

# First example of unsaturated poly(ester-amide)s derived from itaconic acid and their application as bio-based UV-curing polymers

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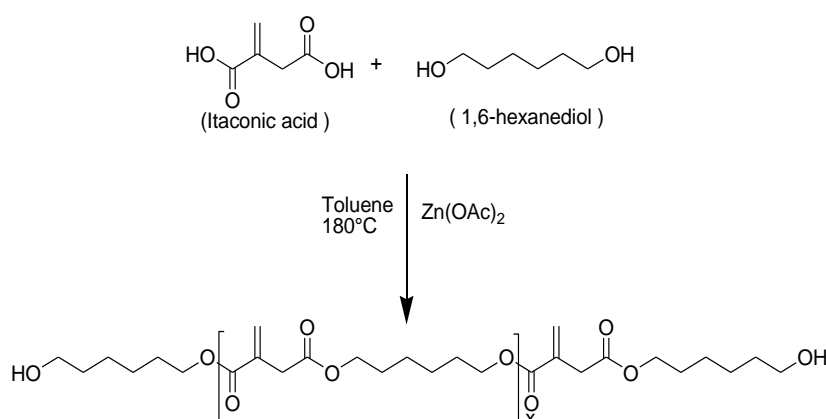
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## Supporting information

### 1. Synthesis of bio-based oligoester

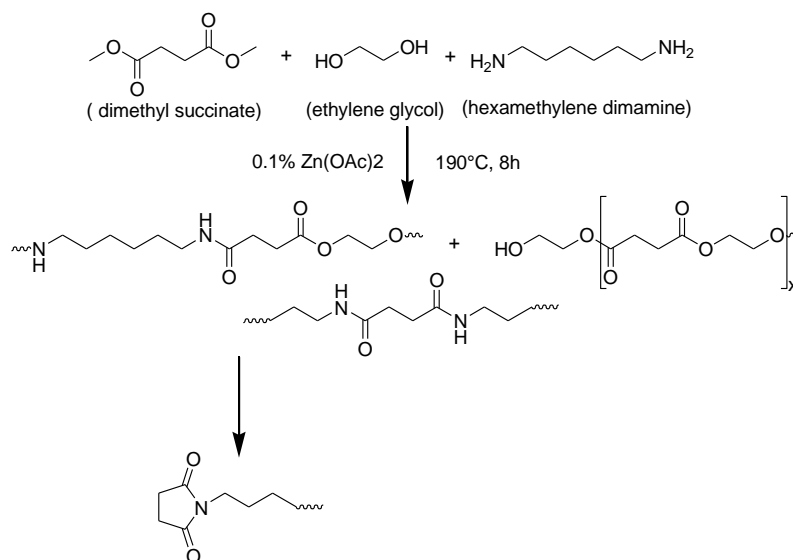


**Scheme S1.** Synthesis of oligoester based on itaconic acid

161.45 g of itaconic acid (1 eq), 183.05 g of 1,6-hexanediol (1.25 eq), BHT (400 ppm) and MEHQ (300 ppm) as the free radical polymerization inhibitors were charged into a three necked flask which was equipped with a mechanical stirrer and Dean-stark. Using toluene as entrainer, the mixture was heated to 130°C and kept at this temperature until all the monomers melted completely and the catalyst (zinc acetate (0.4 wt%)) was added. The mixture was then stirred at 180°C. The course of the reaction was monitored by analysis of the acid value (AV). When the AV reached a value of less than 5 mg KOH/g, the toluene was removed under reduced pressure. The polyester was obtained without any further purification as yellow viscous liquid.

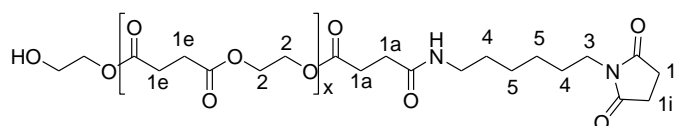
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 6.26 (s, 1H, H1/2), 5.65 (s, 1H, H1/2), 3.27 (s, 2H, H3), 4.01–4.05 (m, 2H, H4), 4.08–4.11 (m, 2H, H9), 3.56–3.59 (m, 4H, H9'), 1.70–1.49 (m, 4H, H5/H8), 1.48–1.32 (m, 4H, H6/H7), Photo-DSC:  $\Delta H_{\text{exp}} = 145.27$  J/g. Viscosity at  $25^\circ\text{C}$  (10021 mPa.s).

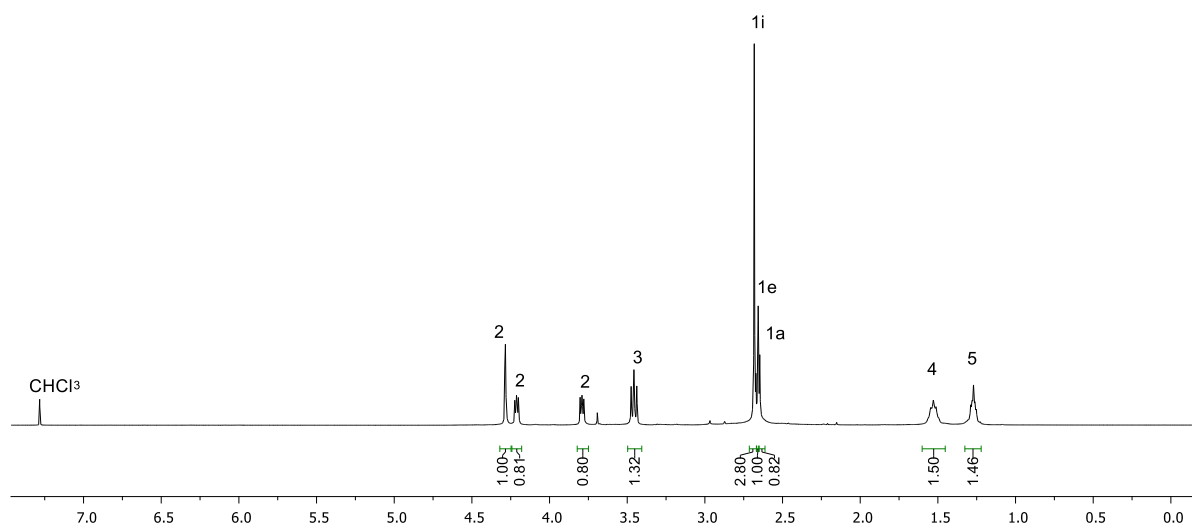
## 2. Oligoimide synthesis:



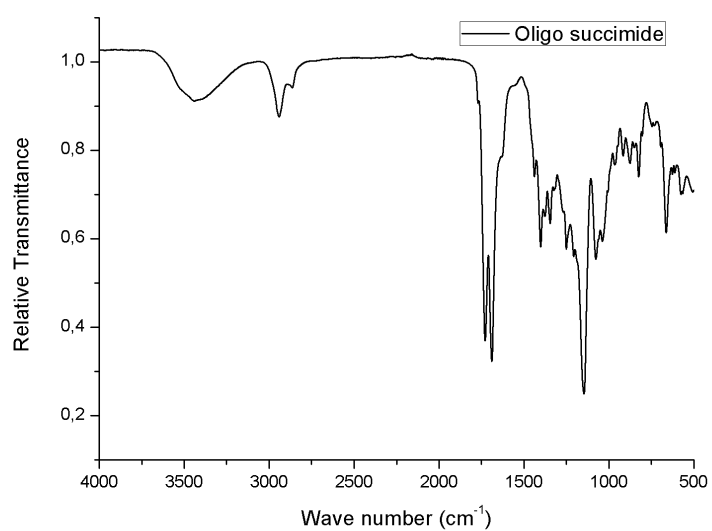
**Scheme S2.** Oligoimide synthesis

In a round bottom flask, 5 g (34.21 mmol) of DMS, 5.94 g (95.79 mmol) of EG and 0.80 g (6.84 mmol) of HMDA were charged with 0.1% (wt%) of zinc acetate under a stream of nitrogen for 8 h. High excess of EG was eliminated by extraction in dichloromethane.



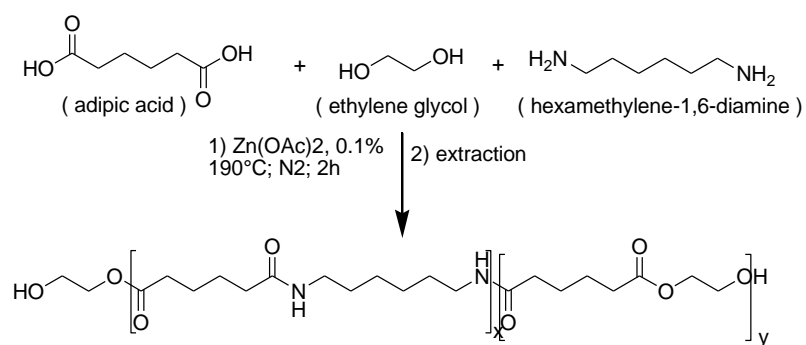


**Figure S1.**  $^1\text{H}$  NMR spectrum of the synthesized oligoimide



**Figure S2.** FTIR spectrum of the synthesized oligoimide

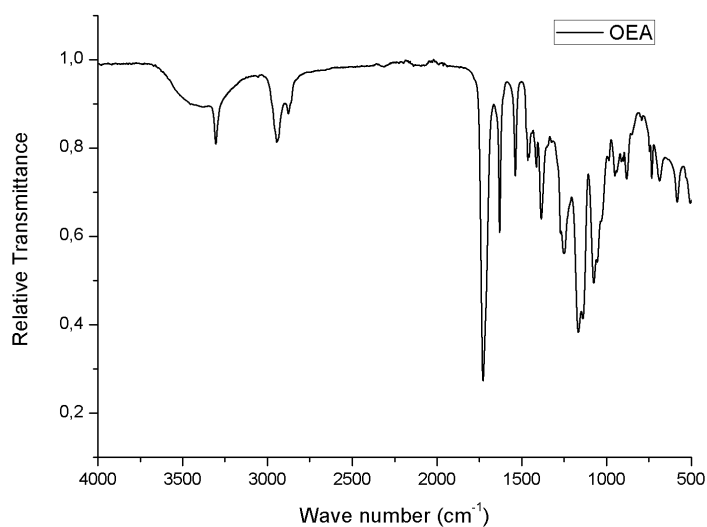
### 3. Oligo(ester amide) synthesis



**Scheme S3.** Oligo(ester amide) synthesis

OEA was synthesized by the condensation of 5g (28.7 mmol) of AA, 4.98 g (80.36 mmol) of EG and 0.66 g (5.74mmol) of HMD with 0.1% (wt%) of zinc acetate as a catalyst under a stream of nitrogen for 2 h. High excess of EG was eliminated by extraction in dichloromethane.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 4.28 (s, 4H, H6), 4.22 (s, 4H, H6'), 3.82 (s, 4H, H6''), 3.22 (m, 4H, H3), 2.38 (m, 4H, H2e), 2.20 (m, 4H, H2a), 1.68 (m, 8H, H1e/H4), 1.49 (m, 4H, H1a), 1.33 (m, 4H, H5). FTIR (Diamond)  $\nu$  = 3700-3100 (O-H), 3306 (N-H), 2938 and 2900 ( $\text{CH}_2$ ), 1731 (C=O), 1631 and 1538 (O=C-NH).



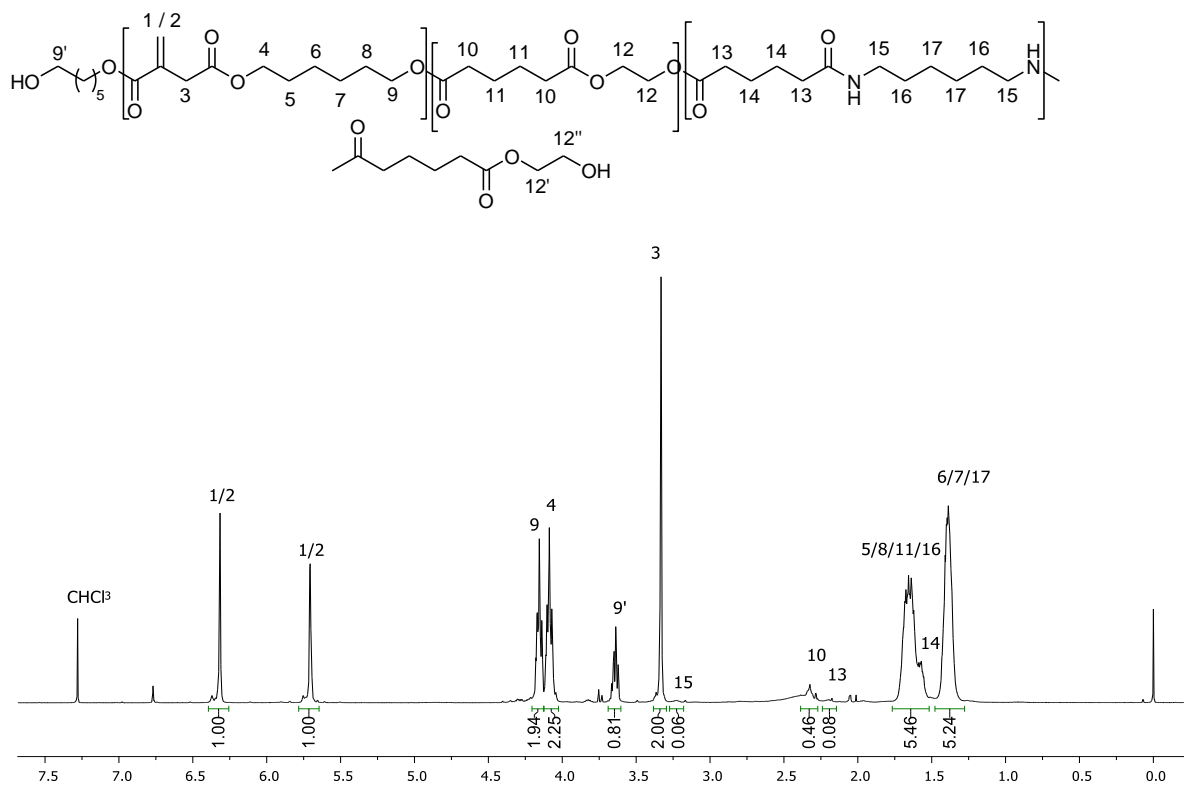
**Figure S3.** FTIR spectrum of oligo(ester-amide)

#### 4. Transesterification:

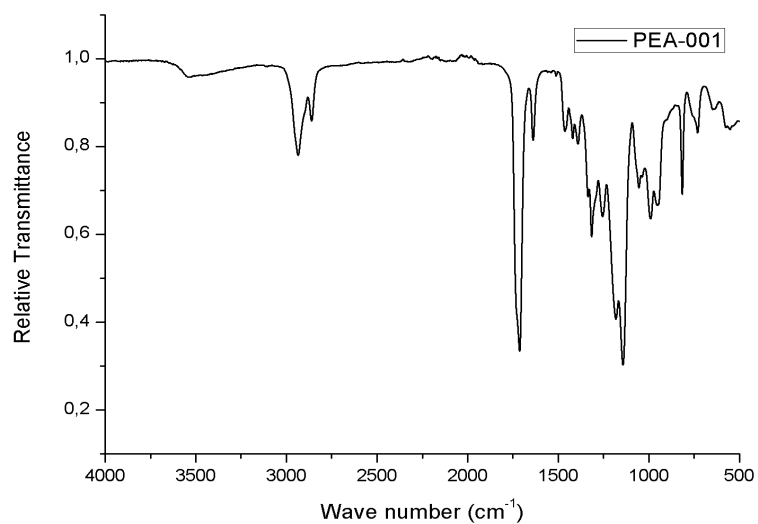
In the transesterification process, we mixed a determinate amount of OE with OEA using 0.1% (wt%) of  $\text{Ti}(\text{OBu})_4$ , 150 ppm of MeQH and 100 ppm of BHT:

##### 4.1. Synthesis of poly(ester-amide) 95/5:

PEA-001 was prepared by mixing 10 g (11.83 mmol) of the synthesized oligoester and 0.49 g (0.62 mmol) of the oligo(ester amide).



**Figure S4.**  $^1\text{H}$  NMR spectrum of the synthesized polyesteramide PEA-001.



**Figure S5.** FTIR of prepared poly(ester amide)s based on itaconic acid PEA-001

#### 4.2. Synthesis of poly(ester-amide) 90/10:

PEA-002 was prepared by reacting 10 g (11.83 mmol) of the oligoester and 1.03 g (1.31 mmol) of OEA.

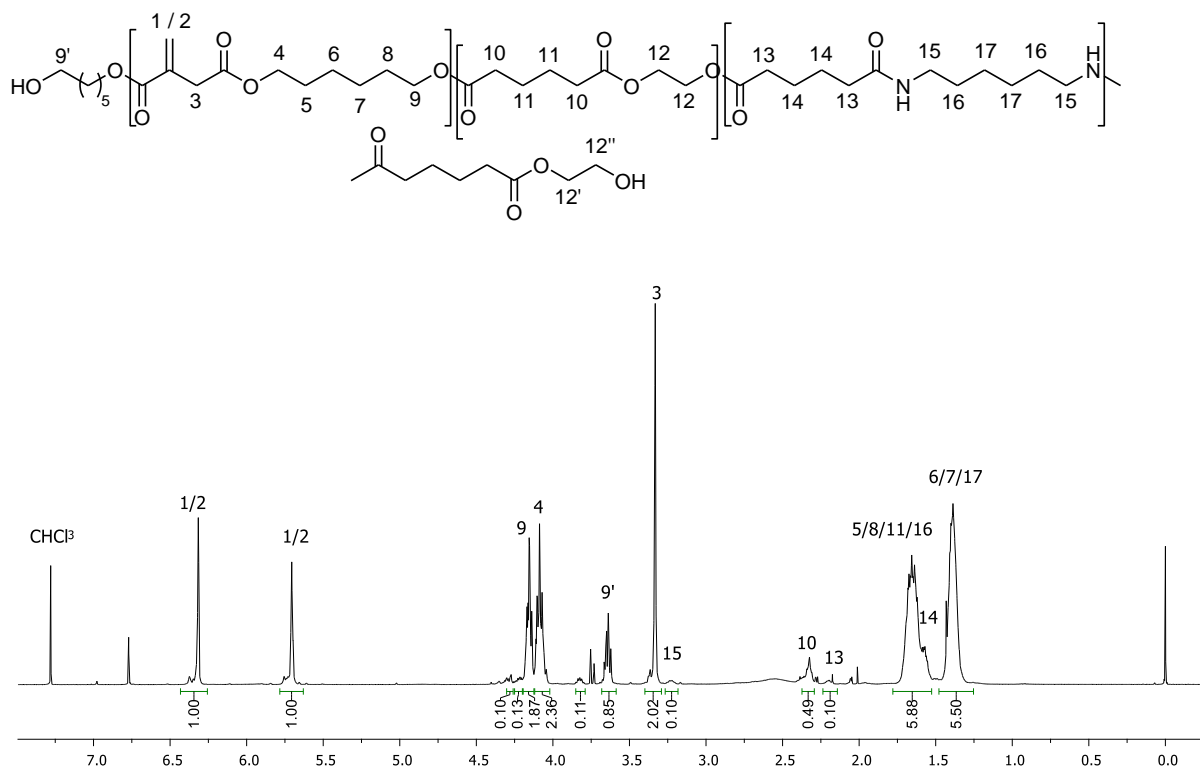


Figure S6. <sup>1</sup>H NMR spectrum of the synthesized poly(ester amide) PEA-002

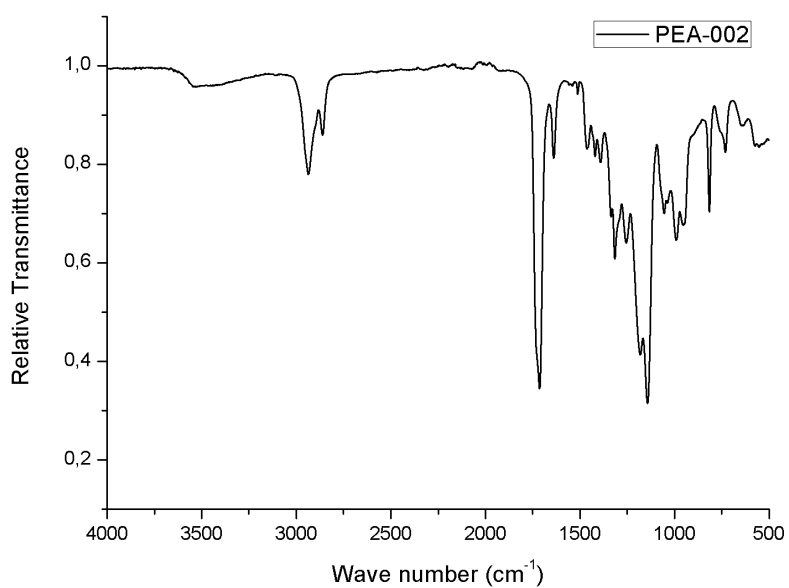
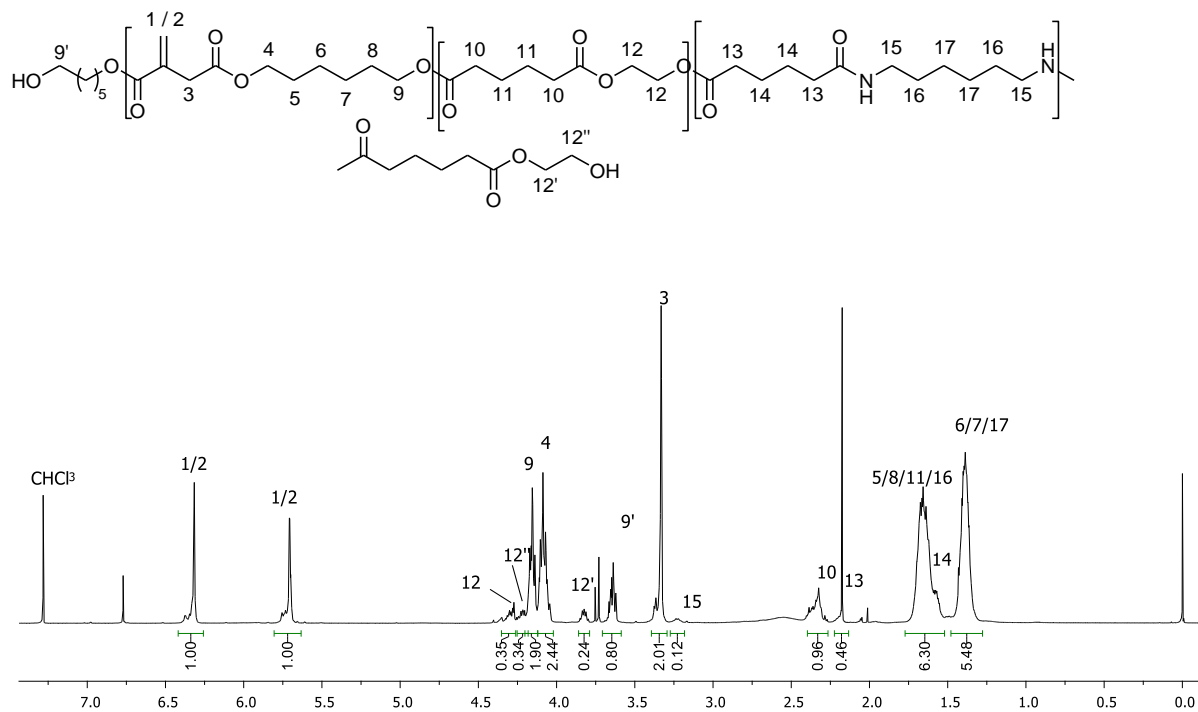


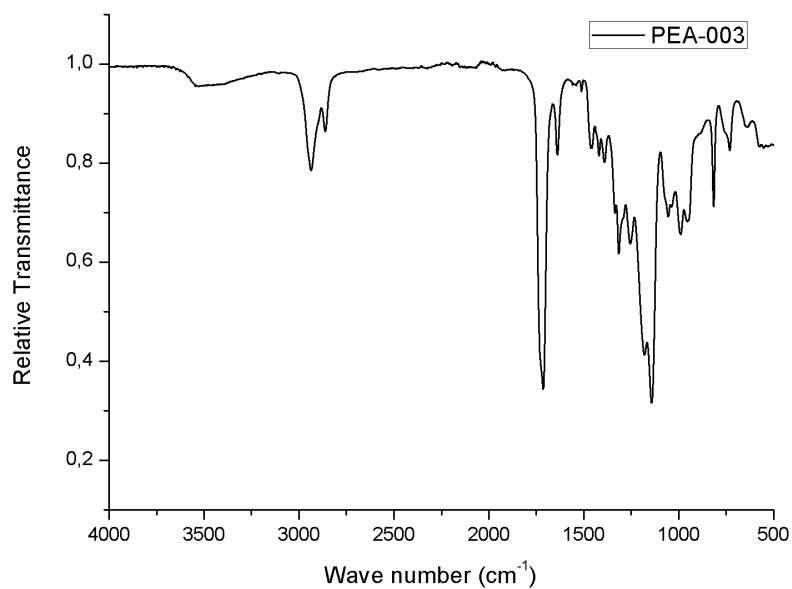
Figure S7: FTIR of prepared poly(ester amide) PEA-002

### 4.3. Synthesis of poly(ester-amide) 80/20:

The PEA-003 was prepared by mixing 10 g (11.83 mmol) of the oligoester and 2.32 g (2.95 mmol) of OEA were reacted.



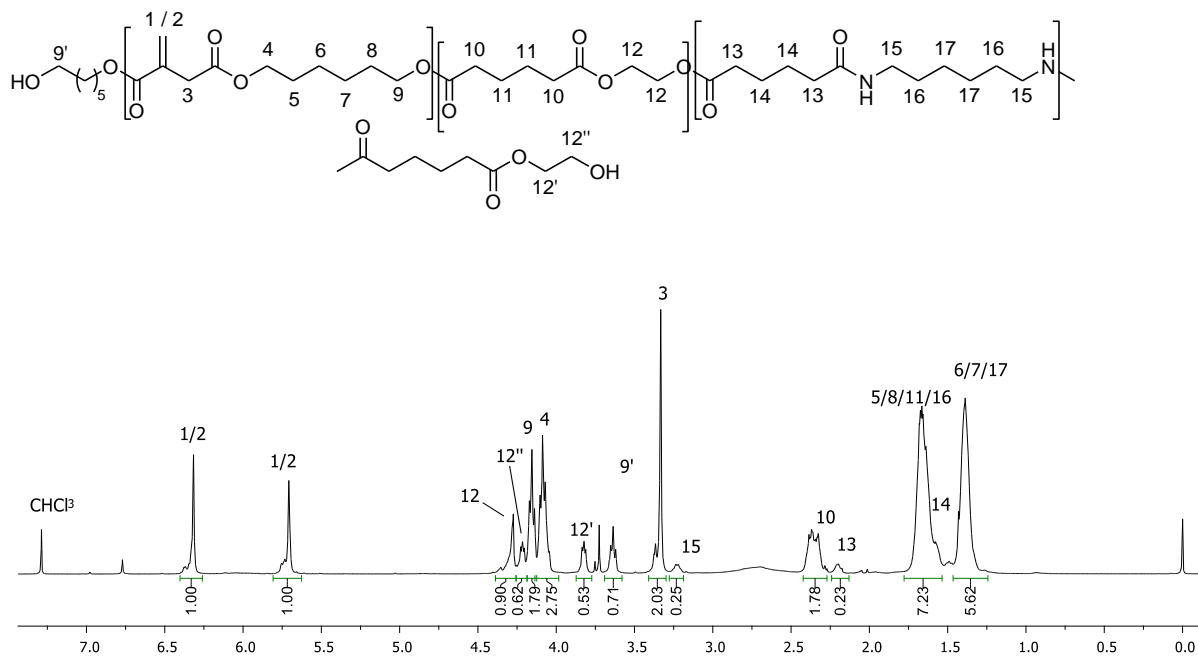
**Figure S8.** <sup>1</sup>H NMR spectrum of the synthesized poly(ester amide) PEA-003



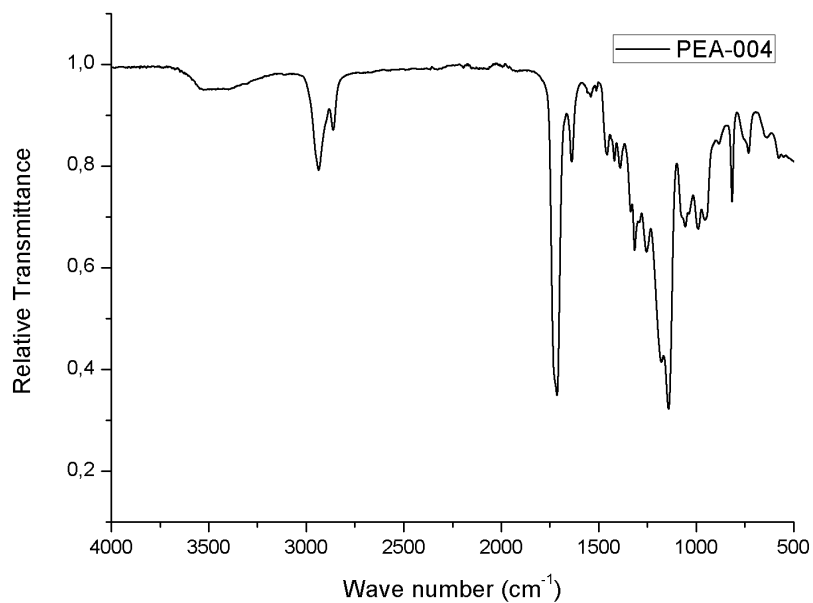
**Figure S9.** FTIR of prepared poly(ester amide) PEA-003 based on itaconic acid

#### 4.4. Synthesis of poly(ester amide) 70/30:

10 g (11.83 mmol) of oligoester and 3.99 g (5.07 mmol) of oligo(ester amide) was mixed to prepare PEA-004.



**Figure S10.** <sup>1</sup>H NMR spectrum of the synthesized poly(ester amide) PEA-004

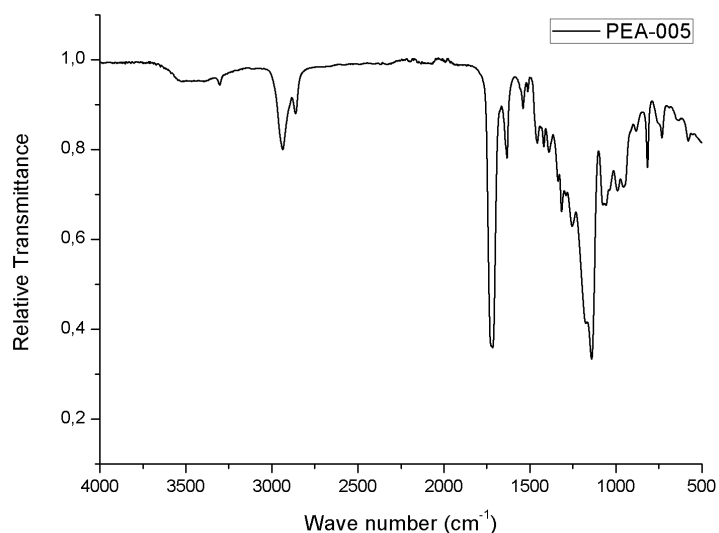


**Figure S11:** FTIR of prepared poly(ester amide) based on itaconic acid PEA-004



#### 4.5. Synthesis of poly(ester-amide) 60/40:

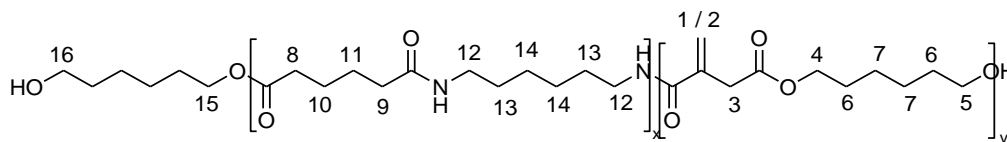
For the PEA-005: 8 g (9.47 mmol) of the oligoester and 4.97 g (6.31 mmol) of OEA were reacted.

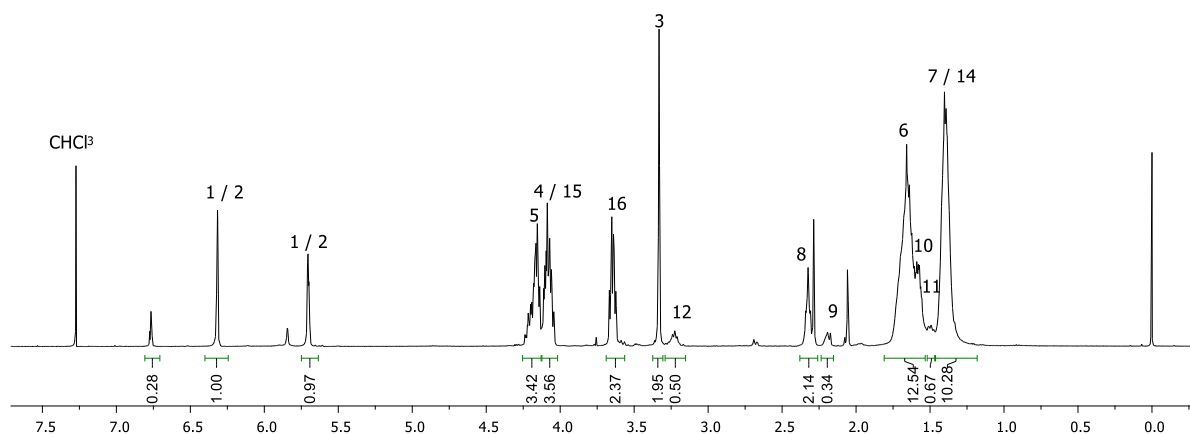


**Figure S12.** FTIR of prepared poly(ester amide) based on itaconic acid PEA-005

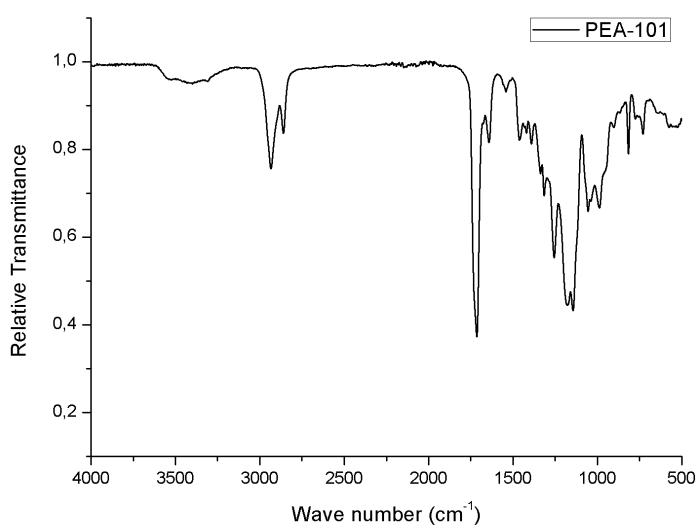
#### 5. Synthesis of poly(ester amide)s via in-situ formed amido diesters

**PEA-101:** In 500 ml three neck , 32.33 g (0.2 mol) of DMA was added to 7.33 g (0.07 mol) of HMDA and 0.04 g (0.1 wt%) of zinc acetate. The mixture was stirred at 150 °C under a stream of nitrogen until all amine groups are reacted to the corresponding amide, which was followed by FT-IR. Then 96.58g (0.8 mol) of itaconic acid, 140.26 g (1.282 mol) of HDO, 0,06 wt% of MeQH, 0,08 wt% of BHT and 0,2 wt% of Fascat 4101 are added at 180°C. Then toluene was slowly added as entrainer over the condenser. The course of reaction was controlled by AV calculation.



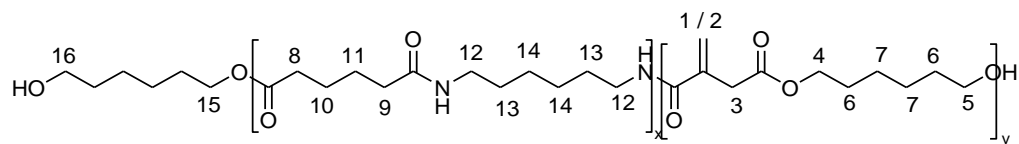


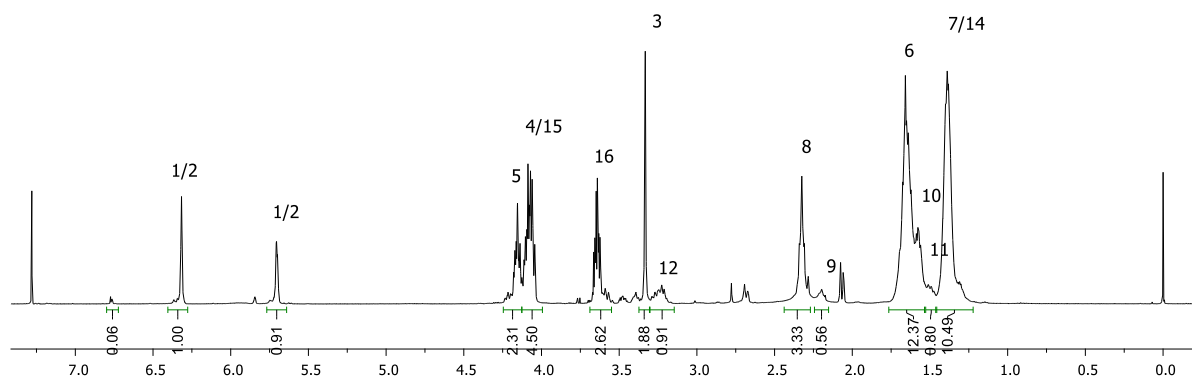
**Figure S13.**  $^1\text{H}$  NMR spectrum of the synthesized poly(ester amide) PEA-101



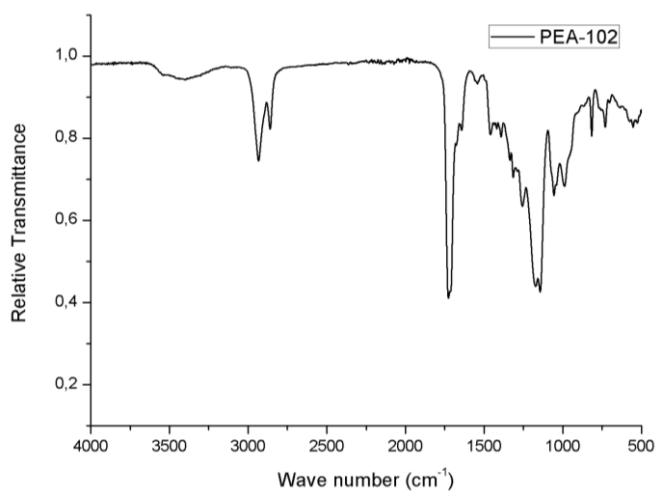
**Figure S14.** FTIR spectrum of the synthesized poly(ester amide) PEA-101

**PEA-102:** In 500 ml three neck, 47.12 g (0.3 mol) of DMA was added to 13.62 g (0.13 mol) of HMDA and 0.067 g (0.1 wt%) of zinc acetate. The mixture was stirred at 150 °C under a stream of nitrogen until all amine groups are reacted to the corresponding amide, which was followed by FT-IR. Then 82.11g (0.7 mol) of itaconic acid, 129.79 g (1.22 mol) of HDO, 0,06 wt% of MeQH, 0,08 wt% of BHT and 0,2 wt% of Fascat 4101 are added at 180°C. Then toluene was slowly added as entrainer over the condenser. The course of reaction was controlled by AV calculation.



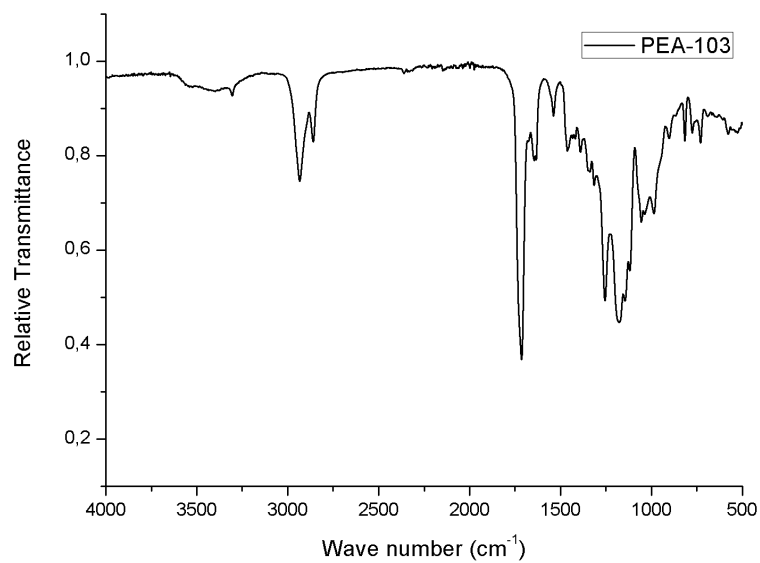


**Figure S15.**  $^1\text{H}$  NMR spectrum of the synthesized poly(ester amide) PEA-102

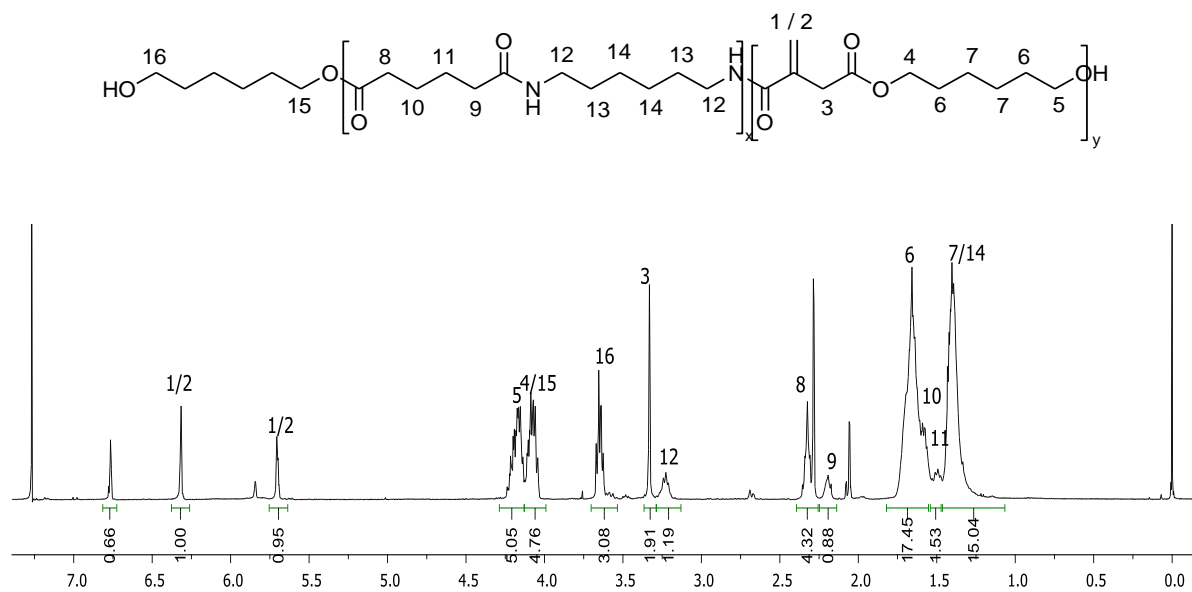


**Figure S16.**  $^1\text{H}$  NMR spectrum of the synthesized poly(ester amide) PEA-102

**PEA-103:** By the same way, 74.29 g (0.5 mol) of DMA, 22.80 g (0.23 mol) of HMDA, 0.096 g (0.1 wt%) of zinc acetate, 55.48 g (0.5 mol) of itaconic acid, 112.42 g (1.12 mol) of HDO, 0,06 wt% of MeQH, 0,08 wt% of BHT and 0,2 wt% of Fascat 4101 are reacted. Then toluene was slowly added as entrainer over the condenser.



**Figure S17.** FTIR spectrum of the synthesized poly(ester amide) PEA-103



**Figure S18.**  $^1\text{H}$  NMR spectrum of the synthesized poly(ester amide) PEA-103