Supporting Information for:

Catalytic Ring-Opening Copolymerization of Fatty Acid Epoxides:
Access to Functional Biopolyesters

Arianna Brandolese,† Francesco Della Monica,¥ Miquel À. Pericàs‡§ and Arjan W. Kleij†‡*

† A. Brandolese, M. À. Pericàs, A. W. Kleij, Institute of Chemical Research of Catalonia (ICIQ), the Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 - Tarragona, Spain. E-mail: akleij@iciq.es
¥ Dipartimento di Biotecnologie e Scienze della Vita, Università degli Studi dell'Insubria, via J. H. Dunant 3, 21100 - Varese, Italy
§ M. À. Pericàs, Departament de Química Inorgànica i Orgànica, Universitat de Barcelona, 08028 Barcelona, Spain
‡ A. W. Kleij, Catalan Institute of Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Spain

Table of Contents:

Page S2:   General information
Page S4:   Additional screening data for the benchmark ROCOP between MOO and PA
Page S6:   General procedure for the epoxy synthesis
Page S8:   General procedure for the synthesis of MOO from duck fat soap
Page S9:   General procedure for ROCOP of epoxy fatty acids esters and cyclic anhydrides with 2+4 as a binary catalytic system
Page S16:  Determination of the variation of $M_n$ and $D$ with the conversion in the ROCOP of MOO and PA using various binary catalysts
Page S20:  Use of a chain transfer agent
Page S23:  Cross-linking of polyesters
Page S24:  NMR Spectra
Page S35:  Gel permeation chromatography
Page S44:  FT-IR spectra
Page S50:  Matrix-assisted laser desorption/ionization mass spectrometry of MOO-based polyesters
Page S53:  Differential scanning calorimetry (DSC) of the polyesters
Page S59:  Thermogravimetric analyses of the polyesters
Page S65:  References
S2: General information
All water-sensitive operations were carried out under a nitrogen atmosphere using an MBraun glovebox, standard vacuum line, and Schlenk techniques. Solvents were purchased from Sigma-Aldrich (HPLC grade) and dried using an MBraun MBSPS800 purification system. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were acquired on either a Bruker Avance II 400 ($^1$H 400 MHz, $^{13}$C 101 MHz) or a Bruker Avance II 500 ($^1$H 500 MHz, $^{13}$C 126 MHz) spectrometers at ambient temperature in the respective deuterated solvents. All chemical shifts are quoted in parts per million (ppm) and referenced to the residual solvent peak (7.26 ppm for CDCl$_3$). All coupling constants, $J$, are quoted in Hz. Multiplicities are indicated by: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). NMR peaks assignments were confirmed using 2D $^1$H correlated spectroscopy (COSY), 2D $^1$H–$^{13}$C heteronuclear multiple-bond correlation spectroscopy (HMBC), and 2D $^1$H–$^{13}$C heteronuclear single quantum coherence (HSQCT) where necessary.

Analytical thin layer chromatography was performed on pre-coated aluminum plates (Kieselgel 60 F254 silica). TLC visualization was carried out with ultraviolet light (254 nm), followed by staining with a 1% aqueous KMnO$_4$ solution. Column chromatography was performed in glass columns fitted with porosity 3 sintered discs over Kieselgel 60 silica using the solvent system stated.

Differential scanning calorimetry (DSC) analyses for glass transition temperatures ($T_g$) determination were measured under a N$_2$ atmosphere using a Mettler Toledo equipment (model DSC822e). Samples were weighed into 40 μL aluminum crucibles and subjected to three heating cycles at a heating rate of 10 °C/min. Thermogravimetric analyses (TGA) were recorded under N$_2$ atmosphere using Mettler Toledo equipment (model TGA/SDTA851). Samples were weighed into 40 μL aluminum crucibles and heated to 600 °C at a heating rate of 10 °C/min. Gel permeation chromatography (GPC) measurements were performed using an Agilent 1200 series HPLC system, equipped with PSS SDV Analytical linear M GPC column (8 x 300 mm; 5 μm particle size) in tetrahydrofuran at 30 °C at a flow rate of 1 mL·min$^{-1}$. Samples were analyzed at a concentration of 1 mg·mL$^{-1}$ after filtration through a 0.45 μm pore-size membrane. $M_n$, $M_w$, and $D$ data were derived from the RI signal by a calibration curve based on polystyrene standards (PS from Polymer Standards Service) for the analysis of the polymers. The GPC samples were prepared by dissolving the polymer (3–5 mg) in THF (2 mL), and filtering the solution through a 0.45 μm pore-size membrane. Mass spectrometry analyses were performed by the Research Support Area at ICIQ.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) was performed using a BRUKER Autoflex spectrometer under the following conditions for the sample preparation: 1 mg of polymers was dissolved in 1 mL of CH$_2$Cl$_2$ (1 mg mL$^{-1}$). 5 μL of this solution was added in a solution of dithranol in CH$_2$Cl$_2$ as a matrix (25 μL, 10 mg mL$^{-1}$) and CF$_3$COONa in THF as an additive (1 μL, 1 mg mL$^{-1}$).

IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Spectra were recorded of thin films, with characteristic absorption wave numbers ($v_{\text{max}}$) reported in cm$^{-1}$.

Reagents and complexes
All reagents were purchased from commercial suppliers (Aldrich and Acros) and used as received if not stated differently. Phthalic anhydride (PA), maleic anhydride (MA) and succinic anhydride (SA) are commercially available and were used after recrystallization from hot chloroform and dried under vacuum for 48 h. The additive bis(triphenylphosphine)iminium chloride (3, PPNCl) and 4-(dimethylamino)pyridine (4, DMAP) are commercially available and were purified by
recrystallization from dichloromethane and dried under vacuum for 48 h. The complexes $1^1, 2^1$ were prepared following previously reported procedures. Methyl oleate epoxide (MOO)$^2$ was prepared according to a previously reported procedure, and further purified through dissolution in dry dichloromethane, stirring over CaH$_2$ for 24 h, and lastly filtered through Celite and vacuum-dried prior to use in the copolymerization reactions. Epoxy fatty acids esters MEO$^{2,3}$ and MDO$^{2,4}$ were prepared according to reported procedures and were dissolved in dry hexane or dichloromethane, stirred over CaH$_2$ for 24 h, filtered through Celite and vacuum-dried prior to use in the copolymerization reactions.
S4: Additional screening data for the benchmark ROCOP between MOO and PA

![Reaction scheme](image)

**Table S1. Reaction conditions screening for the ROCOP of MOO and PA.**

| Entry | [M]/[Nu] | MOO/[M] | Solvent | Temp. (°C) | Time (h) | Conv. (%) | $M_n$ $^b$ (kg/mol) | $D^a$ |
|-------|-----------|---------|---------|-----------|----------|-----------|---------------------|-------|
| 1     | 1/3       | 100     | Toluene | 80        | 6        | 7         | n.d.                | n.d.  |
| 2     | 1/3       | 100     | Toluene | 100       | 6        | 28        | 3.7                 | 1.16  |
| 3     | 1/3       | 100     | Toluene | 110       | 16       | 98        | 6.8                 | 1.21  |
| 4     | 1/3       | 100     | Toluene | 100       | 24       | >99       | 6.5                 | 1.22  |
| 5     | 1/4       | 100     | Toluene | 110       | 16       | 87        | 3.8                 | 1.18  |
| 6     | 1/4       | 100     | Toluene | 110       | 24       | 87        | 5.2                 | 1.21  |
| 7     | 2/3       | 100     | THF     | 60        | 6        | traces    | n.d.                | n.d.  |
| 8     | 2/3       | 100     | Toluene | 60        | 6        | <5        | n.d.                | n.d.  |
| 9     | 2/3       | 100     | Toluene | 80        | 6        | 5         | n.d.                | n.d.  |
| 10    | 2/3       | 100     | Toluene | 100       | 6        | 24        | 4.4                 | 1.15  |
| 11    | 2/3       | 200     | Toluene | 110       | 6        | 10        | n.d.                | n.d.  |
| 12    | 2/3       | 100     | Toluene | 110       | 16       | 72        | 9.8                 | 1.22  |
| 13    | 2/3       | 100     | Toluene | 110       | 24       | >99       | 4.3                 | 1.25  |
| 14    | 2/4       | 100     | Toluene | 110       | 16       | 70        | 8.3                 | 1.23  |
| 15    | 2/4       | 100     | Toluene | 110       | 24       | >99       | 11.2                | 1.24  |
| 16$^c$| -/4       | 100     | Toluene | 110       | 24       | 90        | 2.7                 | 1.55  |
| 17$^d$| -/3       | 100     | Toluene | 110       | 24       | >99       | 5.5                 | 2.17  |
| 18$^e$| -/-       | 100     | Toluene | 110       | 24       | <1        | –                   | –     |

Reaction conditions: MOO (0.75 mmol, 1.0 equiv), PA (0.825 mmol, 1.1 equiv), additive (1.0 mol%), [M] (stated amount), solvent (0.25 mL, 3.0 M). $^a$Determined by $^1$H NMR analysis. $^b$Determined by GPC in THF calibrated with polystyrene standards. $^c$Reaction conditions: MOO (0.75 mmol, 1.0 equiv), PA (0.825 mmol, 1.1 equiv), 4 (1.0 mol%), solvent (0.25 mL, 3.0 M). $^d$Reaction conditions: MOO (0.75 mmol, 1.0 equiv), PA (0.825 mmol, 1.1 equiv), 3 (1.0 mol%), solvent (0.25 mL, 3.0 M). $^e$Reaction conditions: MOO (0.75 mmol, 1.0 equiv), PA (0.825 mmol, 1.1 equiv), 2 (1.0 mol%), solvent (0.25 mL, 3.0 M).
Table S2. Additional experiments with Al-complex 2 and DMAP 4 as a binary catalyst.

| Entry | Solvent                  | Conv. (%) | $M_n$ (kg/mol) | $D^b$ |
|-------|--------------------------|-----------|----------------|------|
| 1     | neat                     | 98        | 9.98           | 1.35 |
| 2$^c$ | toluene                  | 94        | 12.0           | 1.19 |
| 3$^c$ | $m$-xylene               | >99       | 7.9            | 1.33 |
| 4     | toluene/1,4-dioxane 1:1  | 72        | 7.2            | 1.36 |
| 5     | toluene (0.75 M)         | 95        | 1.3            | 1.33 |

Reaction conditions: MOO (0.75 mmol, 1.0 equiv), PA (0.85 mmol, 1.1 equiv), DMAP 4 (stated amount), Al-complex 2 (stated amount), solvent (0.25 mL, 3.0 M), 110 °C, 24 h. 
$^a$Determined by $^1$H NMR. $^b$Determined by GPC in THF calibrated with polystyrene standards. $^c$Addition of 4 Å molecular sieves.
S6: General procedure for epoxide synthesis

Synthesis of MOO, MEO, MDO

MOO, MEO; MDO were prepared following a literature procedure. Spectral data were in accordance with the literature ones.

Synthesis of furlv and propyl oleic acid esters

A solution of oleic acid (1 equiv), DCC (1.1 equiv) and DMAP (0.1 equiv) in dry dichloromethane (25% w/v) was stirred magnetically for 1 h in a two-necked, round-bottomed flask at room temperature. The respective alcohol (1.1 equiv) was then added dropwise through a dropping funnel. The reaction mixture was left stirring overnight at room temperature under nitrogen. N,N'-dicyclohexylurea (DCU) that had precipitated during the reaction was filtered off. The filtrate was washed twice with water, twice with 5% acetic acid solution, and finally again with water until a neutral pH was attained. The organic phase was dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure and the product was used for the further reaction step without any further purification.

Prop-2-yn-1-yl oleate (5)

Following the above reported procedure, oleic acid (8.0 g, 28.3 mmol, 1 equiv), DCC (72 mg, 31.1 mmol, 1.1 equiv), DMAP (43 mg, 0.35 mg, 0.1 equiv) and propargylic alcohol (1.7 g, 31.1 mmol, 1.1 equiv) in DCM (32 mL) were combined at room temperature for 16 h, giving the title compound (8.8 g, 97%) as a yellowish oil that was used without further purification.

\[^1\text{H NMR} (500 \text{ MHz}, \text{CDCl}_3) \delta_{\text{H}} = 5.44 – 5.28 (m, 2H), 4.70 (d, J = 2.5 \text{ Hz}, 2H), 2.49 (t, J = 2.5 \text{ Hz}, 1H), 2.37 (t, J = 7.6 \text{ Hz}, 2H), 2.11 – 1.93 (m, 4H), 1.72 – 1.61 (m, 2H), 1.37 – 1.25 (m, 20H), 0.94 – 0.86 (m, 3H); \[^{13}\text{C NMR} (126 \text{ MHz}, \text{CDCl}_3) \delta_{\text{C}} = 172.99, 130.03, 129.75, 77.82, 74.70, 51.76, 34.00, 31.92, 29.78, 29.71, 29.68, 29.53, 29.33, 29.13, 29.08, 29.04, 27.23, 27.17, 24.81, 22.69, 14.13. \]

HRMS (ESI\(^+\)) C\(_{21}\)H\(_{36}\)O\(_2\)Na [M+Na]\(^+\) found 343.2603, requires 343.2608 (−1.4 ppm).

Furan-2-ylmethyl oleate (6)

Following the above reported procedure, oleic acid (8.0 g, 28.3 mmol, 1 equiv), DCC (72 mg, 31.1 mmol, 1.1 equiv), DMAP (43 mg, 0.35 mg, 0.1 equiv) and (furan-2-yl)methanol (3.0 g, 31.1 mmol, 1.1 equiv) in DCM (32 mL) were combined at room temperature for 16 h giving the title compound (10 g, 98%) as yellowish oil that was used without further purification.

\[^1\text{H NMR} (500 \text{ MHz}, \text{CDCl}_3) \delta_{\text{H}} = 7.44 (dd, J = 2.0, 0.9 \text{ Hz}, 1H), 6.56 – 6.29 (m, 2H), 5.45 – 5.30 (m, 2H), 5.08 (s, 2H), 2.35 (t, J = 7.6 \text{ Hz}, 2H), 2.10 – 1.95 (m, 4H), 1.71 – 1.60 (m, 2H), 1.42 – 1.19 (m, 20H), 0.95 – 0.85 (m, 3H); \[^{13}\text{C NMR} (126 \text{ MHz}, \text{CDCl}_3) \delta_{\text{C}} = 173.47, 149.66, 143.20, 130.01, 129.77, 110.54, 110.48, 57.87, 34.15, 31.92, 29.78, 29.71, 29.68, 29.54, 29.33, 29.14, 29.09, 29.06, 27.23, 27.17, 24.88, 22.70, 14.13. \]

HRMS (ESI\(^+\)) C\(_{23}\)H\(_{38}\)O\(_3\)Na [M+Na]\(^+\) found 385.2713, requires 385.2713 (0 ppm).
**Synthesis of furyl- and alkyne-based epoxidized oleic acid**

1 g of the respective ester was dissolved in CH$_2$Cl$_2$ (40 mL) and cooled to 0 °C. Then meta-chloroperbenzoic acid (1.2 equiv) was slowly added to this solution. The reaction mixture was left stirring for 12 h at r.t. The solution was then washed with an aqueous solution of Na$_2$SO$_3$ (3 × 30 mL, 1 M), a saturated aqueous solution of NaHCO$_3$ (3 × 30 mL) and brine. The organic phase was dried over sodium sulfate and the product was obtained after removal of the solvent *in vacuo* using a rotary evaporator. The product was purified through column chromatography (90:10 cyclohexane/ethyl-acetate) to give the title compound.

**Prop-2-yn-1-yl 8-(3-octyloxiran-2-yl)octanoate (AOO)**

Following the above reported procedure, 5 (1.0 g, 3.12 mmol, 1 equiv) and *m*-CPBA (0.6 g, 3.7 mmol, 1.2 equiv) were combined in DCM (37 mL) at 0 °C for 3 h giving after purification by column chromatography (90:10 cyclohexane : EtOAc) the title compound (0.95 g, 91%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$H= 4.69 (d, $J$ = 2.4 Hz, 2H), 3.02 – 2.78 (m, 2H), 2.48 (t, $J$ = 2.5 Hz, 1H), 2.37 (t, $J$ = 7.5 Hz, 2H), 1.74 – 1.58 (m, 2H), 1.56 – 1.18 (m, 24H), 0.99 – 0.79 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$C= 172.92, 77.80, 74.72, 57.23, 57.18, 51.76, 33.95, 31.86, 29.56, 29.53, 29.32, 29.22, 29.14, 28.95, 27.84, 27.80, 26.61, 26.56, 24.76, 22.67, 14.10. HRMS (ESI$^+$) C$_{21}$H$_{36}$O$_3$Na [M+Na]$^+$ found 359.2550, requires 359.2557 (−1.9 ppm).

**Furan-2-ylmethyl 8-(3-octyloxiran-2-yl)octanoate (FOO)**

Following the above reported procedure, 6 (1.0 g, 2.75 mmol, 1 equiv) and *m*-CPBA (0.57 g, 3.3 mmol, 1.2 equiv) were combined in DCM (33 mL) at 0 °C for 3 h giving after purification by column chromatography (90:10 cyclohexane : EtOAc) the title compound (0.9 g, 90%) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$H= 7.43 (d, $J$ = 2.7 Hz, 1H), 6.55 – 6.23 (m, 2H), 5.07 (s, 2H), 3.01 – 2.80 (m, 2H), 2.34 (t, $J$ = 7.5 Hz, 2H), 1.68 – 1.59 (m, 2H), 1.57 – 1.15 (m, 24H), 0.96 – 0.80 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$C= 173.40, 149.64, 143.20, 110.54, 110.49, 57.87, 57.23, 57.18, 34.11, 31.86, 29.56, 29.54, 29.33, 29.23, 29.15, 28.96, 27.84, 27.80, 26.61, 26.56, 24.82, 22.67, 14.10. HRMS (ESI$^+$) C$_{23}$H$_{38}$O$_4$Na [M+Na]$^+$ found 401.2654, requires 401.2662 (−2.1 ppm).
S8: General procedure for the synthesis of MOO from duck fat soap

A sample of duck fat soap (Sapoval, France) was suspended in MeOH and HCl (6 M) was added. The mixture was allowed to stir at room temperature for 1 h becoming homogeneous. Then, the solvent was removed under vacuum and the residue diluted with water and the oleic acid extracted from the aqueous phase with DCM (three times). Drying over NaSO₄ and concentration under vacuum afforded oleic acid which was used for the synthesis of MOO according to the procedure reported in literature.²
S9: General procedure for ROCOP of epoxy fatty acids esters and cyclic anhydrides with 2+4 as a binary catalytic system

In a glove-box, the respective cyclic anhydride (0.825 mmol, 1.1 equiv), DMAP (50 µL of a stock solution in toluene 0.16 M, 7.5 µmol, 0.01 equiv), complex 2 (3.9 mg, 7.5 µmol, 0.01 equiv), the respective epoxidized fatty acid ester (0.75 mmol, 1.0 equiv), and toluene (200 µL) were added in this order into a 10 mL glass vial equipped with a magnetic stirring bar. The vial was closed with a cap equipped with a Teflon septum for microwaves reactions. Out of the glove-box, the vial was placed in a silicon bath preheated to 110 °C, and the mixture kept stirring for the stated reaction time. After this time, the vial was cooled down to room temperature using cold water, opened to air and the mixture dissolved into a minimum amount of dichloromethane. An aliquot was collected to determine the conversion by 1H NMR analysis. The reaction mixture was poured into acidified methanol (1.0 M) under stirring and the polymeric product precipitated from the solution (NB. typically as an oily substance). After decantation the supernatant was removed and the precipitate was washed twice with cold methanol. After removal of the methanol, the polymer was dried under vacuum at 40 °C for 48 h.

Figure S1. 1H NMR spectra of an aliquot of the reaction mixture for the formation of poly(MOO-alt-PA) to determine the conversion (entry 12, Table 1; CDCl3, 400 MHz).
Figure S2. $^1$H NMR peak assignment for purified poly(MOO-alt-PA).
According to the general procedure, PA (122 mg, 0.825 mmol), DMAP (50 μL of a stock solution in toluene 0.16 M, 7.5 μmol, 0.01 equiv), complex 2 (3.9 mg, 7.5 μmol, 0.01 equiv) and crude MOO (232 mg, 0.75 mmol, 1.0 equiv) and toluene (200 μL) were sealed in a vial and stirred for 24 h at 110 ºC. Hereafter, the reaction mixture was dissolved in a minimum amount of DCM and the polymer product precipitated from MeOH (10 × volume of DCM) at 0 ºC. The precipitate was isolated, washed with cold MeOH and dried under vacuum to afford the product as a white, sticky oil (270 mg, 80%, $M_n = 11.2$ kg/mol, $D = 1.24$) with spectral data in accordance with the literature.$^5$

$^1$H NMR (500 MHz, CDCl$_3$) δH= 7.72 – 7.57 (m, 2H, ArH), 7.55 – 7.38 (m, 2H, ArH), 5.38 (bs, 2H, CHO), 3.65 (s, 3H, CH$_3$COO), 3.19 (m, 6H, terminal (CH$_3$)$_2$NR), 2.28 (t, $J = 7.6$ Hz, 2H, CH$_2$COOCH$_3$), 1.90 – 1.12 (m, 26H, -CH$_2$-), 0.87 (t, $J = 6.8$ Hz, 3H, CH$_2$CH$_3$);$^{13}$C NMR (126 MHz, CDCl$_3$) δC= 174.17, 166.58, 132.38, 130.92, 128.80, 74.94, 51.40, 34.05, 31.89, 31.85, 30.83, 29.60, 29.57, 29.48, 29.40, 29.36, 29.31, 29.30, 29.26, 29.13, 29.11, 25.08, 24.93, 22.67, 14.12. IR (neat) $\nu_{max}$ = 2927, 2856, 1724 (C=O), 1254 cm$^{-1}$.

Synthesis of poly(MOO-alt-PA) using crude MOO obtained from duck fat
According to the general procedure, PA (122 mg, 0.825 mmol), DMAP (50 μL of a stock solution in toluene 0.16 M, 7.5 μmol, 0.01 equiv), complex 2 (3.9 mg, 7.5 μmol, 0.01 equiv) and crude MOO (232 mg, 0.75 mmol, 1.0 equiv) and toluene (200 μL) were sealed in a vial and stirred for 48 h at 110 ºC. Hereafter, the reaction mixture was dissolved in a minimum amount of DCM and precipitated from MeOH (10 × volume of DCM) at 0 ºC. The precipitate was isolated, washed with cold MeOH and dried under vacuum to afford the product as a white sticky oil (200 mg, 60%, $M_n = 1.8$ kg/mol, $D = 1.16$).

Synthesis of poly(MOO-alt-PA) using purified MOO obtained from duck fat
According to the general procedure, PA (122 mg, 0.825 mmol), DMAP (50 μL of a stock solution in toluene 0.16 M, 7.5 μmol, 0.01 equiv), complex 2 (3.9 mg, 7.5 μmol, 0.01 equiv) and purified MOO (232 mg, 0.75 mmol, 1.0 equiv) and toluene (200 μL) were sealed in a vial and stirred for 48 h at 110 ºC. Hereafter, the reaction mixture was dissolved in a minimum amount of DCM and precipitated from MeOH (10 × volume of DCM) at 0 ºC. The precipitate was isolated, washed with cold MeOH and dried under vacuum to afford the product as a white sticky oil (252 mg, 75%, $M_n = 11.975$ kg/mol, $D = 1.19$).
Poly(MOO-alt-SA)

According to the general procedure, SA (83 mg, 0.825 mmol), DMAP (50 μL of a stock solution in toluene 0.16 M, 7.5 μmol, 0.01 equiv) and MOO (232 mg, 0.75 mmol, 1.0 equiv) and toluene (200 μL) were sealed in a vial and stirred for 48 h at 110 ºC. Hereafter, the reaction mixture was dissolved in a minimum amount of DCM and precipitated from MeOH (10 × volume of DCM) at 0 ºC. The precipitate was isolated, washed with cold MeOH and dried under vacuum to afford the product as a white sticky oil (150 mg, 50%, \( M_n = 4.4 \) kg/mol, \( D = 1.16 \)) with spectral data in accordance with the literature.5

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta_H = 5.26 - 4.70 \) (m, 2H, CHO), 3.68 (s, 3H, CH\(_3\)COO), 2.67 (bs, 4H, -COOCH\(_2\)CH\(_2\)COO-), 2.38 – 2.25 (m, 2H, CH\(_2\)COOCH\(_3\)), 1.68 – 1.14 (m, 26H, -CH\(_2\)-), 0.89 (t, \( J = 6.7 \) Hz, 3H, CH\(_2\)CH\(_3\)); \(^{}\)\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta_C = 174.22, 174.19, 172.60, 171.91, 171.85, 74.09, 51.78, 51.43, 34.05, 33.98, 31.92, 31.85, 31.83, 31.62, 30.72, 29.69, 29.66, 29.62, 29.55, 29.45, 29.41, 29.33, 29.28, 29.24, 29.21, 29.19, 29.12, 29.06, 29.04, 29.02, 28.94, 28.89, 25.27, 25.16, 25.12, 25.05, 24.88, 22.66, 22.56, 14.10, 14.05. IR (neat) \( \nu_{max} = 2925, 2855, 1733 \) cm\(^{-1}\).

Poly(MOO-alt-MA)

According to the general procedure, MA (81 mg, 0.825 mmol), DMAP (50 μL of a stock solution in toluene 0.16 M, 7.5 μmol, 0.01 equiv), complex 2 (3.9 mg, 7.5 μmol, 0.01 equiv) and MOO (232 mg, 0.75 mmol, 1.0 equiv) and toluene (200 μL) were sealed in a vial and stirred for 48 h at 110 ºC. Hereafter, the reaction mixture was dissolved in a minimum amount of DCM and precipitated from MeOH (10 × volume of DCM) at 0 ºC. The precipitate was isolated, washed with cold MeOH and dried under vacuum to afford the product as a brownish sticky oil (120 mg, 40%, \( M_n = 5.1 \) kg/mol, \( D = 1.66 \)) with spectral data in accordance with the literature.5

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta_H = 6.91 \) (s, 1H, CH=CH trans), 6.25 (d, \( J = 15.1 \) Hz, 2H, CH=CH), 5.37 – 4.67 (m, 2H, CHO), 3.67 (s, 3H, CH\(_3\)COO), 2.30 (t, \( J = 7.5 \) Hz, 2H, CH\(_2\)COOCH\(_3\)), 1.84 – 0.67 (m, 29H, -CH\(_2\)- and CH\(_2\)CH\(_3\)); \(^{}\)\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta_C = 174.19, 164.48, 129.91, 74.57, 72.59, 51.42, 34.04, 31.88, 30.54, 29.44, 29.27, 29.07, 24.92, 22.67, 14.10. IR (neat) \( \nu_{max} = 2924, 2854, 1784, 1729, 1200, 1159 \) cm\(^{-1}\).
Poly(MDO-alt-PA)

According to the general procedure, PA (122 mg, 0.825 mmol), DMAP (50 µL of a stock solution in toluene 0.16 M, 7.5 µmol, 0.01 equiv), complex 2 (3.9 mg, 7.5 µmol, 0.01 equiv), MDO (150 mg, 0.75 mmol, 1.0 equiv) and toluene (200 µL) were sealed in a vial and stirred for 3 h at 110 ºC. Hereafter, the reaction mixture was dissolved in a minimum amount of DCM and precipitated from MeOH (10 × volume of DCM) at 0 ºC. The precipitate was isolated, washed with cold MeOH and dried under vacuum to afford the product as a white sticky oil (220 mg, 85%, \(M_n = 15.9\) kg/mol, \(D = 1.20\)).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.90 – 7.59 (m, 2H, ArH), 7.59 – 7.38 (m, 2H, ArH), 5.42 (s, 1H, CHO), 4.59 – 4.47 (m, 1H, CHHO), 4.47 – 4.29 (m, 1H, CHHO), 3.66 (s, 3H, CH\(_3\)COO), 2.29 (td, \(J = 7.5, 3.2\) Hz, 2H, CH\(_2\)COOCH\(_3\)), 1.88 – 1.15 (m, 12H, -CH\(_2\)-); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta = 174.18, 166.94, 166.78, 132.32, 131.47, 131.25, 131.10, 129.09, 128.81, 72.94, 72.85, 65.93, 51.43, 34.03, 30.71, 29.31, 29.27, 29.11, 29.09, 29.04, 26.92, 25.04, 24.89. IR (neat) \(\nu_{\text{max}} = 2929, 2856, 1720\) (C=O), 1250 cm\(^{-1}\).

Poly(MEO-alt-PA)

According to the general procedure, PA (122 mg, 0.825 mmol), DMAP (50 µL of a stock solution in toluene 0.16 M, 7.5 µmol, 0.01 equiv), complex 2 (3.9 mg, 7.5 µmol, 0.01 equiv), MEO (232 mg, 0.75 mmol, 1.0 equiv) and toluene (200 µL) were sealed in a vial and stirred for 48 h at 110 ºC. Hereafter, the reaction mixture was dissolved in a minimum amount of DCM and precipitated from MeOH (10 × volume of DCM) at 0 ºC. The precipitate was isolated, washed with cold MeOH and dried under vacuum to afford the product as a white sticky oil (200 mg, 60%, \(M_n = 6.0\) kg/mol, \(D = 1.22\)).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.92 – 7.38 (m, 4H, ArH), 5.40 (s, 2H, CHO), 3.66 (s, 3H, CH\(_3\)COO), 3.19 (m, 6H, terminal (CH\(_3\))\(_2\)NR), 2.42 – 2.13 (m, 2H, CH\(_2\)COOCH\(_3\)), 1.96 – 1.05 (m, 26H, -CH\(_2\)-), 0.99 – 0.76 (m, 3H, CH\(_2\)CH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta = 174.20, 166.71, 132.32, 130.97, 128.89, 75.57, 51.43, 51.40, 34.07, 31.88, 31.86, 29.80, 29.55, 29.47, 29.45, 29.38, 29.31, 29.26, 29.13, 29.11, 26.92, 25.49, 25.39, 24.91, 22.67, 14.11. IR (neat) \(\nu_{\text{max}} = 2925, 2854, 1723\) (C=O), 1253 cm\(^{-1}\).
Poly(AOO-alt-PA)

According to the general procedure, PA (122 mg, 0.825 mmol), DMAP (50 µL of a stock solution in toluene 0.16 M, 7.5 µmol, 0.01 equiv), complex 2 (3.9 mg, 7.5 µmol, 0.01 equiv), AOO (252 mg, 0.75 mmol, 1.0 equiv) and toluene (200 µL) were sealed in a vial and stirred for 24 h at 110 ºC. Hereafter, the reaction mixture was dissolved in a minimum amount of DCM and precipitated from MeOH (10 × volume of DCM) at 0 ºC. The precipitate was isolated, washed with cold MeOH and dried under vacuum to afford the product as a yellowish, sticky oil (295 mg, 82%, $M_n = 9.4$ kg/mol, $D = 1.49$).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta_{H} = 7.94 – 7.32$ (m, 4H, ArH), 5.37 (s, 2H, CHO), 4.67 (d, $J = 2.5$ Hz, 2H, $CH_2C\equiv CH$), 3.20 (s, 6H, terminal ($CH_3)_2NR$), 2.49 (d, $J = 2.6$ Hz, 1H, $CH_2C\equiv CH$), 2.33 (t, $J = 7.5$ Hz, 2H, $CH_2COOCH_3$), 1.93 – 1.11 (m, 26H, -CH$_2$), 0.86 (t, $J = 6.8$ Hz, 3H, $CH_2CH_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta_{C} = 172.83$, 166.59, 132.37, 130.94, 128.81, 77.81, 74.92, 74.79, 51.75, 51.72, 33.94, 33.91, 31.89, 31.86, 30.80, 29.60, 29.57, 29.48, 29.43, 29.38, 29.34, 29.31, 29.30, 29.25, 29.08, 29.03, 29.01, 28.95, 25.05, 24.78, 22.67, 22.66, 14.13, 14.12. IR (neat) $\nu_{max} = 3279$ ($\equiv CH$), 2925, 1721 (C=O), 1253 cm$^{-1}$.

Gram scale synthesis of poly(AOO-alt-PA)

According to the general procedure, PA (488 mg, 3.3 mmol), DMAP (4 mg, 30 µmol, 0.01 equiv), complex 2 (15.6 mg, 30 µmol, 0.01 equiv) and AOO (1.0 g, 0.75 mmol, 1.0 equiv) and toluene (1.0 mL) were sealed in a vial and stirred for 24 h at 110 ºC. Hereafter, the reaction mixture was dissolved in a minimum amount of DCM and precipitated from MeOH (10 × volume of DCM) at 0 ºC. The precipitate was isolated, washed with cold MeOH and dried under vacuum to afford the product as a yellowish, sticky oil (1.08 g, 75%, $M_n = 10.9$ kg/mol, $D = 1.50$).
According to the general procedure, PA (122 mg, 0.825 mmol), DMAP (50 µL of a stock solution in toluene 0.16 M, 7.5 µmol, 0.01 equiv), complex 2 (3.9 mg, 7.5 µmol, 0.01 equiv), FOO (283 mg, 0.75 mmol, 1.0 equiv) and toluene (200 µL) were sealed in a vial and stirred for 24 h at 110 °C. Hereafter, the reaction mixture was dissolved in a minimum amount of DCM and precipitated from MeOH (10 × volume of DCM) at 0 °C. The precipitate was isolated, washed with cold MeOH and dried under vacuum to afford the product as a brownish, sticky oil (307 mg, 78%, $M_n = 7.0$ kg/mol, $D = 1.41$).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta_H = 7.87 – 7.33$ (m, 5H, ArH), 6.50 – 6.22 (m, 2H, ArH), 5.51 – 5.26 (m, 2H, CHO), 5.06 (s, 2H, CH$_2$Furyl), 3.19 (s, 6H, terminal (CH$_3$)$_2$NR), 2.30 (t, $J = 7.5$ Hz, 2H, CH$_2$COOCH$_3$), 1.93 – 1.03 (m, 26H, -CH$_2$-), 0.87 (t, $J = 6.8$ Hz, 3H, CH$_2$CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta_C = 173.32, 166.59, 149.65, 143.22, 143.20, 143.18, 132.38, 130.93, 128.80, 110.58, 110.57, 110.54, 110.49, 74.95, 57.87, 57.83, 34.10, 34.07, 31.90, 31.86, 30.83, 29.60, 29.57, 29.48, 29.44, 29.40, 29.36, 29.30, 29.23, 29.10, 29.06, 29.05, 25.07, 24.84, 22.67, 14.13. IR (neat) $\nu_{max} = 2925, 2855, 1722$ (C=O), 1253 cm$^{-1}$.

Gram scale synthesis of poly(FOO-alt-PA)

According to the general procedure, PA (488 mg, 3.3 mmol), DMAP (4 mg, 30 µmol, 0.01 equiv), complex 2 (15.6 mg, 30 µmol, 0.01 equiv), FOO (1.13 g, 0.75 mmol, 1.0 equiv) and toluene (1.0 mL) were sealed in a vial and stirred for 24 h at 110 °C. Hereafter, the reaction mixture was dissolved in a minimum amount of DCM and precipitated from MeOH (10 × volume of DCM) at 0 °C. The precipitate was isolated, washed with cold MeOH and dried under vacuum to afford the product as a brown sticky oil (1.32 g, 84%, $M_n = 6.8$ kg/mol, $D = 1.61$).
S16: Determination of the variation of $M_n$ and $D$ with the conversion in the ROCOP of MOO and PA using various binary catalysts

Following the general procedure, in a glove-box, PA (122 mg, 0.825 mmol, 1.1 equiv), PPNCl (4.7 mg, 7.5 μmol, 0.01 equiv), Fe-complex 1 (3.9 mg, 7.5 μmol, 0.01 equiv), MOO (233 mg, 0.75 mmol, 1.0 equiv), and toluene (200 μL) were added in this order into a 10 mL glass vial equipped with a magnetic stirring bar. The vial was closed with a cap equipped with a Teflon septum for microwaves reactions. Out of the glove-box, the vial was placed in a silicon bath preheated to 110 °C, and the mixture kept stirring for the stated reaction time. After this time, the vial was cooled down to room temperature in cold water, opened to air and the mixture dissolved into a minimum amount of dichloromethane. An aliquot was collected to determine the conversion by $^1$H NMR analysis. This procedure was repeated several times to collect all the data points as provided in the table below.

| t (min) | Conv. (%)$^a$ | $M_n$ (kg/mol)$^b$ | $D$$^b$ |
|---------|---------------|------------------|--------|
| 60      | 11            | 1.96             | 1.09   |
| 120     | 18            | 2.6              | 1.15   |
| 180     | 40            | 4.0              | 1.17   |
| 240     | 49            | 4.4              | 1.18   |
| 300     | 71            | 5.5              | 1.19   |
| 360     | 90            | 5.2              | 1.18   |

Reaction conditions: MOO (0.75 mmol, 1.0 equiv), PA (0.825 mmol, 1.1 equiv), PPNCl (1.0 mol%), Fe-complex 1 (1.0 mol%), toluene (0.25 mL, 3.0 M). $^a$ Determined by $^1$H NMR analysis. $^b$ Determined by GPC in THF calibrated with polystyrene.

Figure S3. (a) Kinetic plot of ROCOP of MOO with PA promoted by 1/3 as a binary catalytic system. (b) Plot of number-averaged molecular weights $M_n$ and polydispersity $D$ vs. monomer conversion using 1/3 as catalyst for the ROCOP of MOO and PA. Reaction conditions: see entry 5, Table 1.
Following the general procedure, in a glove-box, PA (122 mg, 0.825 mmol, 1.1 equiv), DMAP (50 µL of a stock solution in toluene 0.16 M, 7.5 µmol, 0.01 equiv), complex 1 (3.9 mg, 7.5 µmol, 0.01 equiv), MOO (233 mg, 0.75 mmol, 1.0 equiv) and toluene (200 µL) were added in this order into a 10 mL glass vial equipped with a magnetic stirring bar. The vial was closed with a cap equipped with a Teflon septum for microwaves reactions. Out of the glove-box, the vial was placed in a silicon bath preheated to 110 °C, and the mixture kept stirring for the stated reaction time. After this time, the vial was cooled down to room temperature in cold water, opened to air and the mixture dissolved into a minimum amount of dichloromethane. An aliquot was collected to determine the conversion by 1H NMR analysis. This procedure was repeated several times to collect all the data points as provided in the table below.

| t (min) | Conv. (%)a | $M_n$ (kg/mol)b | $D_b$ |
|--------|-----------|----------------|------|
| 60     | 5         | 1.14           | 1.07 |
| 120    | 15        | 1.54           | 1.12 |
| 180    | 31        | 2.0            | 1.15 |
| 240    | 49        | 3.7            | 1.14 |
| 300    | 67        | 4.4            | 1.15 |
| 360    | 70        | 4.9            | 1.2  |

Reaction conditions: MOO (0.75 mmol, 1.0 equiv), PA (0.825 mmol, 1.1 equiv), DMAP (1.0 mol%), Fe complex 1 (1.0 mol%), toluene (0.25 mL, 3.0 M). a Determined by 1H NMR analysis. b Determined by GPC in THF calibrated with polystyrene standards.

Figure S4. (a) Plot of the ROCOP of MOO with PA promoted by 1/4 as binary catalytic system. (b) Plot of number-averaged molecular weights $M_n$ and polydispersity $D$ vs. monomer conversion using 1/4 as catalyst for the ROCOP of MOO and PA. Reaction conditions: see entry 7, Table 1.
Following the general procedure, in a glove-box, PA (122 mg, 0.825 mmol, 1.1 equiv), PPNCl (4.7 mg, 7.5 μmol, 0.01 equiv), Al-complex 2 (3.9 mg, 7.5 μmol, 0.01 equiv), MOO (233 mg, 0.75 mmol, 1.0 equiv) and toluene (200 μL) were added in this order into a 10 mL glass vial equipped with a magnetic stirring bar. The vial was closed with a cap equipped with a Teflon septum for microwaves reactions. Out of the glove-box, the vial was placed in a silicon bath preheated to 110 °C, and the mixture kept stirring for the stated reaction time. After this time, the vial was cooled down to room temperature in cold water, opened to air and the mixture dissolved into a minimum amount of dichloromethane. An aliquot was collected to determine the conversion by 1H NMR analysis. This procedure was repeated several times to collect all the data points as provided in the table below. 

| t (min) | Conv. (%) | $M_n$ (kg/mol) | $D^b$ |
|--------|----------|----------------|------|
| 90     | 15       | 2.1            | 1.10 |
| 180    | 27       | 4.4            | 1.18 |
| 270    | 41       | 5.5            | 1.19 |
| 360    | 50       | 6.0            | 1.19 |
| 450    | 54       | 7.0            | 1.19 |
| 540    | 61       | 8.5            | 1.23 |

Reaction conditions: MOO (0.75 mmol, 1.0 equiv), PA (0.825 mmol, 1.1 equiv), PPNCl (1.0 mol%), Al-complex 2 (1.0 mol%), toluene (0.25 mL, 3.0 M). aDetermined by 1H NMR analysis. bDetermined by GPC in THF calibrated with polystyrene.

Figure S5. (a) Kinetic plot of ROCOP of MOO with PA promoted by 2/3 as binary catalytic system. (b) Plot of number-averaged molecular weights $M_n$ and polydispersity $D$ vs. monomer conversion using 2/3 as catalyst for the ROCOP of MOO and PA. Reaction conditions: see entry 6, Table 1.
Following the general procedure, in a glove-box, PA (122 mg, 0.825 mmol, 1.1 equiv), DMAP (50 μL of a stock solution in toluene 0.16 M, 7.5 μmol, 0.01 equiv), complex 2 (3.9 mg, 7.5 μmol, 0.01 equiv), MOO (233 mg, 0.75 mmol, 1.0 equiv) and toluene (200 μL) were added in this order into a 10 mL glass vial equipped with a magnetic stirring bar. The vial was closed with a cap equipped with a Teflon septum for microwaves reactions. Out of the glove-box, the vial was placed in a silicon bath preheated to 110 °C, and the mixture kept stirring for the stated reaction time. After this time, the vial was cooled down to room temperature in cold water, opened to air and the mixture dissolved into a minimum amount of dichloromethane. An aliquot was collected to determine the conversion by 1H NMR analysis. This procedure was repeated several times to collect all the data points as provided in the table below.

| t (h) | Conv. (%)<sup>a</sup> | Mn (kg/mol)<sup>b</sup> | Db<sup>b</sup> |
|-------|----------------------|-----------------------|------------|
| 180   | 16                   | 3.3                   | 1.1        |
| 360   | 39                   | 5.3                   | 1.21       |
| 540   | 62                   | 8.1                   | 1.19       |
| 720   | 71                   | 9.5                   | 1.21       |
| 1080  | 87                   | 12                    | 1.19       |

Reaction conditions: MOO (0.75 mmol, 1.0 equiv), PA (0.825 mmol, 1.1 equiv), DMAP (1.0 mol%), Al-complex 2 (1.0 mol%), toluene (0.25 mL, 3.0 M). <sup>a</sup>Determined by 1H NMR analysis. <sup>b</sup>Determined by GPC in THF calibrated with polystyrene standards.

Figure S6. (a) Plot of the ROCOP of MOO with PA promoted by 2/4 as binary catalytic system. (b) Plot of number-averaged molecular weights Mn and polydispersity D vs. monomer conversion using 2/4 as catalyst for the ROCOP of MOO and PA. Reaction conditions: see entry 8, Table 1.
S20: Use of a chain transfer agent

Following the general procedure, in a glove-box, PA (0.825 mmol, 1.1 equiv), DMAP (50 µL of a stock solution in toluene 0.16 M, 7.5 µmol, 0.01 equiv), complex 2 (3.9 mg, 7.5 µmol, 0.01 equiv), BnOH (stated amount), MOO (0.75 mmol, 1.0 equiv) and toluene (200 µL) were added in this order into a 10 mL glass vial equipped with a magnetic stirring bar. The vial was closed with a cap equipped with a Teflon septum for microwaves reactions. Out of the glove-box, the vial was placed in a silicon bath preheated to 110 °C, and the mixture kept stirring for 24 h. After this time, the vial was cooled down to room temperature in cold water, opened to air and the mixture dissolved into a minimum amount of dichloromethane. An aliquot was collected to determine the conversion by $^1$H NMR analysis. The reaction mixture was poured into acidified methanol (1.0 M) under stirring and the polymeric product precipitate from the solution. After decantation the supernatant was removed, and the precipitate was washed with cold methanol twice. After methanol removal, the polymer was dried under vacuum at 40 °C for 48 h.

Figure S7. Example of $^1$H NMR spectra of poly(MOO-alt-PA) in presence of BnOH as chain transfer (entry 15, Table 1).

$^1$H NMR (500 MHz, CDCl$_3$) δ$_H$ = 7.81 – 7.37 (m, 4H, ArH), 5.55 – 5.35 (m, 2H, CHO), 5.30 (m, 2H, CH$_2$Ph), 3.73 – 3.59 (m, 3H, CH$_3$COO), 3.21 (s, 6H, terminal (CH$_3$)$_2$NR), 2.29 (t, J = 7.6 Hz, 2H, CH$_3$COOCH$_3$), 1.89 – 1.10 (m, 26H, -CH$_2$-), 0.87 (t, J = 6.7 Hz, 3H, CH$_2$CH$_3$).
**Figure S8.** GPC trace of poly(MOO-alt-PA) related to Table 1, entry 14, Table 1 (0.01 equiv of BnOH)

| $M_n$ (g/mol) | $M_w$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$   |
|--------------|--------------|--------------|--------------|-------|
| 8.6684e3     | 1.1166e4     | 1.4003e4     | 1.3889e4     | 1.2881|

**Figure S9.** GPC trace of poly(MOO-alt-PA) related to Table 1, entry 15, Table 1 (0.05 equiv of BnOH)

| $M_n$ (g/mol) | $M_w$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$   |
|--------------|--------------|--------------|--------------|-------|
| 4.6969e3     | 5.7178e3     | 7.1814e3     | 4.6735e3     | 1.2173|
Comparison between the molecular weights determined by GPC and $^1$H NMR:

For the DMAP-initiated polymerization reactions leading to various polyesters (see Table below), the calculated values of their average molecular weight, $M_n$ (i.e., via their degree of polymerization, DP) for these polymers by $^1$H NMR using the NMe$_2$ peak of DMAP as a reference was attained through peak integration. The values calculated by NMR are typically higher than the ones determined by GPC. The likely reason for this is the relative large error in peak integration as the peaks associated to the DMAP based end-group are relatively small in intensity.

| Polymer        | $M_n$ ($^1$H NMR) | $M_n$ (GPC) | $M_w$ (GPC) |
|----------------|------------------|-------------|-------------|
| Poly(MOO-alt-PA) | 15.3             | 11.2        | 13.8        |
| Poly(MDO-alt-PA) | 43.0             | 15.9        | 19.2        |
| Poly(MEO-alt-PA) | 15.0             | 6.0         | 7.3         |
| Poly(AOO-alt-PA) | 13.7             | 9.4         | 14.0        |
| Poly(FOO-alt-PA) | 14.8             | 7.0         | 10.0        |
S23: Cross-linking of polyesters

Synthesis of cross-linked polymers through copper(I)-catalyzed alkyne/azide cycloaddition
Poly(AOO-alt-PA) (150 mg), 1,4-bis(azidomethyl)benzene (50 mol% or 15 mol% relative to the alkyne units), CuI (0.10 mol%) and DIPEA (5 equiv) were mixed together in a vial containing DMF (0.1 M). The reaction mixture was heated at 45 ºC for 24 h. After this time, the reaction mixture was cooled down and filtered. The filtrate was sequentially washed with THF (3 × 5 mL), EtOAc (3 × 5 mL) and EtO₂ (3 × 5 mL) and finally dried under vacuum for 48 h at 50 ºC. The cross-linked polymer was analyzed by FT-IR spectroscopy for comparison with the initial mixture of poly(AOO-alt-PA) and 1,4-bis(azidomethyl)benzene.

Synthesis of cross-linked polymers through Diels-Alder chemistry
Poly(FOO-alt-PA) and BM (50 mol% and 15 mol% relative to the difuranic monomer unit) were mixed together in a vial containing DMF (40 wt%). The reaction was heated at 65 ºC for 24 h. Once gelation occurred, the solvent was allowed to evaporate for 48 h at 50 ºC under vacuum. The gel was then analyzed by FT-IR spectroscopy for comparison with the initial mixture of poly(FOO-alt-PA) and BM.

Retro Diels-Alder reaction
The cross-linked polymer (150 mg) obtained from poly(FOO-alt-PA) and BM was suspended in DMF (40 wt%) and heated at 160 ºC for 16 h. Then, the resulting mixture was poured into methanol under stirring and the polymeric product precipitated. After decantation, the supernatant was removed, and the precipitate was twice washed with cold methanol. The polymer was finally dried under vacuum at 40 ºC for 48 h. ¹H NMR and GPC analyses confirmed the re-formation of poly(FOO-alt-PA).
S24: NMR Spectra

Figure S10. $^1$H NMR (CDCl$_3$, 500 MHz) of prop-2-yn-1-yl oleate.

Figure S11. $^{13}$C NMR (CDCl$_3$, 126 MHz) of prop-2-yn-1-yl oleate.
Figure S12. $^1$H NMR (CDCl$_3$, 500 MHz) of furan-2-ylmethyl oleate.

Figure S13. $^{13}$C NMR (CDCl$_3$, 126 MHz) of furan-2-ylmethyl oleate.
Figure S14. $^1$H NMR (CDCl$_3$, 300 MHz) of prop-2-yn-1-yl 8-(3-octyloxiran-2-yl)octanoate.

Figure S15. $^{13}$C NMR (CDCl$_3$, 126 MHz) of prop-2-yn-1-yl 8-(3-octyloxiran-2-yl)octanoate.
Figure S16. $^1$H NMR (CDCl$_3$, 400 MHz) of furan-2-ylmethyl 8-(3-octyloxiran-2-yl)octanoate.

Figure S17. $^{13}$C NMR (CDCl$_3$, 126 MHz) of furan-2-ylmethyl 8-(3-octyloxiran-2-yl)octanoate.
Figure S18. $^1$H NMR (CDCl$_3$, 500 MHz) of poly(MOO-alt-PA).

Figure S19. $^{13}$C NMR (CDCl$_3$, 126 MHz) of poly(MOO-alt-PA).
Figure S20. $^1$H NMR (CDCl$_3$, 400 MHz) of poly(MOO-alt-SA).

Figure S21. $^{13}$C NMR (CDCl$_3$, 101 MHz) of poly(MOO-alt-SA).
Figure S22. $^1$H NMR (CDCl$_3$, 400 MHz) of poly(MOO-alt-MA).

Figure S23. $^{13}$C NMR (CDCl$_3$, 126 MHz) of poly(MOO-alt-MA).
Figure S24. $^1$H NMR (CDCl$_3$, 500 MHz) of poly(MDO-alt-PA).

Figure S25. $^{13}$C NMR (CDCl$_3$, 126 MHz) of poly(MDO-alt-PA).
Figure S26. $^1$H NMR (CDCl$_3$, 500 MHz) of poly(MEO-alt-PA).

Figure S27. $^{13}$C NMR (CDCl$_3$, 126 MHz) of poly(MEO-alt-PA).
Figure S28. $^1$H NMR (CDCl$_3$, 500 MHz) of poly(AOO-alt-PA).

Figure S29. $^{13}$C NMR (CDCl$_3$, 126 MHz) of poly(AOO-alt-PA).
Figure S30. $^1$H NMR (CDCl$_3$, 500 MHz) of poly(FOO-alt-PA).

Figure S31. $^{13}$C NMR (CDCl$_3$, 126 MHz) of poly(FOO-alt-PA).
S35: Gel permeation chromatography

Figure S32. GPC trace of poly(MOO-alt-PA) related to entry 12, Table 1.

Figure S33. GPC trace of poly(MOO-alt-PA) related to entry 9, Table 1 showing a bimodal behavior.
Figure S34. GPC trace of poly(MOO-alt-PA) related to the use of purified MOO derived from duck fat (entry 17, Table 1).

![Figure S34](image1.png)

| $M_n$ (g/mol) | $M_W$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$  |
|--------------|--------------|--------------|--------------|-----|
| 1.1975e4    | 1.4302e4    | 1.6293e4    | 1.5873e4    | 1.1943 |

Figure S35. GPC trace of poly(MOO-alt-PA) related to the use of crude MOO deriving from duck fat (entry 16, Table 1).

![Figure S35](image2.png)

| $M_n$ (g/mol) | $M_W$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$  |
|--------------|--------------|--------------|--------------|-----|
| 1.7859e3    | 2.0673e3    | 2.3854e3    | 1.6070e3    | 1.1576 |
**Figure S36.** GPC trace of poly(MOO-alt-SA) related to entry 2, Table 2.

| Mn (g/mol) | Mw (g/mol) | Mz (g/mol) | Mp (g/mol) | D  |
|-----------|------------|------------|------------|----|
| 4.3730e3  | 5.0886e3   | 6.1797e3   | 4.2036e3   | 1.1636 |

**Figure S37.** GPC trace of poly(MOO-alt-MA) related to entry 3, Table 2.

| Mn (g/mol) | Mw (g/mol) | Mz (g/mol) | Mp (g/mol) | D  |
|-----------|------------|------------|------------|----|
| 5.1538e3  | 8.5532e3   | 1.4834e4   | 3.9882e3   | 1.6596 |
Figure S38. GPC trace of poly(MEO-alt-PA) related to entry 4, Table 2.

![Figure S38](image)

| $M_n$ (g/mol) | $M_W$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$  |
|--------------|--------------|--------------|--------------|-----|
| 5.9898e3     | 7.2983e3     | 8.6297e3     | 8.3305e3     | 1.2185 |

Figure S39. GPC trace of poly(MEO-alt-PA) related to entry 11, Table 2.

![Figure S39](image)

| $M_n$ (g/mol) | $M_W$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$  |
|--------------|--------------|--------------|--------------|-----|
| 3.1939e3     | 3.7229e3     | 4.2336e3     | 3.9197e3     | 1.1656 |
Figure S40. GPC trace of poly(MDO-alt-PA) related to entry 5, Table 2.

| $M_n$ (g/mol) | $M_W$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$       |
|---------------|---------------|---------------|---------------|-----------|
| 1.5927e4      | 1.9165e4      | 1.9165e4      | 2.0987e4      | 1.2033    |

Figure S41. GPC trace of poly(MDO-alt-PA) related to entry 10, Table 2.

| $M_n$ (g/mol) | $M_W$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$       |
|---------------|---------------|---------------|---------------|-----------|
| 6.4631e3      | 8.1915e3      | 1.0012e4      | 6.6197e3      | 1.2674    |
**Figure S42.** GPC trace of poly(AOO-\textit{alt}-PA) related to entry 6, Table 2.

![Figure S42](image)

| $M_n$ (g/mol) | $M_W$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$   |
|----------------|----------------|----------------|----------------|-------|
| 9.3684e3       | 1.3971e4       | 2.1587e4       | 7.6364e3       | 1.4912|

**Figure S43.** GPC trace of poly(AOO-\textit{alt}-PA) obtained from the gram scale synthesis related to entry 7, Table 2.

![Figure S43](image)

| $M_n$ (g/mol) | $M_W$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$   |
|----------------|----------------|----------------|----------------|-------|
| 1.0887e4       | 1.6330e4       | 2.3598e4       | 1.1448e4       | 1.4999|
Figure S44. GPC trace of poly(AOO-alt-PA) related to entry 12, Table 2.

| $M_n$ (g/mol) | $M_W$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$  |
|--------------|--------------|--------------|--------------|------|
| 5.7616e3     | 8.1115e3     | 1.1255e4     | 6.5565e3     | 1.4079 |

Figure S45. GPC trace of poly(FOO-alt-PA) related to entry 8, Table 2

| $M_n$ (g/mol) | $M_W$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$  |
|--------------|--------------|--------------|--------------|------|
| 7.0452e3     | 9.9735e3     | 1.3806e4     | 1.0562e4     | 1.4156 |
Figure S46. GPC trace of poly(FOO-alt-PA) obtained from the gram scale synthesis related to entry 9, Table 2.

|     | $M_n$ (g/mol) | $M_W$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$  |
|-----|---------------|---------------|---------------|---------------|-----|
|     | 6.8077e3      | 1.1001e4      | 1.8318e4      | 8.7477e3      | 1.6159 |

Figure S47. GPC trace of poly(FOO-alt-PA) related to entry 13, Table 2

|     | $M_n$ (g/mol) | $M_W$ (g/mol) | $M_z$ (g/mol) | $M_p$ (g/mol) | $D$  |
|-----|---------------|---------------|---------------|---------------|-----|
|     | 6.7921e3      | 9.1727e3      | 1.2953e4      | 6.0287e3      | 1.3505 |

S42
Figure S48. GPC trace of poly(FOO-alt-PA) obtained after the retro-Diels-Alder derived from the partially cross-linked polymer.

\[
\begin{array}{cccccc}
M_n (\text{g/mol}) & M_W (\text{g/mol}) & M_z (\text{g/mol}) & M_p (\text{g/mol}) & D \\
6.6176e3 & 9.2860e3 & 1.3175e4 & 8.3041e3 & 1.4032 \\
\end{array}
\]

Figure S49. GPC trace of poly(FOO-alt-PA) obtained after the retro-Diels-Alder derived from the fully cross-linked polymer.

\[
\begin{array}{cccccc}
M_n (\text{g/mol}) & M_W (\text{g/mol}) & M_z (\text{g/mol}) & M_p (\text{g/mol}) & D \\
6.0056e3 & 8.6014e3 & 1.2481e4 & 8.0143e3 & 1.4322 \\
\end{array}
\]
S44: FT-IR spectra

Figure S50. FT-IR (neat) of poly(MOO-alt-PA).

Figure S51. FT-IR (neat) of poly(MOO-alt-SA).
Figure S52. FT-IR (neat) of poly(MOO-alt-MA).

Figure S53. FT-IR (neat) of poly(MDO-alt-PA).
Figure S54. FT-IR (neat) of poly(MEO-alt-PA).

Figure S55. FT-IR (neat) of poly(AOO-alt-PA).
Figure S56. FT-IR (neat) of poly(FOO-alt-PA).

Figure S57. FT-IR (neat) of partially cross-linked poly(AOO-alt-PA).
**Figure S58.** FT-IR (neat) of fully cross-linked poly(AOO-alt-PA)$_{\text{CL}}$.

**Figure S59.** FT-IR (neat) of partially cross-linked poly(AOO-alt-PA)$_{\text{CL}}$. 
Figure S60. FT-IR (neat) of fully cross-linked poly(AOO-alt-PA)$_{\text{CL}}$. 
S50: Matrix-assisted laser desorption/ionization mass spectrometry of MOO-based polyesters

Figure S61. MALDI-TOF spectrum of poly(MOO-alt-PA) related to entry 9, Table 1.
Figure S62. MALDI-TOF spectrum of poly(MOO-alt-PA) related to entry 12, Table 1.
Figure S63. MALDI-TOF spectrum of poly(MOO-alt-PA) related to entry 14, Table 1.
S53: Differential scanning calorimetry (DSC) of the polyesters

Figure S64. DSC thermogram of poly(MOO-alt-PA) related to entry 12, Table 1.

Figure S65. DSC thermogram of poly(MOO-alt-SA).
Figure S66. DSC thermogram of poly(MOO-alt-MA).

Figure S67. DSC thermogram of poly(MDO-alt-PA).
Figure S68. DSC thermogram of poly(MEO-alt-PA).

Figure S69. DSC thermogram of poly(AOO-alt-PA).
Figure S70. DSC thermogram of poly(FOO-alt-PA).

Figure S71. DSC thermogram of partially cross-linked poly(AOO-alt-PA)\textsuperscript{CL}.
Figure S72. DSC thermogram of fully cross-linked poly(AOO-alt-PA)\textsuperscript{CL}.

Figure S73. DSC thermogram of partially cross-linked poly(FOO-alt-PA)\textsuperscript{CL}.
Figure S74. DSC thermogram of fully cross-linked poly(FOO-alt-PA)\textsuperscript{CL}.

\[ T_{g} = 95 \, ^{\circ}\text{C} \]
S59: Thermogravimetric analyses of the polyesters

Figure S75. TGA thermogram of poly(MOO-alt-PA).

Figure S76. TGA thermogram of poly(MOO-alt-SA).

$T_{\text{5\%}} (N_2) = 265 \, ^\circ\text{C}$

$T_{\text{5\%}} (N_2) = 312 \, ^\circ\text{C}$
**Figure S77.** TGA thermogram of poly(MOO-alt-MA).

![TGA thermogram of poly(MOO-alt-MA)](image)

\[ T_{5\%} (N_2) = 280 ^\circ C \]

**Figure S78.** TGA thermogram of poly(MDO-alt-PA).

![TGA thermogram of poly(MDO-alt-PA)](image)

\[ T_{5\%} (N_2) = 334 ^\circ C \]
**Figure S79.** TGA thermogram of poly(MEO-alt-PA).

![TGA thermogram of poly(MEO-alt-PA)](image)

$T_{5\%} (N_2) = 289 \, ^\circ C$

**Figure S80.** TGA thermogram of poly(AOO-alt-PA).

![TGA thermogram of poly(AOO-alt-PA)](image)

$T_{5\%} (N_2) = 304 \, ^\circ C$
Figure S81. TGA thermogram of poly(FOO-alt-PA)

Figure S82. TGA thermogram of partially cross-linked poly(AOO-alt-PA)\textsuperscript{CL}.
Figure S83. TGA thermogram of fully cross-linked poly(AOO-alt-PA)\textsuperscript{CL}.

![TGA thermogram of fully cross-linked poly(AOO-alt-PA)\textsuperscript{CL}](image1)

$T_{5\%} (N_2) = 250 \, ^\circ C$

Figure S84. TGA thermogram of partially cross-linked poly(FOO-alt-PA)\textsuperscript{CL}.

![TGA thermogram of partially cross-linked poly(FOO-alt-PA)\textsuperscript{CL}](image2)

$T_{5\%} (N_2) = 285 \, ^\circ C$
Figure S85. TGA thermogram of fully cross-linked poly(FOO-alt-PA)\textsuperscript{CL}.

\[ T_{5\%} (N_2) = 228 \, ^\circ C \]
S65: References

(1) Whiteoak, C. J.; Martin, E.; Martínez Belmonte, M.; Benet-Buchholz, J.; Kleij, A. W. Adv. Synth. Catal. 2012, 354, 469−476.
(2) Peña Carrodeguas, L.; Cristòfol, À.; Fraile, J. M.; Mayoral, J. A.; Dorado, V.; Herrerías, C. I.; Kleij, A. W. Green Chem. 2017, 19, 3535−3541.
(3) Wang, F.; Kawamura, A.; Mootoo, D. R. Bioorg. Med. Chem. 2008, 16, 8413−8418.
(4) Kreye, O.; Tóth, T.; Meier, M. A.R. Eur. Polym. J. 2011, 47, 1804−1816.
(5) Biermann, U.; Sehlinger, A.; Meier, M. A. R.; Metzger, J. O. Eur. J. Lipid Sci. Technol. 2016, 118, 104−110.