

# Green Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



[www.rsc.org/greenchem](http://www.rsc.org/greenchem)



## Green Chemistry

## PAPER

Direct Polymerization of Levulinic Acid *via* Ugi Multicomponent Reaction

Received 00th January 20xx,  
Accepted 00th January 20xx

Manuel Hartweg and C. Remzi Becer\*

DOI: 10.1039/x0xx00000x

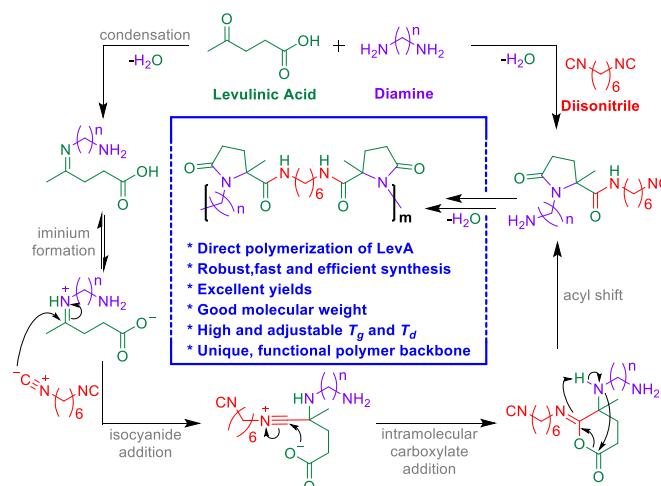
www.rsc.org/greenchem

**A robust, direct and efficient approach has been developed for the utilization of levulinic acid (LevA) as a building block in the synthesis of polyamides. In this approach, there is no need for converting LevA to a cyclic monomer as the carboxylic acid and ketone groups are sufficient for incorporation into a polyamide. Optimization of reaction temperature, solvent, reactants as well as heating source have been performed for the Ugi multicomponent reaction. The obtained polyamides were characterized in details using GPC, NMR, MALDI ToF MS, and TGA.**

## Introduction

The utilization of sustainable chemicals has been of major significance due to the dwindling of fossil resources. Lignocellulosic biomass is one of the most abundant and bio-renewable biomass on earth and converting this into valuable chemicals, materials and plastics has a great economical and environmental potential.<sup>1,2</sup> Various types of sustainable monomers have been polymerized and obtained polymers exhibit excellent material properties. Therefore, sustainable polymers find a broad range of applications and their demands are increasing steadily.<sup>2,3</sup> Levulinic acid is an ideal representative for renewable platform chemicals for several reasons. LevA; (i) is derived from abundant sugar-based cellulose, (ii) is already synthesized in multi-ton scale, and (iii) is cost competitive.<sup>4</sup> Currently, two main methodologies are used in industry for its regeneration from sugar-based cellulose. It can either be synthesized by rehydration of 5-hydroxymethylfurfural (HMF) or by hydrolysis of methyl levulinate, which are both obtained by catalytic dehydration of carbohydrates.<sup>4,5,6</sup> In the last decade, LevA has been used in various chemical processes as a bio-based precursor for additives, pharmaceuticals, and plasticizers. However, it has to be derived to find use as feedstock for polymer

synthesis.<sup>7</sup> Up until now, LevA derivatives, such as ketals and  $\alpha$ -angelica lactone (AAL), as well as  $\gamma$ -valerolactone (GVL), are used as feedstock in polymer synthesis. Indeed, LevA derived diphenolic acid (DPA) may be considered as a renewable substitute for bisphenol A (BPA), whereas other ketals act as monomers for the synthesis of polyurethanes and further thermoplastics.<sup>8,9,9</sup> Furthermore, the derived AAL acts as an intermediate for the synthesis of aliphatic polyesters,<sup>10</sup> whereas the regenerated GVL undergoes a ring-opening reaction to yield diverse polymer precursors.<sup>11</sup> Here, we are reporting a methodology for the first time the direct utilization of LevA in polymer synthesis without any necessity for conversion reactions prior to polymerization (**Scheme 1**). This methodology is benefiting from a more than 50 years old Ugi-multicomponent reaction.<sup>12</sup>



**Scheme 1.** Proposed mechanism for the Ugi-4C8C polymerization from LevA, diamines, and diisocyanides towards polyamides

Multicomponent reactions (MCRs) have become a major interest in polymer science since the introduction of isocyanide-based multicomponent reactions by Meier *et al.* in 2011.<sup>13,14</sup> Multicomponent reactions bear the advantages of being atom efficient and allow convergent syntheses under mild conditions.<sup>15</sup>

Polymer Chemistry Laboratory, School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, E1 4NS London, UK  
E-mail: r.becer@qmul.ac.uk

Electronic Supplementary Information (ESI) available: Experimental details, reaction kinetics, NMR, MALDI ToF MS, GPC, TGA, DSC analysis. See DOI: 10.1039/x0xx00000x

## PAPER

## Green Chemistry

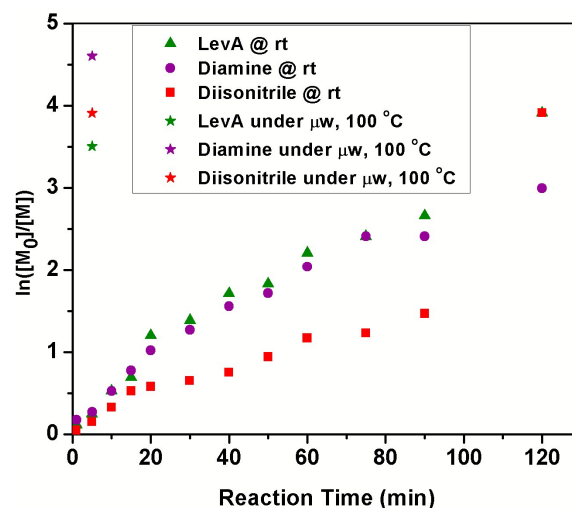
Hence, the selected MCRs, including the Ugi reaction, can be considered as green reactions.<sup>16</sup>

Due to high diversity of substrates, MCRs provide an easy access to complex structural scaffolds in monomer and polymer synthesis, as well as in post polymerization modifications.<sup>13,17</sup> In 2012, Li *et al.* reported the synthesis of sequence regulated poly(ester-amide)s via Passerini three-component reaction (Passerini-3CR).<sup>18,19</sup> In their work, a dicarboxylic acid, two types of monoaldehydes and a diisocyanide were polymerized in a one pot reaction in order to form a linear polymer backbone. Moreover, Meier *et al.* reported the synthesis of monodisperse sequence defined block copolymers *via* Passerini-3CR where an alternating Passerini–thiol-ene cycle was demonstrated using renewable monomers in order to form a well-defined backbone scaffold.<sup>20</sup> Very recently, the same research group significantly improved this methodology by applying the Ugi-MCR in a similar process and obtained sequence-defined oligomers with a dual control over two different side chains per Ugi–thiol-ene reaction cycle.<sup>21</sup> These sophisticated methods benefit from an easy introduction of side chains at precisely defined positions of the polymer backbones.

Considering the scope of monomers that are used in MCR polymerizations, mainly the respective di-compounds, such as diacids, dicarbonyls, diamines, and diisocyanides were employed for polymerization reactions.<sup>22</sup> In our approach, LevA acts as both a carboxylic acid and carbonyl in an Ugi-MCR. We present a novel approach towards sustainable polyamides based on the direct Ugi multicomponent polymerization of LevA. The formation of lactams *via* Ugi four-component reaction of 4-, 5-, and 6-oxo acids with amines and isocyanides has been reported previously.<sup>23</sup> The slightly modified Ugi-MCR polymerization approach of LevA, diamines and diisocyanides is technically a four-component eight-centre (Ugi-4C8C) condensation reaction per repetition unit in this study. Two moles of LevA react with a mole of diamine and a mole of diisocyanide.

## Results and Discussion

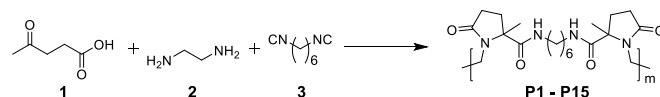
The initial step in the mechanism is the condensation reaction of the carbonyl group of LevA with an amine moiety that results in the formation of an imine while a water molecule is formed as a side product. The formed imine is in equilibrium with its iminium cation due to an intramolecular proton shift with the carboxylic acid moiety. Subsequently, an addition reaction takes place at the electrophilic centre of the iminium ion by a nucleophilic attack of the terminal carbon of the isocyanide, where a nitrilium ion is generated (**Scheme 1**). LevA and ethylenediamine were consumed at the same rate whereas the isocyanide conversion was slightly retarded as evidenced in the GC analysis (**Figure 1**). Next, the nitrilium cation undergoes an intramolecular nucleophilic addition reaction with the carboxylate. An acyl transfer (Mumm rearrangement)<sup>24</sup> finally completes the Ugi reaction under formation of the amide-lactam structure and provides herewith formally one half of the repetition unit within the polymer backbone. It should be noted that, we have not observed the necessity of methanol or other protic solvents within the reaction cycle for the Ugi-polymerization. In our study, even in absence of any solvent polymerization proceeded smoothly (see ESI, **Table S1**).



**Figure 1.** Conversions of the reagents during the Ugi polymerization. Conversions at room temperature ( $\blacktriangle, \bullet, \blacksquare$ ), under microwave irradiation at 100 °C ( $\star, \star, \star$ ). LevA ( $\star, \blacktriangle$ ), ethylenediamine ( $\star, \bullet$ ), 1,6-diisocyanohexane ( $\star, \blacksquare$ ).

### Optimization of the Ugi polymerization

**Table 1.** Optimization of the Ugi-4C8C polymerization of **1**, **2**, and **3**. The reactions were carried out under  $\mu$ w irradiation in MeOH.



Run	Solvent	Temp. [°C]	Time (min)	Conc. LevA [mol·L <sup>-1</sup> ]	M <sub>n</sub> [g·mol <sup>-1</sup> ]	D <sup>[a]</sup>	Yield [%] <sup>[b]</sup>
P1	MeOH	40	30	2.28	3990	1.78	>99
P2	MeOH	70	30	2.28	6660	1.51	>99
P3	MeOH	100	30	2.28	7530	1.42	>99
P4	MeOH	130	30	2.28	6440	1.60	>99
P5	MeOH	100	15	2.28	6690	1.57	>99
P6	MeOH	100	60	2.28	6540	1.60	>99
P7	MeOH	100	30	0.29	3410	2.06	97
P8	MeOH	100	30	1.14	4160	1.78	>99
P9	MeOH	100	30	4.56	8190	1.64	>99
P10	MeOH	100	30	9.13	9460	2.43	>99
P11	Toluene	100	30	2.28	4150	2.06	48
P12	CHCl <sub>3</sub>	100	30	2.28	3810	2.05	83
P13	MeCN	100	30	2.28	3170	1.83	97
P14	DMF	100	30	2.28	1700	1.45	43
P15	H <sub>2</sub> O	100	30	2.28	4280	1.64	>99

[a] Determined by GPC at 50 °C using DMF as the eluent against PMMA standards. [b] Isolated yield after first precipitation.

As a model study we have optimized the Ugi-4C8C polymerization of LevA **1**, ethylenediamine **2**, and 1,6-diisocyanohexane **3**. Therefore, the effect of temperature (room temperature – 100 °C), reaction time (15 – 60 min), concentration (0.29 – 9.13 M), solvent type (MeOH, Toluene, CHCl<sub>3</sub>, MeCN, DMF, and water), and heating source (oil bath, microwave) were investigated at equimolar ratios of the reagents. Initially, several attempts were carried out at various conditions (see ESI, **Table S1**). For instance, the first optimization reactions were carried out in either methanol or bulk, at either room temperature or at 100 °C, and either on bench top or in the microwave ( $\mu$ w). As relatively better results were obtained in the microwave reactor, the rest of the optimization reactions were performed using a  $\mu$ w reactor.

The effect of temperature for the polymerization of the monomers **1**, **2**, and **3** was investigated. The polymerization temperature was altered as 40, 70, 100, and 130 °C (**Table 1**, **P1 – P4**), while the other parameters were kept constant ( $\mu$ w, 2.28 M, MeOH, 30 min). At all reaction temperatures, size exclusion chromatography (SEC) analysis showed formation of polymers with number average molecular weight ( $M_n$ ) in the range of 3990 and 7530 g·mol<sup>-1</sup> and dispersities ( $\mathcal{D}$ ) in the range of 1.42 to 1.78 (**Figure 2A**). However, the best results were obtained at 100 °C (**P3**:  $M_n = 7530$  g·mol<sup>-1</sup>;  $\mathcal{D} = 1.42$ ). Both, an increase and a decrease of the temperature led to significantly lower  $M_n$ . Fortunately, the obtained dispersities are lower than expected for common step growth reactions ( $\mathcal{D} = 2.00$ ), and quantitative yields were isolated after precipitation twice. This indicates that only negligible amount of low  $M_n$  species, such as macrocycles, were formed. Notably, that in case of methanol and other low boiling solvents the pressure in the closed reactor increased dramatically when the boiling point was exceeded. However, the effect of pressure built up during the reaction has not been investigated.

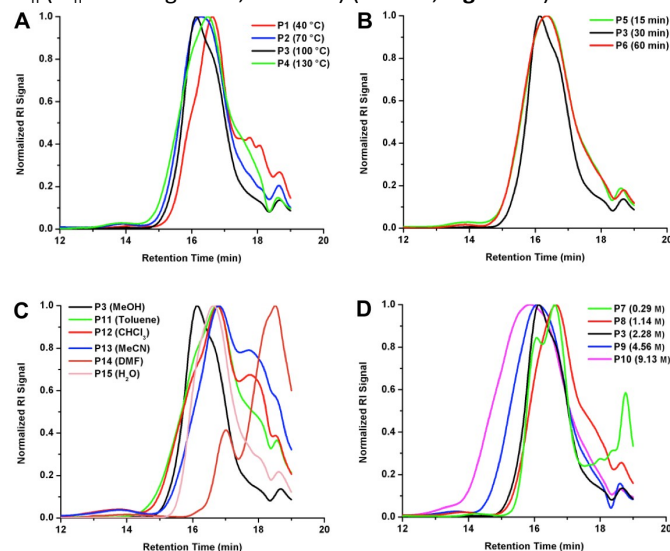
Following to the optimization of the polymerization temperature, the impact of the reaction time was investigated (**Table 1**, **P3**, **P5**, and **P6**, **Figure 2B**). Even at relatively short reaction times (*e.g.* 15 min) quantitative yields were obtained. When the reaction time was decreased to 5 min (see ESI, **Table S1**, **PS4**), only 79% polymer were isolated, displaying lower  $M_n$  and higher dispersities ( $M_n = 3910$  g·mol<sup>-1</sup>,  $\mathcal{D} = 1.86$ ). However, the molecular weight did not increase with extended reaction periods. Therefore, in order to ensure full monomer conversion, following reactions were reacted for 30 min.

The effect of reaction concentration, ranging from 0.29 M to 9.13 M for LevA, has been investigated (**Table 1**, **P3**, **P7 – P10**, **Figure 2D**). At concentrations above 2.28 M, a significant increase of the molecular weight as well as dispersity was observed. For example, at 9.13 M polymer (**P10**;  $M_n = 9460$  g·mol<sup>-1</sup>,  $\mathcal{D} = 2.43$ ) was obtained. In contrary, at concentrations below 2.28 M, the  $M_n$  decreased, while the  $\mathcal{D}$  remained slightly higher in comparison to the polymers formed at 2.28 M. This could be explained by the possible formation of macrocycles with different ring sizes. A similar trend was observed for reactions carried out in bulk (see ESI, **Table S1**).

Another crucial parameter was the choice of an appropriate polar solvent (**Table 1**, **P3**, **P11 – P15**, **Figure 2C**), which influenced the polymer dispersities, and yields of

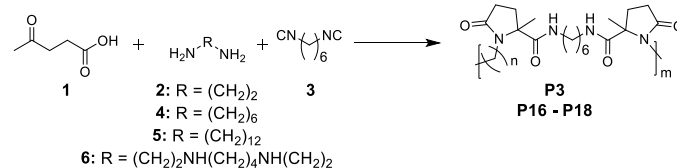
polymers tremendously. Low yields were obtained, especially when toluene or DMF was used. Excitingly, polymers with acceptable properties ( $M_n = 4280$  g·mol<sup>-1</sup>;  $\mathcal{D} = 1.64$ ) could be prepared in water. The best results were obtained when using methanol under  $\mu$ w irradiation with a concentration of 2.28 M at 100 °C after 30 min of reaction time.

As the last step of optimization, the stoichiometric ratio of ethylenediamine was altered as 1.20 and 1.50. Interestingly, at all ratios polymers with almost similar molecular weights were obtained ( $M_n = 8110$  g·mol<sup>-1</sup>;  $\mathcal{D} = 1.48$ ). Moreover, excess of diamine (1.50 eq.) led to bimodal SEC traces with slightly lower  $M_n$  ( $M_n = 5070$  g·mol<sup>-1</sup>;  $\mathcal{D} = 1.39$ ) (see ESI, **Figure S5**).



**Figure 2.** SEC traces of polymers **P1 – P15**. Optimization of the temperature (**A**), reaction time (**B**), solvent (**C**), and concentration (**D**).

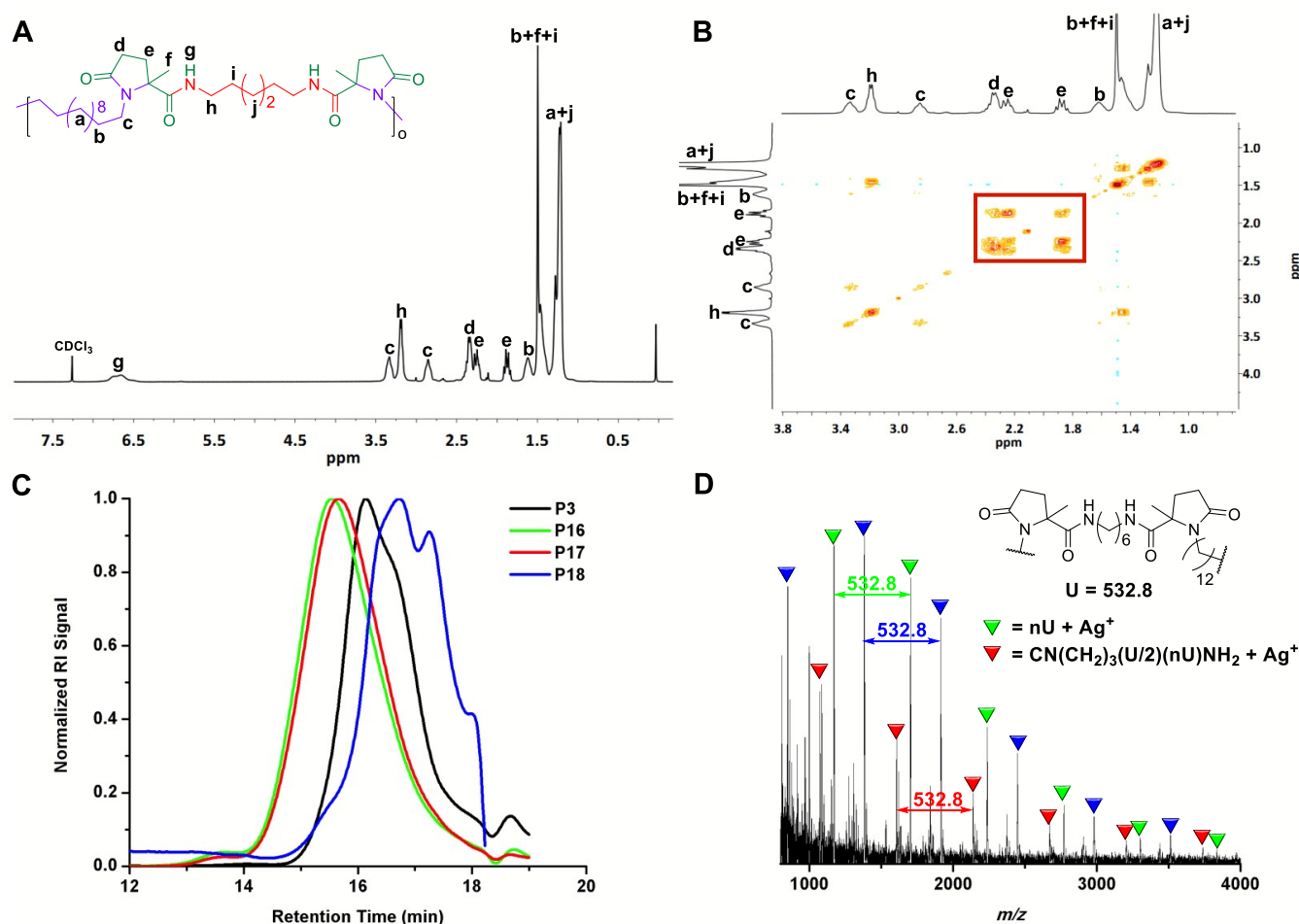
**Table 2.** Ugi-4C8C polymerization of the diamines **2**, **4 – 6** and LevA **1** and diisocyanide **3**. The reactions were carried out under the same conditions ( $\mu$ w, 2.28 M, 100 °C, 30 min).



Run	Diamine	$M_n$ [g·mol <sup>-1</sup> ]	$\mathcal{D}$ <sup>[a]</sup>	Yield [%] <sup>[b]</sup>	[°C]	
					$T_g$	$T_{d, max}$
<b>P3</b>	<b>2</b>	7530	1.42	>99	120	449
<b>P16</b>	<b>4</b>	12 320	1.66	93	86	462
<b>P17</b>	<b>5</b>	11 760	1.63	95	63	462
<b>P18</b>	<b>6</b>	5230	1.36	87	52	377
<b>P19</b>	<b>TREN</b>	n.d.	n.d.	96	n.d.	n.d.

[a] Determined by SEC at 50 °C using DMF as the eluent against PMMA standards. [b] Isolated yield after precipitation. Due to the insolubility of **P19** in common solvents the polymer could not be analyzed further.

In order to study the influence of the chain length between the repetition units of the Ugi-polymer, several different diamines (**Table 2**, **P16 – P18**, **Figure 3C**) were screened.



**Figure 3.** **A**) <sup>1</sup>H NMR analysis of **P17** (400 MHz, CDCl<sub>3</sub>, 25 °C); **B**) COSY NMR analysis of **P17** (400 MHz, CDCl<sub>3</sub>, 25 °C); **C**) SEC analysis of the polymers **P3**, **P16** – **18**; and **D**) MALDI-ToF spectra of **P17** with peak interpretations. The weight distributions represent three polymer species ionized by Ag<sup>+</sup>.

We hypothesized an increasing molecular weight with an increasing chain length due to higher flexibility of the backbone and less steric hindrance of the reaction centers. Reactions employing diamines with a longer chain length, such as hexamethylenediamine or 1,12-diaminododecane, led to a significant increase of the molecular weight ( $M_n = 12\,320$  and  $11\,760\text{ g}\cdot\text{mol}^{-1}$ , respectively) of the polymers while maintaining a comparably low dispersity ( $\mathcal{D} = 1.66$  and  $1.63$ , respectively). In contrary, when spermine was used as a diamine the SEC traces display a multimodal distribution and a comparably low molecular weights. Although, the secondary amines of spermine could potentially take part in a modified Ugi reaction,<sup>25</sup> <sup>1</sup>H NMR analysis of the polymer exhibits the desired formation of the respective polymer (see ESI, **Figure S12–S21**).

Following to this, when TREN (*tris*(2-aminoethyl)amine) was employed as a triamine instead of a diamine in the polymerization, a crosslinked spongy material **P19** was obtained. As expected, it was insoluble in common solvents and could not be analyzed further. Additionally, *p*-phenylenediamine as an aromatic and PEG-diamine as a long chain representative were employed as monomers in the Ugi polymerization (see ESI, **Table S2** and **Figure S2**). In case of the aromatic diamine, mainly low molecular weight oligomers or macrocycles were obtained. When PEG-diamine was employed, a multimodal distribution was revealed by SEC with a slightly higher molecular weight than PEG-diamine ( $M_n = 10\,300\text{ g}\cdot\text{mol}^{-1}$ ;  $\mathcal{D} = 1.78$ ).

In addition to the SEC analysis, the obtained polymers were carefully analyzed by <sup>1</sup>H, <sup>13</sup>C, and COSY NMR spectroscopy, as well as MALDI-ToF mass spectrometry. As representative, the analysis data of polymer **P17** are presented (**Figure 3A**). <sup>1</sup>H NMR spectroscopy clearly indicates the presence of the amide proton (**g**), as well as the characteristic  $\alpha,\beta$ -proton peaks of the amide (**h** and **i**) and the cyclic  $\beta$ -lactam protons (**d** and **e**). COSY NMR spectroscopy (**Figure 3B**, red box) reveals that the methylene protons of the lactams (**d** and **e**) do only correlate with each other and shows the correlation of **h** and **i**, as well as **c** and **b**. Additionally, <sup>13</sup>C NMR spectroscopy (see ESI, **Figure S12–S21**) reveals the formation of characteristic high field shifted amide carbons as well as the presence of the quaternary carbons in  $\alpha$ -position between the lactam and amide bonds. Moreover, MALDI-ToF mass spectra of **P17** is presented (**Figure 3D**) and reveals mainly three different weight distributions each with  $\Delta(m/z) = 532.8\text{ Da}$ , which is assigned to a single repetition unit **U**. The red distribution corresponds to polymer species that are terminated by a primary amine as first and an isonitrile moiety as second terminus. The green distribution on the other hand belongs to macrocyclic components. Unfortunately, the end groups of the blue distribution could not be determined. Nonetheless, the

distance between the repeating units fit to the expected molecular weight of 532.8 Da.

Finally, the thermal properties of the obtained polyamides **P3**, **P16** – **P18** were investigated using thermal gravimetric analyzer (TGA) and differential scanning calorimetry (DSC). (Table 2, and see ESI, Figure S8-S9). The polymers exhibited an amorphous behavior and revealed glass transition ( $T_g$ ) and decomposition temperatures ( $T_d$ ) in the range for common polyamides, e.g. Nylon 6, 12, 4/6, 6/12. As shown in Figure S9 no melting peaks could be detected in the DSC heating curves of the analyzed polymers. Analysis of the polymers **P3**, **P16** – **P18** detected adjustable  $T_g$  values, depending on the chain length of the incorporated amine. A continuous increase of the chain length provided by the incorporated diamine led to a decrease of  $T_g$ . Thus, the short chain derivative **P3** displays the highest  $T_g$  of 120 °C. The polymers with a C<sub>6</sub> or a C<sub>12</sub> chain showed lower  $T_g$  values of 86 °C for **P16** and 63 °C for **P17**. In case of the spermine derivative **P18**, a  $T_g$  of only 52 °C was obtained. This is explained by the increased flexibility of the backbone provided by the incorporation of the heteroatoms alongside the diamine. Moreover, TGA analysis was carried out. The analyzed polymers are found to be stable up to maximum of 462 °C. The decomposition peak maxima were found to be 377 °C for **P18**, 446 °C for **P3**, and 462 °C for **P16** and **P17**.

## Conclusions

In summary, a method for the direct polymerization of levulinic acid, diisonitriles, and different diamines via Ugi-4C8C reaction has been developed and optimized. The process was proved to be robust towards different reaction parameters, fast, and remarkably efficient. Thereby, the polymer structures were analyzed by 1D- and 2D-NMR spectroscopy as well as SEC and MALDI-ToF analysis. The obtained polyamides displayed good dispersities and molecular weights, where the latter can be tuned depending on the chain length of the incorporated diamine, resulting in polyamides with distinct glass transition and decomposition temperatures.

## Notes and references

- F. H. Isikgor and C. R. Becer, *Polym. Chem.*, 2015, **6**, 4497–4559
- R. Mülhaupt, *Macromol. Chem. Phys.*, 2013, **214**, 159–174.
- R. C. Thompson, C. J. Moore, vom Saal, Frederick S and S. H. Swan, *Phil. Trans. R. Soc. B*, 2009, **364**, 2153–2166.
- M. Rose and R. Palkovits, *Macromol. Rapid Commun.*, 2011, **32**, 1299–1311.
- R. Palkovits, *Angew. Chem. Int. Ed.*, 2010, **49**, 4336–4338.
- US patent, US5608105A, 1997.
- F. D. Klingler and W. Ebertz, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2000.
- P. Mäki-Arvela, I. Anugworm, P. Virtanen, R. Sjöholm, J. P. Mikkola, *Ind. Crops Prod.*, 2010, **32**, 175–201.
- C. Leibig, B. Mullen, T. Mullen, L. Rieth and, *Polym. Prepr.*, 2010, **51**, 762–763.
- T. Chen, Z. Qin, Y. Qi, T. Deng, X. Ge, J. Wang and X. Hou, *Polym. Chem.*, 2011, **2**, 1190.
- D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Green Chem.*, 2013, **15**, 584.
- I. Ugi, R. Meyr, U. Fetzer and C. Steinbrückner, *Angew. Chem.*, 1959, **71**, 373–388.
- O. Kreye, T. Tóth and M. A. R. Meier, *J. Am. Chem. Soc.*, 2011, **133**, 1790–1792.
- A. Sehlinger and M. A. R. Meier, *Adv. Polym. Sci.*, 2015, DOI: 10.1007/12\_2014\_298.
- a) I. Ugi, A. Dömling and W. Horl, *Endeavour*, 1994, **18**, 115–122; b) A. Dömling, W. Wang and K. Wang, *Chem. Rev.*, 2012, **112**, 3083–3135; c) E. Ruijter, R. Scheffelaar and R. V. A. Orru, *Angew. Chem. Int. Ed.*, 2011, **50**, 6234–6246;
- B. Yang, Y. Zhao, C. Fu, C. Zhu, Y. Zhang, S. Wang, Y. Wei and L. Tao, *Polym. Chem.*, 2014, **5**, 2704.
- R. Kakuchi, *Angew. Chem. Int. Ed.*, 2014, **53**, 46–48.
- X.-X. Deng, L. Li, Z.-L. Li, A. Lv, F.-S. Du and Z.-C. Li, *ACS Macro Lett.*, 2012, **1**, 1300–1303.
- M. Passerini, *Gazz. Chim. Ital.*, 1921, **51**, 126–129.
- S. C. Solleder and M. A. R. Meier, *Angew. Chem. Int. Ed.*, 2014, **53**, 711–714.
- S. C. Solleder, K. S. Wetzel and M. A. R. Meier, *Polym. Chem.*, 2015, **6**, 3201–3204.
- a) A. Sehlinger, R. Schneider and M. A. R. Meier, *Macromol. Rapid Commun.*, 2014, **35**, 1866–1871; b) A. Sehlinger, L. M. de Espinosa and M. A. R. Meier, *Macromol. Chem. Phys.*, 2013, **214**, 2821–2828; c) N. Gangloff, D. Nahm, L. Döring, D. Kuckling and R. Luxenhofer, *J. Polym. Sci, Part A: Polym. Chem.*, 2015, **53**, 1680–1686; d) Z. Zhang, Y.-Z. You, D.-C. Wu and C.-Y. Hong, *Macromolecules*, 2015, **48**, 3414–3421; e) J. G. Rudick, *J. Polym. Sci, Part A: Polym. Chem.*, 2013, **51**, 3985–3991; f) A. Sehlinger, P.-K. Dannecker, O. Kreye and M. A. R. Meier, *Macromolecules*, 2014, **47**, 2774–2783; g) B. Yang, Y. Zhao, S. Wang, Y. Zhang, C. Fu, Y. Wei and L. Tao, *Macromolecules*, 2014, **47**, 5607–5612; h) W. Lin, T. Sun, M. Zheng, Z. Xie, Y. Huang and X. Jing, *RSC Adv.*, 2014, **4**, 25114–25117;
- a) K. M. Short and A. M. Mjalli, *Tetrahedron Lett.*, 1997, **38**, 359–362; b) G. C. Harriman, *Tetrahedron Lett.*, 1997, **38**, 5591–5594; c) Tye, H., Whittaker, M., *Org. Biomol. Chem.*, 2004, **2**, 813–815; d) M. Jida, S. Malaquin, R. Poulain, G. Laconde and B. Deprez, *Tetrahedron Lett.*, 2010, **51**, 5109–5111.
- O. Mumm, *Ber. Dtsch. Chem. Ges.*, 1910, **43**, 886–893.
- a) G. B. Giovenzana, G. C. Tron, S. Di Paola, I. G. Menegotto and T. Pirali, *Angew. Chem.*, 2006, **118**, 1117–1120; b) G. B. Giovenzana, G. C. Tron, S. Di Paola, I. G. Menegotto and T. Pirali, *Angew. Chem. Int. Ed.*, 2006, **45**, 1099–1102.