mol/mol ratios PA-6,6/MxAd comonomer salt or 'Nylon-6,6 salt'/MxAd salt were used to obtain copolyamides via SSM and MP, respectively, having different compositions. As the SSM transamidation occurs only in the amorphous phase, an important question concerns the solubility of the comonomer salt in the amorphous phase of the PA-6,6. The maximum solubility of the comonomer salt in the PA-6,6 amorphous phase was checked by analyzing the melting temperatures and enthalpies of the unreacted mixtures at different molar feed ratios. The correlation between the chemical microstructure, analyzed using solution ^{13}C NMR spectroscopy, and the thermal properties was established.

In the current chapter, a more detailed analysis is performed to understand the effect of the comonomer composition on the crystalline structure of the blocky or more random copolyamides prepared via SSM, MP or melt-mixing. Wide-angle X-ray diffraction (WAXD), temperature-variable solid-state ^{13}C NMR and dynamic mechanical thermal analysis (DMTA) were used to understand the conformational and structural behavior of the prepared copolyamides. In order to assess the possible advantage of SSM over other methods to make copolyamides, melt-mixing of two homopolymers namely PA-6,6 and MXD6 was performed in a mini-extruder.

The thermal analysis performed using conventional DSC not only has a limitation with respect to the rate of cooling and heating (max. ca. 100 K/min) but also exhibits a slow response and a lower sensitivity with a high signal-to- noise ratio at higher cooling or heating rates. Flash DSC (FDSC) is a recently developed method equipped with an ultra-high cooling rate device, to allow the materials with defined structural properties to be prepared, and with a high heating rate device enabling heating rates up to 1000 K/s. The latter option reduces the measurement times with a faster response sensor over a wide temperature range from -95 to 450 °C. In this chapter, the technique was employed to explore the influence of the chemical microstructure on the cooling rate dependence of the crystallization rate and the crystal structure. The cold-ordering of the SSM copolyamide is studied by quenching the melt and holding it at different dwelling time in the glassy state, followed the cold-ordering above T_g. This is followed by a study on the relation between the chemical microstructure and the moisture absorption of the copolyamides prepared via SSM, MP and melt-mixing in comparison with unmodified

PA-6,6. The chapter concludes with a discussion over the thermal properties of the copolyamides obtained via SSM, MP and melt- mixing.

5.2 Experimental Section

5.2.1 Materials

Poly(amide-6,6) (PA-6,6, Ultramid® A-27) pellets (M_n = 38 kg/mol, M_w = 72 kg/mol) were supplied by BASF SE, Ludwigshafen, Germany. Poly(m-xylyleneadipamide) (MXD6) grade S6001 (M_n = 32 kg/mol, M_w = 65 kg/mol), was obtained from Mitsubishi Gas Chemical Co. Inc., Japan. Adipic acid (AA) and meta-xylylenediamine (MXDA) were purchased from Sigma Aldrich. Ethanol (99%) required for the preparation of the diamine/diacid salt was purchased from Aldrich. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, 99%), obtained from Biosolve (Valkenswaard, the Netherlands), was used for solution mixing of PA-6,6 with the diamine/adipic acid salt. For NMR measurements deuterated trifluoroacetic acid (TFA-d, 99.5% deuterated) was obtained from Cambridge Isotope Laboratories, Inc., USA. All chemicals and solvents were used as received.

5.2.2 Solid-sate modification (SSM)

The experimental setup for SSM consisted of a glass reactor, equipped with a fluidizing purge gas tube. A salt mixture of KNO_3 (53 wt%), $NaNO_2$ (40 wt%), and $NaNO_3$ (7 wt%) was used as the heating medium for the reactor. The reactor consisted of a glass tube (inner diameter ~ 2.4 cm) and a sintered glass-filter plate at the bottom. A small heat exchange glass coil (inner diameter ~ 5 mm) surrounded the reactor. An argon gas flow was heated by passing through this heated coil before entering the inner glass tube at the bottom just below the glass filter plate. The gas flow was controlled by a flow meter. The SSM reaction temperature was measured with a thermocouple inserted into the PA-6,6/Nylon salt mixture.

5.2.3 Melt polymerization (MP)

The melt copolymerization was carried out after dissolving in total 200 g of different salt mixtures of $(HMDA:AA)_x$ and $(MxAd)_y$ in 200 g of water (x,y denotes the mol% of the salt as per feed compositions) placed into a 1.2 L pressure reactor. The reactor was heated to 210 °C at 15 bar for 15 min, and the temperature was raised in steps of 20 °C. Then, the temperature inside the reactor was raised to 220 °C and kept isothermal at that temperature for ca. 55 min under 15 bar pressure while removing water. Subsequently, the temperature and pressure were reduced to ca. 267 °C and 1 bar for 30 min, and the melt polycondensation reaction was carried out at 271 °C for 10 min after which the copolyamide $(PA66_xMxAd_y)_{MP,Feed}$ was granulated in an underwater granulation system. The molecular weight ($M_{n,\mathrm{SEC}}$) of these MP copolyamides is in the range of 25-35 kg/mol.

5.2.4 Melt-mixing of PA-6,6 and MXD6 homopolymers

The transamidation reaction in the solid state and melt was performed to synthesize semi-aromatic polyamides as described earlier in **Chapters 2-4**. To check the advantage of SSM, resulting in copolyamides with a more blocky microstructure compared to the structures obtained by the other methods described in **Chapter 1**, it was decided to investigate also melt-blending with the possibility of forcing the transamidation reactions in the melt state. Cryo-ground powders of the two homopolyamides, i.e. PA-6,6 and MXD6, with a molar ratio of 80/20 were thoroughly mixed by shaking them in a tumbler and this powder mix was fed into a co-rotating twin-screw (Prism TSE 16PC) extruder with a screw diameter of 16 mm. The extruder has two zones, as shown in Figure 5.1, with two electrical heaters and the temperature of the feed and the other zones are controlled by circulating cooling water. The screw is built up of different elements and starts with transport elements in the first zone and in the second zone it has mostly kneading elements to generate high shear rates. At the end of the second zone, there is a short section with transport elements, also with the aim to build-up pressure before the molten polymer is discharged via the die. The residence time of this 16 L/D extruder at 150 rpm was around 2.5 min. No degradation of polyamide due to high shear rate and/or temperature was observed, which was checked by extruding neat PA-6,6 using the same processing parameters. The color didn't change, while the molecular weight ($M_{n,SEC}$) remained constant at ca. 31 kg/mol, similar to the neat starting PA-6,6 (See section 5.3.4).

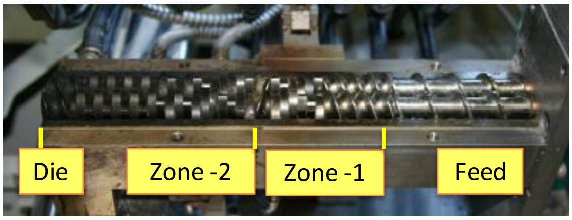


Figure 5.1 Screw configuration of the Prism mini-extruder.

5.2.5 Characterization

5.2.5.1 Wide-Angle X-ray Diffraction (WAXD)

Wide-angle X-ray diffraction (WAXD) patterns were obtained on a Rigaku Geigerflex instrument with the 2θ range from 10° to 40° with a step size of 0.05 and an exposure time of 5 seconds, equipped with a copper target (λ=0.154 nm). Films with similar dimensions and a uniform thickness (ca. 0.2 mm) were prepared by compression molding at 270 °C for 15 min and followed by cooling to room temperature in ca. 15 min. This film was positioned in an aluminum frame. Some of the data were smoothened with an adjacent-averaging method using the Origin 8.5 software.

5.2.5.2 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) was performed on films (with dimensions of about 15 mm × 5.3 mm × 0.5 mm) with a TA Instruments Q800 analyzer in tension film mode, at a maximum strain of 0.1% and a frequency of 1 Hz. The films were prepared by compression molding at 270 °C for 15 min. The sample bars for DMTA were cut to a rectangular shape. The sample was heated from −40 to 290 °C at a heating rate of 3 °C/min. The glass transition temperature was determined as the temperature at the maximum value of the loss modulus (E”) during the transition.

5.2.5.3 Solid-state ^{13}C NMR

Variable-temperature (VT) $^{13}C\{^1H\}$ cross-polarization/magic-angle spinning (CP/MAS) NMR experiments were carried out on a Bruker ASX-500 spectrometer employing a double-resonance probe for rotors with a 4.0 mm outside diameter. These experiments used 10,000 Hz MAS and a 4 μs $\pi/2$ pulse for ^1H. All VT $^{13}C\{^1H\}$ CP/MAS NMR spectra were recorded using a CP contact time of 3.0 ms and two pulse phase modulated (TPPM) decoupling[10] during acquisition. The temperature was controlled using a Bruker temperature control unit in the range from 30 to 180 °C. The VT $^{13}C\{^1H\}$ CP/MAS NMR spectra were recorded under isothermal conditions at intervals of 10 °C, employing a heating rate of 2 °C/min between the temperature-intervals. The reported temperatures were corrected for friction-induced heating due to spinning using ^{207}Pb MAS NMR of $Pb(NO_3)_2$ as the temperature calibrant.[11] Chemical shifts for ^{13}C MAS NMR is reported relative to solid adamantine as external reference.[12] The copolyamide obtained from SSM-reactor as such was packed into the sample rotor and employed for the analysis.

5.2.5.4 Differential Scanning Calorimetry (DSC)

The enthalpies of melting and crystallization and the degrees of crystallinity were measured by a TA Instruments Q100 Differential Scanning Calorimeter (DSC) equipped with an auto sampler and a refrigerated cooling system (RCS). The DSC cell was purged with a nitrogen flow of 50 mL/min. The temperature was calibrated using the onset of melting for indium. The enthalpy was calibrated with the heat of fusion of indium. For the $(PA66_xMxAd_y)_{SSM}$ and $(PA66xMxAdy)_{MP}$ copolymers, samples having a weight of 4–6 mg were prepared in crimped hermetic pans. All samples were measured in the temperature range from -40 to

290 °C using heating and cooling rates of 10 °C/min (unless specified differently), and applying isothermal periods of 5 min at respectively 0 and 290 °C. The degrees of crystallinity (X_c) of PA-6,6 and its copolyamides were calculated from the heat of fusion (ΔH_m) of the second heating run using the following relation:

$$X_c = \{\Delta H_m/\Delta H_{0m})\} \text{ x } 100\%$$

Where ΔH_{0m} is the heat of fusion for 100% crystalline PA-6,6, which was taken as 188 J/g.[13]

5.2.5.5 Fast Scanning Chip Calorimetry (FSC)

In order to study structure formation of crystallizable polymers at high super heating/cooling rates and to overcome the limitations of standard DSC, a special version of a fast scanning chip calorimeter (FSC) as shown in Figure 5.2 (left side) was used.[14-15] FSC has been applied for analysis of the crystallization behavior at rates of cooling between 1 and 10^3 K s^{-1}. The Mettler-Toledo FDSC 1 is a twin-type chip calorimeter, operating in the power-compensation mode and equipped with a refrigerated cooling system (RCS). The chip (code XI-400) is supported by a ceramic base plate for easy handling. It contains two separated silicon nitride/oxide membranes surrounded by a silicon frame, serving as a heat sink. The sensor chip has sample (S) and reference (R) circuits, as shown in Figure 5.2b. Furthermore, the measuring cell has been purged with gaseous nitrogen at a flow of 20 mL/min, to warrant reproducible heat-loss conditions and to avoid both thermal-oxidative degradation of the sample and icing on cold instrument parts.

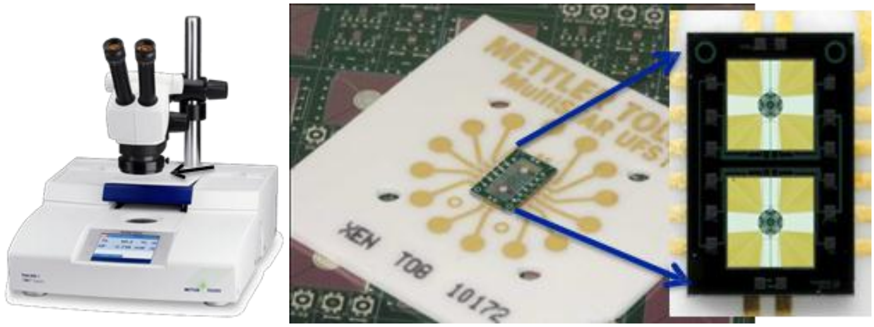


Figure 5.2 Mettler-Toledo FDSC 1 sample mounting unit on the left. Right: the sensor chip (1) and the enlarged chip (2) with the sample part at the top and the reference at the bottom.

Before the sample was placed on the sensor, the sensor was subjected to a 'conditioning' procedure which includes multiple heating and cooling cycles. Then, a temperature-conditioning of the sensor, considering the specific thermal environment, such as gas flow or heat-sink temperature, was performed. Subsequently, approximately few microns size of sample was picked from the cryo-ground copolyamides and placed on the sample sensor. To achieve optimum thermal contact of the sample with the sensor, a heating run was performed up to 280 °C at 100 K/s. Then, the analysis method was created based on the required heating, cooling rate and the isothermal steps for the measurement and the method-program was uploaded to perform the experiments. The evaluation of the analysis was done using STAR^e SW 10.0 software.

5.3 Results and Discussion

In **Chapter 3**, the effect of the concentration of the semi-aromatic comonomer (MxAd) salt on the SSM reaction rate and the effect of the chemical microstructure were investigated using ^{13}C NMR sequence analysis. Thermal analysis of the SSM copolyamides versus MP copolyamides of similar overall chemical compositions was performed and it was found that the SSM copolyamides have higher melting and crystallization temperatures than the copolyamides synthesized via the MP route. The correlation between the chemical microstructures and thermal properties (viz., T_m, T_c) was established in **Chapter 4**. In this chapter, WAXD analysis was used to confirm the influence of the local ordering on the chain packing of xylylenediamine-based copolyamides. To evaluate the transamidation chemistry during melt-mixing, an alternative approach to make a copolyamide, namely from a mixture of the two homopolymers, i.e. PA-6,6 and MXD6, was performed in a lab-scale extruder and the product was investigated for the resulting chemical microstructure and the corresponding thermal properties. This melt- mixed product was included in the further property analysis along with the copolyamides prepared via the SSM or the MP route. To elucidate the conformational changes of the SSM copolyamides and to support the hypothesis of the SSM process that the comonomer modification occurs selectively in the amorphous phase of PA-6,6, temperature-variable $^{13}C\{^1H\}$ CP/MAS NMR was employed. The dynamic-mechanical behavior of the copolyamide products as a function of temperature was studied using DMTA.

5.3.1 WAXD analysis: (PA66$_{80}$MxAd$_{20}$)SSM versus (PA66$_{80}$PxAd$_{20}$)SSM

The crystal modifications can be performed in different ways, such as changing the crystal temperature by subjecting the sample to different temperatures or introducing a comonomer entity and in turn cause a disorder in the lattice is known with PAs. The unit cell of PA-6,6 is a triclinic cell with the dimension of a = 0.49 nm, b = 0.54 nm and c= 1.72 nm. The transformation of the triclinic structure with different interchain/intersheet distances into the pseudo-hexagonal form can be associated to the formation of hydrogen bonds between chains lying in adjacent sheets of the polyamides Generally, for the commercially available PAs the formation of a pseudohexagonal phase is observed upon a solid-state crystal-to-crystal transition upon heating, the so-called Brill transition.[16] The transformation of the triclinic structure with different interchain/intersheet distances into the pseudo-hexagonal form can be associated to the formation of hydrogen bonds between chains lying in adjacent sheets of the polyamides.[17,18] However, more recently, it was proposed that no intersheet H-bonding occurs at the Brill transition temperature and that the intersheet and interchain distances become equal by a kind of cylindrical rotation of the methylene units between the H-bonded amide groups.

The WAXD pattern of semi-crystalline polymers generally consists of distinctive, sharp diffraction peaks from the triclinic unit cell of the crystalline phase, superimposed on a broad halo originating from the non-crystalline phase. For most polyamides, two characteristic diffraction peaks, at d-spacings around 0.44 and 0.37 nm depending on the type of the PA, can be distinguished. The former diffraction peak (indexed 100) of triclinic unit cell yields information about the interchain distance within the hydrogen-bonded β-sheet, whereas the latter (a superposition of the 010 and 110 reflections of the triclinic unit cell) can provide insight into the distance between the β-sheets, which are held together by van der Waals forces. As a result and given Bragg's law, it is possible to interpret the WAXD data obtained for the SSM copolyamides obtained for isomeric xylylenediamine salts, i.e. para (PxAd), meta (MxAd), incorporated into PA-6,6, in terms of interchain and intersheet distances, crystallinity, possible co-crystallization and the built-up of the hydrogen-bonded sheets.

In order to investigate if and how the Px/MxAd-based copolyamide units are built into the crystal structure of PA-6,6 and which conformational modifications this entails, WAXD measurements were performed on materials with a comparable thermal history. Concerning the WAXD studies, the 001 and 002 reflections found to be influenced by the possible co-crystallization of the different repeat units present within the SSM copolyamides. Differences in the peak positions in the reflections can arise directly due to differences in the chemical microstructure with respect to the starting PA-6,6, which determines whether these units would fit in one and the same crystal lattice. The length of the repeat units is particularly important for the c-axis of the unit cell, so the 001 and 002 reflections, but it also influences the chain packing in the 100 and 010/110 direction. These are much more sensitive to changes with respect to pure PA-6,6 if the comonomer would co-crystallize with the 6,6 repeat units. The diffraction pattern obtained for PA-6,6 (see Figure 5.3) clearly displays the two typical reflections at diffraction angles of $2\theta = 20.4°$ and 23.9°. As mentioned above, the first peak (100) represents the interchain distance of the PAs controlled by hydrogen bonding between the polymer chains in one and the same β-sheet and the second peak (010/110) represents the intersheet distances. These indices of the SSM copolyamides are similar to those of PA-6,6. However, the SSM copolyamides consist of several different chemical repeat units due to the nature of the aromatic diamine-based comonomer units, as depicted in Figure 5.4.

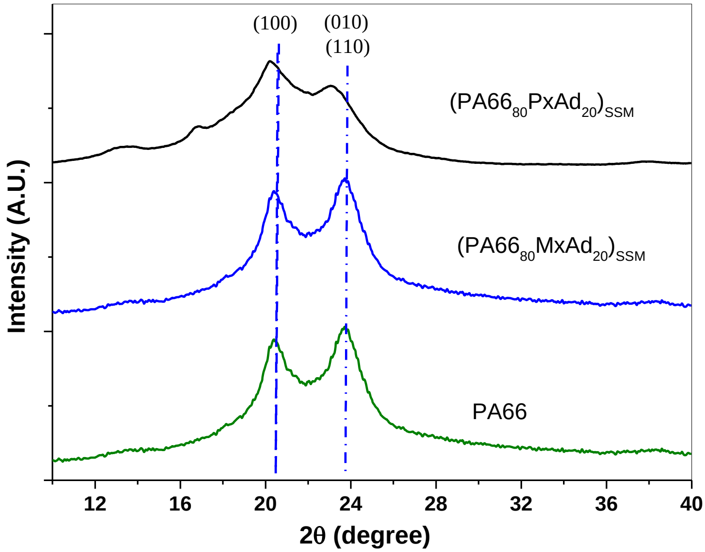


Figure 5.3 Room temperature WAXD diffractograms of an unmodified PA-6,6 and SSM copolyamides obtained after compression molding $(PA66_{80}MxAd_{20})_{Feed}$ and $(PA66_{80}PxAd_{20})_{Feed}$ (They are aligned vertically for clarity).

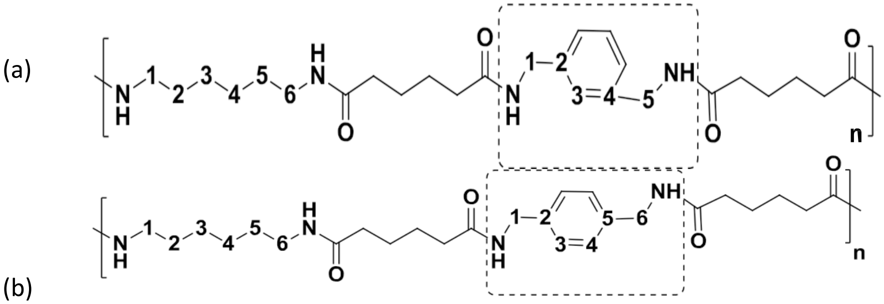


Figure 5.4 Repeating units of the SSM copolyamides of a) $(PA66_{80}MxAd_{20})_{Feed}$ and b) $(PA66_{80}PxAd_{20})_{Feed}$.

Comparing the WAXD diffraction pattern of $(PA66_{80}MxAd_{20})_{SSM}$ and PA-6,6 (Figure 5.3), all obtained after crystallization from the melt, it is evident that the intensity of the 100, 010 reflections of the copolyamide did not change with respect to the starting PA-6,6 pattern, indicating the same interchain and intersheet distances for both polymers. In addition, the extent of ordering is usually reflected by the peak intensities. A careful examination of the peak intensities of the $(PA66_{80}MxAd_{20})_{SSM}$ copolyamide and PA-6,6 revealed that the SSM copolyamide, i.e. $(PA66_{80}MxAd_{20})_{SSM}$, has a very similar crystallinity as PA-6,6. This is in accordance with our earlier conclusion drawn in **Chapters 3** and **4**, namely that during SSM the aromatic MXDA moieties are mostly incorporated into the amorphous phase and do not co-crystallize with homo PA-6,6 chain segments. This was supported by the trend in the melting and crystallization temperatures.

On the other hand, the copolyamide modified with para-xylylenediamine:adipic acid salt (PxAd), having a similar chemical composition as the $(PA66_{80}MxAd_{20})_{SSM}$ copolyamide discussed above, revealed a WAXD pattern that is different from that of PA-6,6 with clearly shifted reflections. Moreover, there is a new diffraction peak observed at approx. 16° (corresponding to 002), pointing to co-crystallization of the repeat units based on the aromatic diamine (PXDA) (as depicted in Figure 5.4) with PA-6,6 repeat units. Remember that like the 1,6- hexamethylenediamine residues the PxAd residues also have six methylene units between the amides groups. The similar distance between the amide groups obviously allows the co-crystallization of the comonomers from the melt into one and the same crystal lattice. Upon the incorporation of the PxAd units into PA-6,6 the intersheet distance increased, as confirmed from the decreased $2\theta_2$ value from ca. 26.8 to ca. 23.2°, due to the presence of the bulkier aromatic moiety (PXDA) in the chain segments. This indicates that the aromatic rings are oriented perpendicular to the β-sheets, thereby pushing them further apart. Also the interchain distance seems to increase a little, but this change is only marginal. It is also interesting to note the different intensities of the crystalline 100 and 010/110 reflections for PA-6,6 and the PxAd based copolyamide, the latter being lower, which points to a lower crystallinity of the ($PA66_{80}PxAd_{20})_{SSM}$ copolyamide with respect to PA-6,6.

5.3.2 Effect of comonomer compositions on WAXD: SSM copolyamides

The change of the chemical microstructure of the SSM and MP copolyamides as a function of aromatic comonomer salt was studied in detail in **Chapter 3**, and the effect on the thermal properties of both series of copolyamides was investigated in **Chapter 4**. In order to complete the structure-analysis of the SSM copolyamides a WAXD study was carried out on samples with two different compositions and the results are presented in Figure 5.5. As described earlier, the WAXD pattern of the melt-crystallized MxAd-modified copolyamides containing 20 mol% MxAd salt in the feed is very similar to the starting PA-6,6 and the same is observed for a different (lower) comonomer concentration (5 vs. 20 mol%). The intersheet (100) and interchain (010) intensity ratios are nearly similar for the 5 and 20 mol% comonomer salt (MxAd) containing SSM copolyamides, indicating that the crystallinities of the two copolyamides after compression molding are in a comparable range. The sharper and more intense peaks evidence a higher crystallinity of ($PA66_{95}MxAd_{5})_{SSM}$ compared to ($PA66_{80}MxAd_{20})_{SSM}$, most probably because lower amounts of comonomer hinder the crystallization of the PA-6,6 blocks to a lesser degree.

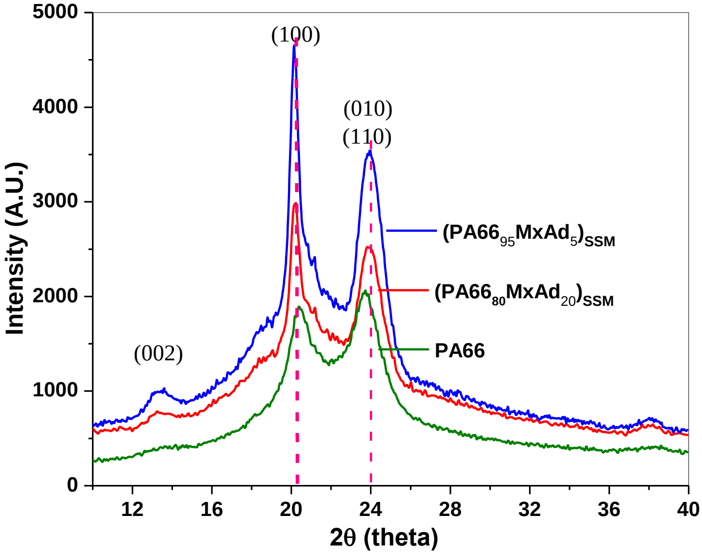


Figure 5.5 Room temperature WAXD diffractograms of unmodified PA-6,6 compared with the $(PA66_{80}MxAd_{20})_{Feed}$, $(PA66_{95}MxAd_5)_{Feed}$ SSM copolyamides. All (co)polyamides were crystallized from the melt.

5.3.3 Effect of comonomer compositions on WAXD: MP copolyamides

The WAXD patterns of the $(PA66_{80}MxAd_{20})_{MP}$ and $(PA66_{50}MxAd_{50})_{MP}$ copolyamides are presented in Figure 5.6. In comparison with $(PA66_{80}MxAd_{20})_{SSM}$ (Figure 5.5), the WAXD pattern of $(PA66_{80}MxAd_{20})_{MP}$ revealed that the intersheet intensity is much lower and the corresponding peak position is also different from that of PA-6,6 and the comparable SSM copolyamide. The $2\theta_1$, $2\theta_2$ values (ca. 21.1 and 23.2° respectively) of the $(PA66_{80}MxAd_{20})_{MP}$ reflections found to be almost identical to the MXD6 homopolymer reflections (ca. 20.8 and 23°). The $(PA66_{80}MxAd_{20})_{MP}$ diffraction pattern reveals that the synthesized copolymer exhibits a lower degree of crystallinity, as also found in **Chapter 4** (see Table 4.2). For this 50/50 melt-synthesized copolyamide also a lower melting temperature was observed (**Chapter 4**).

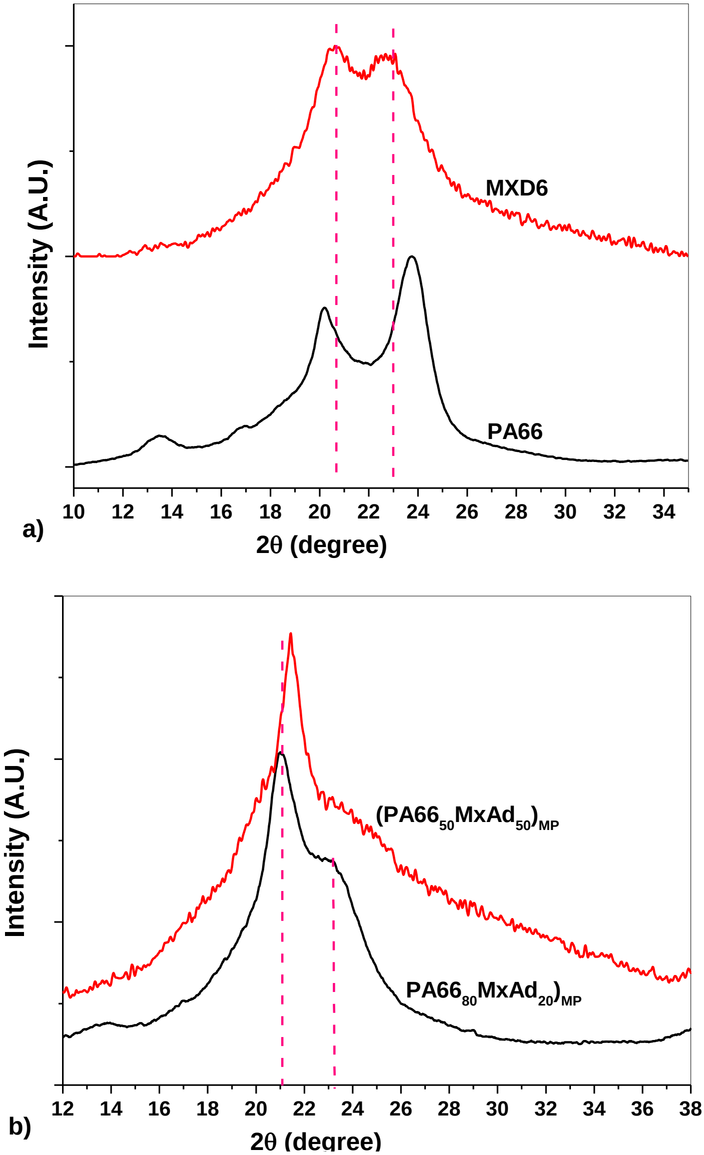


Figure 5.6 Room temperature WAXD diffractograms of: a) homopolymers (PA-6,6 and MXD6) and b) melt copolyamides $(PA66_{80}MxAd_{20})_{MP}$ and $(PA66_{50}MxAd_{50})_{MP}$. All (co)polyamides were crystallized from the melt.

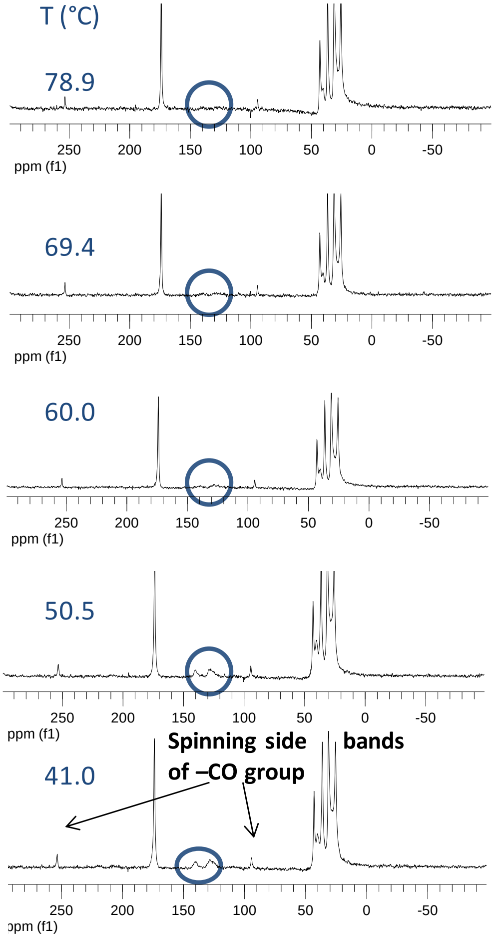
The MP copolyamide containing a higher MxAd comonomer content in the feed revealed a much lower degree of crystallinity of around 21% in comparison w ith the measured value for PA-6,6 of ca. 45 %, as determined by DSC analysis. Further evidence for the presence of the aromatic moiety in the amorphous part of PA-6,6 can be obtained by using temperature-dependent solid-state ^{13}C NMR across the glass transition (T_g) region, which may probe changes in the chain mobility above T_g.

5.3.4 Solid-state ^{13}C NMR Analysis of the SSM copolyamide

From the results presented in **Chapters 2-4** it was evident that by incorporation of the semi-aromatic salts into the PA-6,6 main chain the melting and crystallization temperatures of the SSM copolyamides were retained, while the increase of the glass transition temperature from ca. 55 to ca. 63-65 °C pointed towards the incorporation of the aromatic comonomer into the amorphous phase. The major advantage of the SSM process is that the comonomer moiety is incorporated into the amorphous phase of the starting polymer without disturbing the crystalline phase of the polymer during its chemical incorporation. To reveal this kind of information ^{13}C {^{1}H} CP/MAS NMR spectroscopy was employed, as it is a powerful technique for the analysis of the structural behavior of chain segments of the polyamides and their mobility upon heating. Moreover, the experiments were performed as a function of temperature to characterize the different chain conformations and their populations in the samples. Particular attention was given to investigate the presence of the aromatic moiety (MXDA) in the amorphous phase and the conformational change occurring while heating to a temperature above T_g. The copolyamide obtained from the SSM-reactor as such was employed for the NMR analysis.

In **Chapter 3**, the microstructure analysis was performed by solution ^{13}C NMR, which is regarded as being more or less equivalent to the molten state of the sample with all possible kinetic motions. The temperature-dependent ss- NMR can demonstrate whether the aromatic comonomer moieties are present in the amorphous or crystalline phase. If they are exclusively present in the amorphous phase the corresponding peak will become very diffuse or disappear beyond the glass transition temperature. If the aromatic signals will remain sharp and intense without any broadening if the glass transition is passed, this would imply that the aromatic moieties are predominantly or even only present in the crystalline region. If the signal partly broadens, this would indicate that the aromatic moieties are present in both the amorphous and crystalline regions.

In this section, the temperature dependence of the SSM copolyamide is studied using solid-state ^{13}C NMR across the T_g and the results are shown in Figure 5.7. The aromatic moiety (MXDA) of the SSM copolyamide at room temperature (41 °C) has strong signals around 128- 136 ppm in the ^{13}C NMR spectrum. The chain segments in the amorphous phase do not reveal any motions below T_g. When the sample is stepwise heated to higher temperatures above T_g (10 °C/step), the signals related to the aromatic chain fragments become broader. This phenomenon was observed with $(PA66_{80}MxAd_{20})_{SSM}$. The phenyl peaks around ca. 128-140 ppm (marked in the figure) broaden above 60 °C. On further heating, the transfer of the rotational motion to the hydrogen-bonded moieties becomes even more pronounced.[11]



Spinning side bands of –CO group

Figure 5.7 The variable temperature ss-NMR ^{13}C of the SSM copolyamide (PA66$_{80}$MxAd$_{20}$)$_{SSM}$, indicating the change in the intensity difference across T_g of the aromatic moiety visible in the 128-140 ppm region.

Thus, due to the higher kinetic, rotational moment of the chain segments in the amorphous region there was no signal recorded in ss-NMR at temperatures at 330 K and above this temperature. This confirms that the aromatic comonomer salt (MxAd) was fully incorporated into the amorphous phase of PA-6,6 by SSM or maybe the aromatic moiety in the crystalline phase is too low in concentration to be detected in NMR.

5.3.5 Transamidation via melt-mixing of Pa-6,6 and MXD6

In order to be able to judge the advantage of the SSM process over other routes to make block-like copolyamides, other routes leading to copolyamides exhibiting a blocky structure need to be explored as well. One such route is to perform the transreactions during melt mixing of homopolyamides. Melt-mixing of two homopolymers was performed for two different molar ratios, namely $(PA66_{80}MXD6_{20})_{Ext}$ and $(PA66_{50}MXD6_{50})_{Ext}$. Both these products were examined for transamidation reactions. The chemical microstructure and the thermal properties of these products were analyzed. Unlike in the case of the fully aliphatic PA-6,6 system being gradually modified into a semi-aromatic copolyamide, hence with a gradual development of UV absorption of the transamidation product at 275 nm, the SEC analysis with UV detector is not useful to follow the transamidation reaction for this method, since with one transreaction per macromolecule already a huge amount of UV-active material is introduced into the UV-inactive PA-6,6 and this amount will not change when the transamidation is further extended and the degree of randomness increases. The initial molecular weights of PA-6,6 and MXD6 (M_n ca. 32 kDa) are similar with very similar elution times (ca. 21-22 min). Thus, it is difficult to conclude from UV chromatograms that the UV absorption is mainly caused by fully aromatic MXD6 homopolymer or by the PA-6,6 based semi-aromatic copolyamide product developed via the melt-mixing transreaction. Moreover, the development of molecular weight in time is less spectacular in comparison with the initial PA-6,6/salt mixture. The starting $M_{n,SEC}$ of the starting PA-6,6 powder was material was 31.5 kDa (PDI = 2.06) and the melt-mixed product $(PA66_{80}MXD6_{20})_{Ext}$ and $(PA66_{50}MXD6_{50})_{Ext}$ was 29 kDa (PDI = 2.1) and 32.9 kDa (PDI = 1.9), respectively. The similar molecular weights ensure that the ultimate mechanical properties of all the materials, such as the tensile strength and impact toughness, are only dominated by the chemical microstructure and the concurrent built up of the crystalline morphology.

5.3.5.1 ^{13}C NMR dyad sequence analysis of copolyamides (PA66$_x$MXD6$_y$)Ext

It is evident from the ^{13}C NMR spectra of the melt-mixed PA-6,6/MXD6 samples presented in Figure 5.8 that the transamidation between the two homopolymers indeed occurred, yielding four carbonyl sequence dyads as illustrated in **Chapter 2**. From the melt-mixing studies on two homopolymers, i.e. PA-4,6 and PA6I, carried out by Eersels et al,[22] it was found that the copolymers obtained by reactive blending contain high sequence lengths of the aromatic copolymer. There are many factors, such as the extrusion temperature, residence time and blend composition, that affect the degree of transamidation and, consequently, the sequence length distribution. At optimized processing conditions, the block length decreases with increasing mixing time during the extrusion and this is due to more randomization of the transamidated product with higher residence time. In addition, by increasing the PA6I wt% in the blend composition, the degree of randomness increases linearly beyond 50 wt%.

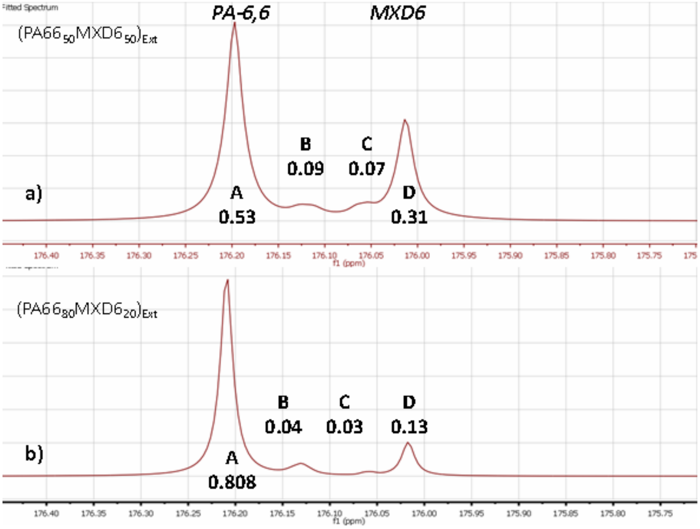


Figure 5.8 Deconvoluted ^{13}C NMR spectra of the melt-blended PA-6,6/MXD6 samples with the carbonyl dyad regions in the 176.5-176.0 ppm region with A-D sequences of a) (PA66$_{50}$MXD6$_{50}$)$_{Ext}$ and b) (PA66$_{80}$MXD6$_{20}$)$_{Ext}$.

In our case, melt mixing of PA-6,6/MXD6 at 80/20 and 50/50 mol/mol compositions was performed at 280 °C in an extruder with a residence time of ca. 2 min. Interestingly, the degree of randomness (R) determined on these products was around 0.25-0.34 (see Table 5.1). The degree of randomness increased with increasing MXD6 content from 20 to 50 mol%. It is apparent from the determined R-values that melt-mixing yielded more blocky copolyamides via melt transamidation than the earlier described SSM route (with R values around 0.4) and that the processing conditions might be favorable to achieve this block-like structure.

Table 5.1 Molar fractions of the four carbonyl dyads and the calculated degrees of randomness (R) for melt- blended polyamides calculated from the ^{13}C NMR spectra presented in Figure 5.8 using eqs. (2.2) to (2.5), presented in **Chapter 2**

Melt blended	$F_{\mathrm{HA\O,total}}$	$F_{\mathrm{HAH,total}}$	$\mathrm{F}_{\mathrm{\O A\O,total}}$	R_{total}
$(\mathrm{PA66}_{50}\mathrm{MXD6}_{50})_{\mathrm{Ext}}$	0.162	0.613	0.387	0.341
$(\mathrm{PA66}_{80}\mathrm{MXD6}_{20})_{\mathrm{Ext}}$	0.066	0.841	0.159	0.248

5.3.5.2 Thermal properties of the melt-mixed polyamides

The thermal properties, such as the glass transition temperature and melting and crystallization temperature, of the melt-mixed polyamides $(\mathrm{PA66}_{50}\mathrm{MXD6}_{50})_{\mathrm{Ext}}$ and $(\mathrm{PA66}_{80}\mathrm{MXD6}_{20})_{\mathrm{Ext}}$ are given in Table 5.2. It can be observed that the melting temperatures of the 80:20 and 50:50 mol% melt-blends (ca. 260 and 255.4 °C, resp.) are much higher than the T_m of the MP copolyamides having similar compositions (ca. 244.7 and 212.1 °C resp.). Due to its longer homopolyamide blocks the $(\mathrm{PA66}_{80}\mathrm{MXD6}_{20})_{\mathrm{Ext}}$ copolyamide even has a higher melting temperature than the T_m of the SSM sample $(\mathrm{PA66}_{80}\mathrm{MXD6}_{20})_{\mathrm{SSM}}$, which was ca. 252.6 °C. The excellent retention of the thermal properties in comparison with PA-6,6 (i.e. higher Tm and T_c) may be caused by the fact that the aromatic homopolymer blocks (MXD6) do not co-crystallize with the pure PA-6,6 blocks and that they are still present in a blocky manner, as proven by the very low R values for the reacted blend. It can be concluded that the presence of the aromatic units leads to some structure in the melt that gives very good nucleation and thus higher T_c and concomitantly a higher T_m. Moreover, this is also supported by the higher T_g values of ca. 65.5 and 71.6 °C (see Table 5.2). The thermal properties of the melt-mixed product are compared with SSM, MP copolyamides later in section 5.3.8.

Table 5.2 Thermal properties of melt-mixed polyamide samples analyzed by DSC

Composition feed		**Composition in copolyamide***		**2nd heating Run**			**1st Cooling Run[a]**	
PA66, feed (mol%)	***MXD6, feed (mol%)***	***PA66 (mol%)***	***MXD6 (mol%)***	**T_g (°C)**	**T_m (°C)**	**X_{cr} (%)**	**T_c (°C)**	**T_m- T_c (°C)^{a,b}**
100.0	0.0	0.0	0.0	55.0	263.3	45.1	221.8	41.5
80.0	20.0	78.7	21.3	65.5	260.0	37.5	232.2	27.8
50.0	50.0	53.1	46.9	71.6	255.4	20.7	217.3	37.1

*Compositions were obtained by ^{1}H-NMR spectroscopy

[a] T_g, T_c, and T_m were determined by means of DSC (TQ100) using a heating/cooling rate of 10 °C/min.

[b] The T_m and T_c values shown are the peak values of the melting endotherms and crystallization exotherms, respectively.

5.3.6 Comparison of the dynamic-mechanical properties

The temperature dependence of the storage and loss modulus of ($PA66_xMxAd_y$) copolyamides synthesized via the SSM and the MP route along with melt-blended samples were studied by using DMTA. The storage modulus (E’) as a function of temperature is given in Figure 5.9a. The E'-modulus of the melt blend below the glass transition temperature is higher than the corresponding value for the SSM and MP copolyamides. This might be due to the higher crystallinity as revealed by DSC for the melt-blended product. The modulus of the melt-mixed blend till 220 °C is higher than any of the other copolyamides, and it almost coincides with the neat PA-6,6. PA-6,6 and melt- blended polymers have nearly the same flow temperature (T_{fl}), being the temperature at which the storage modulus drops to a minimum value. The E'-modulus of the SSM copolyamide is slightly higher than that of the MP copolyamide with a similar composition. This is in agreement with the higher crystallinity of the SSM sample with respect to the MP sample. The differences in the modulus values and in the flow temperatures of the three different copolyamides with quite similar overall compositions can be fully explained by the reported differences in crystallinities (Ext > SSM > MP) and melting temperatures, both being directly related to the PA-6,6 block length (Ext > SSM > MP).

The T_g values were determined from the temperature at which the loss modulus (E") peak maximum occurs. The glass transition temperature of the copolyamides measured from DMTA is given in Table 5.3. The T_g temperatures measured by DMA are within ± 3 °C and in agreement with that of DSC analysis. The higher value (around 66 °C) for the melt-mixed and SSM copolyamides are due to the enrichment of the rigid aromatic moiety incorporated into the amorphous phase. The lower value of MP copolyamide is due to lower crystallinity and random incorporation results a diluting effect of the aromatic entity in the amorphous phase.

Table 5.3 The glass transitions and flow temperatures obtained from DMTA analysis

S. No.	Sample	T_g (°C)*	T_g (°C)-DSC	T_{fl} (°C)*
1.	PA-6,6 unmodified	53.1	55.0	263.0
2.	$(PA66_{80}MxAd_{20})_{SSM}$	66.3	65.1	260.5
3.	$(PA66_{80}MxAd_{20})_{MP}$	58.6	61.8	240.8
4.	$(PA66_{80}MxAd_{20})_{Ext}$	67.3	65.4	261.9

*Obtained from DMTA analysis.

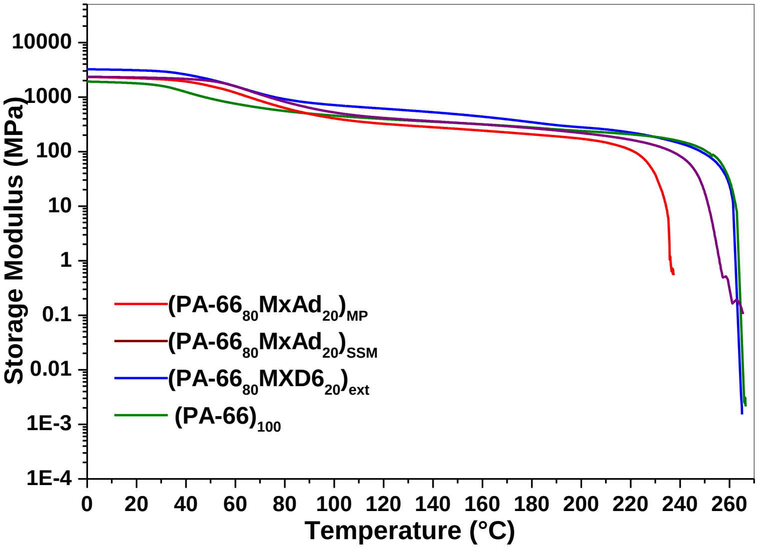


Figure 5.9 DMTA curves of neat PA-6,6 compared with the transamidated $(PA66_xMxAd_y)_{Feed}$ prepared via SSM, MP and melt mixing: Storage modulus (G') as a function of temperature.

5.3.7 Thermal properties of the transamidated copolyamides

The thermal properties of the copolyamides prepared via SSM, MP and melt-mixed method are given in Table 5.4. The melt-mixed product has a higher melting and crystallization temperature which is almost similar to neat PA-6,6. They are better than the copolyamides prepared via SSM and MP route. However, the SSM copolyamides have slightly lower thermal properties than melt-mixed product but higher than that of MP copolyamides. This is also true for the difference between the melting and crystallization temperature, i.e. Tm-T_c (See Table 5.4). This T_m-T_c parameter is especially important in view of the crystallization behavior of the copolyamides products, during injection-molding application. This T_m-T_c value is lower for melt-mixed product, which implies that it can crystallize from the melt faster than the SSM or MP copolyamides. The melt-mixed product has higher block lengths of the MXD6 sequences as studied by sequence analysis (lower R-values) compared to lower blockiness of the aromatic moiety in SSM copolyamides. The SSM copolyamides have comparatively higher values than melt-mixed product but lower than MP copolyamides. MP copolyamides due their most random distribution of the aromatic moiety and lower crystallinity have lower melting and crystallization temperatures. The glass transition temperatures ofthe copolyamides are higher than PA-6,6 due to the rigidity of the aromatic comonomer. They increase linearly with increasing comonomer content. Melt-mixed and SSM copolyamides have higher T_g than MP copolyamide, due to most random distribution the aromatic moiety in MP copolyamides it has lower T_g.

Table 5.4 Summary of the thermal data obtained by DSC on the copolyamides prepared via SSM, MP and melt mixing routes.

	Composition feed		**2nd Heating Run**[a]		**2nd heating Run**	**1st Cooling Run**[a]	
Copolymer process	***PA66*, feed (mol%)**	***MxAd*, feed (mol%)**	***T_g (°C)***	***T_m (°C)***	***% Crys-tallinity***	***T_c (°C)***	***T_m- T_c (°C)***[a,b]
PA-6,6	100.0	0.0	55.0	263.3	39.5	221.8	41.5
SSM	80.0	20.0	65.1	252.6	32.2	220.4	32.2
Melt-mix	80.0	20.0	65.5	260.0	37.5	227.8	32.2
(Ext.)	50.0	50.0	71.6	255.4	20.7	217.3	37.1
MP	80.0	20.0	61.8	244.7	28.0	198.3	46.4
	50.0	50.0	68.3	212.1	21.7	159.3	52.8

*Compositions were obtained by ^{1}H-NMR spectroscopy

[a] T_g, T_c, and T_m were determined by means of DSC (TQ100) using a heating/cooling rate of 10 °C/min.

[b] The T_m and T_c values shown are the peak values of the melting endotherms and crystallization exotherms, respectively.

5.3.8 FSC Analysis of the copolyamides

5.3.8.1 Crystallization kinetics

Conventional DSC has certain limitations in heating and cooling rate (100 K/min). Recently, instruments based on so-called chip calorimeters have been introduced, where the calorimeters are fabricated using semiconductor processes. These chip calorimeters offer heating and cooling rates as high as 10^6 K/s or more using very sample masses with measurement time constants on the order of 10^{-3} sec or less. As such, sample handling and preparation are much more difficult, and it is not possible to directly determine the sample mass, which complicates quantitative measurement of the specific enthalpy and the specific heat capacity.In this part, the effect of the chemical microstructure of the copolyamides prepared via SSM, melt-mix and MP, on the crystallization kinetics is studied at different heating rates and the behavior is compared with the starting material (PA-6,6). The sample was cooled rapidly from the melt at a cooling rate of 1000 K/s. Subsequently, the sample was heated at rates between 5 and 1000 K/s to melting and the crystallization kinetics was analyzed. The FSC curves of this experiment are given in Figure 5.10. The value on the right hand side each thermogram indicates the different heating rate that was employed.

From the non-isothermal cold-ordering of the copolyamides shown in Figure 5.10 reveal information about the glass transition temperature of the fully amorphous PA-6,6 and the copolyamides. The value determined on using a heating rate of 50 K/s was ca. 55 °C, while it is increased to ca. 65 °C on heating at 1000 K/s. A similar increase in T_g (ca. 65-75 °C) with increasing heating rate (50 to 1000 K/s) was observed for the copolyamides. This is due to the specific kinetics of the relaxation process and same trend was observed with the studies on PA-6.[19] From Figure 5.10 it is also evident that the cold-crystallization temperature (T_{cc}) increases with increasing heating rate from 25 to 1000 K/s as expected, as higher heating rate renders less time for a crystal to develop hence the system tend to co-crystallize at higher temperatures.. The non-isothermal crystallization kinetics of the melt-mixed sample ($(PA66_{80}MxAd_{20})_{Ext}$) is similar to unmodified PA-6,6, as can be seen from Figure 5.10d and 5.10a. Both have very comparable crystallization rates, implying that the MXD6 blocks don't co-crystallize and adversely affect the crystallization kinetics of the PA-6,6 blocks in the melt-mixed copolyamide. The copolyamide prepared via SSM has faster crystallization kinetics compared to the copolyamide prepared via MP, yet the crystallization temperature (ca. 226 °C at 1000 K/s) is slightly less than the melt-mixed copolyamide (ca. 236 °C at 1000 K/s). The order of crystallization kinetics and the crystallization temperature is as follows: PA-6,6 ~ $(PA66_{80}MxAd_{20})_{Ext}$ > > > $(PA66_{80}MxAd_{20})_{SSM}$ > $(PA66_{80}MxAd_{20})_{MP}$.

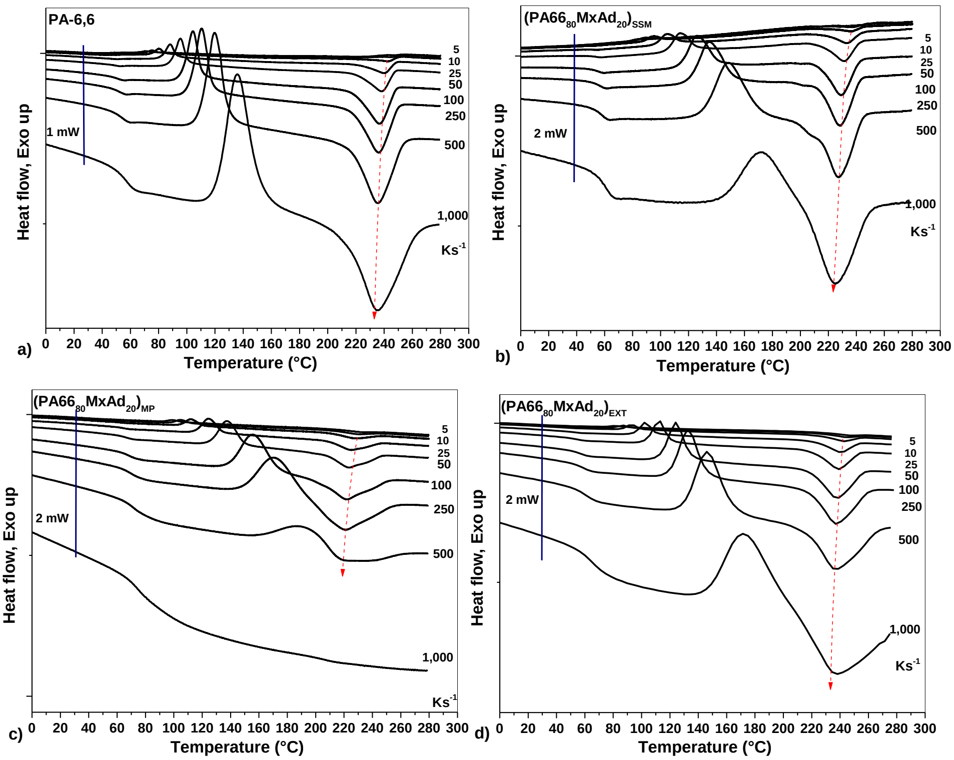


Figure 5.10 The heat flow as a function of temperature obtained on heating fully amorphous samples at different heating rates: a) neat PA-6,6 and b) (PA66$_{80}$MxAd$_{20}$)$_{SSM}$, c) (PA66$_{80}$MxAd$_{20}$)$_{MP}$ and d) (PA66$_{80}$MxAd$_{20}$)$_{Ext}$.

5.3.8.2 Isothermal cold ordering

Crystallizable polymers can crystallize either from the melt or from the glass state depends on the conditions. The latter type of ordering is known as cold-ordering which has considerable significance since many polymer processing methods has so rapid cooling of the molten polymer. The analysis of structure formation of fully amorphous PAs from the glassy state needs a complete inhibition of crystallization. The cooling rate is important to avoid any ordering process due to the formation of homogeneous nuclei during cooling.

Cold- ordering/crystallization, typically, is observed on heating the glass to temperatures higher than the glass transition temperature.

The isothermal kinetics of cold-ordering of initially fully glassy polyamides (PA-6,6 and other copolyamides) has been investigated using an analysis method that was successfully applied for the analysis of mesophase formation of random isotactic copolymers of propylene and 1-butene.[20,21] In the present study, the sample was first molten and quenched at -1000 K/s rate to obtain the fully glassy state. Then, the glass was re-heated after a certain dwell time at an identical rate to a pre-defined temperature between 60 and 200 °C, to permit isothermal cold-ordering. This was studied with different isothermal dwelling time from 0.1 s, 1 s, 10 s and 100 s as shown in Figure 5.11a – 5.11d.

It can be observed from Figure 5.11a that the SSM copolyamide is readily crystallizable even at the shortest dwell time (ca. 0.1 s). The crystallization kinetics with increasing dwell time at 1, 10 s increased the perfection of crystal ordering as seen in Figure 5.11b, 5.11c and they more or less demonstrate a similar effect. The blocky copolyamidehas a better crystal perfectioning at higher dwell time (100.0 s) as can be seen in Figure 5. 11d. From these FSC studies, we can conclude that this modern tool gives the most useful information on the structure changes of the polyamide and copolyamides.

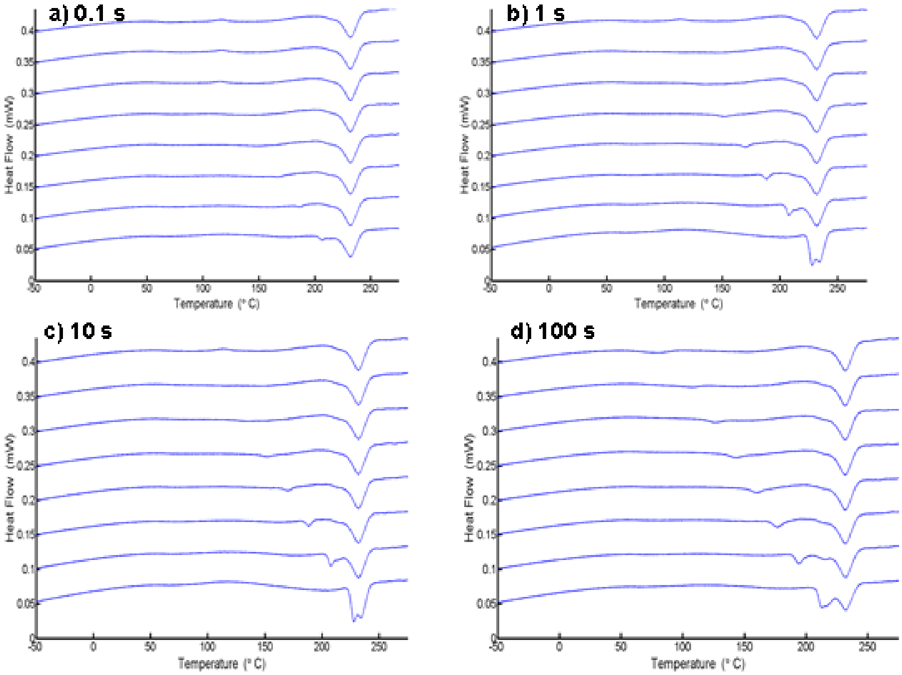


Figure 5.11 Isothermal crystallization studies of the $(PA66_{80}MxAd_{20})_{SSM}$ copolyamide at various dwell times: a) 0.1 s, b) 1.0 s, c) 10.0 s and d) 100.0 s at each temperature in increasing order, i.e. from 60 to 200 °C. (a-d: All Exo up).

5.3.9 Moisture absorption analysis of the copolyamides

The major drawback of PAs is the high moisture absorption (ca. 6 wt % for PA-6,6 after saturation) and this limits the possibilities for high-precision injection-molding applications. The moisture absorption or the water uptake of PAs can be reduced by increasing the degree of crystallinity, so generating a reduced amount of amorphous phase where the moisture is absorbed, or by providing the amorphous phase with a more hydrophobic character, by e.g. the incorporation of aromatic moieties. The reason that the moisture absorption occurs predominantly in the amorphous part is that the amide groups can form H-bonding with water molecules, which cannot penetrate into the crystals. In the SSM process, the aromatic comonomer is selectively incorporated into the amorphous phase and, hence, the obtained copolyamide should have reduced moisture absorption. The moisture absorption was studied by immersing the compression-molded copolyamide thin films of ca. 0.5 mm thickness into water at room temperature for 24 hours and then measuring the weight difference between the initial (dry) and conditioned sample. The weight difference is translated into the percentage moisture absorbed after 24 hrs. The copolyamides prepared via SSM, MP and the melt-mixed process are studied along with the neat PA-6,6 as reference and the results are presented in Figure 5.12. The moisture absorption of PA-6,6, used as a reference, was found within the range as reported in literature (ca. 6.3 vs. 6.0 wt%). The SSM copolyamide has a 31% reduction in moisture absorption, i.e. from 6.3 to 4.6 wt%. However, the melt-mixed copolyamides prepared via the Prism extruder have an even larger reduction, namely from 6.3 to 4.1 wt%. This can be explained based on the different degrees of blockiness of the copolyamides obtained from ^{13}C NMR explained above in section 5.3.4.1. A higher degree of blockiness results in higher degrees of crystallinity, which implies lower moisture absorption. The melt-mixed polymer has a higher MXD6 block length (R ca .0.25) compared to the SSM-copolyamide with a similar composition, reflected by a higher R-value ca. 0.4. A higher PA-6,6 crystallinity implies a lower amount of amorphous PA-6,6 and accordingly an enhanced oncentration of the hydrophobic MXD6 moieties in the amorphous phase, which reduces the moisture absorption. The higher moisture absorption of MP copolyamide is apparently due to its lower crystallinity and the random distribution of aromatic moiety in a diluted manner across the amorphous phase which adversely affected the moisture uptake.

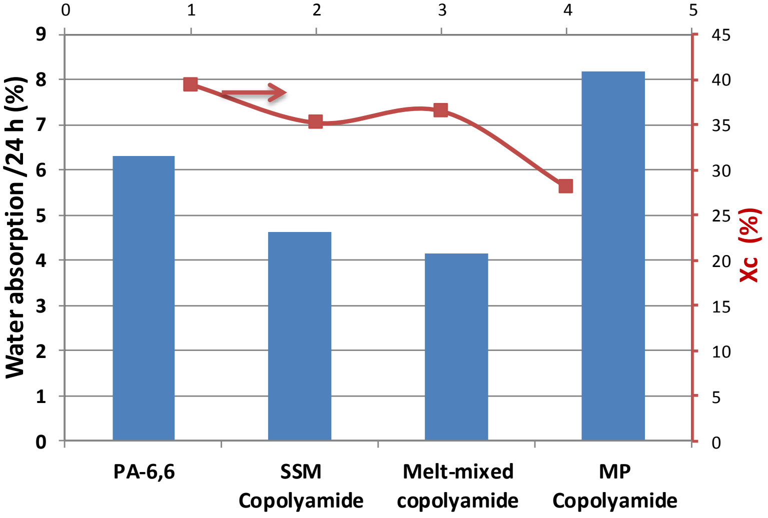


Figure 5.12 Moisture absorption and degree crystallinity of the copolyamides $(PA66_{80}MxAd_{20})_{Feed}$ prepared via SSM, melt-mixing and MP compared to the neat PA-6,6.

5.4 Conclusions

The SSM copolyamides prepared using PA-6,6 and isomeric aromatic comonomers, *viz*. $(PA66_xMxAd_y)$ and $(PA66_xPxAd_y)$, were investigated by using WAXD. It was found that the aromatic PXDA moieties can co-crystallize with the PA-6,6 repeat units. On the other hand, the MXDA-modified SSM copolyamide had a very similar WAXD pattern as the PA-6,6, implying that the MXDA residues do not co-crystallize with the 6,6 repeat units. The dimensions of the unit cell are not affected by increasing in MXDA comonomer content, but the observed change in the ratio of the intensities between the intersheet and interchain reflections indicate that the built-up of the β-sheets gets disturbed. The temperature-variable solid-state ^{13}C NMR study on $(PA66_{80}MxAd_{20})_{SSM}$ confirmed that the aromatic moiety (MXDA) is indeed only present in the amorphous phase, as the peaks corresponding to the phenyl group (ca. 128-140 ppm) became broader during heating and upon further heating beyond the glass transition temperature the peaks disappeared due to the increased dynamics of the chain segments.

The $(PA66_{80}MXD6_{20})_{Ext}$ product obtained by melt-mixing of the two homopolymers, i.e. PA-6,6 and MXD6, was analyzed in detail. The crystallization kinetics of the melt-mix product was examined using FSC and it was found that the melt-mixed product exhibited a higher rate of crystallization compared to copolyamides prepared via SSM and MP route with a similar composition. This may be due to the presence of relatively long sequences of the MXD6 moiety in the melt-mixed product, which may lead to a microphase separated melt structure. This improves the nucleation efficiency resulting in a higher crystallization temperature (T_c) and concomitantly a higher crystallinity and higher melting (T_m) temperature.

The $(PA66_{80}MxAd_{20})_{Ext}$ product has the lowest moisture absorption (ca. 4.1 %) due to the presence of longer sequences of the aromatic MXD6 moieties in the amorphous phase compared to the shorter sequence lengths obtained via SSM using MxAd comonomers. Although the degree of crystallinity of the $(PA66_{80}MxAd_{20})_{SSM}$ copolyamide is comparable (ca. 35%) to PA-6,6 (ca. 40%), it exhibited a lower moisture absorption (ca. 4.6 %) compared to pure PA-6,6 (ca. 6.3 %), which is due the presence the hydrophobic aromatic moiety present in the amorphous phase of SSM copolyamide.

From the overall properties analysis, we can conclude that the melt-mixed copolyamides exhibit the best thermal and mechanical properties of all studied materials, which had a comparable molecular weight. In comparison to the starting PA-6,6, the SSM-product showed some improvement of the properties, while the MP copolyamides demonstrated a deterioration of the properties due to the random distribution of the rigid aromatic moieties.

5.5 References

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Chapter 6

Technology Assessment

6.1 Epilogue

The aim of this research was to successfully synthesize a semi-aromatic copolyamide via the modification of an existing commercial polyamide-6,6 (PA-6,6) with an aromatic, T_g-enhancing comonomer, in such a way that the crystallinity is hardly affected and the thermal (*viz*. T_m, T_c), and mechanical properties are retained or preferably enhanced. The new copolyamide can potentially lead to an interesting material with unique properties. To achieve this goal, it is important to retain blocks with sufficient length of the starting homopolymer material PA-6,6 in the microstructure, so that it can still exhibit easy crystallization from the melt with the formation of thick lamellae with a relatively high melting temperature. Traditionally, PAs are modified in the melt or solution with other monomers or polycondensates (PAs and polyesters). This approach is a well-known method and very easy to adapt but it results in shorter homopolyamide blocks and in a more random distribution of the comonomer. The resulting short homopolyamide blocks exhibit a significantly lower crystallinity and lower melting and crystallization temperatures than the original homo PA-6,6. Moreover, there are many factors (like the blend composition, processing temperature, screw design, shear rates, extent of mixing etc.) during the reactive blending process that can considerably affect the end product properties. Modifying comonomers or polycondensates with a relatively low thermal stability cannot be employed in melt blending, which of course has to be performed above the melting point of PA-6,6, implying a certain limitation in terms of the flexibility of the process in comparison with modification route that could be performed at lower temperature.

Solid-state polymerization (SSP) is a well-known industrial process used to increase the molecular weight of semi-crystalline prepolymers of polycondensates in the solid state via a post-condensation (SSPc) reaction. The key factors affecting the SSP have been explained in detail in **Chapter 1**. The transreaction occurring during SSP is limited to the amorphous phase in which the diffusion of the end groups towards one another is possible, in the meantime leaving the chain segments of the homopolymer present in the crystalline phase unaffected. The exclusion of the chain segments within the crystalline part from the transreactions implies the presence of longer homopolymer chain parts, which should exhibit relatively high thermal transitions and crystallinity. In this work, this mechanism was explored to selectively modify the amorphous phase of PA-6,6 by an aromatic comonomer salt and this process is referred to as 'solid-state modification' (SSM) in the thesis. Other strategies i.e. melt copolymerization (MP) and melt-mixing of two homopolymers, have also been evaluated to prepare similar copolyamides and later compare the advantage of each process over another.

In this research, a solid state modification (SSM)-process was employed for 24 h at 200 and 230 °C to modify PA-6,6 by a selective incorporation of the semi-aromatic comonomer salts para- and meta-xylylenediamine (PXDA and MXDA resp.) into the amorphous phase. The analysis of the melting (T_m) and crystallization (T_c) temperatures of SSM copolyamides modified by PxAd and MxAd revealed that, during cooling of the SSM products from the melt, the PxAd residues have co-crystallized with PA-6,6 repeat units whereas MxAd did not affect the crystalline structure of the PA-6,6. The investigation of the copolyamides by WAXD supported this difference in co-crystallizability with the 6,6 repeat units, as discussed in **Chapter 5**. In this way, PA-6,6-based blocky semi-aromatic copolyamides can be synthesized with almost retention of melting and crystallization temperatures with respect to PA-6,6. In a similar approach, the T_g could be improved and the moisture absorption could be somewhat reduced, again with the approximate retention of the melting temperature of PA-6,6. The selection of the comonomer to be incorporated by SSM can be extended to different diamine comonomers to impart specific properties, such as flame retardancy by e.g. using phosphorous-containing diamines.

It was shown from the sequence analysis by using solution ^{13}C NMR that the SSM copolyamides are indeed blocky in nature with degrees of randomness (R) much lower than one, and accordingly having considerably high amounts of aromatic residues present in the amorphous phase. Therefore, the glass transition temperature of the copolyamides was raised with respect to PA-6,6 from ca. 55 to ca. 65 °C (**Chapter 3**). The retention of the significantly longer homo PA-6,6 blocks in the SSM copolyamides resulted in a nearly similar cystallinity as the homo PA-6,6. On the other hand, MP copolyamides with similar overall composition were found to have an almost random distribution of the comonomer in the entire polymer chain, resulting in deterioration of the chain regularity and, as a consequence, in a reduction of the thermal properties and crystallinity. It should be noted that the lower value of T_m -T_c of the SSM copolyamides (ca. 28-33 °C) is most preferred for an injection-molding grade, since it implies faster crystallization of the product from the melt with less cooling time. On the other hand, the T_m -T_c value for the MP copolyamides was much higher (ca. 38-41 °C) (**Chapter 4**).

The advantages of the SSM-process over MP were clearly demonstrated by the research presented in **Chapters 1- 4**. To assess the real advantages and disadvantages of the SSM-process, the alternative melt-mixing approach was presented and evaluated in **Chapter 5**. Melt-mixing was done with the two homopolymers (PA-6,6 and PA-MXD,6) applying a relatively high shear in a co-rotating twin-screw mini-extruder. The melt-mixed product was analyzed and found to be transamidated by interchange reactions. Interestingly, the sequence analysis revealed that the melt-mixed homopolyamides $(PA66_{80}MxAd_{20})_{Ext}$ exhibited longer aromatic blocks with lower R values (ca. 0.25) than that of the SSM copolyamide (R ca. 0.4) with a similar overall composition. This can be explained by the fact that the starting homopolymer material (MXD6) in the melt-mixing process contains very long aromatic (MXD6) moieties compared to the shorter blocks of the comonomer (MxAd) used in the SSM process. Moreover, the melt-mixed $(PA66_{80}MxAd_{20})_{Ext}$ copolyamide has higher T_m and T_c (ca. 260 and 232 °C, respectively) than that of $(PA66_{80}MxAd_{20})_{SSM}$ (T_m, T_c ca. 252.6 and 220.4 °C resp.) (See Table 5.5). The properties (modulus, % crystallinity, T_m, T_c) of the copolyamide prepared by melt-mixing proved to be slightly better than those of the

SSM copolyamides. The moisture absorption studies on these copolyamides indicated that the melt-mixed homopolyamides (X_{cr} ca. 36 %) as well as the SSM copolyamides (X_{cr} ca. 35 %) exhibit reduced moisture absorptions compared to neat PA-6,6 (X_{cr} ca. 37 %), whereas the most random MP copolyamides show the opposite trend, *viz.* a higher moisture absorption which is also partly due to a lower crystallinity (X_{cr} ca. 28 %), of this random copolymer.

Although, from the comparison of the above-mentioned properties, the melt-mixing technique looks to be an attractive method to obtain copolyamides with the desired properties, one cannot ignore the limitations associated with the melt-blending route as mentioned earlier. It has to be noted that to enable the modifying polymer or monomer to be incorporated into a step-growth polymer (e.g. MXDA or MXD6 incorporated into PA-6,6) the via melt-mixing method, the blend component should be thermally stable and should be able to sustain high shear and high heat during the residence times applied in the extrusion process. The reactive melt-mixing in extrusion may not be reproducible if this melt mixing is by accident carried out for a longer time than the desired duration (e.g. operator's mistake, equipment failure or an electrical shutdown). The transamidated copolyamide can be exposed to more randomization with increasing residence time in melt.

Now, let us discuss what needs to be worked-out to make the SSM process developed here industrially up-scalable. The SSM lab-scale process involves two major steps: first, homogeneous mixing of PA-6,6 and the comonomer salt in a common solvent, such as HFIP, followed by a complete removal of the solvent. The dried reaction mixture is ground to a uniform particle size and the reaction is then carried out in the fluidized bed SSM reactor. It was shown in **Chapter 3** that the homogeneous solvent mixing is important to enable the intimate mixing of the comonomer into the amorphous phase of PA-6,6. This way of mixing of the comonomer salt into the amorphous phase enhances the mobility of and the diffusion within this phase, which later during the SSM reaction accelerates the transamidation kinetics. An unpublished study conducted by us showed that the physical mixing of PA-6,6/MxAd, without applying a common solvent, or swelling the PA-6,6 polymer in an aqueous MxAd salt solution before subjecting the mixture to SSM, exhibited a very low transamidation reaction rate. It has to be noted that the solvent (HFIP) used in the lab-scale solution mixing process is highly irritating to eyes and skin, and also toxic. Moreover, it is expensive and a very large solvent volume is required when the SSM process is scaled-up. Therefore, the common solvent method is not a desirable mixing method for an industrial process. As an alternative, a non-solvent mixing approach could be a quick melt mixing of PA-6,6 with the MxAd salt, which could be achieved in an extruder in which the mixture has a very short residence time to avoid excessive transamidation. Transreactions should be avoided as much as possible here, since the entire amount of PA-6,6 present could participate in these reactions, possibly leading to a random distribution of the aromatic moiety over the entire PA-6,6 chain, thereby excluding the presence of the desired longer PA-6,6 blocks.

Some attempts were made to achieve melt-mixing of MxAd with PA-6,6 in different lab-scale extruders by varying the processing parameters and the feeding methods on different screw designs, as presented in the following section.

6.2 Melt mixing trials of MxAd salt with PA-6,6 : Few approaches

6.2.1 Mini-extruder with more mixing elements

PA-6,6 powder was premixed with MxAd powder and this mixture was fed into the co-rotating twin-screw Prism mini-extruder (TSE 16PC). It has two zones as shown in Figure 6.1, of which the temperature can be independently controlled. The residence time in this 16 L/D extruder at 150 rpm was around 2.5 minutes. The temperature of Zone 1 was set at 250 °C, while Zone 2 was set at 280 °C. First, 30 g of PA-6,6 powder (ca. 80 mol% 6.6 repeat units) mixed with 9.5 g of MxAd (ca. 20 mol% repeat units) powder was premixed in a lab-scale, high-speed mixer and the powder mixture was then fed to the extruder using a gravitational feeder operated in manual mode. The shear heating, generated by the screw configuration, resulted in degradation of the MxAd salt and the output material was very dark colored. Moreover, the melt viscosity dropped significantly yielding a molten liquid flowing through the outlet die. Moreover, together with the dark melt output there was lot of intermittent gas formation observed. To reduce the salt degradation effect, a lower salt content was also tried, but this showed a similar result.

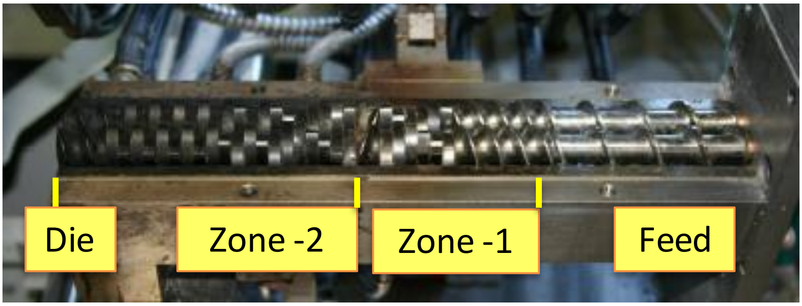

Figure 6.1 Screw configuration of the Prism mini-extruder.

It was concluded that this powder mix approach, using the screw configuration shown in Figure 6.1, was not successful and also that, as there is no downstream feeding available, any improvement was difficult. Further trials were planned, based on the following points:

-The screws contained a lot of kneading elements and not many transportation elements, and the shear rate and the back pressure generated were too high. Further trials could be done with a screw design which has more conveying/transporting elements and merely short mixing elements.

-The degradation could be an oxidative thermal degradation and in the next trials an inert gas blanket should be provided during feeding.

-The comonomer salt (MxAd) started degrading before the melting of PA-6,6 occurred. The melting point of PA-6,6 is ca. 262 °C and onset of the MxAd degradation temperature is ca. 255 °C. So, the thermal degradation of MxAd should be avoided by downstream feeding where the PA-6,6 is fully molten and has developed flow. With this approach the contact time between the molten PA-6,6 and the thermally labile MxAd salt is limited.

6.2.2 Melt-mixing with a mild mixing screw, feeding at different zones

The second experimental approach was followed with the Haake rheomix OS (PTW-16) extruder with an L/D ratio of 40. It has ten zones with two downstream feeding ports at Zones 7 and 9. The screw design used during this trial contains mostly transporting elements, as shown in Figure 6.2, and a short mixing zone just before the exit near to Zone 8. A nitrogen gas blanket was provided around the feeding hopper during feeding. Two trials were performed with premixed powder $(PA66_{80}MxAd_{20})_{Feed}$ followed by purging the extruder with neat PA-6,6 with the set temperature given in Table 6.1. In the first trial, the mix was fed from the main feeder and the residence time was ca. 2 minutes with a screw speed of 100 rpm. The color of the output polymer mix was almost comparable to the color observed using the Prism extruder and some degradation and gas formation was observed.

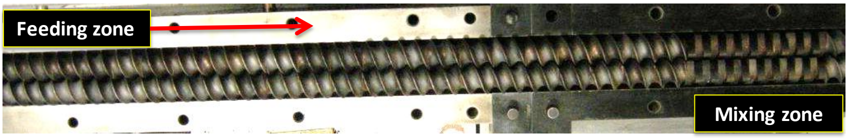

Figure 6.2 Screw configuration of the Haake Rheomix OS extruder (PTW-16) with L/D = 40.

The second set of experiments using this set up was performed as follows. Part of the PA-6,6 was fed from the main feeder and was fully molten, after which manual feeding of the PA-6,6/MxAd powder mix was started in the downstream (Zone-7). The manual feeding downstream was challenging, as there was considerable back pressure exerted from the fully developed PA-6,6 melt. The feeding ratio was calculated and adjusted in such a way that the output had the composition $(PA66_{90}MxAd_{10})_{Feed}$. This trial couldn't be continued successfully as the polymer melt at Zone-7 started to solidify as it was exposed to ambient temperature, thereby hampering the uniform pre-mixed powder feeding.

Table 6.1 Haake extruder (PTW-16) with L/D of 40: processing temperatures.

Zones	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9,10
Set temperature (°C)	250	275	275	275	275	280	280	280	280
PA-6,6/MxAd processing temperature (°C)	250	275	275	275	270	270	270	270	275

6.2.3 Lower residence time approach

Based on the observations done during the above trials and the learnings, some modifications were done with the Haake Rheomix OS extruder (PTW16).

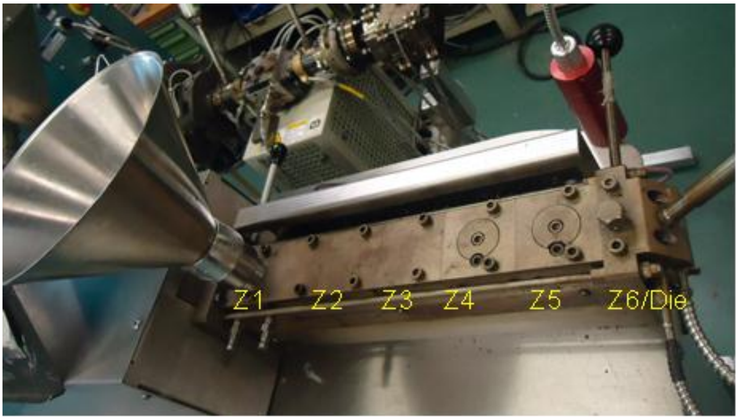

Figure 6.3 Haake Rheomix OS extruder set up (PTW-16) with L/D = 25.

The major measures taken in this trial were as follows:

(a) The length of the screw was reduced to lower the residence time (See Figure 6.3). (b) To delay the thermal degradation of MxAd powder, an aqueous solution of MxAd salt was made from 10 g MxAd and 10 mL of water (see Table 6.3) and this was mixed with PA-6,6 powder in a small tumbler. (C) A different approach was adapted to avoid using the thermally labile MxAd comonomer salt. MXD6 oligomer ($M_{n,SEC}$ ca. 3 KDa) was prepared by melt polymerization of MxAd salt at 250 °C for ca. 3 minutes and was allowed to crystallize.

The MXD6 oligomer in powder form was a priory mixed with PA-6,6 powder, physically at different wt% and fed through the main feeder.

The temperature profile of the PTW16, 25 L/D trial was as given in Table 6.2. The trials and the observations are given in Table 6.3.

Table 6.2 Haake extruder (PTW-16) with L/D of 25: Processing temperatures.

Zones	**Z1**	**Z2**	**Z3**	**Z4**	**Z5**	**Z6/ Die**
Set temperature (°C)	250	275	275	275	275	275
Wet PA-6,6 or oligomer mix trial temperature (°C)	250	265	265	265	265	265

Table 6.3 Haake extruder (PTW-16) with L/D of 25: Trial details and observations.

No.	Trial description	PA-6,6 (wt %)	MxAd/ Oligomer (wt %)	Screw speed (rpm)	Observations
1	Wet mixture fed through the main feeder (10 g MxAd and 10 mL of water).	90	Aq. salt 10	100	Dark polymer output and lots of steam resulted in back flow to the feeding hopper.
2	Same as trial-1	10	Aq. Salt 10	200	Found no change from trial-1, even after increasing screw speed, lower residence time.
3	PA-6,6 was mixed with ground MXD6 oligomer prepared.	50	Oligomer 5	100 200	Feeding was quite smooth; the melt-mix output was lighter in color at both screw speeds.
4	PA-6,6 + MXD6 oligomer	40	10	100 200	Bridging occurred during feeding, leading to fluctuation in the feed, hence the torque oscillated. The powder mix was sticky once it is molten in the first zone.
5	PA-6,6 + MXD6 oligomer	30	20	100 200	Bridging occurred during feeding. With more oligomer the torque decreased to a minimum level (ca. 5 Nm^{-1}).

It was observed that the reduced residence time improved the melt mixing, but still the thermal degradation of the MxAd salt couldn't be totally avoided. The MXD6 oligomer mixing with PA-6,6 successfully resulted in a light colored mix, but when the melt mix was subjected to SSM reactions at 230 °C for 8 h there was no transamidation occurring. This is in line with our reaction mechanism studied and presented in **Chapter 3**, showing that the transreactions are predominantly initiated by a protonated amine group.

6.3 Suggestions

Although the attempts made to mix the comonomer MxAd salt with PA-6,6 in the melt were unsuccessful, these resulted in some learnings. We strongly believe that with a very short residence time the melt mixing can be successfully achieved and we recommend the following routes to obtain this in an industrial process.

a. **Injecting salt-solution downstream:** The comonomer salt (MxAd) is a zwitter-ion pair (A^+B^-) and is readily soluble in water at room temperature. From the solubility experiments it was found that a 1/1 wt/wt ratio salt/water yields a homogeneous solution, stable at room temperature. A salt/water wt/wt ratio of 2:1 was found to be just above the saturation point, resulting in little tiny particles of the MxAd salt dispersed in the solution of the other part of the salt. Thus, the aqueous MxAd salt solution can be injected by a positive displacement pump into the downstream of an extruder where the molten PA-6,6 can be mixed with the aqueous MxAd salt solution within a short time before the transamidation starts to occur. The steam generated can be removed by venting just before the die. Safety consideration is a must, since the solution injection should avoid solidification of the molten polymer and one should avoid or cope with the high back pressure at the injection tip. This can be addressed by providing a non-return valve before the injection point into the extruder and also by providing hot insulation on the liquid injection tubing to avoid temperature loss and temperature differences.

b. **Side feeding of MxAd powder:** The comonomer MxAd is a free flowing powder like for instance talc and it can also be fed by a side feeder with a screw with a proper flight depth to assure efficient feed. Due to the non-availability of such facilities at our labs we could not explore the options a and b by ourselves.

6.4 Conclusions

In this research, taking a single system such as MXDA comonomer and PA-6,6, a nearly complete evaluation of the SSM concept was attempted (*viz*., chemistry, microstructure and conformational structure analysis, thermal, mechanical properties and finally the moisture absorption evaluation). It is more than obvious from the detailed research on the SSM process that it is a versatile and very suitable process to tailor-make the desired copolyamides exhibiting different properties introduced by the incorporated comonomers. Comonomers with a limited thermal stability, such as bio-based or bio-renewable or bio-resourced monomers, for which the incorporation into a polyamide by melt copolymerization is difficult or even impossible, can easily be synthesized via SSM and subsequently studied, as the SSM reaction yielding copolyamides can be done far below the melting point of PA-6,6. By carefully selecting the comonomers we can e.g. reduce the water absorption and/or increase the glass transition temperature and the flame resistance of PA-6,6, or we can prepare functional copolyamides that can be used for specialty applications. The SSM process has a high degree of flexibility in terms of industrial applications. The comonomer feed ratio can be widely varied and a very wide range of comonomers can be incorporated into PA-6,6, improving some crucial physical properties while leaving the melting temperature and crystallinity relatively unaffected. In a nut-shell SSM copolymerization is a mild and versatile process compared to MP and reactive melt-mixing routes. For thermally stabile polymeric blend components for PA-6,6, melt-blending of both homopolymers seems to be even more attractive than SSM, since even longer PS-6,6 blocks are generated after melt-blending than after an SSM reaction between PA-6,6 and the corresponding comonomer salt. Copolyamide production via MP without any doubt is the least attractive route in view of the low attained thermal transitions and crystallinity, which is directly related to the short homopolyamide 6,6 blocks formed.

Summary

Solid-state modification of polyamide-6,6

Polyamide-6,6 (PA-6,6) is well known and used in many applications because of the high dimensional stability under dry conditions, good mechanical and thermal properties, and excellent solvent resistance. Also PA-6,6-based copolymers have gained attention, since additional properties can be introduced while retaining the advantageous properties. PA-6,6 is mainly synthesized by melt polycondensation of hexamethylenediamine and adipic acid to a medium molecular weight (M_n ca. 25 kDa) and later the M_n is increased via a solid-state post-condensation (SSPc) by subjecting the prepolymer to elevated temperatures (ca. 180-200 °C) for 8-24 hours. Copolyamides are conventionally prepared via melt- or solution-polymerization and have a random chemical microstructure. As a result they have a lower crystallinity and lower crystallization (T_c) and melting (T_m) temperatures than the base homopolyamide.

The SSM process of a semi-crystalline polycondensate, *viz.* poly(butylene terephthalate) (PBT), was already reported by Jansen et al. The SSM modification resulted in a non-random incorporation of significant amounts of comonomer (e.g. 2,2-bis[4-(2-hydroxyethoxy)phenyl]propane, bis(2-hydroxyethyl)terephthalate and 2,2'-biphenyldimethanol) into PBT without completely losing the crystallinity of the resulting block-like copolyester. This is due to the fact that the reaction was limited only to the mobile fraction of the amorphous phase, leaving long crystallizable sequences of pure PBT in the main chain. As SSM exclusively occurs in the mobile amorphous fraction of the material, the glass transition temperature can be enhanced depending on the rigidity of the (aromatic) comonomer and the T_c and the T_m of the starting material are nearly retained.

The main objective of this research was to modify the semi-crystalline PA-6,6 with an aromatic comonomer in the solid state resulting in the enhancement of T_g with retention of the crystallization behavior. For the first time for the class of polyamides, a solid-state modification of the amorphous phase of a homopolyamide was performed below the melting temperature. Semi-aromatic para- and meta-xylylenediamine:adipic acid 'nylon salts' were incorporated into the main chain of PA-6,6. Since the PA-6,6 chain segments present in the crystals during the solid-state modification (SSM) process do not participate in the transamidation reactions, the SSM reaction results in relatively long blocks of pure PA-6,6 segments and blocks of copolyamide segments with a reduced mobility. As expected, the kinetics of the transamidation is much faster at 230 than at 200 °C and the SSM-modified copolyamide initially shows a significant molecular weight reduction by chain scission caused by transamidation with the incorporated 'nylon salt', followed by a built-up of the molecular weight by polycondensation to a value close to the starting value after 8-12 h of SSM reaction time. At higher reaction temperatures branching and cross-linking reactions, resulting in gel formation, are observed after 8 h of SSM reaction.

In order to understand the kinetics of the SSM reactions, copolyamides, ($PA66_xMxAd_y$) with different mol% of MxAd were synthesized via solid-state modification (SSM) and melt polymerization (MP). The progress of the transamidation reaction as revealed by the initial decrease in molecular weight during the incorporation of the aromatic comonomer salt was monitored by using SEC. The molecular weight $M_{n,SEC}$ decreases at a higher rate during the first transamidation step when higher molar percentages of MxAd salt were premixed with the PA-6,6 homopolymer. This molecular weight decrease, caused by chain scission, is followed by a built-up of $M_{n,SEC}$ due to post-condensation of the free amine and acid end groups resulting from the first transamidation step.

The SSM reaction mechanism was investigated and it was found that the transamidation or chain scission was initiated by protonated amine species ($-NH_3^+$). It was also observed that neither an excess of diamine nor an excess of dicarboxylic acid in the salt resulted in a significant change in the kinetics of the transamidation reaction with respect to the equimolar salt system, since for both cases no significant change was observed in the number-average molecular weight (M_n) development as a function of time. An in-depth study on the chemical microstructure was performed on the $(PA66_xMxAd_y)_{SSM}$ and $(PA66_xMxAd_y)_{MP}$ samples with similar overall compositions. The sequence analysis based on solution ^{13}C NMR experiments confirmed that the copolyamides prepared via SSM and containing 20-30 mol% of MxAd salt in the feed exhibited a more blocky structure with overall degrees of randomness R_{total} of ca. 0.4. On the other hand, the melt-polymerized copolyamides having a similar overall composition exhibited R_{total} values close to unity, typical for fully random copolymers. The earlier mentioned presumption that during SSM the transamidation reactions selectively occur in the amorphous phase, leaving the chain segments of homopolymer of crystalline PA-6,6 intact, was further supported by the observation that the $(PA66_xMxAd_y)_{SSM}$ products exhibited only slightly lower melting temperatures and degrees of crystallinity as compared to pure PA-6,6, which can only be explained by the presence of long homo PA-6,6 blocks in the SSM products.

The thermal analysis of the copolyamides prepared via SSM and MP showed that SSM copolyamides have a higher melting temperature compared to copolyamides with similar composition prepared via MP. The relatively high crystallization temperature of the SSM copolyamides results in significantly lower super coolings for crystallization from the melt in comparison with MP copolyamides with similar chemical composition. Accordingly, the SSM copolyamides are more suitable for injection-molding applications. The higher degree of crystallinity of the SSM copolyamides compared to the MP samples results a higher glass transition temperature of the SSM copolyamide because of its relatively higher content of the rigid MXDA monomer residues in the amorphous phase. Finally, it turned out that the block-like microstructure of the SSM copolyamides, with all its advantages with respect to thermal transitions and crystallizability, is quite robust with respect to melt processing: even after a residence time in the melt for 15 min at 290 °C the crystallization and melting temperatures remain significantly higher than those of the corresponding random MP counterparts, suggesting that full randomization of the structure does not occur.

Next, the structure of the copolyamides prepared using PA-6,6 and isomeric aromatic comonomers, *viz*. $(PA66_xMxAd_y)$ and $(PA66_xPxAd_y)$, was analyzed by using WAXD, temperature variable ss-NMR and DMTA. It was found that the aromatic PXDA moieties can co-crystallize with the PA-6,6 repeat units. On the other hand, the MXDA-modified SSM copolyamide had a very similar WAXD pattern as the PA-6,6, implying that the MXDA residues do not co-crystallize with the 6,6 repeat units and reside exclusively in the amorphous phase of the copolyamide. A temperature-variable solid-state ^{13}C NMR study on $(PA66_{80}MxAd_{20})_{SSM}$ confirmed that the aromatic moieties (MXDA) are indeed only present in the amorphous phase, as the peaks corresponding to the phenyl group (ca. 128-140 ppm) became broader during heating and upon further heating beyond the glass transition temperature the peaks disappeared due to the increased dynamics of the chain segments.

An alternative approach to investigate the transamidation reaction and to study whether it can also yield a copolyamide containing comparable homoPA-6,6 block lengths was performed by a melt extrusion process. The $(PA66_{80}MXD6_{20})_{Ext}$ product obtained by melt-mixing of the two homopolymers, i.e. PA-6,6 and MXD6, was analyzed in detail. Interestingly, the sequence analysis revealed that the melt-mixed homopolyamides $(PA66_{80}MxAd_{20})_{Ext}$ exhibited longer aromatic blocks with lower R values (ca. 0.25) than that of the corresponding SSM copolyamide (R ca. 0.4) with a similar overall composition. The crystallization kinetics of the melt-mix product was examined using *fast-scanning calorimetry* (FSC) and it was found that the melt-mixed product exhibited a higher rate of crystallization compared to copolyamides prepared via the SSM and MP routes with a similar composition. Furthermore, the moisture absorption studies revealed that the $(PA66_{80}MxAd_{20})_{Ext}$ product has the lowest moisture absorption (ca. 4.1 %) due to the higher degree of crystallinity compared to the copolyamide obtained via SSM using MxAd comonomer. Although the degree of crystallinity of the $(PA66_{80}MxAd_{20})_{SSM}$ copolyamide is comparable (ca. 35%) to PA-6,6 (ca. 40%), it exhibited a lower moisture absorption (ca. 4.6 %) compared to pure PA-6,6 (ca. 6.3 %), which is due the presence the hydrophobic aromatic moieties present in the amorphous phase of the SSM copolyamide.

From the overall properties analysis, it can be concluded that the melt-mixed copolyamides exhibit the best thermal and mechanical properties of all studied materials, which had a comparable molecular weight. In comparison to the starting PA-6,6, the SSM-product showed some improvement of the properties, while the MP copolyamides demonstrated a deterioration of the properties due to the random distribution of the rigid aromatic moieties.

Although the melt-mixed copolyamides exhibited some better properties than the SSM copolyamides (Note: a full mechanical properties study was not performed), the SSM process can be the most preferred industrial route for making tailor-made products and it certainly exhibits a high flexibility for incorporating, in a controlled way, several comonomers that are not available in the form of a (co)polyamide as required for the melt-blending route. So, SSM may impart various properties, such as flame retardancy, flow improvement, and toughening. Furthermore, the SSM route can be the preferred route to prepare copolyamides based on thermally less stable monomers or polymers that cannot be processed via melt-mixing. However, for making copolyamides from monomers, present in commercially available homopolyamides, the melt-blending route seems to be the way to go, although slight variations in the residence time in the melt may have a huge influence on the final product properties.

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Best Regards,
Jey
September, 2012

List of Publications

- **Jeyakumar, A**., C.E. Koning, J.G.P. Goossens , Manoranjan Prusty and Matthias Scheibitz, " Polyamide-6,6 based blocky copoly (amides) obtained by solid-state route", J. Polym. Sci., Part A: Polym. Chem., **2012** – (Submitted after reviewer's comments).
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Curriculum Vitae

A. Jeyakumar (son of P. Albert Sundarraj) was born on the 29th of May 1974 in Madurai, India. After finishing his Bachelor and Masters in Chemistry from The American College, Madurai in 1996, he pursued his second masters (Master of Technology, M.Tech.) in Polymer Science and Engineering at the Indian Institute of Technology (IIT, Delhi 1996-98).

He started his career as an Engineer in one of the biggest petrochemicals (420 KTA of ethylene) in India named Haldia Petrochemicals Limited in 1998. He worked till 2003, in high density polyethylene (HDPE) plant as an quality control, quality analysis Engineer.

Then he moved to Solvay Advanced (India) Polymers Inc. in 2003 (priory known as Gharda chemicals Ltd., Gujarat, India) as a Senior Execute and later as a Deputy Manager of an application development laboratory. He was part of the R&D team to develop and demonstrate the skills on the product development of polysulfones (PES, PSU and PPSU) and poly(ether ether ketone) (PEEK) polymers till 2005.

Subsequently, he joined General Electric Co. (GE Plastics, JFWTC, India) in 2005 as a Research Scientist with Noryl® team and successfully developed a new high performance flexible cable grade and a robust low smoke and flame retardant flexible poly(phenylene oxide) based product for an aircraft wire&cable applications till September end, 2008.

In October 2008, he joined Prof. Dr. Cor Koning's Polymer Chemistry group. The most important results of the research are presented in this thesis. During his PhD he earned a Post graduate Certificate after completing four modules of the course 'Registered Polymer Technologist' (RPK) organized by the National Dutch Graduate School of Polymer Science and Technology (2009-11). From October, 2012 he will be working with MOMENTIVE as a Senior Researcher.