Polyamide-6,6-Based Blocky Copolyamides Obtained by Solid-State Modification

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ABSTRACT: Copolyamides based on polyamide-6,6 (PA-6,6) were prepared by solid-state modification (SSM). *Para*- and *meta*-xylylenediamine were successfully incorporated into the aliphatic PA-6,6 backbone at 200 and 230 °C under an inert gas flow. In the initial stage of the SSM 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 postcondensation during the next stage. When the solid-state copolymerization was continued for a sufficiently long time, the starting PA-6,6 molecular weight was regained. The incorporation of the comonomer into the PA-6,6 main chain was confirmed by size exclusion chromatography (SEC) with ultraviolet detection, which showed the presence of aromatic moieties in the final high-molecular weight SSM product. The occurrence of the transamidation reaction was also proven by ^{1}H nuclear magnetic resonance (NMR) spectroscopy. As the transamidation was limited to the amorphous phase, this SSM resulted in a nonrandom overall structure of the PA copolymer as shown by the degree of randomness determined 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 their nonrandom, block-like chemical microstructure, whereas the melt-synthesized copolyamides were random. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 5118–5129

KEYWORDS: poly(amide-6,6); size exclusion chromatography (SEC); solid-state (co)polymerization; transamidation

INTRODUCTION Since their invention by Carothers,[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, as additional features can be introduced while retaining the original advantageous properties of the homopolyamides.

Solid-state polymerization (SSP), in which the polymerization is performed below the melting temperature but well above the glass transition temperature of semicrystalline polymers, 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 SSP methods,[2–6] SSP reactor-design, and SSP kinetics[7–10] for both polyesters[2] and polyamides.[6,7,11,12] In most cases, these studies focused on solid-state postcondensation. Only a few studies reported on copolymerization or modification reactions using SSP, which in this study is called solid-state modification (SSM).

Copolymers of polyamides can be obtained by either copolycondensation or ring-opening copolymerization in the melt, in solution or 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.[19–24] applied for the first time the SSP process for the chemical modification of a condensation polymer, *viz*. poly(butylene terephthalate) (PBT). The solid-state modification (SSM) resulted in a nonrandom 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.[23] This is due to the fact that the reaction was constrained only to the mobile fraction of the amorphous phase, leaving intact long crystallizable sequences of pure PBT along the main chain.

To our knowledge, SSP copolymerization or SSM has not yet been applied for polyamides of the PA-x.y type, obtained by polymerizing a diamine and a dicarboxylic acid, although the concept has been proven for PA-6 by Cakir et al.[25] A difference with the mentioned PBT SSM is that commercial polyamides usually do not contain a polymerization catalyst. Titanates are used as catalyst in the preparation of polyesters (*viz*. poly(ethylene terephthalate) (PET), PBT) and they are not removed. So, mostly commercial PBT may contain some active titanate catalyst residues. Conversely, the PA-6,6 used in our study contains no such catalyst. In this article, we describe the incorporation of semiaromatic "nylon salts" from *p*- or *m*-xylylene diamine and adipic acid (PxAd resp. MxAd) into the amorphous phase of polyamide-6,6 (PA-6,6) in the solid state using a process very similar to the one described above for the PBT SSM. The main objective of this article is to demonstrate that this SSM 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 those 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 using ultraviolet (UV) detection coupled to size exclusion chromatography (SEC) and using ^{1}H nuclear magnetic resonance (NMR) spectroscopy. In a subsequent article, a more detailed analysis of the crystalline nature of the blocky reaction products obtained after SSM versus the more random copolyamides obtained from the melt route will be presented.

EXPERIMENTAL

Materials

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, MXDA, resp.) 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/AA salt. For NMR measurements, deuterated trifluoroacetic acid (TFA-*d*, 99.5% deuterated) was obtained from Cambridge Isotope Laboratories.

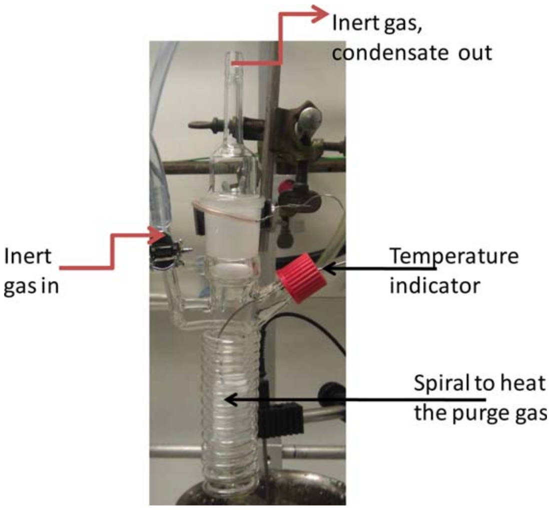


FIGURE 1 Laboratory-scale SSM reactor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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 (either PxAd or MxAd) 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.

SSM and Melt Polymerization

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 (Fig. 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

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

SCHEME 1 Synthesis of the aromatic comonomer salt.

temperature was measured with a thermocouple inserted into the PA-6,6/nylon salt mixture.

For the melt copolymerization, performed at 280 °C, 80 mol % of PA-6,6 salt and 20 mol % of MXDA/adipic acid salt (MxAd) were mixed and reacted for 3 h in the melt under nitrogen atmosphere.

Preparation of Comonomer Salt

The preparation of "comonomer salts" involved mixing the diamine (*p*-xylylene diamine or *m*-xylylene diamine) with AA in equimolar proportions, by mixing equivalent amounts of ethanol solutions of both components (see Scheme 1, where Ar = CH_2-phenyl-CH_2). The nylon salts, *viz.*, *m*-xylylene adipic acid salt (MxAd), *p*-xylylene adipic acid salt (PxAd), 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.

Characterization

Size Exclusion Chromatography

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 UV detectors operating at a wavelength of 275 nm (these detectors were in series, respectively), a Waters 2707 auto sampler, and a polymer standards service (PSS) polar fluoro gel (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 using a calibration performed with 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 poly(tetrafluoroethylene) (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 polydispersity index (PDI) may be underestimated.

NMR Spectroscopy

NMR spectra were recorded on a Varian Mercury Vx (400 MHz) spectrometer at 25 °C. The solvent used was 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 about 1.5 s and a delay time (d1) of about 10 s in the nuclear overhauser effect (NOE)-decoupling mode.

Differential Scanning Calorimetry (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 autosampler and a refrigerated cooling system. 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 melt polymerization (MP), 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), respectively, and isothermal periods of 5 min at, respectively, 0 and 290 °C.

RESULTS AND DISCUSSION

SSM Recipe

For the reactions, 80 mol % of PA-6,6 and 20 mol % of the PxAd or MxAd 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 molar 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 solvent. The SSM 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.

SSM of PA-6,6 with *p*-xylylenediamine

The reaction of PA-6,6 (80 mol %) with the equimolar nylon salt based on PXDA and AA (20 mol %) (denoted as $(PA66)_{80}(PxAd)_{20}$) was performed in the solid state 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 (refractive index (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. 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 AA or deprotonated AA at ca. 28.6 min) are clearly observed [Fig. 2(a)].

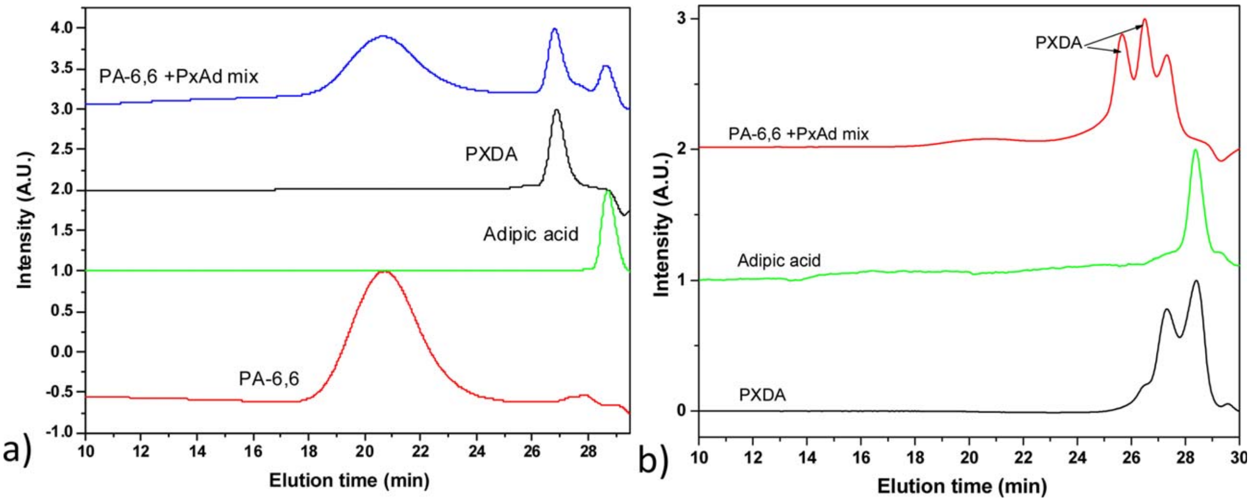


FIGURE 2 SEC chromatograms of SSM reaction starting materials, that is, mixtures of PA-6,6 and PxAd salt, and pure PA-6,6 and salt components PXDA and AA: (a) RI detection and (b) UV detection. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Aliphatic PA-6,6 does not give a strong UV signal [see Fig. 2(b)], so only the PxAd components (PXDA or its protonated form at ca. 25.6 min, respectively, 26.2 min, and AA or its deprotonated form at ca. 27.4 min) give a signal in the UV detection chromatogram [Fig. 2(b)].

The SSM reaction at 200 °C monitored by the SEC RI detector, as shown in Figure 3(a), 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 ~8 h, the peak is no longer visible. However, the diacid signal is only reduced after 4 h. It seems as if first the diamine is incorporated, leading to a decrease in molecular weight, and a corresponding mismatch in stoichiometry. Subsequently, the diacid is incorporated, leading to an increase in molecular weight.

The broad PA-6,6 peak, recorded for the nonmodified 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 about 20–21 min for the initial, nonmodified 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 can at a later stage be postcondensed to form a 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

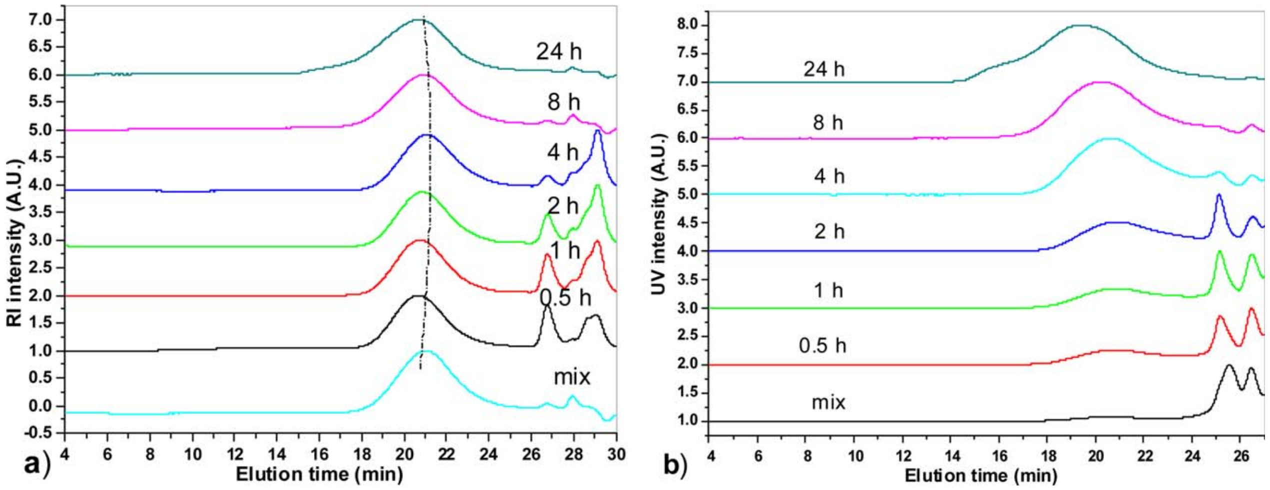


FIGURE 3 SEC chromatograms of SSM reaction products obtained by modification of $(PA66)_{80}(PxAd)_{20}$ at 200 °C: (a) RI detection and (b) UV detection. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

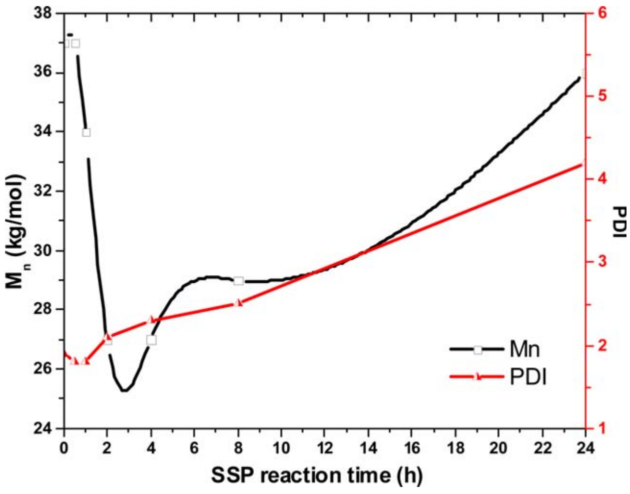


FIGURE 4 Number-average molecular weight (M_n) and PDI (from SEC) for the SSM product $(PA66)_{80}(PxAd)_{20}$ as a function of SSM reaction time at 200 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

after 8 and 24 h of SSM. During this postcondensation, the condensation product (water) is removed from the reaction mixture by the continuous inert gas stream passing through the reactor.

The UV detection chromatogram, shown in Figure 3(b), 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, AA 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, as 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. As 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 breakdown of the chains is a strong indication that not only the PXDA, but also the AA 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 nonequivalence 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 postcondensation (see Fig. 4), is typical for an SSP 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

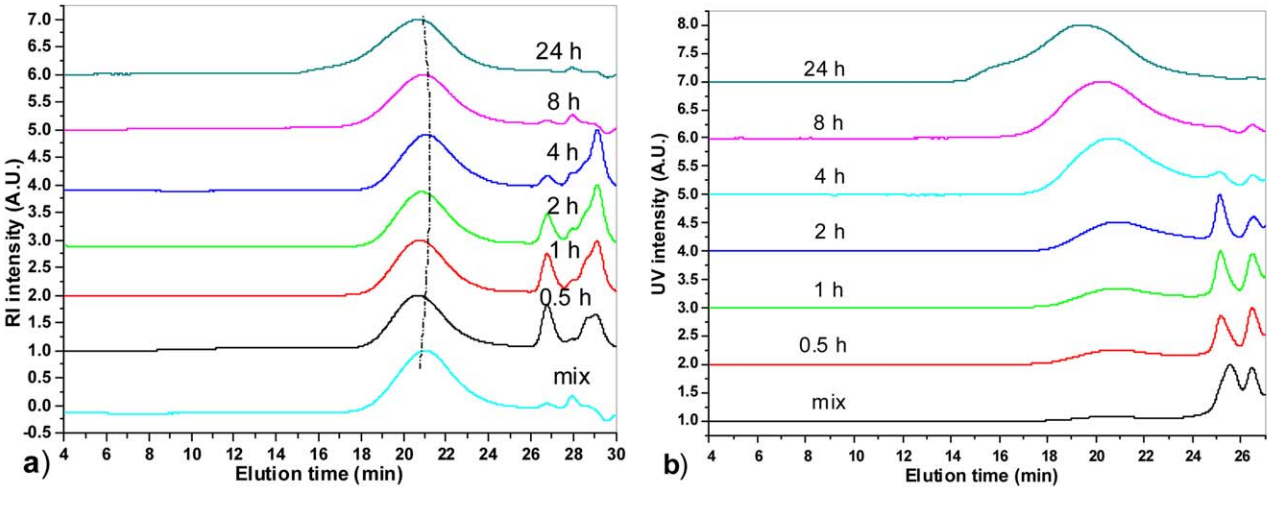
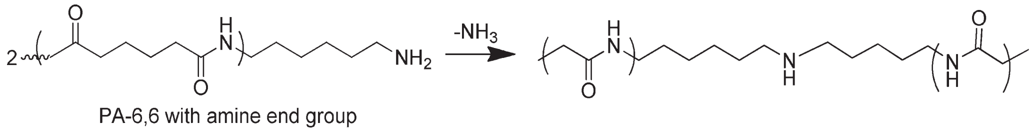


FIGURE 5 SEC chromatograms of SSM reaction products obtained from the sample $(PA66)_{80}(PxAd)_{20}$ upon reaction at 230 °C: (a) RI detection and (b) UV detection. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 2 Origin of cross-linking of PA-6,6 by amine end group reaction, causing higher molecular weight branched PA or even insoluble gels. The secondary amine can react with a carboxylic acid-terminated PA chain.

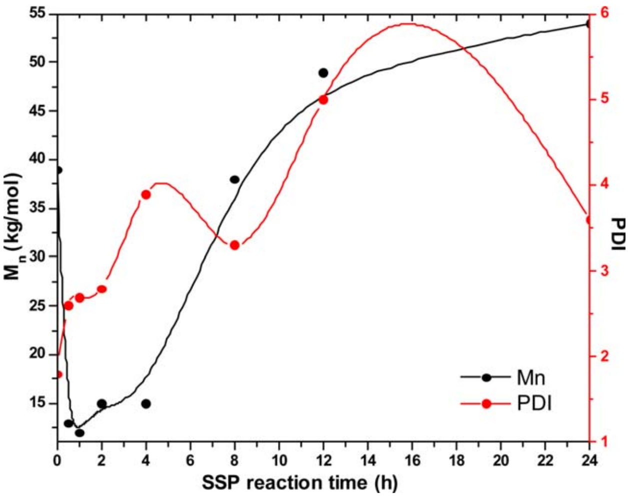


FIGURE 6 Molecular weight (M_n) and PDI as a function of SSM reaction time at 230 °C for $(PA66)_{80}(PxAd)_{20}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

trend, as seen in Figure 4, as during postcondensation some chains gain a lot in weight, whereas some low-molecular weight chains remain present. 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, as in this case after SSM no Flory[27] 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.[28] The resulting secondary amine group, still able to react with carboxylic acid groups, causes branching or even cross-linking (see Scheme 2), which is also confirmed by the development of a tail at lower elution times of about 14–16 min in the UV detection chromatogram of the SSM product [Fig. 3(b)]. Since the nonsoluble 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 postcondensation reaction dominates the chain scission reaction.

The same SSM reaction was done at 230 °C for 24 h under a 1 L/min inert gas stream (see Fig. 5 for SEC results). 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 Fig. 4 compared to Fig. 6). Also, during the second part of the SSM process, a much higher molecular weight was obtained due to a more efficient postcondensation 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 postcondensation already dominates after 1 h.

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 reaction kinetics of the trans-amidation at 230 °C is much faster than that at 200 °C (compare Figs. 4 and 6).

SSM of PA-6,6 with *m*-xylylenediamine

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 could fit in view of their similar distances (1.72 nm) between the hydrogen bonding motifs (*c*-axis of the unit cell of the crystal). So, after melting cocrystallization might be possible in the corresponding SSM products given the rather similar distance between the

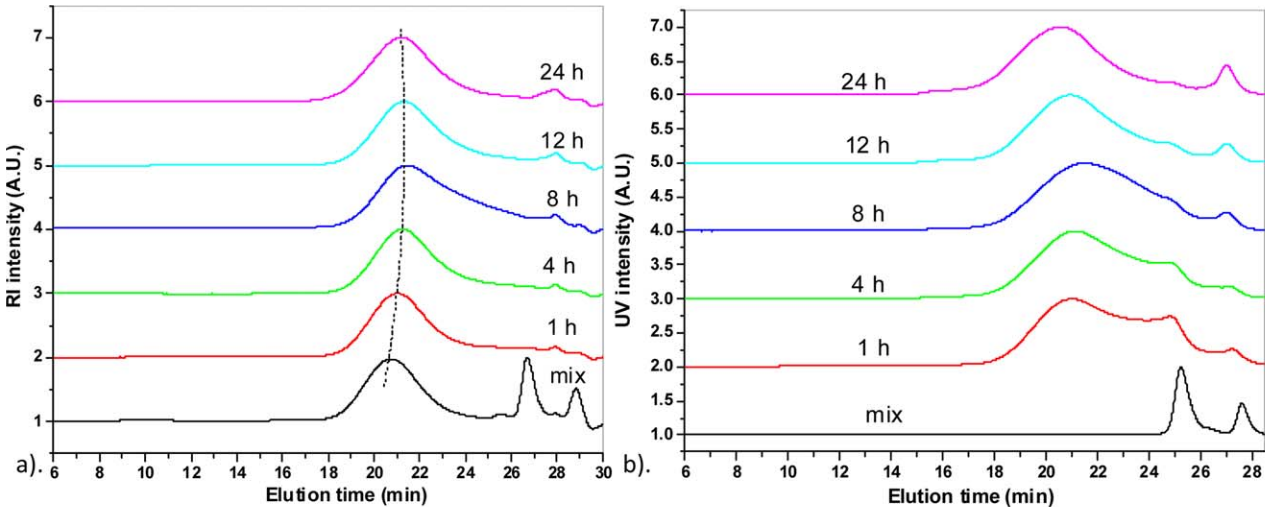


FIGURE 7 SEC chromatograms of SSM reaction products obtained from the sample $(PA66)_{80}(MxAd)_{20}$ at 200 °C: (a) RI detection and (b) UV detection. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

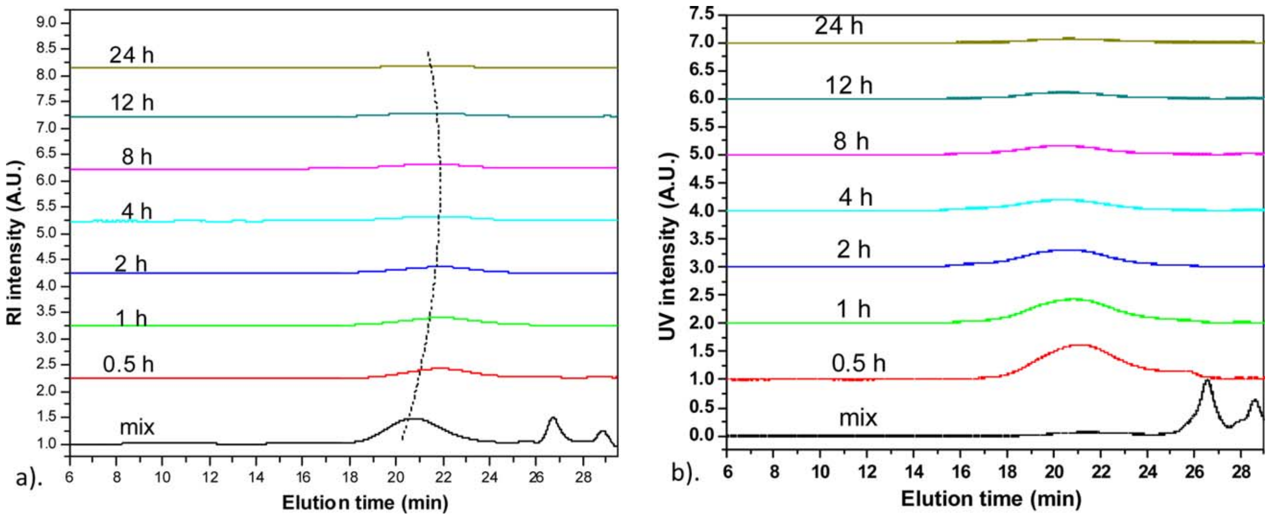


FIGURE 8 SEC chromatograms of SSM reaction products obtained for the sample $(PA66)_{80}(MxAd)_{20}$ at 230 °C: (a) RI detection and (b) UV detection. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nitrogens in PXDA and 1,6-hexamethylenediamine, the major difference being the presence of the phenyl group in PXDA. Therefore, it is interesting to investigate the modification of PA-6,6 with both MxAd and PxAd, as MXDA,6 units are not *a priori* expected to fit into the crystal lattice of PA-6,6. The possible cocrystallization studies will be presented in a subsequent article. 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 °C (see Fig. 7) and 230 °C (Fig. 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 if one compares Figures 6 and 9(b) at one and the same temperature. The higher the rate of transamidation, the faster is the chain scission resulting in a lower molecular weight.

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 initiation of the transamidation reaction of the SSP with MxAd comonomer salt is faster both at 200 and 230 °C. Hence, the comonomer salt disappears as soon as it is incorporated into the PA-6,6 backbone. This is supported by the development of intense UV peaks in the chromatograms.

The ^{1}H NMR spectra of the neat PA-6,6, the starting material, and the comonomer along with the solid state-modified product are given in Figure 10. The benzyl proton (G) of the comonomer is shifted from ∼3.5–4.0 to ∼4.5–5.0 ppm after incorporation into the aliphatic PA-6,6 backbone. The

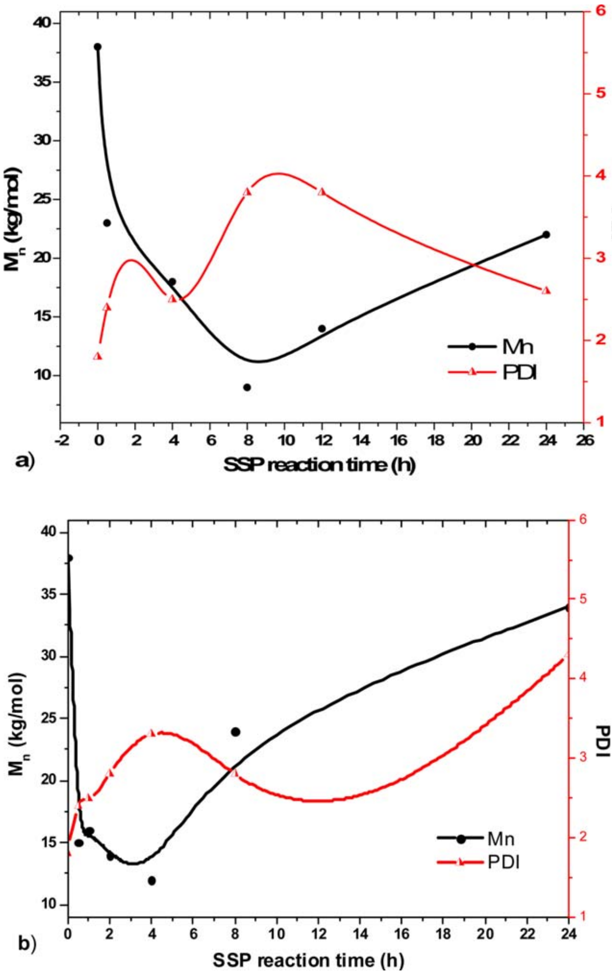


FIGURE 9 $(PA66)_{80}(MxAd)_{20}$: Molecular weight (M_n) and PDI as a function of SSM reaction time at reaction temperatures of (a) 200 °C and (b) 230 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

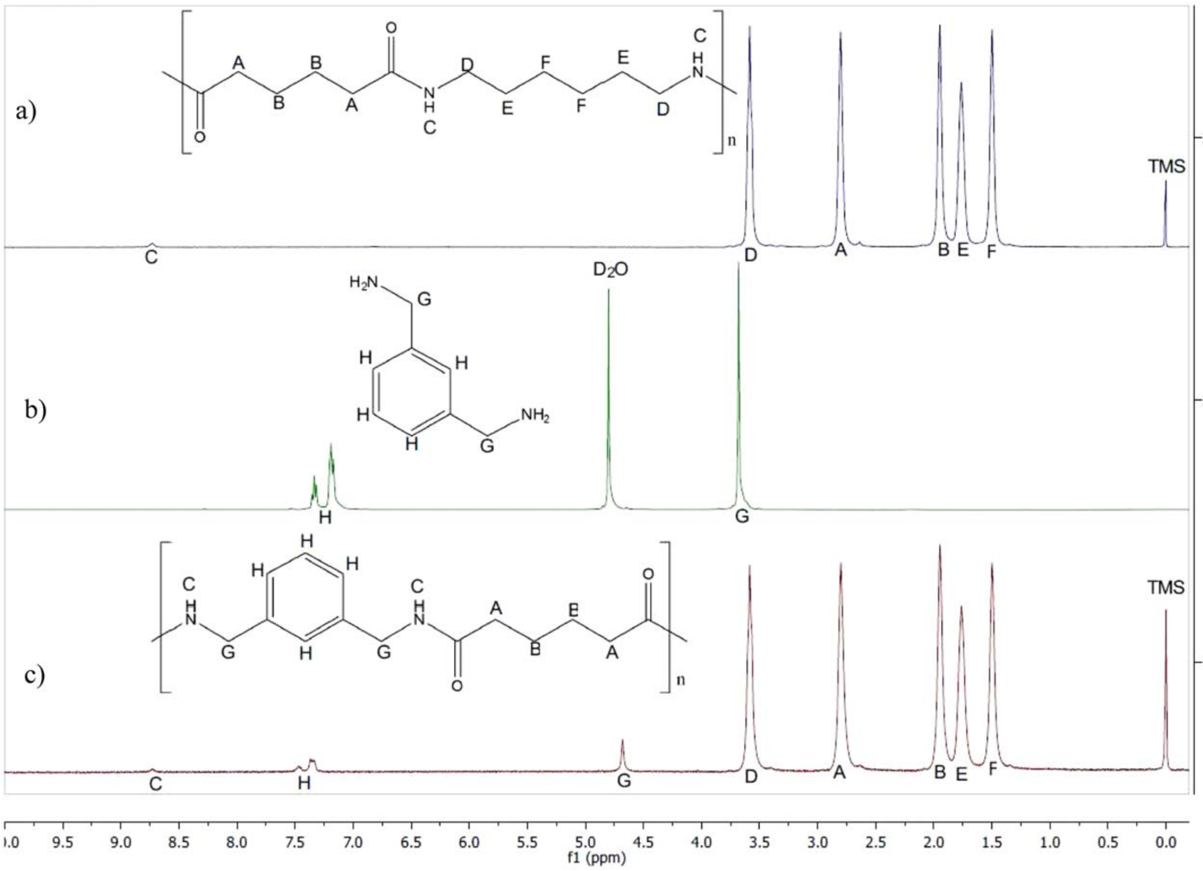


FIGURE 10 ^{1}H NMR spectra of the starting materials and the SSM reaction product of $(PA66)_{80}(MxAd)_{20}$ (top to bottom): (a) PA-6,6, (b) *m*-xylylenediamine, and (c) solid state-modified PA-6,6 with aromatic diamine MXDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amount of comonomer incorporation was calculated, both for the SSM and the corresponding melt copolymerization $(PA66)_{80}(MxAd)_{20}$ 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 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 article the copolyamide will still be identified as $(PA66)_{80}(MxAd)_{20}$).

Chemical Microstructure and its Effect on Thermal Transitions

The reaction products obtained after the SSM 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, as transreactions are expected to occur only in the amorphous phase leaving the crystalline, pure PA-6,6 phase intact. Conversely, the copolyamide prepared via the melt route (MP) is expected to be more random in nature. The microstructures, more specifically the copolyamide sequences, of the copolyamides with comparable molar ratio 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 of ^{13}C NMR spectra (Fig. 11) of polyamides as reported by Novitsky and Mathias.[29]

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 AA and a hexamethylene diamine) have different chemical shifts 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 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 values

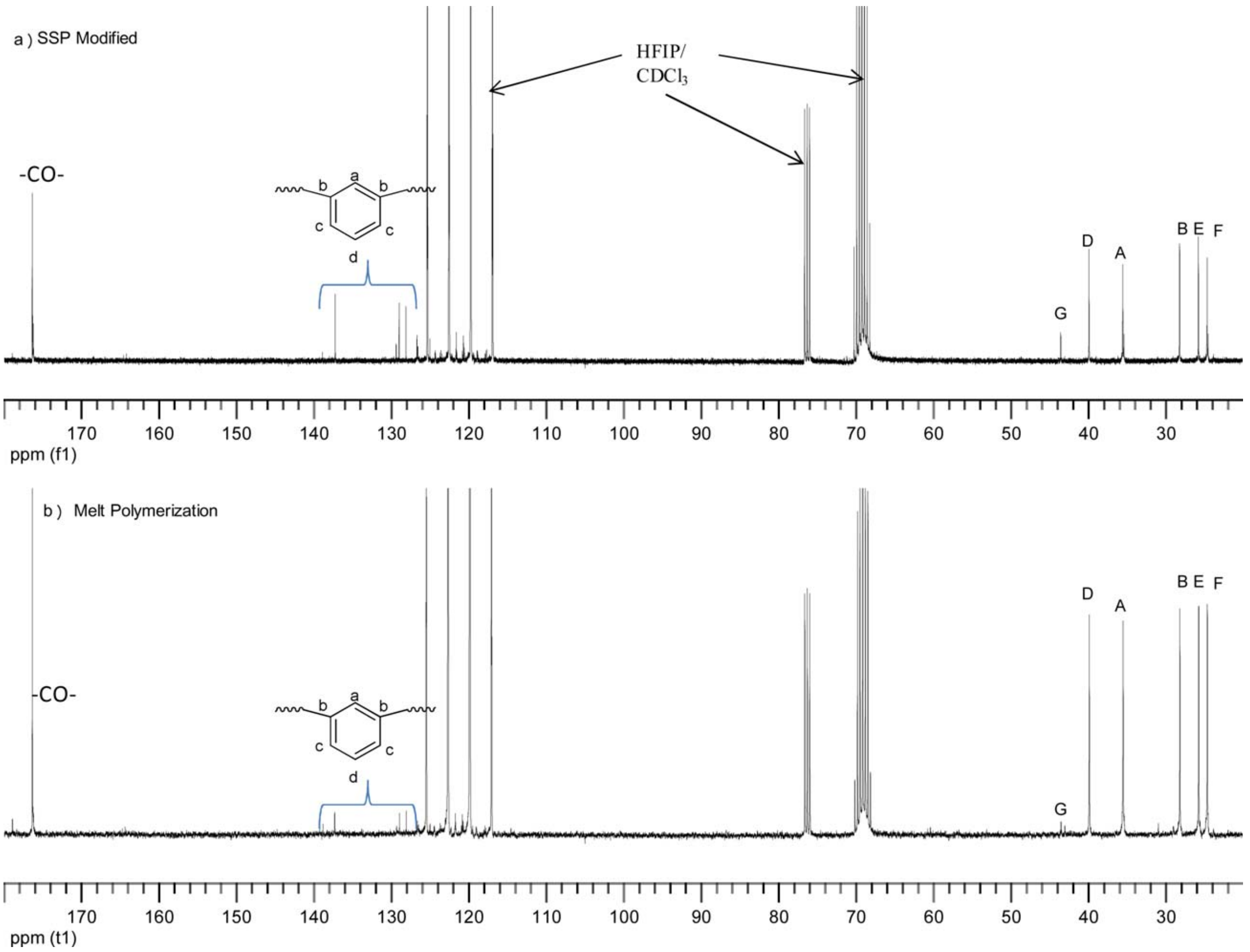


FIGURE 11 ^{13}C NMR spectra of $(PA66)_{80}(MxAd)_{20}$ copolyamide with 20 mol % of MxAd salt in the feed: (a) SSM reaction product and (b) analogous product by melt route. The structure given in Figure 10(c) was used for the peak identification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compared to carbonyl carbons surrounded by lower numbers of methylene diamine residues.[30–32]

The degree of randomness (R) of the copolyamides can be calculated using eqs 1–4, by incorporating the integral values listed under the deconvoluted peaks shown in Figure 13. These integral values of the four sequences are normalized to one.

$$F_{\text{HAØ,total}} = F_{\text{HAØ,HAØ-side}} + F_{\text{HAØ,ØAH-side}} \tag{1}$$

$$F_{\text{HAH ,total}} = \left(F_{\text{HA ØX,total}}\right)/2 + F_{\text{HAH}} \tag{2}$$

$$F_{\text{ØAØ,total}} = \left(F_{\text{HAØ,total}}\right)/2 + F_{\text{ØAØ}} \tag{3}$$

$$R_{\text{total}} = F_{\text{HAØ,total}}/2\left(F_{\text{HA-H ,total}} \times F_{\text{Ø A-Ø,total}}\right) \tag{4}$$

F_i denotes the molar fraction of each sequence, as shown in Figure 13. $F_{\text{HAH,total}}$, $F_{\text{HAØ,total}}$ denote the total molar fractions of the aliphatic and aromatic (MXD) side, respectively.

From Table 1, it is evident that the microstructure of the solid state-modified product is arranged in a more blocky way than that of the melt-route product having the same

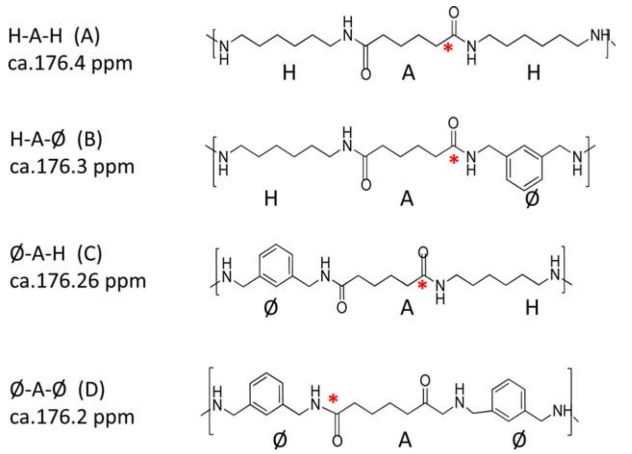


FIGURE 12 Four possible sequences (A–D) of dyads in the PA-6,6/MxAd copolyamides represented by their chemical structure. H = hexamethylene diamine, A = adipic acid, and Ø = *m*-xylylene diamine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

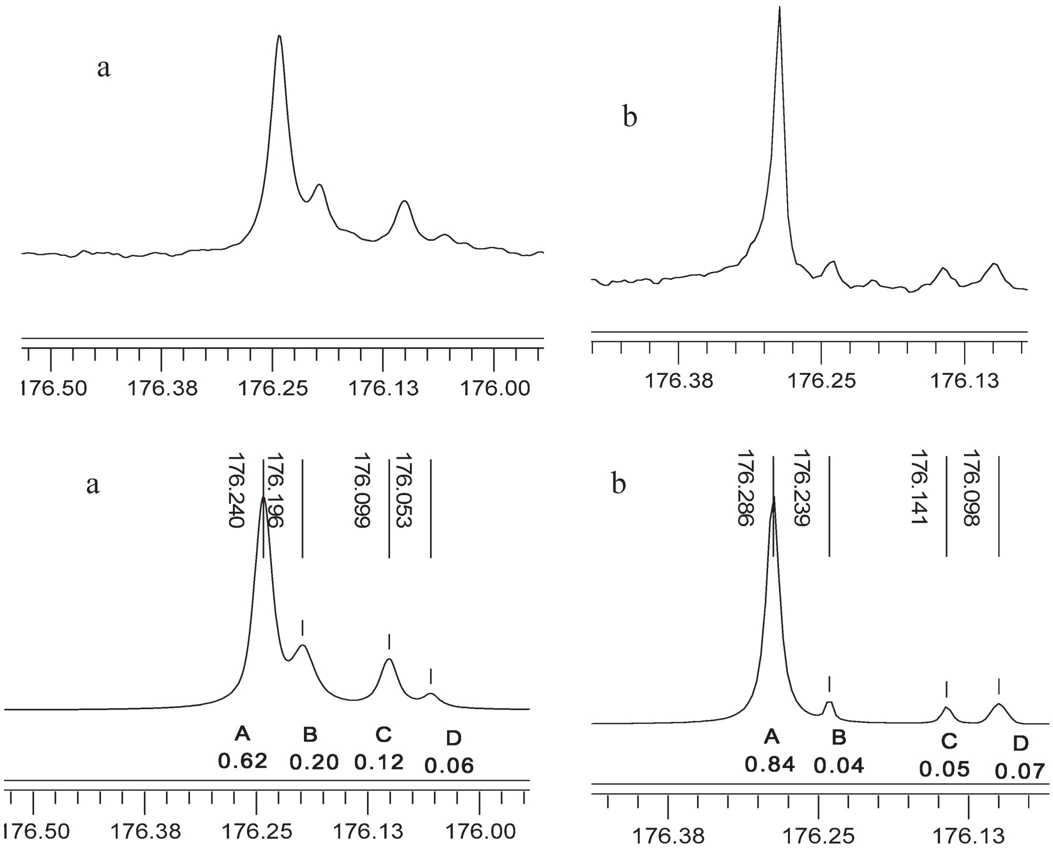


FIGURE 13 ^{13}C NMR spectra of $(PA66)_{80}(MxAd)_{20}$. As-recorded spectra above and deconvoluted spectra below of the carbonyl dyads in the 176.5–176.0 ppm region with A–D sequences of (a) melt-route product (MP) and (b) solid state-modified product.

overall chemical composition, as 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 14(b), it is apparent that the onset of the crystallization peak after the SSM 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 solid state-modified PA-6,6 is increased by ~11 °C [from ca. 55 to 63 °C, see Fig. 14(a)], by the incorporation of 17.0 mol % of MxAd salt. The crystallization temperature as well as the melting temperature determined during the second heating run of the solid state-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). This is due to the block-like structure of the SSM copolyamide, which affords relatively long pure PA-6,6 sequences and concomitantly thicker lamellae 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 cocrystallization of MXDA-based units with PA-6,6 repeat units. On the contrary, the SSM copolyamides modified by similar amounts of PxAd comonomer exhibited

TABLE 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 Solid State-Modified and Melt-Polymerized Copolyamides as Derived from ^{13}C NMR Spectra using eqs 2–5

No.	$(PA66)_{80}(MxAd)_{20}$ Copolyamide Synthesized by	$F_{HAØ,total}$	$F_{HAH,total}$	$F_{ØAØ,total}$	R_{total}
1.	Melt route	0.326	0.779	0.221	0.95
2.	Solid-state modification	0.085	0.844	0.113	0.43

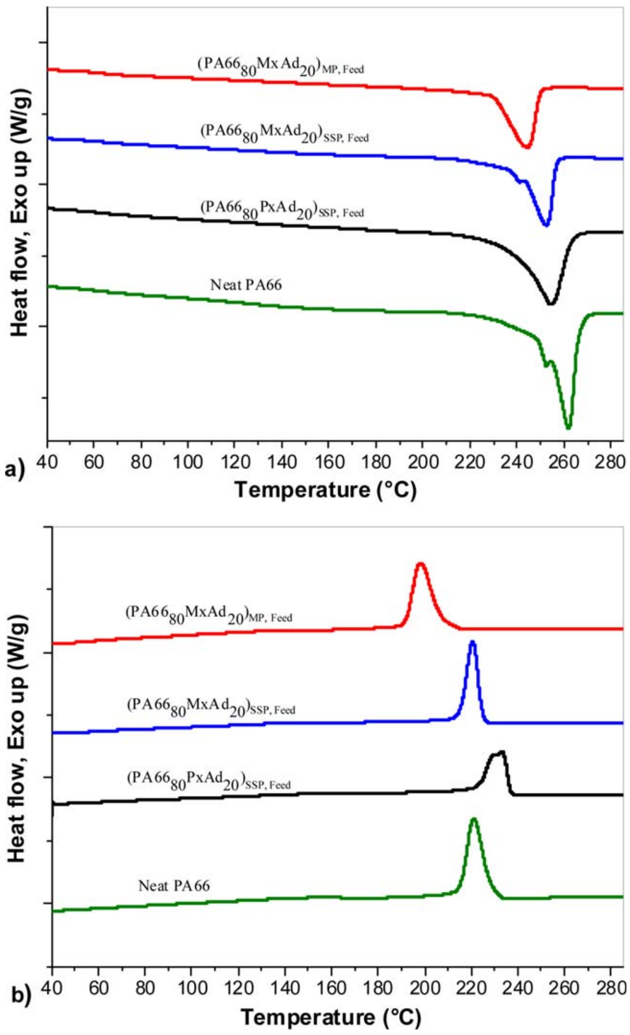


FIGURE 14 The DSC thermograms of unmodified PA-6,6 and PA-6,6 modified with 20 mol % MxAd, PxAd salt: (a) second melting run and (b) second cooling run. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a lower melting temperature than that of PA-6,6 (T_m ca. 254.5 °C, see Table 2), pointing to cocrystallization 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 temperature 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 melting enthalpies in Table 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 a subsequent article.

TABLE 2 Results of DSC Analysis of (PA66)$_{80}$(MxAd)$_{20}$ Copolyamide by Melt- and SSM-Route from Second Heating Cycles (10 °C/min)

No.	Sample	T_g (°C)	T_m (°C)	ΔHm (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

CONCLUSIONS

For the first time for polyamides of the PA-x.y type, a SSM of the amorphous phase of a polyamide was performed below the melting temperature. Semi-aromatic *para*- and *meta*-xylylene diamine/AA “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 cosolvent HFIP. SEC in combination with a UV detector confirmed the presence of the aromatic moiety in the aliphatic PA-6,6 main chain. As the PA-6,6 chain segments present in the crystals during the 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. As expected, the kinetics of the transamidation is much faster at 230 °C than at 200 °C and the solid state-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 products proved to be around 0.4, whereas for a melt-polymerized copolymer with a similar composition an *R* value of about 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 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 semiaromatic salt into the PA-6,6.

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