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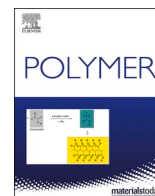
On the way to greener furanic-aliphatic poly(ester amide)s: Enzymatic polymerization in ionic liquid

Dina Maniar [a,1], Fitrilia Silvianti [a,b,1], Viviana M. Ospina [a,c], Albert J.J. Woortman [a], Jur van Dijken [a], Katja Loos [a,*]

[a] Macromolecular Chemistry & New Polymeric Materials, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747, AG, Groningen, the Netherlands
[b] Politeknik ATK Yogyakarta, The Ministry of Industry of the Republic of Indonesia, Jl. Prof. Wirjono Projodikoro, DIY, Indonesia
[c] Grupo Ciencia de Los Materiales, Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia (UdeA). Calle 70 No. 52-21 & Calle 62 No. 52-Medellín, Colombia

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ABSTRACT

The polymerization of 2,5-furandicarboxylic acid (FDCA), one of the key building blocks for the preparation of furan polymers, is often accompanied with side reactions (e.g. decarboxylation). Due to the mild reaction conditions, enzymatic polymerizations became an excellent candidate to address this issue. Here, we present a green and effective method to prepare different furanic-aliphatic poly(ester amide)s (PEAFs) by applying two different approaches. PEAFs with $\overline{M_w}$ up to 21 kg mol^{-1} were successfully synthesized by a Novozyme 435-catalyzed polycondensation of dimethyl 2,5-furandicarboxylate (DMFDCA) with aliphatic diols, diamines or amino alcohols, using toluene at 90 °C. Additionally, we were able to enhance the sustainability of the entire process by performing the polymerization in ionic liquids – BMIMPF$_6$ and EMIMBF$_4$. Using the ionic liquids (ILs) BMIMPF$_6$ and EMIMBF$_4$ as solvents, we were able to produce PEAFs with $\overline{M_w}$ up to 7 kg mol^{-1}. The different polarity of the solvents affects the enzyme activity and product solubility, thus also the final molecular weight of the PEAFs. Despite the lower molecular weight, the tested ILs result products with similar characteristics. All obtained PEAFs are semi-crystalline materials and decompose at a temperature around 390 °C with a T_m of around 77–140 °C and T_g of around 11–46 °C. Although still exemplified on the proof-of-concept production of sustainable materials, these findings pave the way to promote the transition from fossil-to bio-based polymers, as well as more environmentally friendly synthetic routes.

1. Introduction

2,5-Furandicarboxylic acid (FDCA) is a valuable building block for the preparation of high-performance polymers including polyesters and polyamides [1–6]. It is a well-known biobased monomer, which was extensively studied for the synthesis of poly(ethylene furanoate) (PEF), a biobased alternative to poly(ethylene terephthalate) (PET) [7–9]. However, due to side reactions (e.g. decarboxylation) that occur at around 200 °C, different studies have consistently shown that mild reaction conditions are required in the polymerization of FDCA [10]. In this regard, enzymatic polymerizations shows their potential and hence are interesting to be developed for the synthesis of FDCA-based polymers.

In general, enzyme catalysis has been applied in polymer synthesis and proven to be a powerful pathway for polymer production in a sustainable manner [11–13]. Enzymatic polymerizations are known to be more eco-friendly due to the mild reaction conditions and the used renewable non-toxic enzyme catalyst [12,14]. Different studies already reported the enzyme-catalyzed production of FDCA-based polymers [11, 15–20]. To achieve optimum results, enzymatic synthesis of these furan polymers has been conducted through different techniques, e.g., one-step, two-step, two-step with varying temperature [5,15–18,21]. However, due to the poor solubility of the products (e.g. FDCA-based polyamides), early precipitation occurred in the enzyme-catalyzed reaction and leads to low molecular weight products.

Copolycondensation is one of the possible methods to modify

polymer properties. With a combination of polyester and polyamide features, poly(ester amide)s typically possess better solubility compared to polyamides. They are also known to show good thermo-mechanical behavior, as well as biocompatibility and biodegradation [22]. These properties make them attractive for use in biomedical applications or as high-performance polymers with reduced environmental impact. Considering this, the application of enzymatic polymerizations appears to be a promising method for the preparation of poly(ester amide)s. For example, Gross and Scandola et al. performed the synthesis of silicone poly(ester amide)s using N435, the immobilized form of Lipase B from *Candida antartica*, in bulk at 70 °C [23]. Another example was provided by Poojari et al. in which they studied the enzymatic synthesis of silicone fluorinated aliphatic poly(ester amide)s [24]. Additional studies on enzymatic polymerizations of poly(ester amide)s are summarized elsewhere [12]. The preparation of furan poly(ester amide)s by non-enzymatic pathways via bulk copolycondensation was previously reported [25,26]. However, despite the extensive studies on enzymatic syntheses of furan polyesters and polyamides, similar studies on furan poly(ester amide)s are not yet reported [15,16,18,19,21].

Herein, we report the synthesis of furan poly(ester amide)s by lipase catalysis. N435 was used to catalyze a reaction between dimethyl 2,5-furandicarboxylate (DMFDCA) with aliphatic diols and diamines or amino alcohols. To improve the sustainability of the whole synthetic process, we also conducted the reaction in ionic liquids. It has been reported that ionic liquids (ILs) are green solvents with regard to their potential for high recyclability, low flammability, low volatility, and low toxicity [27–29]. In addition, ILs are also regarded as prospective alternatives to traditional metal-based catalyst due to their outstanding catalytic activity and tunabilities [30–32]. By performing a detailed analysis of the enzymatic polymerization, we designed a more efficient and environmentally friendly process for the synthesis of furan poly (ester amide)s.

2. Materials and methods

2.1. Materials

Novozym 435 (N435, Candida antartica lipase B (CALB) immobilized on acrylic resin, 5000+ U/g), 1,6-hexanediol (1,6-HDO, 99%), 1,8-octanediol (1,8-ODO, 98%), 1,10-decanediol (1,10-DDO, 98%), 1,12-dodecanediol (1,12-DODO, 99%), 1,6-hexanediamine (1,6-HDA, 98%), 1,8-octanediamine (1,8-ODA, 98%), 1,10-decanediamine (1,10-DDA, 97%), 1,12-dodecanediamine (1,12-DODA, 98%), 6-amino-1-hexanol (6-AH, 97%), toluene (anhydrous, 99.8%), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF$_6$, ≥97.0%), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF$_4$, ≥98.0%), chloroform (CHCl$_3$, Chromasolv HPLC, ≥99.8%, amylene stabilized), potassium trifluoroacetate (KTFA, 98%), deuterated chloroform (CDCl$_3$, 99.8 atom% D), and deuterated dimethyl sulfoxide (DMSO- d_6) were purchased from Sigma Aldrich. Dimethyl 2,5-furandicarboxylate (DMFDCA, 97%) was purchased from Fluorochem UK. 8-amino-1-octanol (8-AO, > 98.0%), 10-amino-1-decanol (10-AD, > 98.0%), and 12-amino-1-dodecanol (12-ADO, > 98.0%), 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, ≥ 99%) were acquired from TCI Europe. Absolute methanol (MeOH, AR) was obtained from Biosolve Chemicals. Dithranol (≥98%) was purchased from Fluka.

N435 was pre-dried as reported previously [33]. The molecular sieves (4 Å) were pre-activated at 200 °C in vacuo. The diamines, including 1,6-HDA, 1,8-ODA, 1,10-DDA, and 1,12-DODA, were purified by sublimation under reduced pressure and stored in a desiccator. All the other chemicals were used as received.

2.2. CALB-catalyzed polycondensation of DMFDCA with various diamines and diols

Based on our previously reported studies [16], the following one-step

enzymatic polymerization procedure was applied. As an example, the experimental polymerization of DMFDCA, 1,12-DODO, and 1,12-DODA is described in the following. Pre-dried N435 and pre-activated molecular sieve (15 wt % and 150 wt % in relation to the total amount of the monomer, respectively) were inserted to a 25 mL round bottom flask under a nitrogen environment. Subsequently, DMFDCA (4.675 mg, 2.59 mmol), 1,12-DODO (2.618 mg, 1.29 mmol), 1,12-DODA (2.592 mg, 1.29 mmol) and solvent (5 mL) were added into the flask. The flask was magnetically stirred in an oil bath and heated to 90 °C under a nitrogen atmosphere. After a reaction time of 72 h, the reaction was allowed to cool down and stopped. Chloroform (20 mL) was added to dissolve the products under vigorous stirring. N435 and molecular sieve were filtered by normal filtration (Folded filter type 15 Munktell 240 mm) and then washed with chloroform (3 10 mL). All the obtained solutions were combined and concentrated by the use of a rotary evaporator at 40 °C under a reduced pressure of 400–480 mbar. The concentrated solution was precipitated in an excess amount of methanol. The solution with the precipitated products were then stored overnight at −20 °C. After that, the precipitated product was collected by centrifugation (30 min, 4500 rpm, 4 °C in a Thermo/Heraeus Labofuge 400 R and dried under vacuum at 40 °C for 3 days, which yielded a white or light brown powder depending on the reaction conditions. The powders were stored under vacuum at room temperature prior to analysis.

2.3. CALB-catalyzed polycondensation of DMFDCA with various amino alcohols

A typical reaction is described as follows: In a 25 mL round bottom flask, 1 g monomer (DMFDCA: amino alcohols = 1:1, mol ratio), pre-dried N435, and pre-activated molecular sieve (15 wt % and 150 wt % in relation to the total amount of the monomer, respectively) were mixed with solvent (5 mL). The flask was magnetically stirred in an oil bath and heated to 90 °C under a nitrogen atmosphere for 72 h. At the completion of the reaction, the reaction mixture was purified and dried according to the same procedure as described above. The samples were stored under vacuum at room temperature before analysis.

2.4. Furan-based poly(ester amide)s

ATR-FTIR (ν, cm^{-1}): 3317–3334 (N–H stretching vibration); 3108–3120 (=C–H stretching vibration of the furan ring); 2922–2935, 2850–2858 (asymmetric and symmetric C–H stretching vibrations); 1720–1724 (C=O stretching vibration of ester); 1645–1650 (C=O stretching vibration of amide); 1573–1576 (aromatic C=C bending vibration); 1550–1552 (N–H bending vibration); 1491–1493, 1468–1475 (C–H deformation and wagging vibration); 1392 (C–H rocking vibration); 1142–1144, 1270–1284 (asymmetric and symmetric stretching vibrations of the ester C–O–C group); 1230–1234, 1010–1016 (=C–O–C = ring vibration, furan ring); 966–977, 820–822, 764 (=C–H out-of-plane deformation vibration, furan ring).

2.5. Poly(hexamethylene furanoate-co-hexamethylene furanamide) (PEAF6)

^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.17 (2H, m, –C**H** = , DMFDCA), 6.89 (1H, m, –N**H**–CO–, from 6-AH), 4.31 (2H, m, –CO–O–C**H$_2$**–, from 6-AH), 3.43 (2H, m, –CO–NH–C**H$_2$**–, from 6-AH), 1.79 (2H, m, –CO–O–CH$_2$–C**H$_2$**–, from 6-AH), 1.64 (2H, m, –CO–NH–CH$_2$–C**H$_2$**–, from 6-AH), 1.44 (4H, m, –CO–O–CH$_2$–CH$_2$–C**H$_2$**– C**H$_2$**–, from 6-AH), 3.91 (s, –O–C**H$_3$**, end group from DMFDCA), 3.66 (t, –C**H$_2$**–OH, end group from 6-AH).

2.6. Poly(octamethylene furanoate-co-octamethylene octanamide) (PEAF8)

^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.16 (2H, m, –C**H** = , DMFDCA),

6.74 (1H, m, –NH–CO–, from 8-AO), 4.30 (2H, m, –CO–O–**CH₂**–, from 8-AO), 3.41 (2H, m, –CO–NH–**CH₂**–, from 8-AO), 1.73 (2H, m, –CO–O–CH₂–**CH₂**–, from 8-AO), 1.61 (2H, m, –CO–NH–CH₂–**CH₂**–, from 8-AO), 1.35 (8H, m, –CO–O–CH₂–CH₂–CH₂– **CH₂**– **CH₂**– **CH₂**, from 8-AO), 3.92 (s, –O–**CH₃**, end group from DMFDCA), 3.64 (t, –**CH₂**–OH, end group from 8-AO).

2.7. Poly(decamethylene furanoate-co-decamethylene furanamide) (PEAF10)

¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.16 (2H, m, –**CH** = , DMFDCA), 6.72 (1H, m, –N**H**–CO–, from 10-AD), 4.30 (2H, m, –CO–O–**CH₂**–, from 10-AD), 3.41 (2H, m, –CO–NH–**CH₂**–, from 10-AD), 1.73 (2H, m, –CO–O–CH₂–**CH₂**–, from 10-AD), 1.59 (2H, m, –CO–NH–CH₂–**CH₂**–, from 10-AD), 1.30 (12H, m, –CO–O–CH₂–CH₂–**CH₂**–**CH₂**–**CH₂** –**CH₂**–**CH₂**–**CH₂**, from 10-AD), 3.91 (s, –O–**CH₃**, end group from DMFDCA), 3.64 (t, –**CH₂**–OH, end group from 10-AD).

2.8. Poly(dodecamethylene furanoate-co-dodecamethylene furanamide) (PEAF12)

¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.16 (2H, m, –**CH** = , DMFDCA), 6.69 (1H, m, –N**H**–CO–, from 12-ADO), 4.30 (2H, m, –CO–O–**CH₂**–, from 12-ADO), 3.42 (2H, m, –CO–NH–**CH₂**–, from 12-ADO), 1.74 (2H, m, –CO–O–CH₂–**CH₂**–, from 12-ADO), 1.59 (2H, m, –CO–NH–CH₂–**CH₂**–, from 12-ADO), 1.26 (16H, m, –CO–O–CH₂–CH₂–**CH₂**–**CH₂**–**CH₂**–**CH₂** –**CH₂**–**CH₂**–**CH₂**–**CH₂**, from 12-ADO), 3.91 (s, –O–**CH₃**, end group from DMFDCA), 3.64 (t, –**CH₂**–OH, end group from 12-ADO).

2.9. Analytics

Proton and carbon nuclear magnetic resonance (¹H NMR and ¹³C NMR; 400 MHz) spectra were recorded on a Varian VXR Spectrometer, using CDCl₃ or DMSO-d_6 as the solvent. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra were recorded on a Bruker VERTEX 70 spectrometer equipped with an ATR diamond single reflection accessory. The measurement resolution was 4 cm⁻¹ and the spectra were collected in the range of 4000–400 cm⁻¹, with 16 scans for each sample. Atmospheric compensation and baseline correction were applied to the collected spectra using OPUS spectroscopy software (v7.0) (Bruker Optics).

Molecular weights (number-average, $\overline{M_n}$, and weight-average, $\overline{M_w}$) of PEAFs were determined by size exclusion chromatography (SEC) equipped with a triple detector, consisting of a Viscotek Ralls detector, Viscotek Viscometer model H502, and Schambeck RI2912 refractive index detector. The separation was carried out by utilizing two PLgel 5 μm MIXED-C, 300 mm columns from Agilent Technologies at 35 °C. THF 99+%, extra pure, stabilized with BHT was used as the eluent at a flow rate of 1.0 mL/min. Data acquisition and calculations were performed using Viscotek OmniSec software version 5.0. Molecular weights were determined based on a conventional calibration curve generated from narrow dispersity polystyrene standards (Agilent and Polymer Laboratories, $\overline{M_w}$ = 645–3001000 g mol⁻¹). The samples were filtered over a 0.2 μm PTFE filter prior to injection.

Matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-ToF MS) measurements were performed on a Biosystems Voyager-DE PRO spectrometer in positive and linear mode. The used matrix, cationization agent, and solvent were dithranol, KTFA, and HFIP respectively. At first, dithranol (20 mg/mL), KTFA (5 mg/mL) and a polymer sample (1–2 mg/mL) were premixed in a ratio of 5:1:5. Then the mixture was hand-spotted on a stainless steel plate and left to dry afterwards. Polyamide species having different end groups were determined by the following equation:

$$M_P = M_{EG} + (n \times M_{RU}) + M_{K^+} \tag{1}$$

where M_P is the molecular masses of a poly(ester amide)s species, M_{EG} is the molecular mass of the end groups, n is the number of the repeating units, M_{RU} is the molecular mass of the repeating units, and M_{K^+} is the molecular mass of the potassium cation.

The analysis of the thermal properties was performed on a TA-Instruments Q1000 DSC calibrated on indium standard. The heating rate was 10 °C min⁻¹ under nitrogen flow. PEAFs melting points (T_m) were derived from the first heating curve; glass transition temperatures (T_g) were measured by Temperature Modulated DSC (TMDSC) at 2 °C min⁻¹ with a temperature modulation of ±0.50 °C for every 60 s. The thermal stability and degradation temperatures were analyzed on a TA-Instruments Discovery TGA 5500 using a heating rate of 10 °C min⁻¹ in a nitrogen environment.

Wide-Angle X-ray diffraction (WAXD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 0.1542 nm) in the angular range of 5-50° (2θ) at room temperature.

## 3. Results and discussion

3.1. Synthesis and structural characterization of furanic-aliphatic poly (ester amide)s (PEAFs)

Furanic-aliphatic poly(ester amide)s (PEAFs) were successfully prepared via two different procedures, as outlined in Scheme 1. In the first procedure, PEAFs were synthesized by the N435-catalyzed reaction between DMFDCA, diols, and diamines, while in the second approach DMFDCA and linear amino alcohols were used. The number of methylene units (n) in the aliphatic linear diols, diamines, and amino alcohols is 6, 8, 10, and 12 respectively. In this work, this number is defined as the chain length of the tested aliphatic linear monomers. The obtained PEAFs are listed in Table 1. To evaluate the influence of the aliphatic linear monomers on the enzymatic synthesis of PEAFs, a comparative study between the two approaches was performed.

We found that DMFDCA can react with 1,8-octanediamine (1,8-ODA) and 1,8-octanediol (1,8-ODO) or 8-amino-1-octanol (8-AO) in the absence of N435. After the reaction, small amounts of product were obtained with a yield less than 5%. Although EMIMBF₄ have been reported to be an effective catalyst for PEF synthesis, we observed differently in the PEAFs synthesis [34]. Without the presence of enzyme as the catalyst, only oligomers ($\overline{M_n}$ = 900–2100 g mol⁻¹) are obtained with the yield less than 10% (see Table S1 in Supplementary Information). In the presence of N435, the polymerization efficiency was significantly improved, which was supported by higher yields and molecular weights (Table 4). This underlines that the polymerization is catalyzed by the enzyme. This finding is also in agreement with our previous results, which showed that the polymerization of DMFDCA with 1,8-ODA was improved by the presence of the enzyme [15].

Fig. 1 shows the Attenuated total reflection-Fourier transform infrared (ATR-FTIR) and proton nuclear magnetic resonance (¹H NMR) spectra of the acquired PEAFs. The ATR-FTIR spectra confirm the presence of amide and ester linkages by the appearance of a sharp band around 1720 cm⁻¹ and 1650 cm⁻¹ indicating the C=O stretching vibration of the ester and amide groups, respectively. The successful polymerization and chemical structure of the PEAFs were further supported by the -COO-CH₂- and -CONH-CH₂- signals present in the ¹H NMR spectra at around 4.3 and 3.4 ppm. Detailed NMR and IR peak assignments are provided in the Materials and Methods Section.

The microstructure of the products was further analyzed by MALDI-ToF MS spectroscopy. Fig. 2 depict the representative mass spectrum of PEAF12 synthesized from DMFDCA and 12-ADO, ranging from *m/z* 600 to 10000. A main peak separation Δ(*m/z*) value of 321 is detected, which is characteristic for the PEAF12 repeating unit with a molecular weight of 321 g mol⁻¹. This result confirms that the reaction yielded PEAF12. The MALDI-ToF patterns of all tested polymers were similar, a total of seven species were observed in the spectra and their proposed
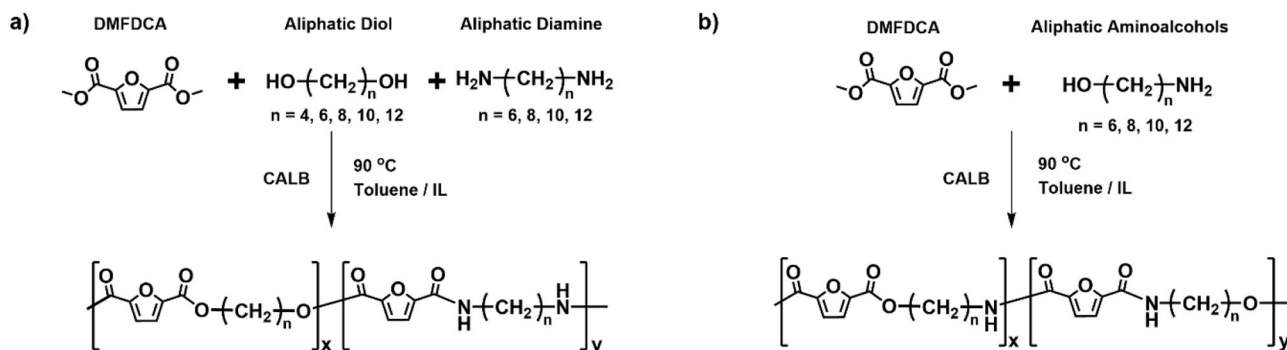
Scheme 1. Enzymatic synthesis of furan-based poly(ester amide)s from a) DMFDCA, aliphatic diols, and aliphatic diamines and b) DMFDCA and aliphatic amino alcohols.

Table 1
Abbreviations of the obtained furanic-aliphatic poly(ester amide)s (PEAFs).

n[a]	Poly(ester amide)s	Abbreviation
6	Poly(hexamethylene furanoate-*co*-hexamethylene furanamide)	**PEAF6**
8	Poly(octamethylene furanoate-*co*-octamethylene octanamide)	**PEAF8**
10	Poly(decamethylene furanoate-*co*-decamethylene furanamide)	**PEAF10**
12	Poly(dodecamethylene furanoate-*co*-dodecamethylene furanamide)	**PEAF12**

[a] The number of methylene units in aliphatic linear diols, diamines, and amino alcohols.

structures are given in Table 2. They were terminated by ester/alcohol or ester/amine, ester/ester, aminoalcohol/aminoalcohol, acid/alcohol or acid/amine, acid/acid, ester/acid, and cyclic polyesteramide (without end groups). As previously reported by our group, the acid end group is formed by hydrolysis of the esters during the polymerization by N435 [15,16,35].

In the first approach, aliphatic linear diols and diamines with different chain lengths were screened to evaluate their influence on the preparation of PEAFs (Fig. 3). The results indicate that the aliphatic linear diols and diamines with a chain length of n > 6 are preferred by *Candida antartica* lipase B (CALB). The weight-average degree of polymerization ($\overline{DP_w}$) of the obtained PEAFs increased from 56 to 78 upon increasing the chain length of the diols and diamines from n = 6 to 8,

respectively. PEAF10 with a similar $\overline{DP_w}$ of 74 was obtained when the diol and diamine chain lengths were increased to n = 10. PEAF12 with the highest $\overline{DP_w}$ of 128 was obtained from the enzymatic polymerization between DMFDCA, 1,12-dodecanediol (1,12-DODO), and 1,12-dodecanediamine (1,12-DODA). These results are in accordance with our previous studies on the synthesis of furan polyesters and polyamides, which suggest that CALB, in general, prefers longer aliphatic linear diols and diamines [5,16,17].

In the second approach, an increasing trend of the number-average degree of polymerization ($\overline{DP_n}$) and $\overline{DP_w}$ with respect to the amino alcohol chain length was observed. As illustrated in Fig. 3, the $\overline{DP_w}$ value steadily increases from 23 to 97, if the chain length of the amino alcohols is increased from n = 6 to 12. Interestingly, these results are similar to the ones from the first approach where diols and diamines were used as the aliphatic monomers. This finding further supports our studies that CALB shows a preference towards monomers bearing longer aliphatic chains. Moreover, Couturier et al. [36] reported comparable findings in their study of the lipase-catalyzed aminolysis of various amino alcohols with fatty acids. They observed an increase in yield with increasing aliphatic amino alcohol chain lengths (n = 2, 3, 4, 5 and 6).

A comparison of the degree of polymerization (DP) of PEAFs obtained from the first and second synthetic approach shows that both methods result in similar $\overline{DP_w}$, although the $\overline{DP_n}$ of the first approach is marginally higher (Fig. 3). This can be again explained by the substrate selectivity of CALB. However, the reactivity of these aliphatic monomers and the solubility of end products in the reaction medium needs to be
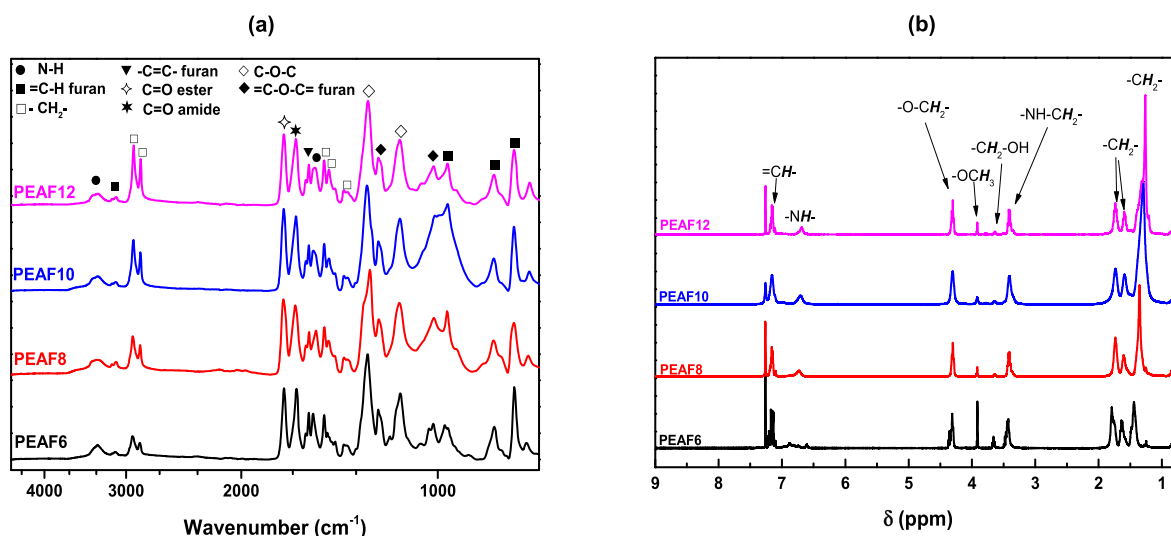

Fig. 1. (a) ATR-FTIR, and (b) ^{1}H NMR spectra of the obtained poly(ester amide)s from DMFDCA and aliphatic amino alcohols in CDCl₃.
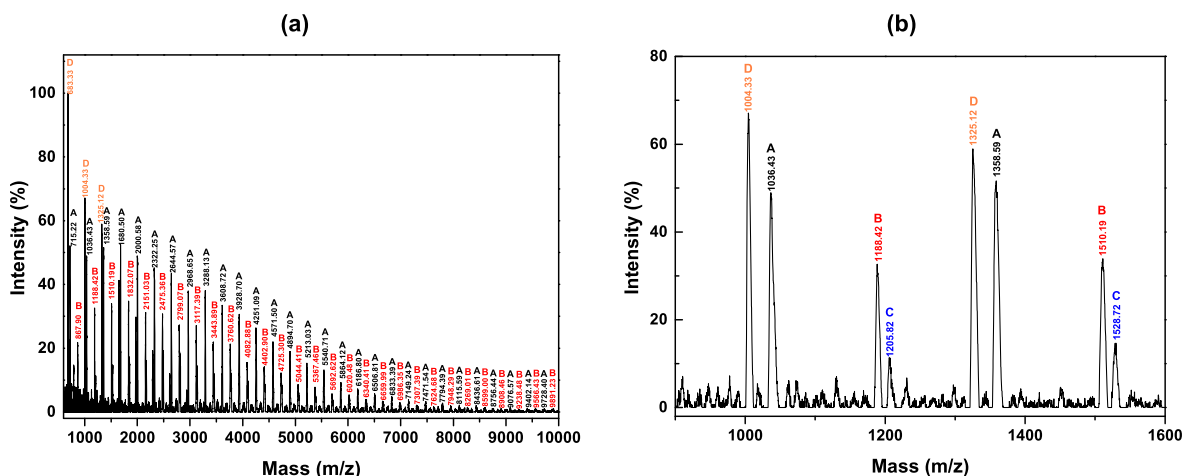
Fig. 2. (a) MALDI-ToF MS spectrum of the obtained PEAF12 and (b) magnified part with peak interpretation. Influence of linear monomers on the enzymatic synthesis of the PEAFs.

Table 2
MALDI-ToF MS Analysis: End Groups of the obtained PEAFs.

Entry	Polymer species	End groups	Remaining mass (amu)
A		Ester/Alcohol; Ester/Amine	32.04
B		Ester/Ester	184.15
C		Aminoalcohol/ Aminoalcohol	x = 6: 117.19 x = 8: 145.25 x = 10: 173.3 x = 12: 201.36
D		Cyclic	0
E		Acid/Alcohol; Acid/Amine	18.02
F		Acid/Acid	156.1
G		Ester/Acid	170.03

Fig. 3. and $\overline{DP_w}$ of the obtained poly(ester amide)s from the first and second synthetic approach plotted against the chain length of the linear monomers.

no specificity was shown by CALB for amide or ester formation in the reaction between linoleyl ethyl ester with several aliphatic amino alcohols.

taken into account as well. Typically, the amino alcohols are more reactive than their diols, but less active compared to their diamine counterparts. Apart from reactivity, the DP may also be affected by the corresponding polymer solubility in the reaction solvent. Premature precipitation of the oligomers causes a contact loss with the enzyme active site and thus, results in a low degree of polymerization. Despite of the change in the aliphatic monomers from diols and diamines to amino alcohols, different PEAFs were successfully obtained with this CALB-catalyzed polymerization.

Interestingly, we also observed that CALB shows no specificity for the formation of amide or ester bonds. As summarized in Table 3, the molar fractions X of amide and ester in PEAFs obtained from the first approach are consistent with their molar feed values F. There are similarities of the CALB behavior in this study and those described by Couturier et al. on transesterification/transamidation reactions [36]. They observed that
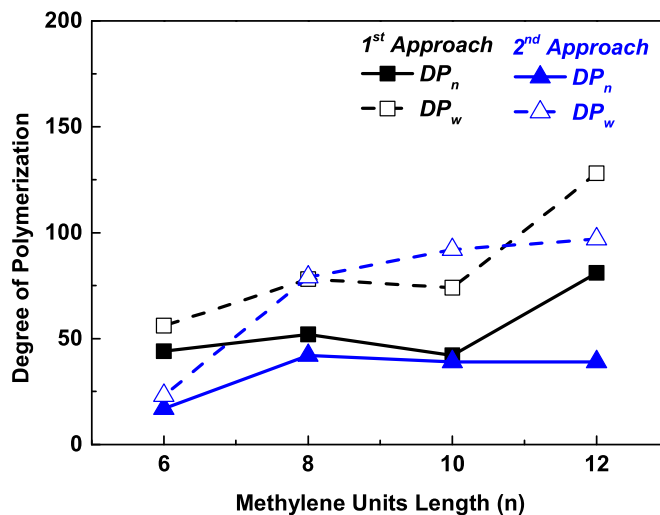
Table 3
Molar fraction and degree of polymerization of the PEAFs obtained from DMFDCA, aliphatic diols, and aliphatic diamines.

Polymers	Molar Fraction [%]				$\overline{DP_n}$[a]	$\overline{DP_w}$[b]
	Feed		Poly(ester amide)s			
	F_{ester}	F_{amide}	X_{ester}	X_{amide}		
PEAF6	50	50	52	48	44	56
PEAF8	75	25	76	24	33	56
	50	50	54	46	52	78
	25	75	44	56	28	40
PEAF10	50	50	55	45	42	74
PEAF12	50	50	53	47	81	128

[a] $\overline{DP_n}$ (number-average degree of polymerization) $= 2 \times [(\overline{M_n} - 32.03) / ((X_{ester} \times M_{ester}) + (X_{amide} \times M_{amide}))]$
[b] $\overline{DP_w}$ (weight-average degree of polymerization) $= 2 \times [(\overline{M_w} - 32.03) / ((X_{ester} \times M_{ester}) + (X_{amide} \times M_{amide}))]$.

3.2. Influence of different solvents on the enzymatic synthesis of the PEAFs

Typically, the enzymatic polymerizations described in this work were conducted in toluene as solvent. In order to create a sustainable polymerization process, we replaced the toluene with ionic liquids (ILs), BMIMPF$_6$ and EMIMBF$_4$. The reason why these two ILs were chosen is, although CALB can be also dissolved in [BMIM] acetate, lactate and nitrate, which are environmentally more acceptable ILs as they do not contain fluorinated anions, we decided to use BMIMPF$_6$ and EMIMBF$_4$ as the enzyme activity is higher in these ILs. As reported by Sheldon et al. for transesterification of ethyl butanoate with 1-butanol, CALB can maintain their activity better in fluorinated anions ILs [37]. In addition, BMIMPF$_6$ was reported to possess a remarkable performance in enzymatic ring-opening polymerization of lactides and lactones, which makes it a promising candidate for the CALB-catalyzed syntheses of poly (ester amide)s [38]. With excellent catalytic activity, selectivity, and stability, EMIMBF$_4$ is also reported as the best catalyst for PEF synthesis via metal-free direct esterification method [34].

Using the first approach, PEAFs were successfully obtained independent of the alkyl chain lengths in the tested monomers, while the second approach was limited to alkyl chain lengths n > 6. In general, the enzymatic polymerization performed in BMIMPF$_6$ and EMIMBF$_4$ clearly resulted in lower molecular weight PEAFs compared to those prepared in toluene (Table 4). For example, the first approach conducted in toluene resulted in $\overline{M_n}$ values of 5300–13000 g mol^{-1}, while the polymerization in BMIMPF$_6$ and EMIMBF$_4$ yielded $\overline{M_n}$ values between 1500 and 4400 g mol^{-1}. These results match those observed by Heise et al. [39], who reported a higher molecular weight for poly(caprolactone) (PCL) synthesized by a N435-catalyzed ROP in toluene in comparison to PCL prepared in BMIMPF$_6$. They suggested that this might be due to the better solubility of PCL in toluene. A similar explanation might be applied in our case. The different polarity of the solvents may also affect the final molecular weight of the poly(ester amide)s. Comparing the two ILs, polymerization in EMIMBF$_4$ yielded in slightly lower molecular weight PEAFs. This can be explained by the slight decrease of enzyme activity due to the increase in acidity of the IL. In the presence of water, BF$_4^-$ anions can be hydrolyzed to generate hydrogen ions, that responsible for the change in the pH [40].

Besides the effect on molecular weight, the use of the ILs also caused a coloration of the PEAFs. All PEAF samples synthesized in BMIMPF$_6$ and EMIMBF$_4$ showed a yellow to brownish color, while PEAFs obtained from the polymerization in toluene are white to light yellow powders (Fig. 4 and Fig. S3 in Supplementary Information). In most cases, the coloration of FDCA-based polymers is due to the decarboxylation of FDCA. However, in our case, the coloration of PEAFs cannot be explained in a similar manner since the same polymerization in toluene yields white powders, clearly indicating that no decarboxylation is occurring during the polymerization. In fact, the formation of colored products can be attributed to solvent impurities of BMIMPF$_6$ and EMIMBF$_4$ in the final product. This is supported by the presence of proton peaks of BMIMPF$_6$ and EMIMBF$_4$ in the ^{1}H NMR spectra of the PEAFs obtained from the reaction in ILs (Fig. 4c and Fig. S2 in Supplementary Information). The PEAFs coloration can be reduced, however excessive re-precipitaion purification steps are needed, and thus will significantly reduce the product yield.

To explore the potential application of PEAFs, it is essential to study their thermal properties. Therefore, we analyzed the thermal properties and degradation behaviors of the obtained PEAFs by performing differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) measurements. The values of the thermal transitions and the degradation temperatures of the obtained PEAFs are summarized in Table 5. The representative thermal degradation profiles of the PEAFs are depicted in Fig. 5a. They typically show a two-step degradation pattern and start to decompose at a temperature around 390 °C. The first decomposition step is attributed to the decomposition of ester bonds, and is subsequently followed by the amide bond cleavage at the second step. In general, the PEAFs obtained from enzymatic polymerization in toluene appear to possess a higher thermal stability, which can be explained by their higher molecular weights. Importantly, we found that the chain length of the aliphatic diols, diamines, and amino alcohols have no significant influence on the decomposition temperatures of the resulting PEAFs.

The representative DSC curves of PEAF6 from the second approach in toluene are shown in Fig. 5b. Two endothermic peaks were obtained in the first heating cycle at around 120 and 140 °C. Similar to what we observed in furan polyamides, the first small endothermic peak at around 120 °C results from crystal-crystal phase transition [16]. The melting peak (T_m) of the PEAF6 was identified as the second endothermic peak at around 140 °C. In the second heating scan, the T_m disappeared and no crystallization was detected in the cooling curve. This indicates that the obtained PEAFs cannot crystallize in bulk at the tested conditions due to their slow crystallization rate [15]. The T_g of the obtained PEAFs was observed during the second heating scan with values ranging from 11 to 46 °C. The T_m and T_g of all obtained PEAFs show a decreasing trend with increase of the chain length of the amino alcohols. A similar trend was observed in FDCA-based semi-aromatic polyesters

Table 4
Molecular weights, dispersities, and yields of the obtained PEAFs.

Polymers	Solvent	First Approach[a]				Second Approach[b]			
		$\overline{M_n}$[c] [g mol^{-1}]	$\overline{M_w}$[c] [g mol^{-1}]	Đ[c] ($\overline{M_w}/\overline{M_n}$)	Yield[d] [%]	$\overline{M_n}$[c] [g mol^{-1}]	$\overline{M_w}$[c] [g mol^{-1}]	Đ[c] ($\overline{M_w}/\overline{M_n}$)	Yield[d] [%]
PEAF6	Toluene	5300	6720	1.3	28	2100	2780	1.3	45
	BMIMPF$_6$	2210	2840	1.3	19	-[e]	-[e]	-[e]	-[e]
	EMIMBF$_4$	1500	1900	1.3	5	-[e]	-[e]	-[e]	-[e]
PEAF8	Toluene	6940	10390	1.5	47	5650	9360	1.7	43
	BMIMPF$_6$	2800	4030	1.4	40	3090	4490	1.5	39
	EMIMBF$_4$	2100	3000	1.4	23	-[e]	-[e]	-[e]	-[e]
PEAF10	Toluene	6140	10930	1.8	54	5780	10980	1.9	61
	BMIMPF$_6$	4390	7490	1.7	47	4100	6800	1.7	32
	EMIMBF$_4$	3300	6800	2.1	40	-[e]	-[e]	-[e]	-[e]
PEAF12	Toluene	12990	20630	1.6	39	6300	11500	1.8	81
	BMIMPF$_6$	4150	7450	1.8	44	2600	4700	1.8	30
	EMIMBF$_4$	2500	4800	1.9	35	-[e]	-[e]	-[e]	-[e]

[a] PEAFs synthesized from DMFDCA, aliphatic diols, and aliphatic diamines.
[b] PEAFs synthesized from DMFDCA and amino alcohols.
[c] The number-average molecular weight ($\overline{M_n}$), weight-average molecular weight ($\overline{M_w}$), and dispersity (Đ, $\overline{M_w}/\overline{M_n}$) were determined by SEC using THF as the eluent.
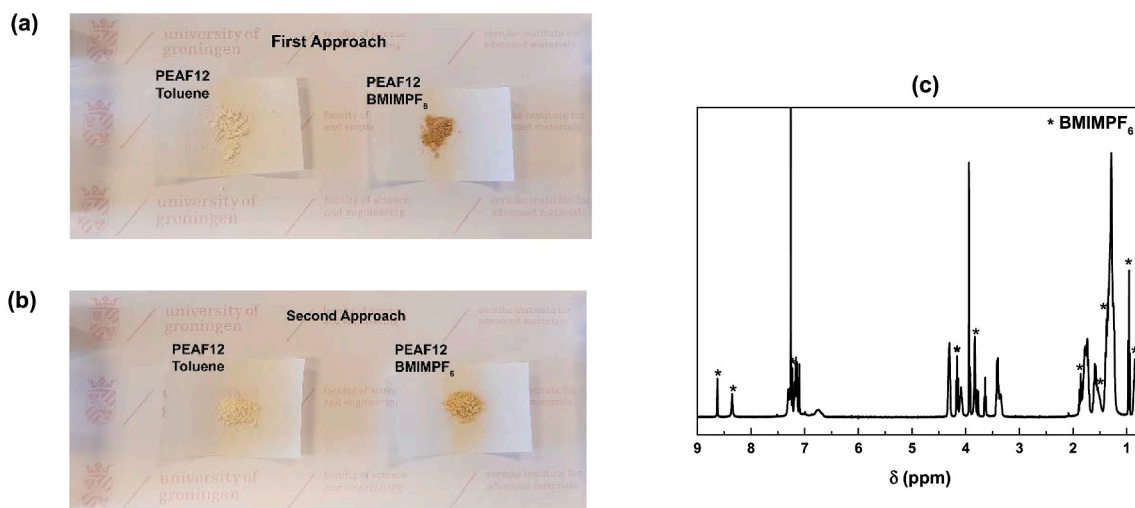[d] Isolated yield.
[e] Not determined.

Fig. 4. PEAF12 synthesized from (a) DMFDCA, 1,12-DODO, and 1,12-DODA and (b) DMFDCA and 12-ADO. (c) ^{1}H NMR spectrum of PEAF10 obtained from the reaction in BMIMPF$_6$. Crystallinity and thermal analysis of the obtained PEAFs.

Table 5
Thermal properties of the obtained PEAFs from DMFDCA and amino alcohols.

Polymers	Solvent	DSC[a]		TGA[b]
		T_g (°C)	T_m (°C)	$T_{d\text{-}max}$ (°C)
PEAF6	Toluene	44	140	390
	BMIMPF$_6$	-[c]	-[c]	-[c]
	EMIMBF$_4$	8	91	366
PEAF8	Toluene	46	130	390
	BMIMPF$_6$	22	110	360
	EMIMBF$_4$	-[c]	-[c]	374
PEAF10	Toluene	35	90	390
	BMIMPF$_6$	22	82	380
	EMIMBF$_4$	15	72	379
PEAF12	Toluene	25	92	395
	BMIMPF$_6$	11	77	350
	EMIMBF$_4$	6	66	377

[a] T_g = glass transition temperature from the modulated DSC heating scan, T_m = melting temperature from the first DSC heating scan.
[b] $T_{d\text{-}max}$ = temperature at the maximum rate of decomposition.
[c] not determined.

and polyamides. As previously reported by our group, this can be explained by an enhancement in the chain flexibility and a reduction in the density of hydrogen bonds and π- π stacking [16].

The Wide-Angle X-ray diffraction (WAXD) spectra confirmed that the obtained PEAFs possess semi-crystalline properties. As shown in Fig. 6, PEAF6 exhibits WAXD patterns that display four diffraction peaks at 28.40°, 23.64°, 18.11°, and 12.23°. Similarly, PEAF8 shows three diffraction peaks at 23.93°, 17.37°, and 12.92° with additional low-intensity peaks at 34.22°, 29.91°, 27.09°, 21.66° and 10.19°. Two diffraction peaks located at the same position around 23.95–24.00° and 17.37–18.33° are detected in PEAF10 and PEAF12 spectra, while they also showed multiple low-intensity peaks at 34.20°, 29.94°, 27.11°, 26.07°, 21.68°, 20.42°, 16.11°, 12.47°, 10.19° and 7.18°. This result indicates that the crystal phase of PEAF6 is similar to PEAF8, and PEAF10 is similar to PEAF12.

4. Conclusions

We designed an enzymatic synthesis pathway for the production of furanic-aliphatic poly(ester amide)s (PEAFs). A better understanding of the processes involved in the enzymatic polymerization of PEAFs was
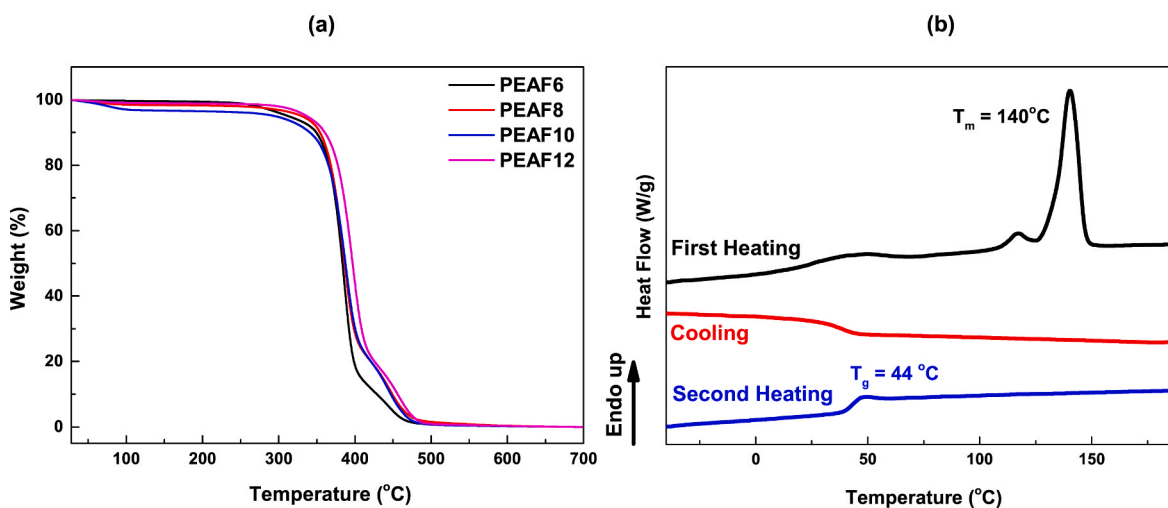

Fig. 5. (a) Representative TGA traces of the obtained PEAFs from the second approach conducted in toluene (b) DSC curves of PEAF6 from the enzymatic polymerization of DMFDCA and 6-AH in toluene.
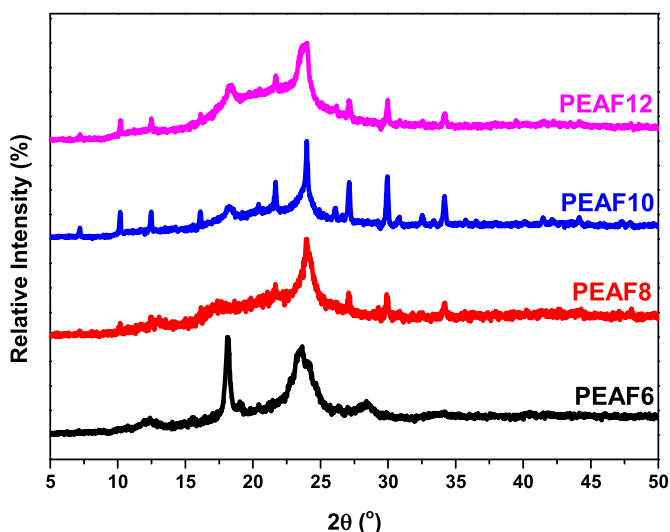
Fig. 6. WAXD spectra of the obtained PEAFs from DMFDCA and amino alcohols.

achieved by introducing two different synthetic approaches, which included the introduction of different aliphatic monomers with varying alkyl chain lengths. Both synthetic approaches yielded PEAFs with comparable $\overline{DP_w}$, although the $\overline{DP_n}$ of the first approach in which diols and diamines were used as the monomers, is marginally higher. This can be explained by the substrate selectivity of CALB, in which aliphatic diamines and diols are preferred compared to the analogous amino alcohols. On the other hand, the reactivity of the aliphatic monomers and the solubility of the products have to be taken into consideration as well. To show that these synthetic processes could be even greener, we performed the polymerization in an ionic liquid. Using BMIMPF$_6$ and EMIMBF$_4$ as the reaction solvent, we were able to produce different PEAFs with $\overline{M_w}$ up to 7490 g mol^{-1}. In the case of enzymatic synthesis of PEAFs, compared to toluene, the tested ILs still gives products with similar characteristics. All obtained PEAFs are semi-crystalline materials and possess a two-step degradation profile. They start to decompose at a temperature around 390 °C, display a T_m of around 77–140 °C and T_g of around 11–46 °C.

CRediT authorship contribution statement

Dina Maniar: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Fitrilia Silvianti:** Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing. **Viviana M. Ospina:** Validation, Investigation. **Albert J.J. Woortman:** Formal analysis. **Jur van Dijken:** Formal analysis. **Katja Loos:** Conceptualization, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2020.122662.

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