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Redefining polyamide property profiles via renewable long-chain aliphatic segments: Towards impact resistance and low water absorption

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ABSTRACT

A series of renewable, long-chain, fatty acid-derived polyamides (PA) ranging from PA 6,14 to PA 6,18 were synthesized via polycondensation, yielding very high molecular weights and a remarkable property profile distinct from short-chain commercial grades. Most notably, synthesized polyamides exhibited good impact resistance, excellent stiffness-to-toughness balance and very low water absorption yet high oxygen and water vapour permeability; with this property profile being exemplified by PA 6,18. The increased repeating unit length and reduced number of amide linkages able to participate in interchain hydrogen bonding imparted a strong influence on material properties. The data highlights the benefits and technical advantages of utilising long-chain polyamides, while also significantly expanding the repertoire, knowledge and property profile of the long-chain aliphatic polyamide family, and providing a basis for further development of polyamides from renewable sources.

KEYWORDS

Polyamide, molecular weight, renewable, impact strength, water absorption

INTRODUCTION

Within all polyamides, inter- and intramolecular hydrogen bonding between amide groups are amongst the most important and interesting phenomena, appearing in both crystalline and amorphous domains. Their presence and the extent to which they occur is responsible for a range of different material characteristics and properties, including melting temperature, the degree of water absorption, tensile strength, impact strength, density, solvent resistivity, etc ¹. Short aliphatic-segment polyamides such as polyamide 6 (PA 6) or polyamide 6,6 (PA 6,6) have a relatively high ratio of amide:methylene groups per repeating units; this correlates to a high degree of hydrogen bonding between polymer chains. The strong nature of these bonds results in polyamides that typically exhibit high melting temperatures, superior tensile strength and resilience values, and good abrasion resistance. However, one negative consequence of the presence of amide groups is their high sensitivity to moisture. The adsorbed water molecules behave as plasticizing agents, while also reducing the number of potential sites that can participate in inter-polyamide chain hydrogen bonding. As a result, strength and stiffness are reduced and dimensional instability increases. Furthermore, polyamidation is a reversible reaction in which amide linkages can be broken and lead to chain scissoring. Thus, water molecules which are adsorbed during polymerisation are able to cause hydrolysis degradation for polyamides ².

Long-chain, aliphatic PAs are a well-established class of polyamides, which for the purpose of this manuscript will be defined as possessing a repeating unit with a carbon number of 10 or higher. Within AABB-type polyamides, this increased repeating unit length is usually derived from the dicarboxylic acid segment (eg. PA 6,10, PA 6,12), however it can also stem from the diamine component (eg. PA 10,10). These PAs possess a range of attractive properties, including high mechanical strength, good solvent stability/resistance, lower melting temperatures and low moisture absorption ^{3,4}. In particular, reduced moisture absorption gives long-chain PAs a competitive edge over their shorter-chain counterparts, such

as PA 6 and PA 6,6. This stems from the longer segments of aliphatic chain, and higher ratio of methylene:amide linkages per repeating units. As such, they have found use in a broad field of applications, including packaging, automotive components, sporting equipment, cables and tubing ⁴.

As with many classes of polymer, the push towards bio-based or renewable source materials and monomers has caused a search for new polyamide synthesis techniques ⁵. This generally involves the use of di-acids which are derived (eg. hydrolysis or alcoholysis) from fatty acid triglycerides, which constitute up to 95 %wt of vegetable oils and fats. One common example involves the extraction of ricinoleic acid from castor oil, which can be further subjected to pyrolysis to yield fatty acid derivatives for subsequent use as monomers in polyamide synthesis. A wide range of polyamides have already been synthesized utilising these fatty acid derivatives ⁶⁻⁹. Furthermore, fully- or partly- bio-based long-chain PAs have already been commercialized by a range of industrial polymer manufacturers ¹⁰, including Rilsan® (PA 11) from Arkema S.A., Zytel® (PA 6,10, PA 10,10) from DuPont and Vestamid® Terra (PA 6,10, PA 10,10, PA 10,12) from Evonik Industries AG. This growing interest from both academia and industry, the increased availability and production of bio-sourced fatty acid reserves and the recent developments into the preparation bio-base diamines ¹¹ encourages further study and development of this class of polymers.

Despite the volume of research interest and literature regarding long chain PAs, there exists a need to expand the repertoire and knowledge of these materials. For example, although a variety of long-chain polyamides have been synthesized utilising repeating units containing up to 34 carbons ¹²⁻²¹, a rather limited overview of basic intrinsic properties is presented, without exploring practical properties (eg. impact strength, tear strength, etc.). Similarly, the possibility to modify and manipulate polyamide behaviour and characteristics by increasing segment length and reducing amide linkage density provides great potential for expanding the applicability and limitations of this class of polymers. Furthermore, several of the aforementioned long-chain PAs possess various other functional groups along the backbone

chain^{22,23}; this provides the opportunity to characterise and identify the effect of non-modified long-segments of aliphatic chains, establishing crucial structure-property correlations in the process. Finally, the ongoing commercialisation of vegetable oil-derived, long-chain fatty acids possesses, in addition to bio-fuel production, a viable and renewable resource for the production of next-generation polymers with increased aliphatic segment length. This serves to heighten the need to synthesize, characterise and profile these long chain polyamides, providing a basis and understanding for synthesizing and developing similar polyamides from bio-based, renewable resources.

Herein, a series of AABB-type, aliphatic long-chain polyamides were synthesized via polycondensation, utilising a number of renewable long-chain dicarboxylic acids with varying repeating unit lengths. The molecular weight, crystallinity, thermal, mechanical, barrier and water absorption properties of the synthesized polyamides are presented and compared with several commercially-available polyamides. Key structure-property relationships are identified and presented, in particular focusing on the influence of repeating unit length and molecular weight.

EXPERIMENTAL

Raw materials

All reagents were used as received. Tetradecanedioic acid (TDA), hexadecanedioic acid (HAD) and octadecanedioic acid (ODA) were supplied by Zito Guantong Chemical Company Ltd, Zibo City, China. Hexamethylenediamide (HMDA), hexafluoroisopropanol (HFIP) and dodecanedioic acid were purchased from Aldrich. Dodecamethylenediamine (DMDA) was purchased from TCI. Ethanol was purchased from Altia. All other solvents were purchased from Aldrich. Commercial polyamides were obtained from GoodFellow, Sigma Aldrich and DuPont. Their specifications are listed in Table 1.

Table 1 Commercial polyamides utilised

Polyamide	Manufacturer/Supplier	Product number/trade name
PA 6	BASF	B3S
PA 6,6	Sigma Aldrich	429171
PA 6,10	DuPont	RS LC3090 NC010
PA 10,10	Evonik	Terra DS 18
PA 11	Sigma Aldrich	181153
PA 12	GoodFellow	AM376010

Synthesis of long-chain aliphatic polyamides

Polyamides were synthesized via a two-step method; firstly, a crystalline, solid nylon salt was prepared from dicarboxylic acid and diamine. The respective diamine and dicarboxylic acids utilised, as well as polyamide nomenclature are summarized in Table 2. This was done to ensure a precise 1:1 molar ratio of both components, which subsequently encourages polymer chain growth (i.e. high molecular weight) and prevents premature termination of the polycondensation reaction. Secondly, the nylon salt was fed into the reaction vessel and subjected to melt polycondensation at elevated temperature and high vacuum.

Table 2 Nomenclature, composition and reaction conditions of synthesized polyamides

Polyamide	Monomers/constituent materials		Reaction temperature (°C)	Reaction time (h)^a	Yield (%)
	<i>Diamine</i>	<i>Dicarboxylic acid</i>			
PA 6,14	Hexamethylenediamine	Tetradecanedioic acid	250	20	98
PA 6,16	Hexamethylenediamine	Hexadecanedioic acid	240	20	99
PA 6,18	Hexamethylenediamine	Octadecanedioic acid	230	20	95

a) In addition to the 20 h reaction times, polyamides were synthesized for shorter reaction times and analyzed. These specimens synthesised for <20 h will be identified in the Results and Discussion section as they are introduced

Nylon salt preparation

In general, fatty acids have limited solubility in water, thus nylon salts were prepared in ethanol solution. The nylon salt preparation procedure was applied to all polyamides synthesized in this project. Dicarboxylic acids were dissolved in absolute ethanol at approximately 75 °C to obtain 10 %-wt clear transparent solutions. Then, 5 %-mol excess of HMDA dissolved in ethanol solution was added under vortex stirring to the dicarboxylic acid solution. The nylon salt precipitated as soon as it was formed. After the addition was complete, the reaction mixture was continuously stirred for 1 h at 75 °C, following by an additional stirring period of 1 h at 0 °C (achieved with an ice bath). The resulting product was vacuum filtered, and the precipitate was washed with ethanol. The product was dried in a vacuum oven overnight at 40 °C. The yield and purity of the nylon salts is summarized in Table 3.

Table 3 Yield and purity of nylon salts

Nylon salt	Yield (%-wt)	Purity (%)
PA 6,14	95	98
PA 6,16	98	99
PA 6,18	93	98

Melt polycondensation

Polymerization was conducted for 24 h utilizing a 1 L stainless-steel reactor, with the reaction temperatures being summarized in Table 2. The reactor consists of a 1 L stainless-steel vessel, surrounded by a heating element that encompasses the sides of the vessel. A lid which includes a mechanical stirrer column, and inlets for vacuum and nitrogen was fastened to the top of the reaction vessel/heating element ‘base’ during the polycondensation reaction. The vessel was charged with nylon salt at room temperature, after which the temperature was increased (under nitrogen purge) to the reaction temperatures described in Table 2. Upon reaching the desired temperature, the nitrogen purge was

stopped, the valves of the reactor were closed, and these conditions maintained for 2 h. Nitrogen purge was subsequently reapplied for 1 h to remove any water polycondensate. Finally vacuum of less than 0.07 mbar was applied and the reaction proceeded for a total of 24 h. To harvest, the polyamides were soaked immediately into liquid nitrogen to cool and prevent any possible thermal degradation.

Preparation of test specimens

Film specimens for subsequent use (XRD, DSC, water vapour- and oxygen transmission analysis) were prepared via a heated press (Fontijne TP 400). Samples were heated to 30 °C above their melting temperatures, 150 kPa of was pressure applied, held for 5 min and cooled to ambient (within 2 min). Dog-bone specimens (for tensile analysis) and rectangular bar specimens (for Charpy impact- and water absorption analysis) were prepared using a Babyplast 6/10P micro-injection moulding device. Dog bone specimens were prepared using an ISO 527-6B standard mould, while the rectangular specimens displayed average dimensions of $\sim 20 \times 5 \times 1 \text{ mm}^3$. The temperatures utilized during specimen fabrication are summarized in Table 4.

Table 4 Injection moulding temperatures utilized during specimen fabrication

Polyamide	Injection Temperature (°C)	Mold Temperature (°C)
<i>Commercial polyamides</i>		
PA 6	245 - 265	40
PA 6,6	280 - 300	40
PA 6,10	240 - 280	45
PA 6,12	220 - 270	50
PA 10,10	235 - 250	30
PA 11	210 - 240	40
PA 12	210 - 250	45

<i>Synthesized polyamides</i>		
PA 6,14	250 - 265	30
PA 6,16	250 - 260	30
PA 6,18	250 - 270	30

Characterization

¹H Nuclear magnetic resonance (NMR)

¹H NMR spectra were recorded with a Bruker AVANCE-III 400 MHz spectrometer operating at 400.13 MHz for ¹H. The spinning speed of samples was 8000 Hz, contact time 2 ms and delay between pulses 5 s. Samples were dissolved in chloroform-d₁ (deuteration at no less than 99.8 %) with 10 %v/v trifluoroacetic anhydride added, in 5 mm NMR tubes, at room temperature.

Size exclusion chromatography (SEC)

SEC analyses were performed at room temperature with a Waters 717plus Autosampler, Waters 515 HPLC pump, and a Waters 2414 refractive index (RI) detector. A set of two columns in series (HFIP-803 and HFIP-804 ‘Shodex’ columns, Showa Denko Europe GmbH.) was utilised. Hexafluoroisopropanol (HFIP) with 5 mM sodium trifluoroacetate (CF₃COONa) was used as eluent at 0.5 mL·min⁻¹, and calibration was done against PMMA standards. All samples were prepared at 1 mg·mL⁻¹ concentrations using the eluent solvent.

X-ray powder diffraction (XRD)

The crystallinity of the synthesised polyamides were calculated from XRD analysis data obtained with a PANalytical X’pert Pro/Pw 3040/60, with Cu K α radiation (λ = 0.154 nm). Data was collected in the 2 θ range from 2 to 70 ° with a scanning speed of 3 °·min⁻¹. All specimens were heated above their melting temperature and cooled to ambient at 20 °·min⁻¹ prior to analysis at room temperature. Radiation conditions were 45 kV and 40 mA. Crystallinity (χ_c) values were calculated as detailed in Pagacz et al ²¹.

Density measurements

The density calculations were based on Archimedes' principle. The specimens were weighed in both air and water (23 °C), with Equation 1 being used to determine the volume of the specimen:

$$V = \frac{m_1 - m_2}{\rho_{H_2O}} \quad (1)$$

where V is the volume of the specimen (cm^3), m_1 and m_2 are the mass of the specimen (g) in air and water, respectively, and ρ_{H_2O} is the density of water ($1 \text{ g}\cdot\text{cm}^3$). The mass of the object in air was then divided by this calculated volume to yield the density. Specimens were analysed in triplicate.

Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was conducted with a TA Q2000 Modulated Temperature DSC in order to observe the melting and crystallization processes. Nitrogen was used as the purge gas. Approximately 5 mg of sample was sealed in T-zero aluminum pans. The heating-cooling was programmed from 25-250 °C at a heating rate of $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$, with the samples being subjected to two heating-cooling cycles. The transition temperatures were measured the second heating/cooling cycle. All the measured temperatures were recorded at the peak values (T_m , T_c) or values in the middle of the heat capacity signal (T_g). Crystallinity (χ_c) values were calculated utilising Equation 2:

$$\chi_c(\%) = \frac{\Delta H_{melt} - \Delta H_{crys}}{\Delta H_{melt}^0} \cdot 100 \quad (2)$$

where ΔH_{melt} is the experimental enthalpy of melting, ΔH_{crys} is the experimental enthalpy of crystallization and ΔH_{melt}^0 is the melting enthalpy of a 100 % crystalline specimen. Melting enthalpy values of purely crystalline commercial polyamides were obtained from literature²⁴, with the value of purely crystalline PA 6,12 ($258 \text{ J}\cdot\text{g}^{-1}$) being used for the synthesized long-chain polyamides. Due to a lack of literature values

for PA 6,14, 6,16 and 6,18 (to the best of the authors knowledge), the value of PA 6,12 was used since it is the closest structural counterpart to the aforementioned synthesized polyamides.

Dynamic mechanical analysis (DMA)

The glass transition temperatures were measured by dynamic mechanical analysis (DMA). The samples were heated from room temperature to 100 °C at 3 °C·min⁻¹, while subjected to a 1 Hz frequency within 0.5 % strain. The glass transition temperatures were determined from the peak of tan delta curve which is the ratio of the loss modulus and the storage modulus. Test specimens were equilibrated at 50 % relative humidity and 23 °C for at least 10 days prior to testing. Samples were analyzed in duplicate.

Tensile analysis

Tensile analysis was conducted using an Instron 4204 Universal Tensile Tester with a 1 kN static load cell. The measurements were strain-control with an increasing strain-rate of 10 mm·min⁻¹. Specimens were allowed to equilibrate in a humidity-controlled atmosphere, (0 or 50 % relative humidity) at 23 °C for at least 10 days prior to testing. Each measurement was repeated at least 5 times. The Young's modulus, yield stress, yield strain and, where possible, tensile strength and elongation at break were determined. Results presented are the average of five reproducible repeats.

Charpy (V-notch) impact analysis

Impact analysis was conducted using a Zwick pendulum impact tester, utilising an impact energy of 1 J. A 45 ° v-notch with 2 mm depth was cut into the test specimens following moulding. Test specimens were equilibrated at 50 % relative humidity and 23 °C for at least 10 days prior to analysis. The results presented are the average of five reproducible repeats.

Water absorption

The water absorption content of polymers were measured by soaking a known-mass of polyamide (pre-dried overnight, under vacuum, at 100 °C) in distilled-water for 10 days. After this, the samples were taken out and excess water from the surface of the samples was dried gently with tissue paper. The water absorption percentages were calculated by the weight ratios of dry to wet samples. Three specimens were measured for each sample.

Water vapour transmission rates (WVTR)

WVTR of the films were determined gravimetrically using a modified ASTM E-96B (wet cup) procedure. Samples with a test area of 30 cm² were mounted on a circular aluminum dish (68-3000 Vapometer EZ-Cups), which contained deionized water. Dishes were stored at 23 °C and 50 % RH and weighed periodically until a constant rate of weight reduction was attained. Water vapour permeability was determined by normalizing the transmission rates to the thickness of the films.

Oxygen transmission rates (OTR)

OTR of the polyamide films were determined according to standard ASTM D3985 using an Oxygen Permeation Analyzer Models 8001 (Systech Instruments Ltd, UK). The test area of the sample was 50 cm². The measurements were carried out at 23 °C and 50 or 90 % RH, using 100 % oxygen as a test gas. Oxygen permeability was determined by normalizing the transmission rates to the thickness of the films.

RESULTS AND DISCUSSION

Chemical structure

Figure 1 displays the ¹H-NMR spectra of the synthesized long-chain polyamides. Peaks at chemical shifts of 3.7 and 2.8 ppm were attributed to the protons adjacent to the -NH and -CO groups, respectively. The remaining peaks are derived from protons along the aliphatic chain, and are assigned as displayed within the Figure. The spectra are in correlation with previously reported data ^{16,18}, and confirm the anticipated

chemical structure of these polyamides. Furthermore, there is no apparent evidence of branching within the synthesized polymers.

Figure 1 ^1H NMR spectra of synthesized long-chain polyamides; i) PA 6,14, ii) PA 6,16, iii) PA 6,18

Molecular weight distribution

The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index ($\mathcal{D}$) were obtained via SEC are summarized in Table 5. The bulk of the commercial PAs exhibited M_n values in the range of 12,000-37,000 $\text{g}\cdot\text{mol}^{-1}$, which is quite typical of commercial polyamide grades. A noticeable exception was the PA 6,6 (Sigma) which yielded a maximum commercial M_n value of 68,000 $\text{g}\cdot\text{mol}^{-1}$. The novel, synthesized PAs possessed a M_n range of 41,000-72,000 $\text{g}\cdot\text{mol}^{-1}$ (for specimens with identical reaction times, 20 h). This increased number average molecular weight can be attributed to the synergy of a number of factors. Firstly, the reaction times used to synthesize the PAs (20 h). Since the degree of polycondensation is a function of reaction time, the desired molecular weight can be obtained by quenching the reaction at an approximate time; therefore the reaction process allows for a degree of

control of polymer chain length. This is confirmed when comparing the M_n values of PA 6,14 and 6,16 which were synthesized using shorter reaction times (8 and 15 h, respectively). Furthermore, effective water removal and mechanical agitation during the polycondensation reaction encourage chain growth and reduce the likelihood of chain scission (degradation) or reaction termination. Finally, the filtration method employed during nylon salt preparation encourages high monomer purity and precise stoichiometric control; eliminating any potential contaminants or the likelihood of premature termination of reaction.

Table 5 Molecular weight, density and thermal data of commercial and synthesized polyamides

Polyamide	M_n (g·mol ⁻¹)	M_w (g·mol ⁻¹)	$\bar{D}$	ρ (kg·m ⁻³)	T_g (°C)	T_c (°C)	T_m (°C)
Commercial polyamides							
PA 6	37,000	64,000	1.78	1.20	78	194	220, 216
PA 6,6	68,000	109,000	1.60	1.14	80	219	260, 251
PA 6,10	36,000	83,000	2.30	1.08	65	179	222
PA 10,10	18,000	45,000	2.53	1.05	62	163	200, 189
PA 11	17,000	43,000	2.53	1.03	68	158	191, 180
PA 12	12,000	24,000	2.00	1.07	58	152	178, 172
Synthesized polyamides							
PA 6,14	18,000 ^a /49,000 ^b	93,000 ^b	1.90 ^b	1.06	71	185	208, 197, 170
PA 6,16	20,000 ^c /41,000 ^b	87,000 ^b	2.12 ^b	1.06	66	182	196, 171
PA 6,18	72,000 ^b	713,000 ^b	9.90 ^b	1.00	66	179	200, 193, 172

b) Table 6 PA 6,14 synthesized for 8 h

c) PA 6,14, 6,16 and 6,18 synthesized for 20 h

d) PA 6,16 synthesized for 15 h

When comparing the M_w and $\bar{D}$ behaviour, the synthesized PAs displayed remarkably higher values on average than their commercial counterparts. The most noticeable values were that of PA 6,18 polymerized for 20 h, displaying M_w and $\bar{D}$ of 713,000 g·mol⁻¹ and 9.90, respectively. This indicates that

significant segments of very-high molecular weight PA are present within the greater polymer. Although such high $\bar{M}_w$ values for polyamides are not common, the possibility of their occurrence has been previously documented^{25,26}. These large deviations in polydispersity have been attributed to the effect of changes in end-group reactivity with chain length and additional side reactions²⁷. If these principles are applied to PA 6,18, it is hypothesized that they may arise from the increased melt viscosity which accompanies increased molecular weight. The M_n of PA 6,18 ($72,000 \text{ g}\cdot\text{mol}^{-1}$) was highest of all PAs; as such this would result in an increase in melt viscosity. As such, this increased viscosity would increase the torque and energy required to evenly and effectively mix the polyamide melt. This combination of increased viscosity and seemingly ineffective mixing may result in a number of factors which can ultimately influence PDI. Firstly, reduced mixing efficiency may hinder chain mobility; this is important since all functional groups are assumed to have an equal probability of reaction. Restrictions on chain mobility may effectively hinder this reactivity potential. Secondly, ineffective mixing which doesn't break the surface of the melt may result in the formation of a 'skin'. This can serve as a barrier to prevent escape of water molecules, while further 'trapping' pockets of polyamide and limiting the effectiveness of mixing. This can result in segments of polyamide continuing to polymerize, while others remain stagnant or even degrade via hydrolysis reactions with entrapped water molecules. This disparity in chain growth behaviour may lead to the large deviation in polydispersity.

Crystallinity and morphology

The XRD patterns of the synthesized and commercial polyamides are presented in Figures 2a and b, respectively. The synthesized, long chain polyamides all exhibited spectra with similar features. The peak at $2\theta = \sim 38^\circ$ stems from the amorphous segments within the polyamides, while the two small peaks at $2\theta = \sim 8^\circ$ (001) and 13° (002) correlate to the length of the chemical repeat unit²¹. The two distinct peaks were most prominent for specimen PA 6,14, while PA 6,16 displayed less-intense peaks and PA 6,18 a

single peak at $2\theta = \sim 11^\circ$. This phenomenon within polyamides has been attributed to the effects of destructive interference, evidenced by the (001) peak gaining intensity as the distance between carbonyl groups becomes more equal²⁸. Commercial polyamides displayed similar behaviour (Figure 2b), with single peaks becoming more prevalent and shifting to lower 2θ values as repeating-unit length increased.

Figure 2 XRD profiles of a) synthesized long-chain polyamides, b) commercial polyamides

The profile of all synthesized and commercial AABB-type PAs displayed a sharp, intense peak (100) is visible at $2\theta = \sim 20^\circ$, attributed to the inter-chain distance of the α -crystalline phase, with a shoulder at $2\theta = \sim 21^\circ$ suggesting the presence of β -pseudo-hexagonal crystal structure. Furthermore, a smaller peak at $2\theta = \sim 23^\circ$ ($010/110$) was attributed to the inter-sheet distance of the γ -crystalline phase²⁹. Both (100) and ($010/110$) peaks shifted slightly towards lower 2θ values as repeating unit length increased, indicative of an increase in inter-chain- and inter-sheet distance. It was apparent for all synthesized polyamides that the α -crystalline phase dominated the structure, with the ratio of (100):($010/110$) peak intensities increasing with repeating unit length. Pagacz et al.²¹ compared the XRD profiles of various long-chain AABB-type polyamides, observing that reducing the methylene:amide linkage ratio may increase (100) peak intensity relative to the ($010/110$) peak. Although this increase in (100) peak intensity with repeating unit length was also evident for the commercial AABB-type polyamides (PA 6,6, 6,10 and 10,10), the XRD

profiles indicated a higher presence of the γ -crystalline phase, especially within specimen PA 6,10. Furthermore, the AB-type commercial PAs displayed much broader and overlapped peaks.

The percentage crystallinities (χ_c) of commercial and synthesized PAs determined using XRD are summarized in Table 6. Synthesized polymers exhibited crystallinity values within the range 18-23 %. Typically crystallinities of polyamides do not exceed 40%²², which indicate that crystal formation is favored by hydrogen-bonding in an overall less-efficient way than crystallization induced by van der Waals interaction, that is the driving force in long-chain polyester and polyolefins^{9,23}. The dominance of hydrogen-bonding in the crystallization behaviour of long-chain aliphatic polyamides has also been confirmed³⁰, with the α -phase, triclinic crystalline structure being dominant. Synthesized polyamides displayed an increase in crystallinity with increasing repeat unit (and methylene unit) length, as highlighted in Figure 3. This was in stark contrast to the reduction in χ_c displayed by commercial AABB-type polyamide with increasing repeat unit length. Despite this inconsistency, an increase in χ_c with repeat unit length has been reported by both Michalska et al³¹ and Pagacz et al²¹, however, neither elaborated on the behaviour. One hypothesis for this behaviour may stem from a combination of the even spacing of amide linkages throughout the backbone (encouraging efficient hydrogen-bonding), and the reduced stiffness which accompanies an increase in repeating unit length. This increased flexibility may encourage more-effective rearrangement of polymer chains, allowing van der Waals interactions to contribute a greater degree towards crystalline domain formation.

Table 6 Crystallization- and melting enthalpies, and crystallinity values of synthesized and commercial polyamides

Polyamide	ΔH_{melt} (J·g ⁻¹)	ΔH_{crys} (J·g ⁻¹)	$\chi_{\text{c DSC}}$ (%)	$\chi_{\text{c XRD}}$ (%)
<i>Commercial polyamides</i>				
PA 6	74.35	54.10	9	16
PA 6,6	81.90	58.32	10	16
PA 6,10	72.75	51.85	8	13
PA 10,10	55.08	37.44	7	12
PA 11	57.93	51.52	3	6
PA 12	55.02	42.32	5	14
<i>Synthesized polyamides</i>				
PA 6,14	86.52	56.10	12	18
PA 6,16	85.20	51.43	13	21
PA 6,18	84.35	46.55	15	23

Crystallization is dependent on a number of factors, including the energies of both amide and methylene groups, chain folding and inter-chain bonding²¹. These aforementioned factors are time-temperature phenomena; as such, formation of the less-stable γ -phase is encouraged via quenching, while slower cooling rates lead towards a more-stable crystalline domain³². Despite all polyamides having similar cooling profiles prior to analysis, it should be mentioned that crystallization may still occur at different time scales. Furthermore, commercial polyamides are likely to contain various additives (eg. processing aids, anti-oxidants) which are lacking from the synthesized long-chain polyamides. These additives can impart influence on crystallization behaviour, including the rate of crystal formation and preferential formation of specific crystalline phases. A future in-depth study of these polyamides (with all PA specimens synthesized utilizing the same reactor) will provide further clarity and insight into crystallization behaviour.

Density

The density (ρ) values of commercial and synthetic polyamides are summarized in Table 5. Although polyamides displayed arguably similar values, a general trend of reduced density with increasing length of repeating unit was apparent. Although it is anticipated that increasing repeating unit length and reducing the overall amide-group density would result in greater chain flexibility and/or increased likelihood of entanglement (leading to a looser-packed, less-dense polymer structure), the observed reduction in density is in stark contrast to the increased crystallinity displayed from specimens PA 6,14 to PA 6,18. Generally speaking, crystallinity is expected to increase with density, as the higher prevalence of ordered polymer chains reduces the proportion of unoccupied ('free') volume throughout the macromolecule structure. This unexpected behaviour has previously been reported by Saitome and Komoto³³, who observed increased crystallinity with repeat unit length in AB-type polyamides. They attributed the phenomena to the difference in densities of amide and methylene groups (with amide being larger), and the increasing contribution/dominance of less-dense methylene groups within crystal domains.

Thermal properties

The glass transition, crystallization and melting temperatures of the polyamides are summarized in Table 5. When comparing the T_g of commercial and synthetic long-chain polyamides, a similar temperature range was observed. An evident reduction in glass transition temperature with increasing repeating unit length was observed. The same behaviour was also displayed for crystallization and melting temperatures. Increasing the length of the repeating unit leads to several occurrences that reduce the aforementioned transition temperature;

- Increasing repeating unit length enhances the flexibility of the main backbone chain. This reduces the activation energy required for glass transition, while also allowing easier and

more effective packing of polymer chains (reduced T_c) and increasing the entropy change upon melting (reduced T_m). It should be noted that high molecular weights, such as those seen here, lead to reduced free volume via a smaller number of chain ends per total units – this was certainly evident in the higher T_g values. However, the influence of the **repeating unit length** rather than molecular weight, appears to dominate the melting and transition behaviour.

- The ratio of methylene:amide linkages also increases with increasing unit length. This reduces the number of amide linkages per repeat unit which could potentially partake in hydrogen bonding; these hydrogen bond sites restrict chain motion and increase the energy required for glass-rubber transition (T_g) and melting (T_m). Subsequently, a reduction in amide linkage density results in reduced T_g and T_m values ³³.

The DSC curves of the polyamides are shown in Figure 4. All polyamides displayed multiple melting curves, as displayed in Figures 4a and b. Synthesized polyamides all displayed a distinct main melting peak with a broad shoulder at lower temperatures. Specimens PA 6,14 and 6,18 exhibited an additional peak at temperatures above the main melting peak. This behaviour may be due to a number of factors. Li et al. ³⁴ and Millot et al. ³⁵ suggested that the multiple melting peaks of polyamides may be attributed to the presence of crystallites of the same type but different thickness. Pagacz et al. ²¹ further elaborated on this, by attributing the multiple peaks to the fusion of imperfect crystals with lower thermal stability, secondary crystallization upon heating, and/or re-melting of more perfect crystals. This behaviour is not uncommon for polyamides which can experience polymorphic transitions upon heating, and form lamellae with varying thickness ^{21,34}. Indeed, the occurrence of multiple melting peaks has previously been documented for long-chain polyamides ^{12,15,18,20} and been generally attributed to melting of less-perfect crystallites and their subsequent re-crystallization, or the melting of crystallites of varying thickness.

Cooling curves of the synthesized and commercial polyamides are displayed in Figures 4c and 4d, respectively. Commercial polyamides displayed a single crystallization peak, while synthesized polyamides appear to display two small and broad shoulders at temperatures below the primary crystallization peak. Cui et. al¹⁸ observed similar behaviour for long-chain polyamides, but did not elaborate. One hypothesis is that these shoulders may be related to the crystallization of different lamellae types or thicknesses, and may account for the additional peaks observed in the melting curves which could be attributed to recrystallization or melting of crystallites with imperfections or varying thickness. Furthermore, synthesized long-chain PAs generally displayed narrower crystallization curves than commercial PAs. This has been related to chain mobility, in particular the influence hydrogen bonding between amide linkages and their influence on ordering crystalline nuclei in the melt and subsequent crystallization kinetics¹. Above the melt, a large fraction of amide groups remain hydrogen bonded³⁶. And although these linkages are important in helping form ordered arrays of polymer chain, excessive bonding may restrict chain motion and act as hindrance to effective chain folding and/or packing. Reducing the amide:methylene ratio (or increasing the aliphatic segment in the repeating unit) reduces the likelihood of these chain restrictions, leading to reduced energy requirements for effective chain packing and crystallite growth. The increased presence of methylene units may also lead to van der Waals interactions contributing a greater degree towards crystalline domain formation.

a)

b)

c)

d)

Figure 3 DSC heating curves of a) synthesized polyamides, b) commercial polyamides. Cooling curves of c) synthesized polyamides, d) commercial polyamides

The enthalpies of melting and crystallization, and crystallinity values calculated from DSC data are summarized in Table 6. Generally speaking, the calculated crystallinities obtained via DSC were lower than those from XRD, however trends were similar suggesting good correlation between the two techniques. As was mentioned in the Experimental section, the pure enthalpy of melting of purely crystalline PA 6,12 was used to determine χ_c values of the synthesized long-chain polyamides; this should be considered when observing the results. As with T_m , the enthalpy of melting was observed to reduce with increasing repeat unit length and was attributed to the reduced likelihood of hydrogen bonding between amide linkages reducing energy requirements for melting. Although the synthesized polyamides displayed a negligible reduction in melting enthalpy with increasing repeating unit, the crystallization enthalpy displayed a more apparent reduction. As mentioned previously, the increased flexibility which can arise with increasing repeating unit length may encourage more-effective rearrangement of polymer chains and increase the rate of crystallization, as evidenced by the narrower crystallization curves of the synthesized long-chain PAs.

Tensile properties

The tensile properties of the commercial and synthesized polyamides are summarized in Table 7 (conditioned at 50 % RH), and Table 8 (conditioned at 0 % RH), while the stress-strain curves are presented in Figure S1 of the Supplementary Data. All polyamide samples yielded curves with a similar profile and features; following the linear-viscoelastic region, samples experienced yield, which is typical of polyamide specimens. A slight degree of increasing stress (strain hardening) was apparent prior to sample failure, with this effect being more apparent for specimens analysed at 50 % RH. This may be due to the plasticizing influence of water, which may encourage chain alignment and orientation during elongation during extension.

Table 7 Tensile data of polyamides conditioned at 50 % RH

Polyamide	Young's Modulus (MPa)	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Work to Break (kJ·m²)
<i>Commercial PA</i>					
PA 6	721 ± 54	54 ± 2	75 ± 10	545 ± 74	27.1 ± 2.4
PA 6,6	744 ± 24	51 ± 1	85 ± 5	660 ± 35	31.6 ± 5.2
PA 6,10	506 ± 24	45 ± 2	60 ± 10	632 ± 153	29.4 ± 4.7
PA 10,10	437 ± 46	42 ± 2	60 ± 10	583 ± 121	24.0 ± 3.7
PA 11	397 ± 24	37 ± 3	60 ± 5	655 ± 60	25.0 ± 2.2
PA 12	478 ± 11	39 ± 2	50 ± 5	464 ± 65	17.3 ± 1.5
<i>Synthesized PA</i>					
PA 6,14	602 ± 6	40 ± 1	50 ± 3	402 ± 48	17.2 ± 1.9
PA 6,16 (5 h)	514 ± 30	40 ± 2	50 ± 5	545 ± 30	22.5 ± 1.4
PA 6,16 (20 h)	598 ± 20	40 ± 1	50 ± 5	510 ± 36	21.8 ± 1.8
PA 6,18	550 ± 33	46 ± 4	75 ± 10	807 ± 113	41.8 ± 3.1

The synthesized long-chain PAs displayed tensile properties most similar to commercial PA 6,10 and PA 12; given the similar ratio of amide groups:carbons, this was anticipated and suggests this as a key factor which influences stiffness and strength behaviour. This hypothesis is further supported when the influence of repeating unit length on tensile properties is analysed. Increasing the length of the repeating unit leads to reduced strength and moduli values, accompanied by an increase in flexibility. As the number of carbon per repeat unit increases, the reduced prevalence of amide groups results in a subsequent reduction in degree of inter-amide hydrogen bonding between chains. Consequently, long chain PAs are more likely to experience reduced modulus and tensile strength values, while exhibiting an increase in ductility and strain at break. Furthermore, the reduced number of amide linkages decrease the number

of potential sites that can hydrogen bond with water. This is important due to the plasticizing effect bound water imparts on polyamides and that the test specimens were equilibrated at 50 % RH prior to testing. Additionally, PA 6,18 displayed remarkably higher work to break values compared with all other specimens; this behaviour will be discussed in greater detail in the ‘impact resistance’ section.

Table 8 Tensile data of polyamides conditioned at 0 % RH

Polyamide	Young's Modulus (MPa)	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Work to Break (kJ·m²)
<i>Commercial PA</i>					
PA 6	1190 ± 96	90 ± 4	90 ± 4	100 ± 50	6.4 ± 1.8
PA 6,6	1070 ± 12	83 ± 4	82 ± 5	446 ± 160	23.2 ± 5.9
PA 6,10	748 ± 19	64 ± 5	65 ± 10	475 ± 90	20.4 ± 3.2
PA 10,10	653 ± 20	53 ± 4	60 ± 10	568 ± 68	19.0 ± 2.4
PA 11	572 ± 39	54 ± 2	55 ± 5	478 ± 4	18.2 ± 1.4
PA 12	639 ± 26	53 ± 1	50 ± 5	386 ± 28	15.7 ± 1.7
<i>Synthesized PA</i>					
PA 6,14	721 ± 21	51 ± 3	50 ± 5	277 ± 50	16.5 ± 2.3
PA 6,16 (5 h)	697 ± 15	50 ± 1	55 ± 5	511 ± 36	20.8 ± 1.0
PA 6,16 (20 h)	734 ± 22	48 ± 1	55 ± 5	490 ± 37	19.2 ± 1.4
PA 6,18	700 ± 51	52 ± 8	55 ± 10	630 ± 50	24.8 ± 3.6

To further probe the effect of moisture on polyamide tensile behaviour, specimens were analysed following condition at 0 % RH; the results are summarized in Table 8. Conditioning under these dryer conditions resulted in increased stiffness and strength values for all polyamides, with a reduction in elongation. The contrast was most drastic for PA 6 and PA 6,6, with the dry conditions imparting a distinct

brittling influence. Increasing repeating unit length (and subsequently, hydrophobicity) reduced the extent of which water can impart a plasticizing/softening effect on polyamides; this is highlighted in Figure 5, which shows the percentage difference in modulus and yield strength for 0 and 50 % RH. The values displayed represent the moduli and yield strength of specimens analysed at 50 % RH, as a percentage of '100 %' values corresponding to specimens analyzed at 0 % RH. Synthesized polyamides generally displayed a higher retention of moduli and strength values, indicating they are less susceptible to the influence of moisture, and can maintain higher mechanical stability in both dry and humid conditions.

Figure 4 (50 % RH / 0 % RH · 100 %) Young's modulus and yield strength values for commercial and synthesized polyamides analyzed at 50 % RH, displayed as a percentage of those analyzed at 0 % RH. Values were calculated as follows: (50 % RH / 0 % RH · 100 %). The closer the values are to '100 %', the smaller the difference between values for specimens tested at 50 and 100 % RH.

In order to determine the influence of molecular weight (and reaction time) on tensile properties, a PA 6,16 specimen synthesized for 5 h was analysed. This is important in order to further develop structure-property relationships, and to allow/confirm suitable comparison with commercial polyamides; usually they are industrially polymerized for shorter time periods. Both PA 6,16 specimens displayed similar tensile values, with data falling within standard deviation ranges. The one exception here is the modulus at 50 % RH; with the 5 and 20 h polymerized sample displaying values of 514 and 598 MPa, respectively. This difference may be related to the increased molecular weight and distribution which is associated with longer reaction times and the humid environment in which the polyamides were exposed. Increasing molecular weight/distribution may encourage entanglement formation amongst segments of polymer chain, which can act as physical barriers to water penetration and plasticization. This may also account for the higher modulus values displayed by synthesized long-chain polyamides for commercial equivalents with similar or higher repeating unit lengths (namely, PA 6,10 and PA 10,10). The data highlights the influence moisture (and subsequently repeat unit length and amide density) has on tensile properties of polyamides, while also demonstrating how increased molecular weight may help retain stiffness at elevated humidities.

Impact resistance

The Charpy (V-notch) impact test was utilised to evaluate the impact strength of the commercial and synthesized polyamides are summarized in Table 9. For both hot-pressed and injection moulded specimens, similar impact strength values were displayed by both commercial and synthesized specimens (correlating with work-to-break data obtained during tensile testing). One notable exception to this is specimen PA 6,18, which displayed impact strength values of 32 and 83 kJ·m⁻², for injection moulded and hot pressed specimens, respectively. This behaviour may be a consequence of the increased repeating-unit length; with the increased ductility and elongation experienced by the long-chain polyamides (refer

to Tensile properties) encouraging dissipation of applied energy through various chain motions, rather than breakage or failure. However, given the drastic increase in impact strength value, the influence of increased molecular weight and broad polydispersity must also be considered. Perron and Lederman³⁷ postulated that the increased volume of chain entanglements between fractions of very high molecular weight PA contribute towards energy absorption upon impact.

Table 9 Impact strength of selected polyamides

Polyamide	Impact strength (kJ·m²)	
<i>Commercial polyamides</i>	<i>Injection moulded</i>	<i>Hot pressed</i>
PA 6	15 ± 2	30 ± 17
PA 6,6	19 ± 3	14 ± 5
PA 10,10	20 ± 1	28 ± 11
PA 11	28 ± 2	30 ± 6
PA 12	32 ± 4	33 ± 4
<i>Synthesized polyamide</i>	<i>Injection moulded</i>	<i>Hot pressed</i>
PA 6,14	22 ± 2	39 ± 4
PA 6,16	25 ± 4	35 ± 3
PA 6,18	32 ± 1	83 ± 6

Additionally, drastic differences in values between specimen preparation techniques are apparent. This may be attributed to factors³⁸. Firstly, chain orientation is attained during injection moulding, while specimens prepared via heated press exhibit a random chain distribution. Since the impact during analysis is perpendicular to the direction of orientation, the ability to resist deformation is less effective. This may also partly contribute to the exceptional performance of the hot pressed PA 6,18 specimen. Secondly, the mold temperature, exposure times and rate of cooling may influence factors such as crystallization rate, or allowing the onset of oxidation or chain scissioning. Finally (and somewhat related to the previous

factor), is the presence of additives, including stabilizing agents, anti-oxidants, processing aids pigment, etc. Commercial PAs most-likely contain a mixture of these aforementioned additives, while the synthesized PAs contain none. This makes them more susceptible to the effects of oxidation and chain degradation. In order to probe this hypothesis further, the crystallinity and molecular weight values of the injection moulded polyamides were compared; these are summarized in Table S2 of the Supplementary Data. As seen, injection moulded specimens displayed increased crystallinity compared with the hot pressed samples, which could be attributed to the chain orientation which occurs during injection moulding. This added crystallinity may impart a stiffening effect and diminish chain flexibility, reducing effective dissipation of energy. The molecular weights of commercial polyamides were similar for both hot pressed and injection moulded specimens, with negligible differences observed. In contrast, synthesized PAs exhibited a more drastic reduction in M_n for injection moulded specimens. This confirms a significant degree of chain scissioning has occurred during processing within the synthesized PAs, while it is likely the presence of additives (anti-oxidants, stabilizers, etc.) within the commercial polyamides prevented the same extent of scission from occurring.

Water absorption

Due to amide linkages, polyamides undergo hydrogen bonding not only between polymer chains but also with water molecules in the surrounding environment. The property of moisture absorption of polyamides is a challenge for processing, storage and extended use. Moisture is known to affect polymer characteristics such as dimensional stability, mechanical, chemical and physical properties. Adsorbed moisture within polyamides acts as a plasticizing agent that reduces the interaction bonding and entanglement between polymer chains. This results in an increase in 'free' (unoccupied) volume and chain mobility.

The moisture absorption ability of polyamides is dependent on a number of factors; firstly, the density of amide linkages within the polymer chain. A smaller number of amide linkages leads to reduced moisture attraction, as the overall hydrophobicity of the polyamide increases with repeating unit length. This is highlighted in Figure 6, where the influence of repeating unit length on water absorption is displayed. The water absorption values and their standard deviations are summarized in Table S1 of the Supplementary Data. Compared with commercial PA 6,6, the long-chain aliphatic segments polyamides have remarkably less moisture absorption, with average values of $\sim 1\text{--}2\%$ wt, and a minimum value of 0.8% wt displayed by PA 6,18. Secondly, the influence of reaction time (molecular weight) on moisture absorption is quite evident, as observed for PA 6,16, reducing from 1.8 to 1.6 and 1.2% with 15, 24 and 30 h reaction time, respectively. Apart from the increased hydrophobicity with longer repeating unit lengths (aliphatic segments), increased likelihood of entanglement formation may lead to as physical barriers to water penetration and subsequent adsorption. Thirdly, increased crystallinity is expected to reduce overall water absorption and uptake. When comparing synthesized specimens PA 6,14, 6,16 and 6,18, water absorption was observed to reduce with increasing crystallinity. In contrast, commercial specimens PA 6,6, 6,10 and 10,10 displayed reducing water absorption values along with reducing crystallinity (refer Table 6). Similarly, PA 6 and PA 11 displayed crystallinity values of 16 and 6% , respectively, while the water absorption value of PA 11 was considerably lower than PA 6. The data indicates that the influence of repeating unit length (and methylene:amide group ratio per repeat unit) may impart the strongest influence on water absorption behaviour, more so than molecular weight and crystallinity. Furthermore, the water absorption data correlates with the tensile data, where the long-chain synthesized polyamides maintained superior tensile properties following equilibration at elevated humidity.

Figure 5 Water absorption as a function of repeating unit length

Barrier properties

The oxygen transmission rates (OTR) and water vapour transmission rates (WVTR) of selected commercial and synthesized PA 6,18, and various polymer films are summarized in Table 10. PA 6,18 displayed slightly lower WVTR values than the commercial PA 6, which could be attributed to the reduced water absorption described previously. However, the values were still quite higher than the polyolefins, PET, EVOH and PA 11. This was somewhat surprising given the excellent water absorption performance. When comparing the OTR values, the results are even more drastic, with the synthesized PAs displaying increasing oxygen permeability. This increase in permeation is attributed to the increased length of repeating unit which can lead to increased likelihood of entanglement formation. This results in less-efficient packing/arrangement of polymer chains, leading to a greater proportion of unoccupied/free volume which can facilitate a higher degree of permeation.

Table 10 OTR and WVTR data of commercial and synthesized polyamides, and other polymer films

Polyamide	OTR (23 °C, 50 % RH) cm³×μm/(m²×24h×kPa)	OTR (23 °C, 90 % RH) cm³×μm/(m²×24h×kPa)	WVTR (23 °C, 50 % RH) g×μm/(m²×24h×kPa)
<i>Other polymers</i>			
LDPE	2180	2180	41
HDPE	240	240	6
PP	550	550	21
EVOH	0.09	0.81	225
PET	14.8	16.8	79
<i>Commercial polyamides</i>			
PA 6	8 ± 4	18 ± 7	738 ± 5
PA 11	65 ± 5	71 ± 6	133 ± 4
<i>Synthesized polyamides</i>			
PA 6,18	164 ± 5	171 ± 7	200 ± 27

CONCLUSIONS

A series of long-chain fatty acid-derived polyamides, were synthesized utilising polycondensation. Polyamides with very high molecular weight were able to be synthesized without the need of additional stabilizers or catalysts. The use of a precise stoichiometric ratio of nylon salt, sufficient shear, temperature and reaction times and water removal were crucial to the attainment of high molecular weight polyamides. The synthesized polyamides displayed glass transition temperatures comparable to commercial PAs, while showing a reduction in melting temperature. Stiffness, yield strength and moduli values were comparable with commercial equivalents, while specimen PA 6,18 displayed exceptionally higher impact resistance. Water absorption was exceptionally low, while higher oxygen permeability to gas and water vapour was evident with polyamides containing the longest chain segments.

In considering the structure-property relationships displayed by the synthesized polyamides, the influence of repeating unit length and methylene:amide linkage ratio was apparent. Increasing the aforementioned factors lead to greater hydrophobicity and chain flexibility, while also reducing the number of amide linkages able to participate in interchain hydrogen bonding. Molecular weight and polydispersity contributed towards impact strength, moisture absorption and material stiffness at elevated humidity, encouraging the formation of entanglements which may impart restrictions on chain motion and prevent water uptake. The most notable properties exhibited by the long-chain polyamides were superior impact resistance, excellent stiffness-to-toughness balance and very low water absorption yet high oxygen and water vapour permeability. This unique combination of properties strongly encourages the use of these long chain polyamides in a number of applications where dimensional stability, high impact resistance, low moisture absorbance and lower processing temperatures are desirable and/or important. Furthermore, the results highlight the potential and applicability of such polymers derived from renewable sources, utilizing conventional techniques and infrastructure.

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DATA AVAILABILITY

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

REFERENCES

1. Murthy NS. Hydrogen bonding, mobility, and structural transitions in aliphatic polyamides. *Journal of Polymer Science Part B: Polymer Physics*. 2006;44(13):1763-1782.

2. Meyer A, Jones N, Lin Y, Kranbuehl D. Characterizing and modeling the hydrolysis of polyamide-11 in a pH 7 water environment. *Macromolecules*. 2002;35(7):2784-2798.
3. Ortmann P, Lemke TA, Mecking S. Long-spaced polyamides: Elucidating the gap between polyethylene crystallinity and hydrogen bonding. *Macromolecules*. 2015;48(5):1463-1472.
4. Stempfle F, Ortmann P, Mecking S. Long-chain aliphatic polymers to bridge the gap between semicrystalline polyolefins and traditional polycondensates. *Chem Rev*. 2016;116(7):4597-4641.
5. Biermann U, Bornscheuer U, Meier MAR, Metzger JO, Schäfer HJ. Oils and fats as renewable raw materials in chemistry. *Angewandte Chemie International Edition*. 2011;50(17):3854-3871.
6. Islam MR, Beg MDH, Jamari SS. Development of vegetable-oil-based polymers. *J Appl Polym Sci*. 2014;131(18):n/a-n/a.
7. Yamano N, Kawasaki N, Oshima M, Nakayama A. Polyamide 4 with long-chain fatty acid groups – suppressing the biodegradability of biodegradable polymers. *Polymer Degradation and Stability*. 2014;108:116-122. doi: <http://dx.doi.org/10.1016/j.polymdegradstab.2014.06.011>.
8. Hablot E, Tisserand A, Bouquey M, Avérous L. Accelerated artificial ageing of new dimer fatty acid-based polyamides. *Polymer Degradation and Stability*. 2011;96(6):1097-1103. doi: <http://dx.doi.org/10.1016/j.polymdegradstab.2011.03.006>.
9. Stempfle F, Ritter BS, Mulhaupt R, Mecking S. Long-chain aliphatic polyesters from plant oils for injection molding, film extrusion and electrospinning. *Green Chem*. 2014;16(4):2008-2014.

10. Brehmer B. Polyamides from biomass derived monomers. In: *Bio-based plastics*. John Wiley & Sons Ltd; 2013:275-293. 10.1002/9781118676646.ch10.
11. Becker J, Wittmann C. Diamines for bio-based materials. In: *Industrial biotechnology*. Wiley-VCH Verlag GmbH & Co. KGaA; 2017:391-409. 10.1002/9783527807833.ch13.
12. Bennett C, Mathias LJ. Synthesis and characterization of polyamides containing octadecanedioic acid: Nylon-2,18, nylon-3,18, nylon-4,18, nylon-6,18, nylon-8,18, nylon-9,18, and nylon-12,18. *Journal of Polymer Science Part A: Polymer Chemistry*. 2005;43(5):936-945.
13. Stempfle F, Quinzler D, Heckler I, Mecking S. Long-chain linear C19 and C23 monomers and polycondensates from unsaturated fatty acid esters. *Macromolecules*. 2011;44(11):4159-4166.
14. Saotome K, Komoto H. Polyamides having long methylene chain units. *Journal of Polymer Science Part A-1: Polymer Chemistry*. 1966;4(6):1463-1473.
15. Huang Y, Li W, Yan D. Preparation and characterization of a series of polyamides with long alkylene segments: Nylons 12 20, 10 20,s 20,6 20, 4 20 and 2 20. *Polymer Bulletin*. 2002;49(2):111-118.
16. Li W, Yan D. Synthesis and characterization of nylons based on hexadecane diacid. *J Appl Polym Sci*. 2003;88(10):2462-2467.
17. Ehrenstein M, Smith P, Weder C. Polyamides X.34: A new class of polyamides with long alkane segments. *Macromolecular Chemistry and Physics*. 2003;204(13):1599-1606.
18. Cui X, Li W, Yan D, Yuan C, Di Silvestro G. Synthesis and characterization of polyamides X 18. *J Appl Polym Sci*. 2005;98(4):1565-1571.

19. Garca-Martn M, de Gracia, Benito Hernndez E, Ruiz Prez R, Alla A, Muoz-Guerra S, Galbis JA. Synthesis and characterization of linear polyamides derived from l-arabinitol and xylitol. *Macromolecules*. 2004;37(15):5550-5556.
20. Mutlu H, Meier MAR. Unsaturated PA X,20 from renewable resources via metathesis and catalytic amidation. *Macromolecular Chemistry and Physics*. 2009;210(12):1019-1025.
21. Pagacz J, Raftopoulos KN, Leszczyska A, Pielichowski K. Bio-polyamides based on renewable raw materials. *Journal of Thermal Analysis and Calorimetry*. 2016;123(2):1225-1237.
22. van Velthoven JIJ, Gootjes L, Noordover BAJ, Meuldijk J. Bio-based, amorphous polyamides with tunable thermal properties. *European Polymer Journal*. 2015;66(Supplement C):57-66. doi: <https://doi.org/10.1016/j.eurpolymj.2015.01.040>.
23. Firdaus M, Meier MAR. Renewable polyamides and polyurethanes derived from limonene. *Green Chem*. 2013;15(2):370-380.
24. Blaine R. Polymer heats of fusion. . ;TN048.
25. Kilson H. Effect of reaction path and initial distribution on molecular weight distribution of irreversible condensation polymers. *Ind Eng Chem Fund*. 1964;3(4):281-293.
26. Tadmor Z, Biesenberger JA. Influence of segregation on molecular weight distribution in continuous linear polymerizations. *Ind Eng Chem Fund*. 1966;5(3):336-343.
27. Stepan D. *The design of continuous polycondensation reactors*. [PhD]. University of Massachusetts Amherst; 1989.

28. Jones NA, Atkins EDT, Hill MJ, Cooper SJ, Franco L. Chain-folded lamellar crystals of aliphatic polyamides. investigation of nylons 4 8, 4 10, 4 12, 6 10, 6 12, 6 18 and 8 12. *Polymer*. 1997;38(11):2689-2699. doi: [https://doi.org/10.1016/S0032-3861\(97\)85603-0](https://doi.org/10.1016/S0032-3861(97)85603-0).
29. Jasinska L, Villani M, Wu J, et al. Novel, fully biobased semicrystalline polyamides. *Macromolecules*. 2011;44(9):3458-3466.
30. Kaya E, Mathias LJ. Investigation of melting behaviors and crystallinity of linear polyamide with high-aliphatic content. *J Appl Polym Sci*. 2012;123(1):92-98.
31. Michalska ZM, Ostaszewski B, Zientarska J. Preparation and catalytic activity of rhodium and platinum complexes attached to polyamides having a pyridine moiety. *Journal of Molecular Catalysis*. 1989;55(1):256-267. doi: [http://dx.doi.org/10.1016/0304-5102\(89\)80259-7](http://dx.doi.org/10.1016/0304-5102(89)80259-7).
32. Murthy NS. Hydrogen bonding, mobility, and structural transitions in aliphatic polyamides. *J Polym Sci B Polym Phys*. 2006;44(13):1763-1782.
33. Saotome K, Komoto H. Polyamides having long methylene chain units. *Journal of Polymer Science Part A-1: Polymer Chemistry*. 1966;4(6):1463-1473.
34. Li Y, Zhu X, Tian G, Yan D, Zhou E. Multiple melting endotherms in melt-crystallized nylon 10,12. *Polym Int*. 2001;50(6):677-682.
35. Millot C, Fillot L, Lame O, Sotta P, Seguela R. Assessment of polyamide-6 crystallinity by DSC. *Journal of Thermal Analysis and Calorimetry*. 2015;122(1):307-314.

36. Garcia D, Starkweather HW. Hydrogen bonding in nylon 66 and model compounds. *J Polym Sci Polym Phys Ed.* 1985;23(3):537-555.
37. Perron PJ, Lederman PB. The effect of molecular weight distribution on polyethylene film properties. *Polymer Engineering & Science.* 1972;12(5):340-345.
38. Simpson EH, Polleck RE. Tensile impact properties of thermoplastics. *Polym Eng Sci.* 1964;4(1):25-28.