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Polyamides based on a partially bio-based spirodiamine

Aleksandra A. Wróblewska^a, Sophie Lingier^b, Jurrie Noordijk^a, Filip E. Du Prez^b,
Stefaan M.A. De Wildeman^a, Katrien V. Bernaerts^{a,*}^a Bio-based Materials, Faculty of Humanities and Sciences, Maastricht University, P.O. Box 616, 6200 MD Maastricht, The Netherlands^b Polymer Chemistry Research Group, Centre of Macromolecular Science, Department of Organic and Macromolecular Chemistry, Ghent University, Krijgslaan 281 S4bis, 9000 Ghent, Belgium

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ABSTRACT

In this study novel, fully and partially bio-based polyamides containing spiroacetal moieties in the backbone derived from bio-glycerol and bio-ethanol were prepared and characterized. The renewable diamine employed to obtain a series of polyamides was synthesized by means of thiol-ene click chemistry and therefore contains flexible thioether as well as rigid spiroacetal moieties. Two different chemical pathways for the polymerization were investigated and evaluated. The polymerization of polyamide salts proved to be the most promising method and therefore salt polymerization was applied in the synthesis of polyamides with aliphatic and aromatic dicarboxylic acids. Subsequently, the structure of the polymers was confirmed by Maldi-ToF analysis and additionally thermal and mechanical properties were investigated revealing T_g 's between 24 and 80 °C and ductile materials with moduli between 1.0 and 1.5 GPa. Both semicrystalline and amorphous polyamides were thermally stable and therefore suitable for thermal processing. In the end, degradation studies were performed on the acetal containing polyamides which showed that the polymers were stable at pH 3 and higher.

1. Introduction

Spiropolymers are a subclass of ladder polymers in which adjacent rings share a common atom [1,2]. This class of polymers is known for its high rigidity and high thermal stability. In the early work on spiropolymers, it was shown that the regular structure of these polymers resulted in highly crystalline materials with limited solubility in organic solvents [3–9]. There have been two strategies to enhance the solubility of rigid polymers; enriching the polymer backbone with solubilising groups (e.g. alkyl groups) [10,11] or introducing irregularities which diminish linearity of the polymer [12]. In more recent years, the last strategy has shown to be the most versatile and promising [13,14]. In order to completely understand what these strategies mean, it is necessary to learn how spiropolymers are made.

One way of obtaining spiropolymers is by direct polyacetalization of tetraols with dialdehydes/diketones [10,11,15,16]. On the other hand, spiropolymers can be obtained by the reaction of bifunctional monomers that already contain spirocenter(s). Among these bifunctional monomers, diols, diamines or diesters are reported and when they are used in polymerization, polyamides [17–20], polyesters [18,21], polyethers [13,22], polyurethanes [23,24] and polycarbonates [25] containing spirocenters are realized.

Few articles reported the synthesis of spiro containing polyamides and when synthesized, it was mostly done from pentaerythritol containing benzylic diamines and terephthaloyl chloride or similar aromatic derivatives via interfacial polymerization [17–19,26]. Even though interfacial polycondensation very often proves to be an efficient approach, it is not applicable for large scale synthesis

* Corresponding author.

E-mail address: katrien.bernaerts@maastrichtuniversity.nl (K.V. Bernaerts).<http://dx.doi.org/10.1016/j.eurpolymj.2017.08.056>

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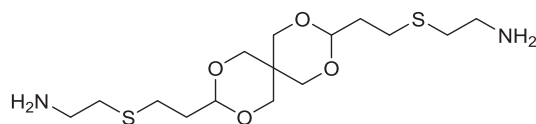


Fig. 1. The structure of the partially bio-based spirodiamine (3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane).

and therefore the more challenging high temperature melt polycondensation is preferable. To our knowledge, only one aliphatic polyamide containing spirocenters was reported up till now [20]. A diester was synthesized from pentaerythritol and methyl 9(10) formyl stearate. This diester was in a next step combined with diamines and diols in a polycondensation reaction, which resulted in polyamides and polyesters. The long alkane side chains (C_8 – C_9) reduced the crystallinity to such a degree that the polymers were soluble in ordinary solvents like chloroform and tetrahydrofuran. Moderate molecular weights ($< 12,000$ g/mol) but broad dispersities (3.9–15.5) were reported [20]. Due to the introduction of long flexible alkyl groups in the polymer chain, only low T_g 's (-10 °C) could be realized. From these results and the limited amount of articles on spiro containing polyamides, it can be concluded that it is challenging to obtaining spiro containing polyamides that are soluble in ordinary solvents and have good thermal properties like high T_g 's and T_d 's.

In this work, a partially bio-based spirodiamine, shown in Fig. 1, was synthesized from pentaerythritol and acrolein [27,28] with subsequent post-polymer modification by thiol-ene addition [29,30]. Pentaerythritol and acrolein can be produced from renewable resources, by extraction and chemical modification of glycerol [31–33]. Thiol-ene chemistry is a straightforward method to introduce functional groups like hydroxy/ester/amines into monomers [23,34]. This new rigid diamine extends the range of bio-based diamines [35–38], which is an important contribution towards fully bio-based polyamides, polyimides, epoxies or polyurethanes. The synthesized diamine has medium long alkyl chains with a spirocyclic moiety, which should lead to improved thermal properties but still soluble polyamides in analogy with a study on polyurethanes with a similar diol [23].

In an effort to obtain fully renewable polyamides from this spirodiamine, two different polymerization routes were explored; melt polycondensation with the ethyl ester and melt polycondensation of the amide salts. Hereafter, the methods were evaluated and the best method will be used on a series of (renewable) aliphatic and aromatic diacids. The polymer structures were confirmed by 1H -NMR and Maldi-*ToF* measurements and the formation of possible side products was investigated. The molecular weights as well as the thermal and mechanical properties were determined. As these polyamides contain acetals, which can be prone to degrade in acid conditions, a hydrolytic stability test at different pH's was executed.

2. Experimental part

2.1. Materials

Cysteamine hydrochloride $> 95.0\%$ and 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane $> 98.0\%$ were purchased from TCI. 2,2-Dimethoxy-2-phenylacetophenone 99% (DMPA), methanol (MeOH), diethylsulfide 98%, Irganox 1330, adipoyl chloride, trimethylamine 99%, pentafluorophenol- d_1 98% (PFP), sodium hypophosphite monohydrate $> 99\%$ ($NaHPO_3 \cdot H_2O$), sodium hydroxide (NaOH), decane $> 99.9\%$, dithranol and potassium trifluoroacetate (KTFA) were purchased from Sigma Aldrich and used as delivered. 1,1,1,3,3,3-hexafluoro-2-propanol, dimethylsulfoxide- d_6 (DMSO- d_6), chloroform- d ($CDCl_3$), succinic acid, adipic acid 99%, sebacic acid 98%, suberic acid 99%, terephthalic acid 99+%, isophthalic acid 99+%, diethyl adipate 99%, N-methylpyrrolidone (NMP), dimethyl sulfoxide 99.7% (DMSO) and dry chloroform 99.9% were purchased from Acros Organics.

2.2. Methods

1H - and ^{13}C - 1H HSQC-NMR spectra were recorded on a Bruker Avance 300 at 300 MHz for 1H -NMR and 75 MHz for ^{13}C -NMR in $CDCl_3$ /25 wt% PFP- d_1 or in DMSO- d_6 . Chemical shifts are presented in parts per million (δ) relative to DMSO- d_6 (2.50 ppm in 1H - and 39.51 ppm in ^{13}C -NMR respectively) or $CHCl_3$ - d_1 (7.26 ppm in 1H - and 77.16 ppm in ^{13}C -NMR respectively). The resonance multiplicities are described as s (singlet), d (doublet), t (triplet) or m (multiplet).

^{13}C -NMR spectra of 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane hydrochloride (2) were recorded on a Bruker Avance 400 at 100 MHz in DMSO- d_6 . Chemical shifts are presented in parts per million (δ) relative to DMSO- d_6 (39.51 ppm in ^{13}C -NMR).

LC-MS and HR-ESI-MS analyses were performed on an Agilent Technologies 1100 series LC/MSD system with a diode array detector (DAD) and a single quad MS. Analytical reversed phase HPLC-analyses were performed with a Phenomenex Luna C18 (2) column (5 μm , 250 mm \times 4.6 mm) and a solvent gradient (0–100% acetonitrile in H_2O in 15 min), the eluted compounds were analysed via UV detection (214 nm).

TGA analysis (TA Instruments Q500) was used to determine the thermal stability of the prepared polyamides and monomers. Around 10 mg of the material was heated at 10 °C/min from 25 °C to 700 °C in a nitrogen atmosphere.

Tensile testing was performed on a Tinius-Olsen H10KT tensile tester, equipped with a 5000 N load cell, using a flat dog bone type specimen with an effective gage length of 13 mm, a width of 2 mm, and a thickness of 1.3 mm. The samples were cut out using a RayRan dog bone cutter. The tensile tests were run at a speed of 10 mm min $^{-1}$.

Matrix-assisted laser desorption/ionization time-of-flight (Maldi-*ToF*) mass spectra were recorded on a Bruker

UltrafleXtreme spectrometer with a 355 nm Nd:Yag laser (2 kHz repetition pulse/Smartbeam-II™) and a grounded steel plate. All mass spectra were obtained in reflector mode. Dithranol (20 mg/mL in THF) was used as a matrix, KTFA (5 mg/mL) was used as a cationating agent, and polymer samples were dissolved in THF (1 mg/mL). The applied ratio of polymer:matrix:salt was 20:200:10. Poly(ethylene glycol) standards with M_n equal to 5000, 10,000, 15,000 g/mol were used for calibration. All data were processed using the FlexAnalysis (Bruker Daltonics) software package.

Molecular weight of polyamides was determined via Gel Permeation Chromatography (GPC). The polymers were dissolved in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) with 0.019 % NaTFA salt. The sample for GPC measurement was prepared by dissolving 5.0 mg of the polymer in 1.5 ml of the solvent. The solutions were filtered over a 0.2 μm PTFE syringe filter before injection. The GPC apparatus was calibrated with poly(methyl methacrylate) (PMMA) standards. Two PFG combination medium microcolumns with 7 μm particle size (4.6×250 mm, separation range 100–1,000,000 Da) and a precolumn PFG combination medium with 7 μm particle size (4.6×30 mm) with a Refractive Index detector (RI) were used in order to determine molecular weights and dispersities. The molecular weights during hydrolysis were measured on a Waters instrument, equipped with 3 Polymer Standards Services GPC serial columns (1 X GRAM Analytical 30 Å, 10 μm and 2 x GRAM Analytical 1000 Å, 10 μm) at 35 °C with a RI detector (2414 Waters). PMMA standards were used for calibration and dimethylacetamide (DMA) containing LiBr (0.42 g mL^{-1}) was used as a solvent at a flow rate of 1 mL min^{-1} . Molecular weights and dispersities were determined using Empower software.

Infrared spectroscopy (IR) of samples in the powder form was recorded on a Szimadzu IR affinity Single Reflection ATR and processed using the SpectraGryph 1.0.3 software package.

Melting profiles were recorded using differential scanning calorimetry (DSC) on a Netzsch Polyma 2014 DSC. DSC data was obtained from about 5 mg of polymer at heating/cooling rates of $10^\circ\text{C min}^{-1}$ under a nitrogen flow of 20 mL min^{-1} . Indium, zinc, tin and bismuth were used as standards for temperature and enthalpy calibration. DSC heating and cooling cycles were performed from 0 to 250 °C. The melting temperatures (top value) and the enthalpy values reported correspond to the second heating cycle.

Melting points of salts were measured on Mettler Toledo Melting Point System MP70. The sample was placed in a capillary and heated with a heating rate of 10°C/min . The melting point was determined visually.

Solubility tests was performed by dissolving approximately 10–20 mg of polymer in 1 mL of solvent at room temperature.

Hydrolytic stability study of the polyamides was performed by placing 0.1 g of polymer into test tubes, to which 10 mL of an aqueous HCl solution of a specific pH was added. Parallel experiments were carried out with four different pH solutions, namely pH 1, 3, 5 and 7 at temperatures of 50 °C. The test tubes were sealed to avoid evaporation of the solutions. After two weeks, the samples were rinsed with water and dried. The degradation of the polymers was monitored gravimetric and by SEC measurements.

2.3. Synthesis

2.3.1. Synthesis of 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane hydrochloride (2)

In a 1-neck flask of 100 mL, 5 g (23.6 mmol, 1 eq.) of 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane and 8 g (70.4 mmol, 3 eq.) of cysteamine hydrochloride were dissolved in 50 mL methanol. 0.3 g (1.2 mmol, 0.05 eq.) of 2,2-dimethoxy-2-phenylacetophenone (DMPA) was added as the catalyst. The solution was stirred under UV for 5 h after which the flask was put overnight in the freezer. The obtained product was filtered off and washed with MeOH. The diamine was then dried at 50 °C in vacuum overnight. Yield: 80 %. The obtained diamine consisted of white crystals with $T_m = 230^\circ\text{C}$.

LC-MS (m/z): 367.20 [$M - 2\text{HCl}$].

HR-ESI-MS calculated m/z [$M - 2\text{HCl}$]: 366.1647; experimental m/z [$M - 2\text{HCl}$]: 367.2000.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) = 8.00 (s, 6H, $\text{NH}_3^+ \text{Cl}^-$), 4.58 (t, 2H, OCHCH_2), 4.26 and 3.59 ($2 \times$ d, 4H, $\text{CCH}_2(\text{eq})\text{O}$), 3.36 and 3.39 ($2 \times$ s, 4H, $\text{CCH}_2(\text{ax})\text{O}$), 2.94 (t, 4H, $\text{CH}_2\text{NH}_3^+ \text{Cl}^-$), 2.72 (t, 4H, $\text{SCH}_2\text{CH}_2\text{NH}_3^+ \text{Cl}^-$), 2.56 (t, 4H, $\text{CHCH}_2\text{CH}_2\text{S}$), 1.78 (t, 4H, $\text{CHCH}_2\text{CH}_2\text{S}$).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) = 100.25 (2C, CH), 69.38 (2C, CH_2), 68.86 (2C, CH_2), 38.31 (2C, CH_2), 34.30 (2C, CH_2), 31.89 (1C, C_q), 27.97 (2C, CH_2), 25.09 (2C, CH_2).

FT-IR: wavenumber (cm^{-1}) = 2500–3000 $\nu(\text{N-H})/\text{NH}_3^+$, stretching (broad signal) 2800–2000 $\text{N-H}/\text{NH}_3^+$ stretching vibration/overtone (multiple peaks), 2915 CH_2 $\nu(\text{C-H})/\text{CH}_2$ asym. stretching vibration, 2841 $\nu(\text{C-H})/\text{CH}_2$ sym. and S-CH_2 asym. stretching, 1603, 1506 $\delta(\text{N-H})/\text{NH}_3^+$, 1432, 1373 $\delta(\text{C-H})/\text{C}(\text{CH}_2)$ deformation, 1194 C–C skeletal stretching, 1172, 1122, 1030 $\nu(\text{C-O-C})$ spiroacetal.

2.3.2. Synthesis of 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane (2)

Prior to the polymerization 10 g (22.8 mmol) of 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane hydrochloride was dissolved in 683 mL of 0.1 M aqueous NaOH solution. The solution was magnetically stirred for 3 h and free diamine was extracted with 3×200 mL chloroform. The chloroform was evaporated and free diamine was dried overnight in the vacuum oven at 50 °C (7.9 g, 21.4 mmol, 94 %).

$^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ (ppm) = 4.56 (t, 2H, OCHCH_2), 4.24 and 3.59 ($2 \times$ d, 4H, $\text{CCH}_2(\text{eq})\text{O}$), 3.37 and 3.39 ($2 \times$ s, 4H, $\text{CCH}_2(\text{ax})\text{O}$), 2.64 (t, 4H, $\text{SCH}_2\text{CH}_2\text{NH}_2$), 2.50 (t, 4H, CH_2NH_2), 2.48 (t, 4H, $\text{CHCH}_2\text{CH}_2\text{S}$), 1.76 (t, 4H, $\text{CHCH}_2\text{CH}_2\text{S}$), 1.54 (s, 4H, NH_2).

2.3.3. Melt polycondensation of diethyl adipate and 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane

To a 100 mL three-necked round bottom flask equipped with a vacuum tight mechanical stirrer, a vigreux column and a distillation condenser, diethyl adipate (1.66, 8.2 mmol), 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane (3.02,

8.2 mmol) and Irganox 1330 (0.05 g, 0.1 wt %) as an antioxidant were added. The reactants were slowly heated to 220 °C and after the ethanol was fully released vacuum was applied for 1–3 h. The crude product was a viscous material with yellowish color.

¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 6.58 (s, 2H, NH), 4.72 (t, 2H, OCHCH₂), 4.57 (d) 3.71 (t) 3.54 (d) (8H, CCH₂O), 4.25 (q, 2H, OCH₂CH₃), 3.33 (t, 4H, CH₂NH), 2.76 (t, 4H, SCH₂CH₂NH), 2.66 (t, 4H, CHCH₂CH₂S), 2.41 (s, 4H, CH₂CONH), 1.98 (t, 4H, CH₂CH₂CO), 1.78 (s, 4H, CHCH₂CH₂S), 1.32 (t, 3H, OCH₂CH₃).

2.3.4. 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane and adipic acid salt

To a solution of adipic acid (0.80 g, 5.4 mmol) in ethanol (10 mL) at 50 °C, a solution of 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane (2.0 g, 5.4 mmol) in ethanol (6 mL) was added. During the addition, a precipitate was formed. The mixture was stirred at 80 °C for 2 h. The crude product was filtered and recrystallized from an ethanol to afford the salt as white crystals (2.4 g, 4.6 mmol, 86%) with a melting point of 172–175 °C.

¹H-NMR (300 MHz, DMSO-*d*₆): δ = 4.70–3.90 (broad signal, 6H, NH₃⁺), 4.58 (t, 2H, OCHCH₂), 4.28 (d) 3.59 (t) 3.55 (d) (8H, CCH₂O), 3.38 (t, 4H, CH₂NH), 2.68 (t, 4H, SCH₂CH₂NH), 2.51 (t, 4H, CHCH₂CH₂S), 2.16 (s, 4H, CH₂CONH), 1.74 (s, 4H, CHCH₂CH₂S), 1.49 (s, 4H, CH₂CH₂CO),

3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane – succinic acid, 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane – suberic acid, 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane – sebacic acid and 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane – isophthalic acid salts were synthesized according to the procedure presented above.

2.3.5. 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane and terephthalic acid salt

To a solution of terephthalic acid (0.906 g, 5.4 mmol) in DMSO (20 mL) at 50 °C a solution of 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane (2.0 g, 5.4 mmol) in DMSO (6 mL) was added dropwise. During the addition, a precipitate was formed. The mixture was stirred at 80 °C for 2 h. The crude product was filtered and the salt was isolated as white crystals (2.7 g, 5.1 mmol, 97%) with a melting point of 252–253 °C.

2.3.6. Melt polycondensation of adipic acid and 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane salt

To a 100 mL three-necked round bottom flask equipped with a vacuum tight mechanical stirrer, a vigreux column and a distillation condenser, 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane and adipic acid salt (3.0 g, 5.8 mmol), NaHPO₃·H₂O (0.3 mg, 0.1 wt%) as a catalyst and Irganox 1330 (0.05 g, 0.1 wt%) as an antioxidant were added. The reactants were slowly heated to 220 °C and after the water was fully released vacuum was applied. The crude product was a viscous material with a yellowish color.

¹H-NMR (300 MHz, CDCl₃/PFP-*d*₁): δ (ppm) = 6.58 (s, 2H, NH), 4.72 (t, 2H, OCHCH₂), 4.57 (d) 3.71 (t) 3.54 (d) (8H, CCH₂O), 3.48 (t, 4H, CH₂NH), 2.76 (t, 4H, SCH₂CH₂NH), 2.65 (t, 4H, CHCH₂CH₂S), 2.41 (s, 4H, CH₂CONH), 1.98 (s, 4H, CH₂CH₂CO), 1.78 (s, 4H, CHCH₂CH₂S).

The presented procedure was applied to the melt polycondensation of all abovementioned salts, except 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane and terephthalic acid salts, which were heated to 250 °C.

2.4. Polymer film preparation

First of all, the polymer material was pre-dried for 30 min. in a vacuum oven at a temperature above the melting point of the polymer. Hereafter, the material was placed between two layers of Teflon and pressed at 3 metric tons. This step was repeated up to three times until the material was free of bubbles.

3. Results and discussion

3.1. Monomer synthesis

A new spiroacetal containing diamine monomer was synthesized via thiol-ene chemistry. 3,9-Divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane (1) was reacted photochemically with cysteamine hydrochloride and DMPA as initiator (see Fig. 2). The resulting molecule (2) has a similar structure as a diol, which was already reported by us [23]. The synthesis was straightforward and the product could easily be purified by filtration. As seen from the ¹H-NMR (Fig. S1 in the supporting information) and ¹³C-NMR (Fig. S2 in the supporting information) spectra, all the signals of the diamine could be assigned and no double bond or thiol signals are present

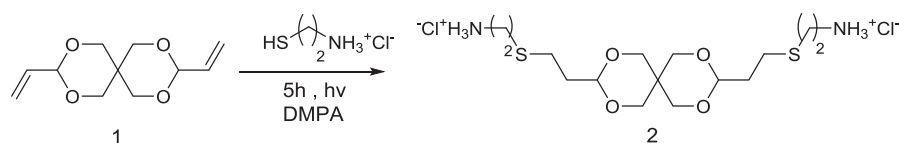


Fig. 2. Synthesis of the partially bio-based spiroacetal diamine (2), starting from 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane (1) and cysteamine hydrochloride.

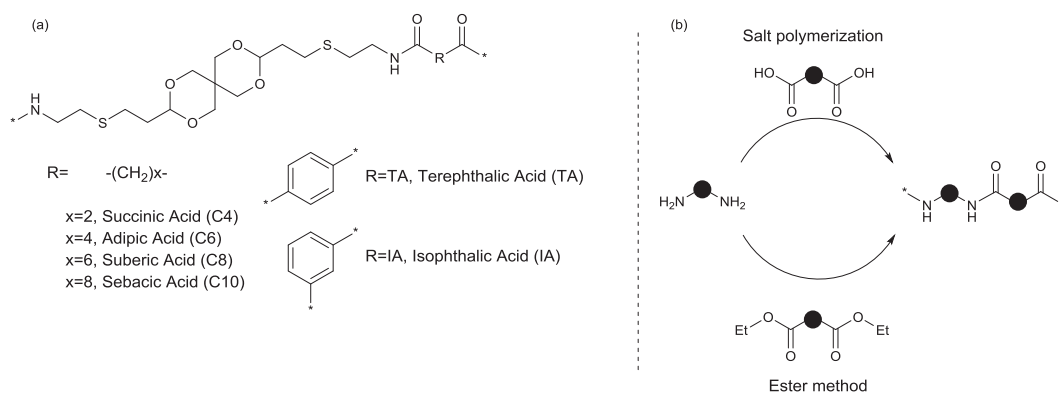


Fig. 3. Overview of the general structure of the synthesized polymers (a) and the two different methods to obtain polyamides (b). x – number of methylene units in the aliphatic chain.

anymore. The purity of the product was confirmed by LC-MS and HR-ESI-MS measurements, where a single signal with a mass of 367.20 (M – 2HCl) could be observed. It was necessary to make the protonated diamine as a thiol-ene reaction is not compatible with amines. Before polymerization, a basic deprotection step followed by an extraction, needs to be performed in order to get the unprotected diamine.

3.2. Polymer synthesis and structural analysis

The deprotected diamine has been used for the synthesis of polyamides. In Fig. 3a, a series of polymers based on the synthesized diamine and different (renewable or potentially renewable) diacids is presented. Four aliphatic diacids with varying alkyl chain length (C4–C6–C8–C10) and two aromatic diacids were used in the polymerization reaction. In part b of Fig. 3, an overview of the two different synthetic polymerization routes is shown. Either the diamine could be reacted with diesters, or the diamine could first be transformed in a salt with a dicarboxylic acid which is subsequently polymerized.

Firstly, the aminolysis of diethyl adipate by the spirodiamine (2) in the melt, at 220 °C was tested. The application of this method resulted in an oligomer PA1 (Table 1) with a molecular weight of 1300 g/mol and molecular weight distribution 3.8. The polymer is thermally stable and 10 % weight loss is registered at 346 °C. From literature it is known that it is challenging to obtain high molecular weight polyamides with the ester-amide bond exchange method due to the alkylation of amine groups in the monomer by the present alkyl ester [39]. The ethylation of the diamine is a significant chain stopping agent (limiting high molecular weights) as secondary amines are more sterically hindered and exhibit lower reactivity than primary amines. The polymer structure was determined by Maldi-ToF. The analysis of the collected spectra (Fig. 4(a)) revealed the presence of three main distributions and side

Table 1
Composition, molecular weights and thermal properties of polyamides with 50/50 diacid/diamine in the feed.

Entry	Method ^b	Diacid ^c	Molar ratio diacid/diamine ^d	M _{n, GPC} [g/mol] ^e	Đ ^e	TGA T _{10%} [°C] ^f	TGA T _{max} [°C] ^f	m.r. salt [°C] ^g
PA1	Ester method	C6	48.5:51.5	1300	3.8	346	358	–
PA2	Salt polymerization	C4	50.1:49.9	2500	2.0	295	351	172–175
PA3		C6	49.9: 50.1	20,000	2.4	350	374	156–162
PA4		C8	50.6:49.4	13,500	2.3	334	360	155–158
PA5		C10	50:50	19,000	2.9	348	365	148–149
PA6 ^a		TA	49.7:50.3	2600	5.9	–	–	252–253
PA7		IA	45.5:54.5	6000	5.4	344	366	199–201

^a the properties were measured for a sample collected before the vacuum stage of the synthesis due to degradation of polymer during the vacuum.

^b ester method refers to melt polycondensation of a diethylester and a diamine, salt polymerization refers to polymerization of amide salts.

^c C4 – succinic acid unit, C6 – adipic acid unit, C8 – suberic acid unit, C10 – sebacic acid unit, TA – terephthalic acid unit, IA – isophthalic acid unit.

^d The molar composition determined by integration of the ¹H-NMR spectra.

^e Molecular weight of polyamides determined by GPC in HFIP with RI detection, calibrated with PMMA standards.

^f T_{10%} – temperature corresponding to 10% weight loss in TGA [°C], T_{max} – temperature corresponding to maximum peak of weight loss [°C] in first derivative curve of TGA.

^g Melting range of corresponding amide salts.

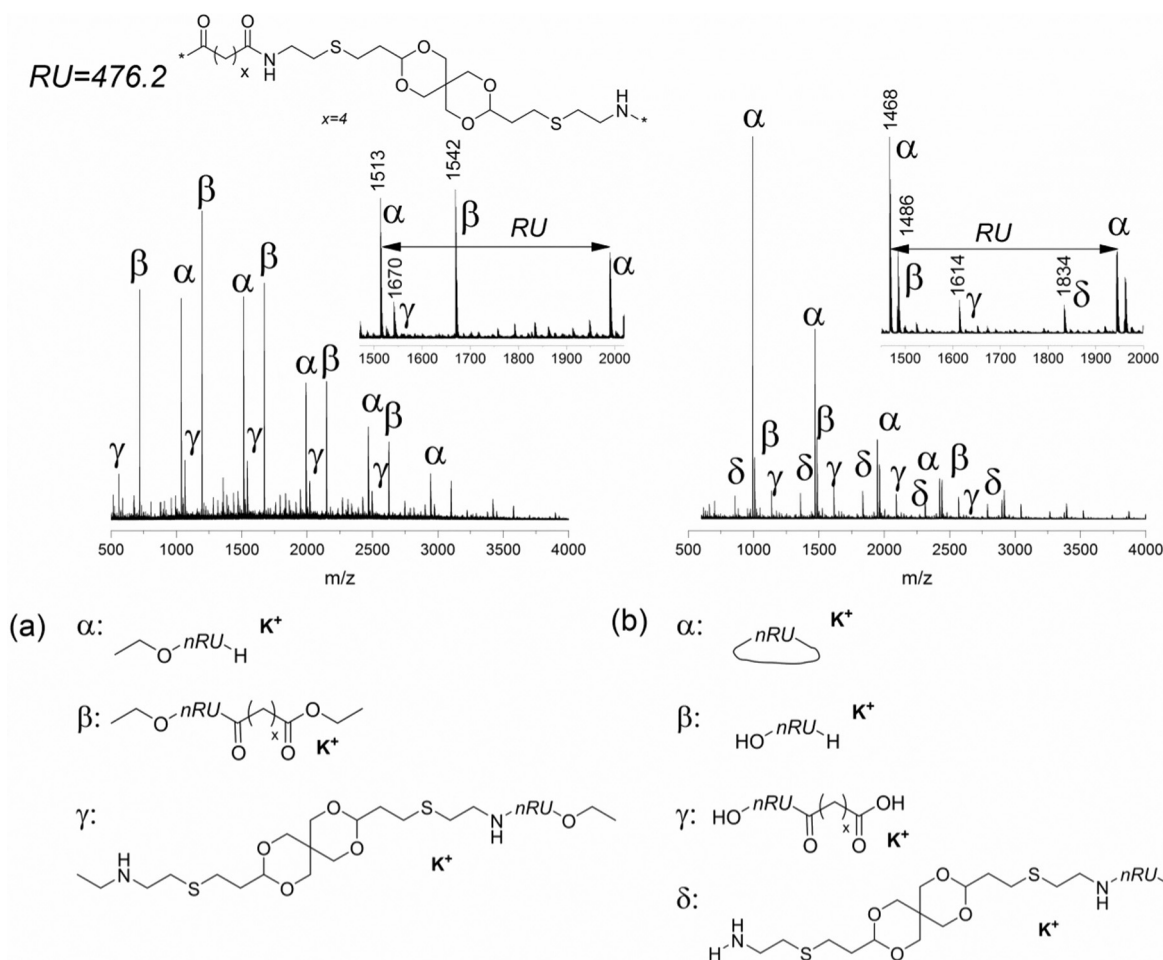


Fig. 4. Maldi-Tof results for PA composed of the spirodiamine with an adipic acid unit: (a) PA1 obtained via aminolysis of diethyl adipate (GPC: $M_n = 1300$ g/mol, $\bar{D} = 3.8$), (b) obtained via salt polymerization (GPC: $M_n = 14500$ g/mol, $\bar{D} = 2.4$) recorded in reflectron mode with dithranol as a matrix and KTFA as a salt.

products formed during the melt polycondensation. The repeating unit is 476.2 g/mol, which corresponds to the diamine-adipic acid unit. The main distribution α on the spectra corresponds to the desired linear chains with both ester and amine end groups. Besides this, the presence of linear chains, which are terminated by the adipic ethyl ester unit are present as distribution β . Interestingly, the distribution γ on the presented graph corresponds to the linear chains terminated with adipate on one side and ethylated diamine on the other. This observation confirms that one of the limiting factors in this type of polymerization is indeed the ethylation of amines.

In a next step, polyamides were prepared by melt polycondensation of the amide salts as the melt polymerization of the diamine with diethyl adipate resulted in oligomers. The polymerization can be conducted at relatively low temperatures as the salts have quite low melting temperatures (salts of spirodiamine and aliphatic diacids melt between 140 and 180 °C). With adipic acid (PA3 in Table 1), molecular weights up to 20,000 g/mol could be reached.

Salt polymerization proved to be the most effective method for polyamide synthesis with 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane because it allows to sustain equimolarity during the synthesis. The equimolar ratio of monomers is ensured by the synthesis of the salt prior to polycondensation. To confirm the structure of the synthesized polyamide, a Maldi-*ToF* spectrum of PA3 was recorded (Fig. 4(b)). Due to the saturation of the detector, only a part of the chains is visible in the spectrum. The analysis revealed the presence of four main distributions. The distribution α corresponds to the formation of cyclic chains. Distributions β , γ and δ correspond to linear chains terminated by acid and amine end groups, two acid end groups and two amine

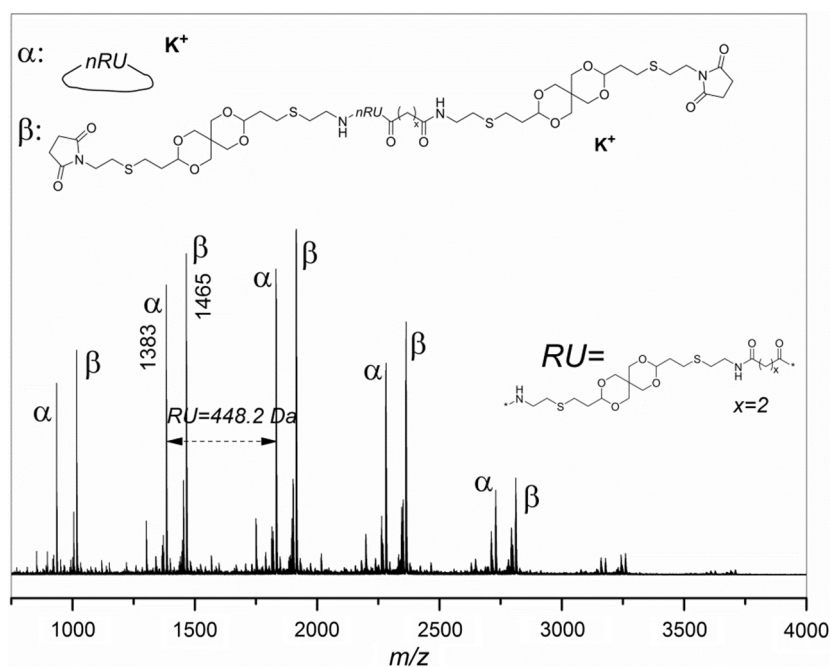


Fig. 5. Maldi-ToF results for PA2 composed of the spirodiamine with succinic acid (GPC: M_n = 1100 G/mol, \bar{D} = 1.8) recorded in reflectron mode with dithranol as a matrix and KTFA as a salt.

end groups, respectively. Additionally, ^1H – ^{13}C NMR spectra of PA3 can be found in Fig. S3 of the supporting information. As salt condensation in the melt yields the highest molecular weights of the two polymerization methods, it was decided to vary the structure of the diacid in order to map some trends in thermal and mechanical properties and show the versatility of the method and of the synthesized diamine.

Polyamides PA3 (C6), PA4 (C8) and PA5 (C10) were successfully synthesized and reached molecular weights of 20,000 g/mol, 13,500 g/mol and 19,000 g/mol, respectively. The above mentioned polymers have typical dispersities for polycondensates (between 2 and 3), which are lower than for PA1 made via transamidation. Furthermore, the polymers obtained via salt condensation showed high thermal stability (Table 1). The polyamides synthesized with aromatic diacids have lower molecular weights (and broader dispersities), i.e. 2600 g/mol for terephthalic and 6000 g/mol for isophthalic acid, respectively. The polyamide of terephthalic acid and 3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane (PA6) degraded upon application of vacuum in the last stage of the synthesis. The temperature of the synthesis of this one polyamide was higher compared to the other polymers (250 °C instead of 220 °C), which contributed to the formation of side products and the degradation of monomers. Moreover, it is generally known that polymerization with terephthalic acid is challenging due to its very limited solubility in the reaction medium.

In contrast to the successfully synthesized polymers with the aliphatic acids C6, C8 and C10, polymer PA2 containing succinic acid C4 has a low molecular weight. The Maldi-ToF analysis of this polymer revealed that the succinic acid is end-capping the polymer by the formation of succinimide, a phenomenon already reported in the literature [40,41]. On the spectra presented in Fig. 5 two distributions can be distinguished. The distribution α corresponds to cyclic chains and distribution β to the polymer with $-\text{NH}_2$ groups that are end capped by the succinic acid.

FT-IR measurements of PA2 confirmed that succinimide carbonyl groups occur in significant amount in the polymeric chains. The presence of amide protons in the FT-IR spectrum for PA2 (Fig. 6 bottom) and PA3 (Fig. 6 top) confirms that the polycondensation resulted for both polymers in the formation of polymeric material. However, for the low molecular weight PA2, in which normally more end groups should be present, a clear signal corresponding to the stretching vibration of $-\text{OH}$ from the carboxylic acid is expected above 3000 cm^{-1} . Instead, a strong signal at 1703 cm^{-1} , corresponding to the stretching vibration of succinimide carbonyl groups, confirms the occurrence of this particular side reaction. The list of FT-IR peaks for PA2 and PA3 together with the peak assignment can be found in Table S1 of the supporting information.

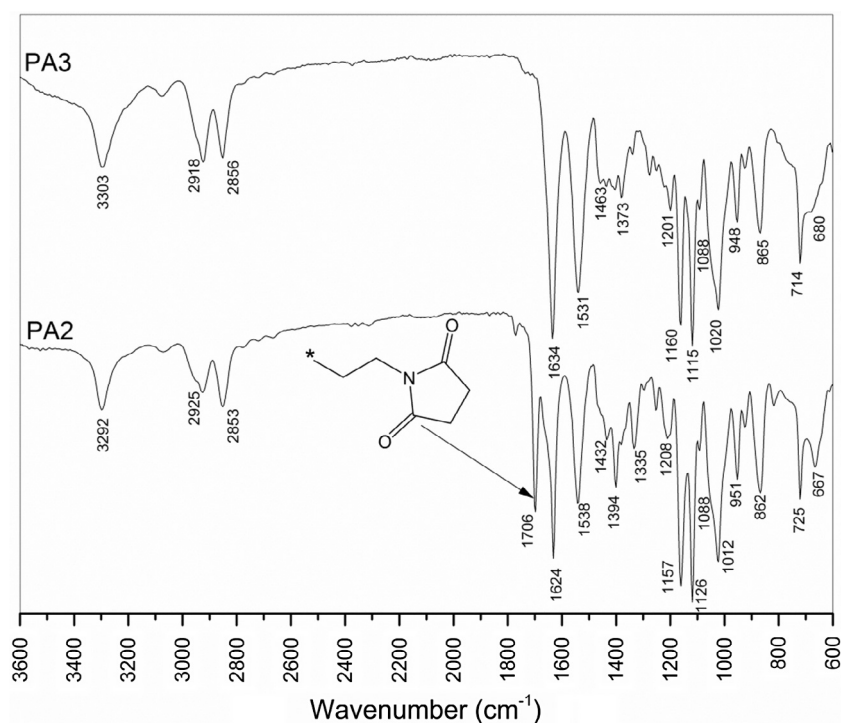


Fig. 6. FT-IR spectrum of (top) poly(adipic acid-co-3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane) PA3 and (bottom) poly(succinic acid-co-3,9-(2-ethylthio)ethanediamine-2,4,8,10-tetraoxaspiro[5.5]undecane) PA2.

3.3. Solubility of polyamides

A reoccurring problem of spiro containing polyamides is the insolubility of the polymers in common organic solvents. Therefore, the solubility of PA5 (C10) and PA7 (isophthalic acid) was tested (Table 2). Both polyamides were soluble in NMP, HFIP, DMA with 5 g/L LiBr and a mixture of chloroform and phenol. PA7, in contrast to PA5, is well soluble in DMSO. It is suspected that the lower molecular weight of PA7 in respect to PA5 as well as the amorphous character of this polyamide (Fig. 7) contributes to the better solubility. Additionally, both polymers are not soluble in ethanol, chloroform and tetrahydrofuran.

Table 2

The solubility of two polyamides obtained upon melt condensation.

Entry	Diacid	EtOH	CHCl ₃	CHCl ₃ /25 wt% PhOH	THF	DMSO	HFIP	NMP	DMA/5 g/l LiBr
PA5	C10	–	–	+	–	–	+	+	+
PA7	IA	–	–	+	–	+	+	+	+

3.4. Thermal analysis

Thermogravimetric analysis for this new series of polyamides showed good thermal stability ($T_d > 300$ °C). The thermal profiles of the polyamides obtained by DSC measurements showed that the aliphatic polyamides are semi-crystalline while the aromatic ones are amorphous. The thermal profile of the aliphatic polyamides shows a glass transition (T_g), a melting region and a cold crystallization region (Fig. 7). The presence of the cold crystallization region indicates a reorganization of the amorphous regions of the polymer to a crystalline one upon heating when the mobility of aliphatic fragments of the polymer chains increases. The amorphous aromatic polyamides have T_g 's of around 83 °C. PA2, which is a low molecular weight polymer, end-capped with succinimide, has a T_g of 24 °C and a melting point of 125 °C, which is the lowest value among the synthesized aliphatic polyamides. For polyamides with adipic acid, suberic acid and sebacic acid, the T_g and melting point decreases with an increase of the number of methylene units present in the aliphatic chain of the acids. The T_g 's are between 36 °C and 48 °C and all melting points have values below 144 °C.

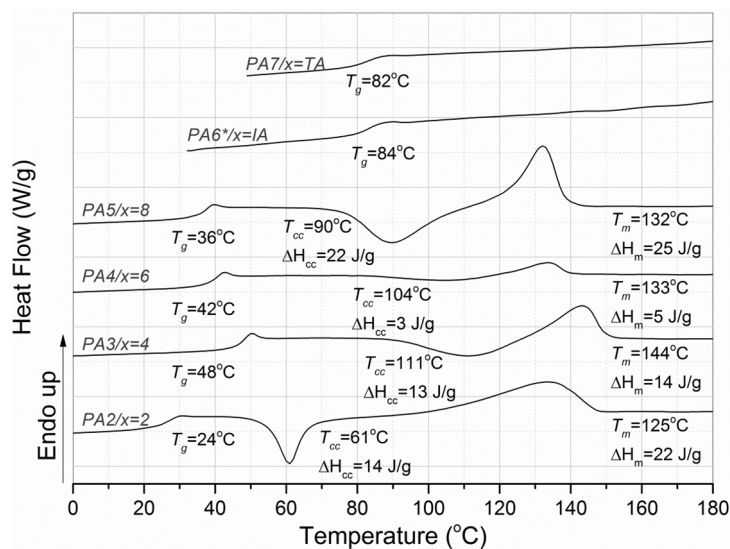


Fig. 7. DSC curves of polyamides synthesized by melt polycondensation of polyamide salts. The melting temperatures (top value), the T_g 's (midpoint) and the enthalpy values reported correspond to the second heating cycle.

3.5. Mechanical analysis

Three of the synthesized polyamides, PA3, PA4 and PA5, were processed via compression moulding and all three polyamides resulted, after fast cooling, in transparent yellowish materials. The synthesized polyamides bear low crystallinity and were cooled fast, which explains the transparency of the materials. Hereafter, tensile measurements were performed on the samples and the results of modulus, yield stress and strain at break can be found in Table 3. The shorter the chain of the diacid, the higher the value of the modulus and yield stress because of a higher rigidity of the polymer chains. The strain at break values of PA5 and PA4 were much higher than the value of PA3 as it behaved more like an elastomeric material due to the longer chain of the diacid.

This difference in ductile behaviour can also be observed in Fig. 8. Both profiles of PA4 and PA5 show a yielding region followed

Table 3
Mechanical properties of three aliphatic polyamides.

Entry	Diacid	E (MPa)	Yield Stress (MPa)	Strain at break (%)
PA3	C6	1520	31.2	43.5
PA4	C8	1130	28.8	400
PA5	C10	975	23.0	523

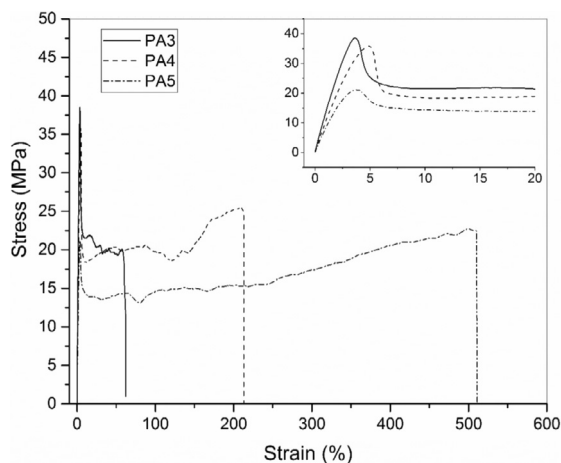


Fig. 8. Strain vs. stress plot for polyamides PA3 (C6) PA4 (C8) and PA5 (C10).

by a long plateau region before break. High modulus, elongation at break and yield stress are typical characteristics of hard and tough materials [42].

3.6. Hydrolytic stability

The hydrolytic stability of one of the polyamides (PA4) was tested at different pH-values. The polymer was immersed in an aqueous solution for two weeks, after which the samples were weighted and SEC analyses was performed to investigate if degradation took place [43]. Four different pH values were tested, namely pH 1, 3, 5 and 7. Already after one day, the transparent polymer changed into an opaque white material. Upon hydration, the water molecules occupy the intermolecular space of the amorphous chains and the inter-chain hydrogen bonds are replaced by interactions with water [44]. The solution and polymer were heated to 50 °C, which made the molecular chains realign resulting in a cold crystallization and therefore a change from a transparent to an opaque material [45]. This phenomenon was already reported and is referred to as water induced crystallization [46]. After two weeks no significant decrease in the weight of the polymer could be observed as for all samples at least 99% of the mass was retained. The SEC results in Fig. 9 show that degradation only took place for the lowest pH-value.

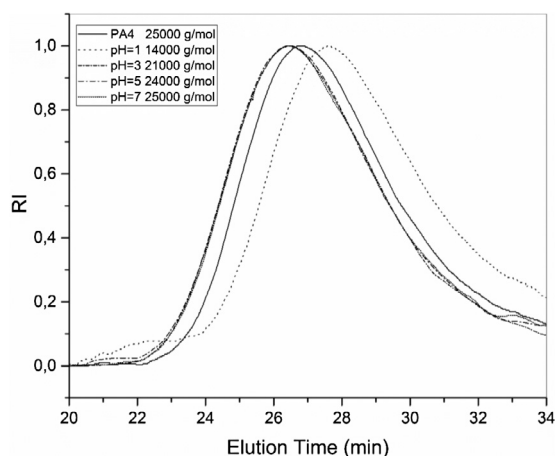


Fig. 9. DMA SEC curves of PA 4 measured after 2 weeks in pH 1, 3, 5 & 7.

4. Conclusions

Polyamides were successfully synthesized from a new, partially bio-based spirodiamine with different diacids. Two approaches towards the synthesis were investigated and the most promising results were obtained via melt polymerization of the polyamide salts. The melt polycondensation with diethyl adipate resulted in low molecular weight polyamides due to ethylation of the diamine, which resulted in a disturbed equimolarity and therefore low molecular weight polyamides. The polycondensation of polyamide salts showed to be the best method for making polyamides out of the spiroacetal containing diamine. In combination with aliphatic diacids, polyamides with molecular weights between 10,000 and 20,000 g/mol were obtained. The polycondensation of succinic acid – spirodiamine salts resulted in a low molecular weight polymer end capped with the succinimide. All synthesized polyamides were soluble in a chloroform/phenol mixture, 1,1,1,3,3,3-hexafluoropropanol and N-methylpyrrolidone. DSC revealed that polymers composed of aliphatic diacids and the investigated diamine were semicrystalline with glass transition temperatures between 24 °C and 48 °C and melting points between 144 °C and 125 °C. The aromatic polyamides were amorphous with glass transition temperatures above 80 °C. The processed polyamides were transparent when rapidly cooled and the materials showed ductile behaviour. The moduli of the investigated polyamides had values between 1.0 and 1.5 GPa. The strain at break value was much higher for polyamides with longer aliphatic chains as they behaved more like elastomeric materials. Hydrolytic stability tests revealed a degradation of the polyamide at a pH of 1 and no degradation above a pH of 3.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.eurpolymj.2017.08.056>.

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