A Novel Production Route for Nylon-6: Aspects of Microwave-Enhanced Catalysis

J. Meuldijk,[1] B.H.P. van de Kruijs,[2] J.A.J.M. van Vekemans,[2] L.A. Hulshof,[2] R. Duchateau,[3] C.E. Koning[3]*

Summary: Microwave irradiation was used for the amidation of a nitrile with an amine with a freshly prepared zirconium-based heterogeneous catalyst. Microwave irradiation selectively heats the catalyst which enhances its activity as compared to conventional heating. The difference between microwave heating and conventional heating disappears when $Zr(OH)_4$ is used instead of ZrO_2, indicating a microwave-induced shift in the hydrolysis equilibrium, i.e. the distribution of ZrO_2, $ZrO(OH)_2$ and $Zr(OH)_4$, of the zirconium-based catalyst. The catalyst efficiently catalyzes the amidation of valeronitrile with *n*-hexylamine with conventional as well as with microwave heating. $Zr(OH)_4$ was also used for the polymerization of 6-aminocapronitrile using conventional and microwave heating. With both heating methods a relatively low molecular weight polymer with a M_n of 4000 g/mol was obtained in a sealed vessel, due to the presence of water and ammonia. A post-polymerization step under microwave irradiation, with active removal of water and ammonia shifts M_n to 10000 g/mol. Pressure decrease to facilitate water removal resulted in products with higher molecular weights. A pressure reduction to 50 Pa and operation in an argon atmosphere at 230 °C resulted in nylon-6 with a M_n of 65000 in rather short reaction times. Lower pressures led to end-biting and evaporation of the volatile ε-caprolactam at 230 °C. As a consequence the resulting product has than a much lower molecular weight. The combination of a heterogeneous zirconium based catalyst and microwave heating is promising for process intensification for nylon-6 production.

Keywords: 6-aminocapronitrile; amidation; microwave heating; nylon-6; polycondensation; porous zirconium based catalyst

Introduction

Nylon-6 is a commodity polymeric material with an annual production of (0.6–0.7) $\times 10^6$ kg in Western Europe alone.[1] This production scale makes a small reduction of the production costs economically relevant. Nylon-6 is produced commercially by ring opening polymerization of ε-caprolactam, which in turn is produced industrially from benzene, see Scheme 1. This ring opening polymerization process has been studied intensively and has been optimized.[1]

One way of reducing raw materials and energy consumption as well as reduction of overall production costs is short-cutting the chemical route by using an alternative starting material. A promising starting material is butadiene, which is industrially converted into 6-aminocapronitrile, see Scheme 2.[2]

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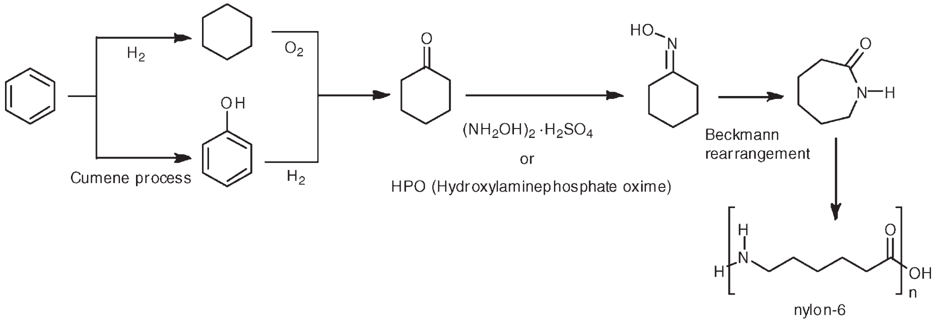
[1] Laboratory of Chemical Reactor Engineering, Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, P.O. Box 513, NL 5600 MB Eindhoven, The Netherlands
Fax (+31) 40 2446653; E-mail: j.meuldijk@tue.nl
[2] Applied Organic Chemistry Group, Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, P.O. Box 513, NL 5600 MB Eindhoven, The Netherlands
[3] Laboratory of Polymer Chemistry, Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, P.O. Box 513, NL 5600 MB Eindhoven, The Netherlands



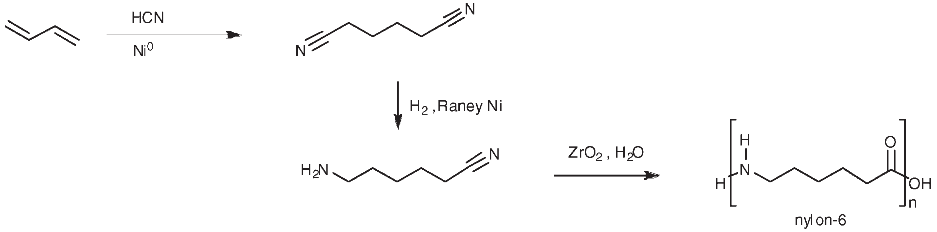
Scheme 1.
Commercial route to nylon-6 starting from benzene.

The conversion of 6-aminocapronitrile into nylon-6 only occurs in the presence of a catalyst. ZrO_2 is thought to catalyze the hydrolysis of the nitrile and subsequently the amidation.[3,4] Also TiO_2 has been reported as a good catalyst.[5] The influence of microwave heating on the ZrO_2-catalyzed production of nylon-6 from 6-aminocapronitrile is still unknown. So ZrO_2 was selected to investigate the influence of microwave irradiation on its catalytic activity. The use of microwave irradiation to activate a zirconium-based catalyst has been reported in a few articles.[6–8] The work reported in this paper focuses on the application of Zr-based catalysts for a novel route towards the production of nylon-6.[3,4]

Selective heating of the catalyst may lead to higher activities and enhanced selectivities. Application of microwave irradiation for the production of polymers in the melt has high potential.[9,10] For conventional heating the increase of the viscosity of the reaction mixture during the polymerization process may hamper the heat transfer from the reactor wall to the reactor content. Volumetric heating by microwave irradiation avoids these heat transfer limitations. However, the limited penetration depth of the microwaves limits the overall reactor size, hampering large scale production. This paper describes the performance of zirconium based catalysts towards nitrile amidation for microwave and conventional heating. An optimized procedure for the production of nylon-6 out of 6-aminocapronitrile with a high enough molecular weight using microwave heating is reported.

Experimental Part

The ZrO_2-catalyst was prepared by calcination of $Zr(OH)_4$. One batch was calcinated dynamically with an airflow of 300 °C in a packed bed of crushed compressed $Zr(OH)_4$ tablets, sieved on a 125–250 mesh sieve track. This dynamic calcination pro-



Scheme 2.
Alternative route to nylon-6 starting from butadiene.

Table 1.
Surface area and porosity of the zirconium catalyst.

	BET-surface area (m^2/g)	Pore diameter (nm)
Statically calcinated	155	5.3
Dynamically calcinated	226	4.1
Dynamically calcinated[3,4,12]	288	4.9

cess lasted 3 hours. Another batch was calcinated in an oven at 300 °C, i.e. static calcination. The specific surface area (BET) [11] as well as the average pore diameter for both calcination procedures are collected in Table 1.

Unless dynamic calcination resulted in the highest specific surface area, the catalyst performance in terms of activity and selectivity for both calcination methods towards the ZrO_2 catalyzed amidation of valeronitrile with *n*-hexylamine in the presence of water (see Scheme 3) was not significantly different. The reason for equal catalyst performance is the dynamic nature of the ZrO_2 - $Zr(OH)_4$ surface at the reaction temperature. For all experiments described the dynamically calcinated catalyst was used.

For microwave heated reactions a commercially available, automated multimode microwave oven MicroSynth from Milestone s.r.l. (Italy) was used. This oven operates at 2.45 GHz and is temperature controlled by a fiber-optic sensor. To eliminate significant temperature distributions the temperature was monitored by insertion of the fiber-optic sensor in the reaction mixture while stirring properly. The maximum power input could be adjusted between 0 and 1000 Watt.

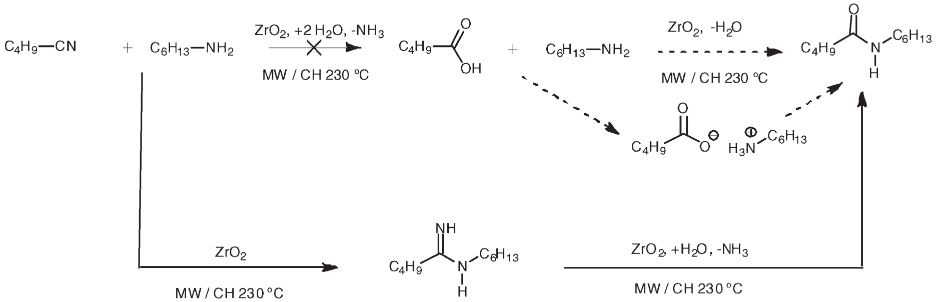
The reactions of valeronitrile with *n*-hexylamine and the polymerization of 6-aminocapronitrile were performed in the presence of water at 230 °C. During the reaction NH_3 is formed. In a closed system the pressure quickly rose to 3 MPa. These conditions require an autoclave setup. Figure 1 shows the autoclaves used for conventional and microwave heating.

Although the reactor for the conventionally heated experiment was much smaller, the loading of the reactors was chosen in such a way that the gas/liquid contact area and filling ratios were similar for both heating methods.

The detailed experimental procedures used for the amidation of valeronitrile with *n*-hexylamine (*i.e.* the model reaction) and the polymerizations of 6-aminocapronitrile are described hereafter.

Amidation of Valeronitrile with n-Hexylamine with Conventional Heating

Valeronitrile (0.87 g, 8.6 mmol), *n*-hexylamine (0.71 g, 8.6 mmol), water (0.31 g, 17.2 mmol) and $Zr(OH)_4$ (0.4 g, 2.5 mmol) were introduced in a stainless-steel reactor that contained a glass insert. The vessel was purged with argon for 10 min before sealing. The reaction mixtures were stirred with a magnetic stirring bar. The vessel was heated with a heating mantle to 230 °C for the mentioned time. The whole reaction mixture was cooled and the autoclave was



Scheme 3.
Model reaction for the determination of catalyst activity. Pathways of the zirconia-catalyzed amidation of valeronitrile with n-hexylamine.

Figure 1.
Autoclaves used for the zirconium-catalyzed amidation. Left: the conventionally heated reactor, stainless steel.[12] Right: microwave reactor, modified PTFE/PEEK (Milestone s.r.l., MedCHEM Kit, Reactor 45111T, MW radiation 2.45 GHz, temperature control with a fiber optic sensor). The relevant dimensions are collected in Table 2.

opened. A small aliquot was dissolved in $CDCl_3$ and filtered. The conversion was determined by ^{1}H-NMR and GC/MS. *N*-hexylpentanamide: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.68 (br s, 1H), 3.20 (q, 2H), 2.21 (t, 2H), 1.58 (m, 2H), 1.46 (m, 2H); 1.26 (m, 8H), 0.86 (m, 6H); GC/MS: r.t. 7.0 min., m/z: 185.2. Maximum yield = 1.51 g (95%).

Amidation of Valeronitrile with *n*-Hexylamine with Microwave Irradiation

Valeronitrile (8.7 g, 86 mmol), *n*-hexylamine (7.1 g, 86 mmol), water (3.1 g, 172 mmol) and $Zr(OH)_4$ (4 g, 25 mmol) were introduced the microwave reactor The vessel was purged with argon for 10 min before sealing. The reaction mixtures were stirred with a magnetic stirring bar. The vessel was heated by microwave irradiation (maximum power = 300 W) to 230 °C for the time mentioned. The reaction mixture was cooled to room temperature and the autoclave was opened. A small aliquot was dissolved in $CDCl_3$ and filtered. The conversion was determined by ^{1}H-NMR and GC/MS. *N*-hexylpentanamide**:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.68 (br s, 1H), 3.20 (q, 2H), 2.21 (t, 2H), 1.58 (m, 2H), 1.46 (m, 2H); 1.26 (m, 8H), 0.86 (m, 6H); GC/MS: r.t. 7.0 min., m/z: 185.2. Maximum yield = 15.2 g (97%).

Polymerization of 6-Aminocapronitrile with Microwave Irradiation

6-Aminocapronitrile (9.0 g, 80 mmol), water (2.9 g, 160 mmol) and $Zr(OH)_4$ (4.0 g, 25.3 mmol) were introduced in the microwave reactor The vessel was purged with argon for 10 min before sealing. The reaction mixtures were stirred with a magnetic stirring bar. The vessel was heated by microwave irradiation (maximum power = 300 W) to 230 °C for the time mentioned. The complete reaction mixture was cooled to room temperature and the autoclave was opened. Either a small aliquot was taken and the vessel was resealed or the complete reaction mixture was subjected to the work-up procedure. For the polymerizations the reactor setup did not allow the polymer-catalyst separation in the melt. The separation was achieved by first dissolving the polymeric product in formic acid. The zirconia catalyst was removed by centrifugation during 30 min at 4000 rpm and subsequent decantation. The polymer was precipitated by pouring the liquid phase into water. The precipitate was separated from the liquid phase by centrifugation during 30 min at 4000 rpm followed by decantation. The polymer was redispersed in ethanol and separated from the liquid phase by centrifugation for 30 min at 4000 rpm and subsequent decantation. The polymer was dried in a vacuum-oven at 50 °C for 24 h. This method resulted in the loss of the low molecular weight fraction of the product (mainly ε-caprolactam). The yield was 80%.

Post-Polymerization Treatment

A three-neck 50 mL flask was charged with 10 g of crude product of the sealed-vessel polymerization (*i.e.* not subjected to the precipitation procedure). A temperature probe was inserted and an air-inlet (or argon-inlet) tube was connected to the neck of the flask. The air-inlet (or argon-inlet) tube was connected to a capillary tube. The capillary tube ensured a constant air-flow (or argon-flow). The flask was held at a constant pressure of 5 kPa (or 50 kPa) by an oil pump connected to the other neck. A Dean-Stark apparatus was connected to the flask and the reaction mixture was heated to 230 °C by temperature-controlled microwave irradiation ($P_{max} = 350$ W). The temperature was maintained for the described times by microwave irradiation ($P_{max} = 200$ W). The reaction mixture was subjected to the work-up procedure described above.

Polymerization of 6-Aminocapronitrile with Conventional Heating

6-Aminocapronitrile (0.90 g, 8.0 mmol), water (0.29 g, 16.0 mmol) and $Zr(OH)_4$ (0.40 g, 2.53 mmol) were introduced in a stainless-steel reactor that contained a glass insert. The same procedure was used as described above, substituting microwave heating by a heating mantle.

The molecular weight distributions of the polymerization products were determined by Size Exclusion Chromatography (SEC).

The SEC system was equipped with a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector (40 °C), a Waters 2707 autosampler and a PSS PFG guard column followed by 2 PFG-linear-XL (7 μm, 8 × 300 mm) columns in series operated at 40 °C. Hexafluoroisopropanol (HFIP, Apollo Scientific Limited) with potassium trifluoroacetate (3 g/l) was used as eluent at a flow rate of 0.8 $mL \cdot min^{-1}$. The molecular weights were calculated against polymethyl methacrylate standards (Polymer Laboratories, $M_p = 580$ Da up to $M_p = 7.1 \times 10^6$ Da).

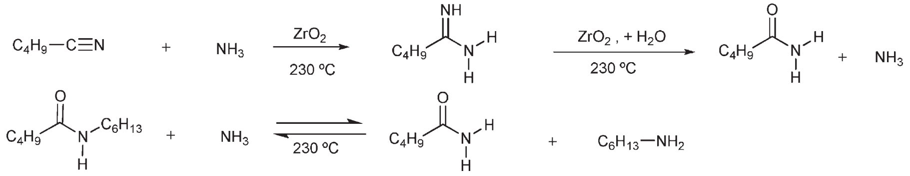
Microwave-Zirconium Interactions

Selective heating is the main reason that microwave irradiation may lead to different reaction rates, products and selectivities. Selective heating occurs when the preferred absorption of microwaves by the dispersed component, *i.e.* the Zr-based catalyst, leads to a substantial temperature difference between the dispersed and the continuous phase. The results of thermographic imaging experiments as well as heating measurements of mixtures of valeronitrile and *n*-hexylamine (*i.e.* the reaction mixture of the model reaction see Scheme 3) with and without the Zr-based catalyst demonstrate that MW-irradiation results in selective heating of the catalyst. [13]

Amidation of Valeronitrile with *n*-Hexylamine

The amidation of valeronitrile with *n*-hexylamine was performed with conventional and MW heating at 230 °C. Since in this reaction no polymerization can take place it is suitable to monitor the influence of microwave heating on the activity of the ZrO_2-catalyst towards amidation, see Scheme 3.

To prove whether ZrO_2 actually catalyzes the hydrolysis of valeronitrile, the nitrile was first treated with both water and the catalyst at a temperature of 230 °C. Surprisingly, even after prolonged heating, no significant hydrolysis of valeronitrile was observed, indicating that the reaction pathway does not follow nitrile hydrolysis and subsequent amidation. However, the reaction to the amide proceeds in the presence of *n*-hexylamine. These observations strongly indicate that the pathway involves addition of *n*-hexylamine to valeronitrile yielding *N*-hexyl pentane-amidine followed by



Scheme 4.

Reactions leading to pentanamide and *n*-hexylamine caused by the presence of ammonia in the reaction mixture.

in-situ hydrolysis to *N*-hexyl pentanamide. During this hydrolysis NH_3 is formed. Scheme 4 shows possible reactions of the ammonia formed. NH_3 acts as a nucleophile and reacts with valeronitrile yielding pentane-amidine which is hydrolyzed to the primary amide (pentanamide). Alternatively, pentanamide as well as *n*-hexylamine may also be formed by transamidation of *N*-hexyl pentanamide and ammonia.

Removal of NH_3 will accelerate the formation of N-hexylpentanamide and leads then to a higher valeronitrile conversion, see Figure 2. However, the cooling and heating cycles, required for removal of NH_3 safely, are undesirable. On larger scale this may be overcome by a proper equipment solution, see Meuldijk *et al.* [14]

The high temperature and the required presence of water in the reactor raised the question whether calcination of $Zr(OH)_4$ is essential before use. The dynamic character of the water chemisorption on the ZrO_2 surface at these temperatures could lead to an *in-situ* generation of $Zr(OH)_4$, thus blurring the distinction between both zirconium species in the reaction mixture. Therefore, determining which is actually the active catalytic species, ZrO_2 or $Zr(OH)_4$, is difficult. The dynamic nature of the zirconium species was tested by starting with $Zr(OH)_4$. The catalytic activity of the $Zr(OH)_4$ form of zirconium outperformed the non-hydrated ZrO_2-catalyst, making the cumbersome calcination step obsolete. As compared to ZrO_2, the difference between microwave and conventional heating using $Zr(OH)_4$ diminished, indicating an influence of microwave irradiation on the transformation of ZrO_2 into $Zr(OH)_4$ and vice versa, see Scheme 5.

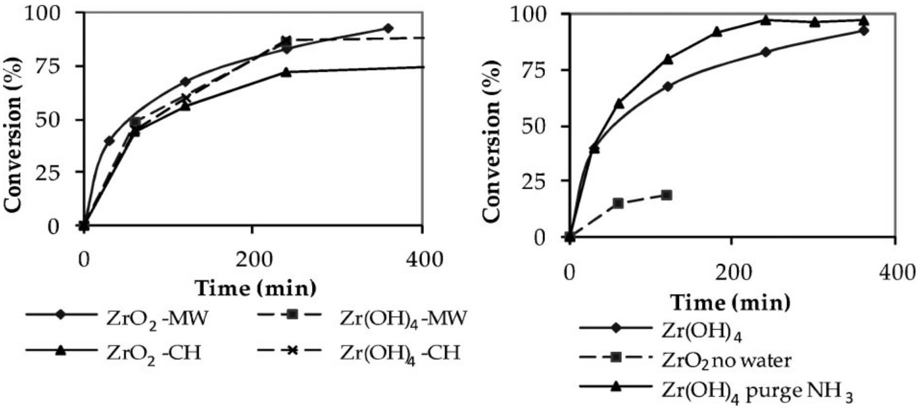
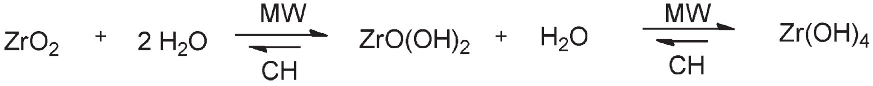


Figure 2.

Conversion-time histories of the amidation of valeronitrile with n-hexylamine. Left: various ZrO_2 and $Zr(OH)_4$ grades under microwave and conventional heating. Right: the effect of NH_3 removal on the conversion-time history under microwave irradiation.



$$ZrO_2 + 2\,H_2O \underset{CH}{\overset{MW}{\rightleftharpoons}} ZrO(OH)_2 + H_2O \underset{CH}{\overset{MW}{\rightleftharpoons}} Zr(OH)_4$$

Scheme 5.
Reversible reactions between ZrO_2 and $Zr(OH)_4$.

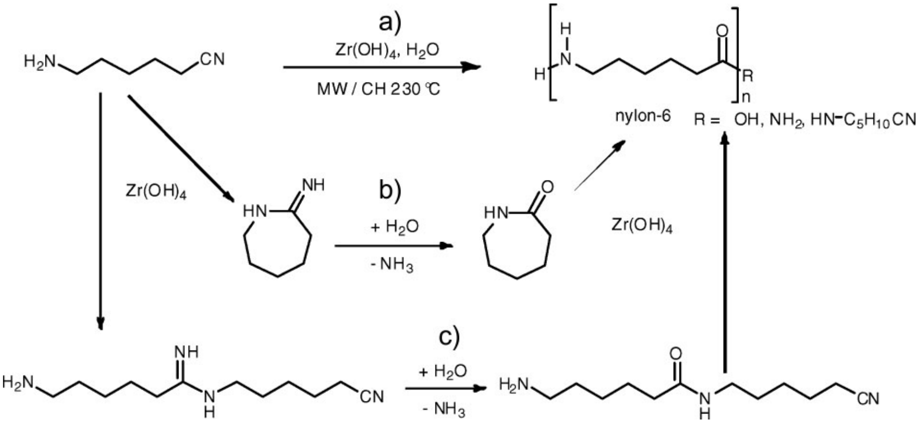
This can be rationalized by the observation that both ZrO_2 and $Zr(OH)_4$ heat very rapidly with microwave irradiation. The enhanced reaction rate with ZrO_2 under microwave irradiation, compared to conventional heating, and the disappearance of this effect with $Zr(OH)_4$ as catalyst is a strong indication that $Zr(OH)_4$, or $ZrO(OH)_2$, are the active species. This is confirmed by the low conversion of the reaction when performed with ZrO_2 in the absence of additional water, see Figure 2 (right).

Producing Nylon-6 out of 6-Aminocapronitrile

The synthesis of nylon-6 starting from 6-aminocapronitrile was performed using $Zr(OH)_4$ as catalyst, see Scheme 6.

The polymerization of 6-aminocapronitrile, pathway a, may proceed via numerous intermediates. A selection of anticipated pathways is also illustrated in Scheme 6. The zirconia-catalyzed intramolecular addition of the amine to the nitrile, generating azepan-2-imine, pathway b, leads to polymerization via hydrolysis of the imine to ε-caprolactam. ε-caprolactam is able to polymerize under the influence of heat and/or the zirconium-based catalyst. This polymerization route yields nylon-6 with terminal amide groups. These end groups can in principle be hydrolyzed into the corresponding carboxylic acid. The intermolecular addition to a nitrile can also occur, see pathway c in Scheme 6. Subsequent hydrolysis and repeated addition of another amine molecule would generate nylon-6 with terminal nitrile groups. Note, that hydrolysis of these nitrile end-groups to the primary amide or the carboxylic acid does not occur, see Scheme 3.

Polymer scission during the reaction may also occur either by reaction with ammonia, generated by the polymerization process, or by reaction with water, necessary for the hydrolysis, yielding oligomers with terminal primary amide or terminal carboxylic acid groups, respectively. These



Scheme 6.
Postulated reaction pathways for the conversion of 6-aminocapronitrile into nylon-6.

Table 2.
Dimensions of the autoclaves used for comparing microwave heating (MW) with conventional heating (CH).

	Diameter (cm)	Height (cm)	Contact area (cm^2)	Volume (cm^3)	Filling ratio (%)
MW	3.5	9	9.6	86.6	27
CH	1.1	7.3	0.95	6.9	34

oligomers may further polycondensate into higher molecular weight nylon-6.

The produced polymer was analyzed using FT-IR. A typical absorption band for a nitrile end group (2300 and 2200 cm^{-1}) was not present in the IR-spectra, clearly indicating the absence of nitrile end-groups in the product. Maldi-TOF analysis of the oligomers showed that the end-groups are primary amide and carboxylic acid functions. These FT-IR and Maldi-TOF results point to the intermolecular addition, see pathway c in Scheme 6, to be not significant in the polymerization process.

The results of the polymerizations of 6-aminocapronitrile are collected in Table 3 for conventional heating and in Table 4 for microwave irradiation.

The molecular weight distribution data of the nylon-6 samples, as given in these tables, indicate that the reaction goes to equilibrium within one hour, yielding a polymer with a number average molecular weight (M_n) of 4000–4500 g/mol applying conventional heating. The polydispersity index ($PDI = M_w/M_n$) was in the range of

Table 3.
Molecular weight distribution of nylon-6 samples prepared under conventional heating conditions.

Time (min)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	Remark
60	4202	5163	1.27	Closed[a]
120	4315	5983	1.34	Closed[a]
240	4445	5172	1.39	Closed[a]
60 + 60	4276	5845	1.37	NH_3 removal[b]
60 + 60 + 60	4929	7083	1.44	NH_3 removal[b]

[a]Closed vessel, 230 °C,[b]Vessel was cooled to room temperature and opened for the removal of NH_3 after 1 h reaction. After NH_3 removal the reaction vessel was reclosed and heated again to the reaction temperature.

Table 4.
Molecular weight distribution of nylon-6 samples prepared under microwave heating conditions.

Time (min)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	Remark
30	3819	4365	1.41	Closed[a]
60	4600	6048	1.31	Closed[a]
240	3543	4855	1.37	Closed[a]
30 + 20[b]	6183	12360	1.99	Closed[a] + Reflux[c]
60 + 10[b]	6625	12455	1.88	Closed[a] + Reflux[c]
30 + 40[b]	10234	20061	1.96	Closed[a] + Dean Stark[d]
30 + 10[b]	7474	12727	1.70	Closed[a] + 5 kPa[e]
30 + 30[b]	7176	12181	1.70	Closed[a] + 5 kPa[e]
30 + 10[b]	7668	13303	1.73	Closed[a] + 50 kPa[f]
30 + 20[b]	6756	12016	1.77	Closed[a] + 50 kPa[f]
30 + 30[b]	6399	11505	1.80	Closed[a] + 50 kPa[f]
20	8163	14896	2.85	ε-Caprolactam[g]
30 + 40	65336	179288	2.74	Closed[a] + 50 kPa argon[h]

[a]Closed vessel and T = 230 °C,[b]second time corresponds to treatments listed under the remarks column,[c]Reflux condenser and T = 230 °C,[d]T = 230 °C with Dean-Stark apparatus for the removal of water,[e]Reduced pressure (5 kPa with airflow) 230 °C,[f]Reduced pressure (50 kPa with air-flow) T = 230 °C with Dean-Stark apparatus for the removal of water,[g]ε-Caprolactam and $Zr(OH)_4$ at 230 °C with Dean-Stark apparatus for the removal of water,[h]Reduced pressure (50 kPa with argon-flow) T = 230 °C with Dean-Stark apparatus for the removal of water.

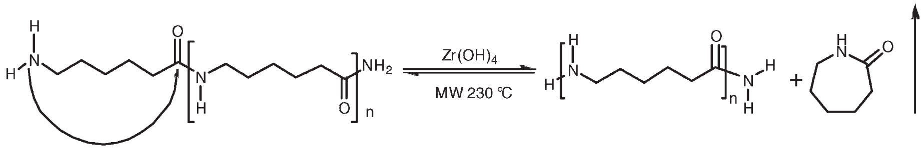
1.3–1.4 for all equilibrium situations. This is lower than the expected final PDI of 2 for polycondensation reactions.[15] This deviation is caused by the work-up procedure of the polymer. During the precipitation step, low molecular-weight fractions stay dissolved in the water, thus shifting M_n to higher values but having limited influence on the M_w. The reaction was performed in a closed vessel, causing ammonia, being generated during the reaction, and water, which is necessary for the hydrolysis of the amidine, to be trapped, resulting in an equilibrium between oligomers, 6-aminocaproamide and 6-aminocapronic acid. In analogy with amidation of valeronitrile with *n*-hexylamine (see the previous section), removal of ammonia shifts this equilibrium towards higher molecular weight material, see Table 3.

Unfortunately, the effect of ammonia removal is modest, increasing M_n to 5000 g/mol after three consecutive heating and ammonia removal steps. This modest effect and the cooling and heating cycles, that are required for safe NH_3 removal, are undesirable, limiting the value of this way of operation.

Additionally, the polymerization reaction was performed applying microwave heating in a closed system. The results collected in the Tables 3 and 4 demonstrate that a molecular weight of 15000 g/mol, required for commercial nylon-6, could not be reached in a closed system for conventional as well as for microwave heating. Therefore, a post-polymerization under reflux was performed. Selective heating of the catalyst by microwave irradiation facilitated rapid heating of the reaction mixture. Also the heat transfer limitations, caused by the high viscosity of the reaction mixtures with high molecular weight material, did not play a role with microwave heating. The post-polymerization under reflux increased M_n to 6000–6500 g/mol. Active removal of water by a Dean-Stark setup shifted this molecular weight to even higher values. After 40 min a product with a M_n of 10000 g/mol was obtained. This is relatively close to the M_n for commercial products. The polydispersity index of the polymer produced at atmospheric pressure was around 2, corresponding with the equilibrium state at high conversion. The low molecular-weight fraction is small in these polymers, limiting the influence of the work-up procedure on the polydispersity index.

Reaction at 5 kPa with a constant air flow over the reaction mixture to guarantee continuous removal of water and ammonia increased M_n and M_w to respectively 7000 and 12000 g/mol. The molecular weight of the polymer was limited and the yield of the polymer was low as a result of a reversible degradation reaction of the nylon-6 and subsequent evaporation of ε-caprolactam, see Scheme 7. Note that the boiling point of ε-caprolactam is 160 °C at 5 kPa.

To circumvent the removal of ε-caprolactam from the reaction mixture, a reduced pressure of 50 kPa was employed. At this pressure the reaction temperature was well below the boiling temperature of ε-caprolactam. An M_n of 7600 g/mol was obtained in 10 min and this molecular weight steadily decreased in time. The air-flow over the sample removed the generated water but also introduced oxygen in the system. Oxygen is responsible for degradation and discoloration of the molten polymer, limiting its molecular weight.



Scheme 7.
Degradation of nylon-6 by "end-biting" and subsequent removal of ε-caprolactam.

Substituting the air-flow by an argon-flow at a reduced pressure of 50 kPa prevented oxidation. After 40 min of microwave treatment a product with a M_n of 65000 g/mol was obtained. For the polymer produced from 6-aminocapronitrile as well as from ε-caprolactam by microwave irradiation, the polydispersity indices are in the range between 2.7 and 2.9. For conventional heating it was reported that the same procedure resulted in a product with a M_n of 10000 g/mol after 24 hours and at 250 °C.[3,12] The polydispersity indices of the polymers produced by microwave irradiation as well as that of the reported polymer [3,12] were in same range. The polydispersity indices point to a different reaction mechanism for the $Zr(OH)_4$ catalyzed polymerizations and the conventional polymerization of ε-caprolactam (*i.e.* PDI = 2).

The microwave-assisted ring opening polymerization of caprolactone[16] and ε-caprolactam[17] without heterogeneous catalyst has been reported. The ring opening polymerization of ε-caprolactam at 220 °C was reported not to proceed and an increase of process temperature to 250 °C with a nitrogen flow for more than 2 hours was necessary to yield a polymer with sufficient molecular weight (24000 g/mol).[17] Therefore, the polymerization of ε-caprolactam with $Zr(OH)_4$ as catalyst was studied. This resulted in a number-averaged molecular weight of 8160 in only 20 min, stressing the high catalytic activity of the zirconia-based catalyst.

Conclusion

Microwave irradiation selectively heats the zirconia-based catalyst. This selective heating causes a shift in the hydrolysis equilibrium of the catalyst governed by three equilibrated Zr-species, *i.e.* ZrO_2, $ZrO(OH)_2$ and $Zr(OH)_4$. The catalyst proved to be suitable for the amidation of valeronitrile with *n*-hexylamine, making it a promising catalyst for the polymerization of 6-aminocapronitrile into nylon-6.

The polymerization of 6-aminocapronitrile in a sealed vessel yielded limited molecular weight polymer with conventional as well as microwave heating. A post-polymerization step increased the molecular weight by the active removal of water and ammonia. The combination of the $Zr(OH)_4$ catalyst with microwave irradiation resulted in a very high molecular weight nylon-6 from 6-aminocapronitrile as well as from ε-caprolactam. Reaction times were short reaction times and the reaction conditions were relatively mild. So the application of a $Zr(OH)_4$ catalyst in combination with microwave heating is a promising concept for process intensification for nylon-6 production.

Acknowledgements: The authors like to thank the Senter-Novem (The Netherlands) for financial support.

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