Electronic Supplementary Information (ESI)

for

Ambient Temperature Catalyst-Free Light-Induced Preparation of Macrocyclic Aliphatic Polyesters

Thomas Josse,[a,b] Ozcan Altintas,[c] Kim K. Oehlenschlaeger,[c] Philippe Dubois,[a] Pascal Gerbaux,[b] Olivier Coulembier*[a] and Christopher Barner-Kowollik*[c]

[a] *Center of Innovation and Research in Materials and Polymers (CIRMAP), Laboratory of Polymeric and Composite Materials, University of Mons, 23 Place du Parc, B-7000, Mons, Belgium; E-mail: olivier.coulembier@umons.ac.be; Fax: +32 (0)65 373484; Tel: +32 (0)65 373481*
[b] *Interdisciplinary Center for Mass Spectrometry (CISMa), Organic Synthesis and Mass Spectrometry Laboratory, University of Mons, 23 Place du Parc, B-7000 Mons, Belgium*
[c] *Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany and Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology (KIT), Herrmann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. E-mail: christopher.barner-kowollik@kit.edu; Fax: +49 721 608-45740; Tel: +49 721 608-45641*

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1. Materials and Analytic Instrumentation

Materials

L-Lactide (L-LA) (GALACTIC, Belgium) was recrystallized twice from dried toluene and stored in a glove box. ε-Caprolactone (ε-CL, Sigma-Aldrich) and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU, 98%, Aldrich) were distilled from CaH_2 and stored over molecular sieves (4Å). Dichloromethane (DCM, extra dry, water < 0.005%, Acros), tetrahydrofurane (THF, extra dry, water < 0.005%, Acros), acetonitrile (MeCN, > 99%, VWR), hexane (> 98%, VWR), 5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Sigma-Aldrich), benzoic acid (99.5%, Sigma-Aldrich), acryloyl chloride (96%, Alfa-Aesar), magnesium sulfate (99%, ROTH) and triethylamine (Et_3N, > 99%, Merck) were used as received. 2-

((11-Hydroxyundecyl)oxy)-6-methylbenzaldehyde was synthesized according to published procedures.[1]

Analytic Instrumentation

Electro-Spray Ionization-Mass Spectrometry (ESI-MS)

ESI-MS spectra were recorded on an LXQ mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the *m/z* range 195-1822 using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Sigma-Aldrich). A constant spray voltage of 4.5 kV was used and nitrogen was applied with a dimensionless sweep gas flow-rate of 2 (approx. 3 L min^{-1}) and a dimensionless sheath gas flow-rate of 12 (approx. 1 L·min^{-1}). The capillary voltage, the tube lens offset voltage and the capillary temperature were set to 60 V, 110 V and 275°C, respectively. The sample was measured with a concentration of 1 mg.mL^{-1} in acetronitrile solution [dopped with NaI (0.014 mg mL^{-1})] and a flow rate of 10 μL min^{-1}.

Size-Exclusion Chromatography

SEC measurements were performed on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 μm bead-size guard column (50×7.5 mm) followed by three PLgel 5 μm Mixed-C and one PLgel 3 μm Mixed-E columns (300×7.5 mm) and a differential refractive index detector using THF as the eluent at 35 °C with a flow rate of 1 mL min^{-1}. The SEC system was calibrated using linear poly(styrene) (PS) standards ranging from 160 to 6.10^6 g.mol^{-1}. Calculation of the molecular weights proceeded via the Mark-Houwink parameters ($K = 13.95\ 10^{-5}$ dL.g^{-1}, $\alpha = 0.786$) and a correction value of 0.58 for poly(ε-caprolactone)[2] and poly(L-lactide)[3], respectively.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR spectroscopy was carried out on a Bruker AM 400 MHz spectrometer. The samples were dissolved in $CDCl_3$. The δ-scale is referenced to tetramethylsilane ($\delta = 0.00$ ppm) as internal standard. Abbreviations used in the description of the synthetic procedures include singlet (s), doublet (d), triplet (t), quartet (q), broad multiplet (bm), and unresolved multiplet (m).

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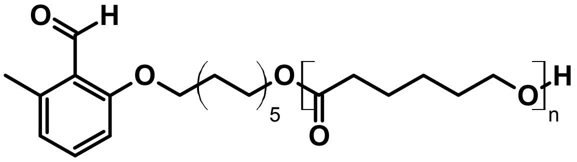
[1] K. K. Oehlenschlaeger, J. O. Mueller, N. B. Heine, M. Glassner, N. K. Guimard, G. Delaittre, F. G. Schmidt and C. Barner-Kowollik, *Angew. Chem. Int. Ed.*, 2013, **52**, 762.

[2] A. Schindler, Y. M. Hibionada and C. G. Pitt, *Journal of Polymer Science*, *Polymer Chemistry Edition*, 1982, **20**, 319.

[3] A. Kowalski, A. Duda and S. Penczek, *Macromolecules*, 1998, **31**, 2114.

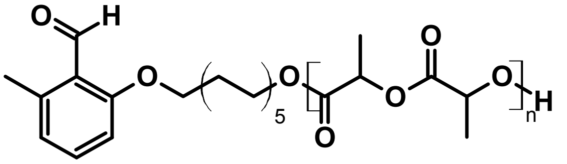
2. Synthetic Procedures



Photoenol end-capped poly(ε-caprolactone) (1):

2-((11-Hydroxyundecyl)oxy)-6-methylbenzaldehyde (53.5 mg, 0.175 mmol, 0.04 eq) and TBD (24.4 mg, 0.175 mmol, 0.04 eq) were dissolved in CH_2Cl_2 (3.75 mL) in an inert atmosphere. ε-CL (500 mg, 4.4 mmol, 1 eq) was added and the solution was stirred under argon atmosphere at ambient temperature for 90 min. The reaction was quenched with benzoic acid (50.0 mg, 0.40 mmol, 0.09 eq) and the polymer was precipitated in cold *n*-hexane (30 mL).[4]

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 10.67 (s, 1H, C*H*O), 7.34 (t, J = 8.0 Hz, 1H, Ar*H*), 6.80 (dd, J = 14.3, 8.0 Hz, 2H, Ar*H*), 4.05 (t, J = 6.7 Hz, 2nH, C(O)OCH_2 along polymer backbone; t, 4H, OCH_2 initiator), 3.64 (t, J = 6.5 Hz, 2H, CH_2OH), 2.56 (s, 3H, CH_3), 2.30 (t, J = 7.5 Hz, 2nH, OC(O)CH_2 along polymer backbone), 1.86-1.24 (m, 6nH, C(O)CH_2-CH_2-CH_2-CH_2-CH_2-O along polymer backbone; m, 18H, OCH_2-(CH_2)$_9$-CH_2 initiator). Conv.^{NMR} = 75%; $M_n^{th} = M_n^{targeted}$ x Conv.^{NMR} (%) = 2450 g.mol^{-1}; M_n^{NMR} = 2350 g.mol^{-1}. SEC (THF): M_n^{SEC} = 2700 g.mol^{-1}, $Đ_M$ = 1.09.



Photoenol end-capped poly(L-lactide) (4):

2-((11-Hydroxyundecyl)oxy)-6-methylbenzaldehyde (42.5 mg, 0.14 mmol, 0.04 eq) and DBU (21 mg, 0.14 mmol, 0.04 eq) were dissolved in CH_2Cl_2 (3.75 mL) in an inert atmosphere. L-LA (500 mg, 3.4 mmol, 1.00 eq) was added and the solution was stirred under argon atmosphere at ambient temperature for 2 min. The reaction was quenched with benzoic acid (50.0 mg, 0.40 mmol, 0.11 eq) and the polymer was precipitated in cold *n*-hexane (30 mL).

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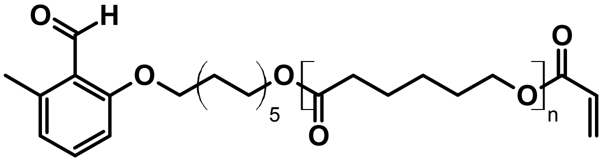
[4] The purification procedure of the crude polymer is based on a simple recovery of the polymer by precipitation in *n*-hexane since aromatic aldehyde slowly reacts with methanol (conventional solvent for the recovery by precipitation of aliphatic polyesters) and the methanol/hydrochloric acid (usually used to remove the organic catalyst by extractions) mixture leading to the corresponding hemiacetal and acetal, respectively, as reported by J. M. Bell *et al* (*J. Org. Chem.*, 1965, **30**, 4284).

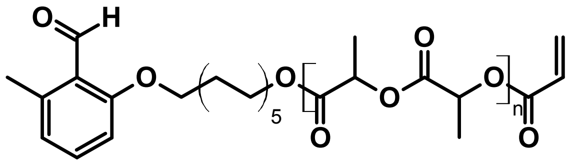
^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 10.68 (s, 1H, C*H*O), 7.35 (t, J = 8 Hz, 1H, Ar*H*), 6.79 (dd, J = 13.2, 8.0 Hz, 2H, Ar*H*), 5.18 (q, J = 7.1 Hz, 2nH, $C(O)C\mathit{H}CH_3O$ along polymer backbone), 4.36 (q, J = 7 Hz, 1H, $C(O)C\mathit{H}CH_3OH$), 4.11 (m, 2H, $C\mathit{H}_2OC(O)$ initiator), 4.04 (t, J = 6.3 Hz, 4H, $OC\mathit{H}_2$ initiator), 2.56 (s, 3H, $C\mathit{H}_3$), 1.56 (d, J = 7.1 Hz, 6nH, $C(O)CHC\mathit{H}_3O$ along polymer backbone), 1.28 (m, 18, $OCH_2\text{-}(C\mathit{H}_2)_9\text{-}CH_2$ initiator). Conv.^{NMR} > 99%; $M_n^{th} = M_n^{targeted}$ x Conv.^{NMR} (%) = 3900 g.mol^{-1}; M_n^{NMR} = 4100 g mol^{-1}. SEC (THF): M_n^{SEC} = 4400 g mol^{-1}, $Đ_M$ = 1.09.



PCL-acrylate (2)

α-*o*-Methylphenyl aldehyde-*ω*-hydroxyl-PCL (**1**) (250 mg, 0.092 mmol, 1 eq) was weighed into a round-bottom flask and set under argon atmosphere. THF (10 mL) was added and the reaction mixture was stirred for 5 min. Subsequently, acryloyl chloride (0.041 g, 0.46 mmol, 5 eq) and, after further 5 min of stirring, Et_3N (0.056 g, 0.55 mmol, 6 eq) were added. The mixture was stirred for 3 h at ambient temperature. The solvent was evaporated under reduced pressure and the crude mixture was dissolved in CH_2Cl_2 (50 mL) prior to extraction in distilled water (1x50 mL), saturated $NaHCO_3$ aqueous solution (1x50 mL) and brine (1x50 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum. The polymer was precipitated in cold *n*-hexane (30 mL).

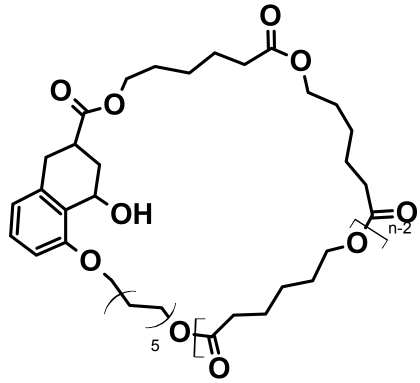
^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 10.67 (s, 1H, C*H*O), 7.35 (t, J = 8 Hz, 1H, Ar*H*), 6.80 (dd, J = 14.0, 8.0 Hz, 2H, Ar*H*), 6.37 (dd, J = 17.3, 1.4 Hz, 1H, $C(O)CH{=}C\mathit{H}_2$), 6.10 (dd, J = 17.3, 10.4 Hz, 1H, $C(O)C\mathit{H}{=}CH_2$), 5.81 (dd, J = 10.4, 1.4 Hz, 1H, $C(O)CH{=}C\mathit{H}_2$), 4.15 (t, J = 6.6 Hz, 2H, $C\mathit{H}_2OC(O)CH{=}CH_2$), 4.05 (t, J = 6.7 Hz, 2nH, $C(O)OC\mathit{H}_2$ along polymer backbone; t, 4H, $OC\mathit{H}_2$ initiator), 2.56 (s, 3H, $C\mathit{H}_3$), 2.30 (t, J = 7.5 Hz, 2nH, $OC(O)C\mathit{H}_2$ along polymer backbone), 1.86-1.24 (m, 6nH, $CH_2\text{-}C\mathit{H}_2\text{-}CH_2$ along polymer backbone; m, 18H, $OCH_2\text{-}(C\mathit{H}_2)_9\text{-}CH_2$ initiator). Conv.^{NMR} > 99.9%; M_n^{NMR} = 2430 g mol^{-1}. SEC (THF): M_n^{SEC} = 2750 g mol^{-1}, $Đ_M$ = 1.09.



P(L-LA)-acrylate (5)

α-*o*-Methylphenyl aldehyde-*ω*-hydroxyl-P(L-LA) (**4**) (250 mg, 0.057 mmol, 1 eq) was weighed into a round-bottom flask and set under argon atmosphere. THF (10 mL) was added and the reaction mixture was stirred for 5 min. Subsequently, acryloyl chloride (0.026 g, 0.285 mmol, 5 eq) and, after further 5 min of stirring, Et_3N (0.035 g, 0.34 mmol, 6 eq) were added. The mixture was stirred for 3 h at ambient temperature. The solvent was evaporated under reduced pressure and the crude mixture was dissolved in CH_2Cl_2 (50 mL) prior to extraction in distilled water (1x50 mL), saturated $NaHCO_3$ aqueous solution (1x50 mL) and brine (1x50 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum. The polymer was precipitated in cold *n*-hexane (30 mL).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 10.68 (s, 1H, C*H*O), 7.35 (t, J = 8 Hz, 1H, Ar*H*), 6.79 (dd, J = 13.0, 8.0 Hz, 2H, Ar*H*), 6.45 (dd, J = 17.3, 1.3 Hz, 1H, C(O)CH=C*H*$_2$), 6.19 (dd, J = 17.3, 10.4 Hz, 1H, C(O)C*H*=CH$_2$), 5.91 (dd, J = 10.5, 1.1 Hz, 1H, C(O)CH=C*H*$_2$), 5.18 (q, J = 7.1 Hz, 2nH, C(O)C*H*CH$_3$O along polymer backbone), 4.11 (m, 2H, C*H*$_2$OC(O) initiator), 4.04 (t, 2H, J = 6.3 Hz, OC*H*$_2$ initiator), 2.57 (s, 3H, C*H*$_3$), 1.57 (d, J = 7.1 Hz, 6nH, C(O)CHC*H*$_3$O along polymer backbone), 1.28 (m, 18, OCH$_2$-(C*H*$_2$)$_9$-CH$_2$ initiator). Conv.^{NMR} > 99.9%;; M_n^{NMR} = 4170 g mol^{-1}. SEC (THF): M_n^{SEC} = 4450 g mol^{-1}, $Đ_M$ = 1.09.



Representative procedure for the synthesis of cyclic polymers

PCL precursor **(2)** was weighed and dissolved in MeCN to give a polymer concentration of 25 mg L^{-1}. The stock solution was transferred into a headspace vial (Pyrex, dia. 20 mm), which was crimped airtight using a styrene/butadiene rubber seal with a PTFE inner liner. The solution was deoxygenated by bubbling with argon during 15 min. The polymer solution was irradiated during 12 h at ambient temperature by revolving the vial around a compact low-pressure fluorescent lamp (Arimed B6, Cosmedico GmbH, Stuttgart, Germany) emitting at 320 nm (±30 nm) at a distance of 40-50 mm in a custom-built photo reactor. After ending the reaction, the solvent was evaporated under reduced pressure without any further purification.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.16 (t, J = 7.9 Hz, 1H, Ar*H*), 6.72 (t, J = 8.8 Hz, 2H, Ar*H*), 4.19 (t, J = 6.5 Hz, 2H, CH_2OC(O)-cycloadduct), 4.05 (t, J = 6.7 Hz, 2nH, C(O)OCH_2 along polymer backbone; t, 2H, OCH_2 initiator), 3.00-2.50 (bm, cycloadduct) 2.30 (t, ^{3}J = 7.5 Hz, 2nH, OC(O)CH_2 along polymer backbone), 1.86-1.24 (m, 6nH, CH_2-CH_2-CH_2 along polymer backbone; m, 18H, OCH_2-$(CH_2)_9$-CH_2 initiator). Conv.^{NMR} > 99 %; M_n^{NMR} = 2450 g mol^{-1}. SEC (THF): M_n^{SEC} = 2 050 g mol^{-1}, $Đ_M$ = 1.11.

Setup used for the photochemically activated Diels-Alder cycloaddition reactions:

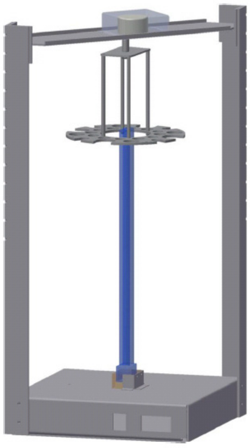


Figure S1. Schematic representation of the photoreactor employed in the current study.

3. Spectroscopic Data

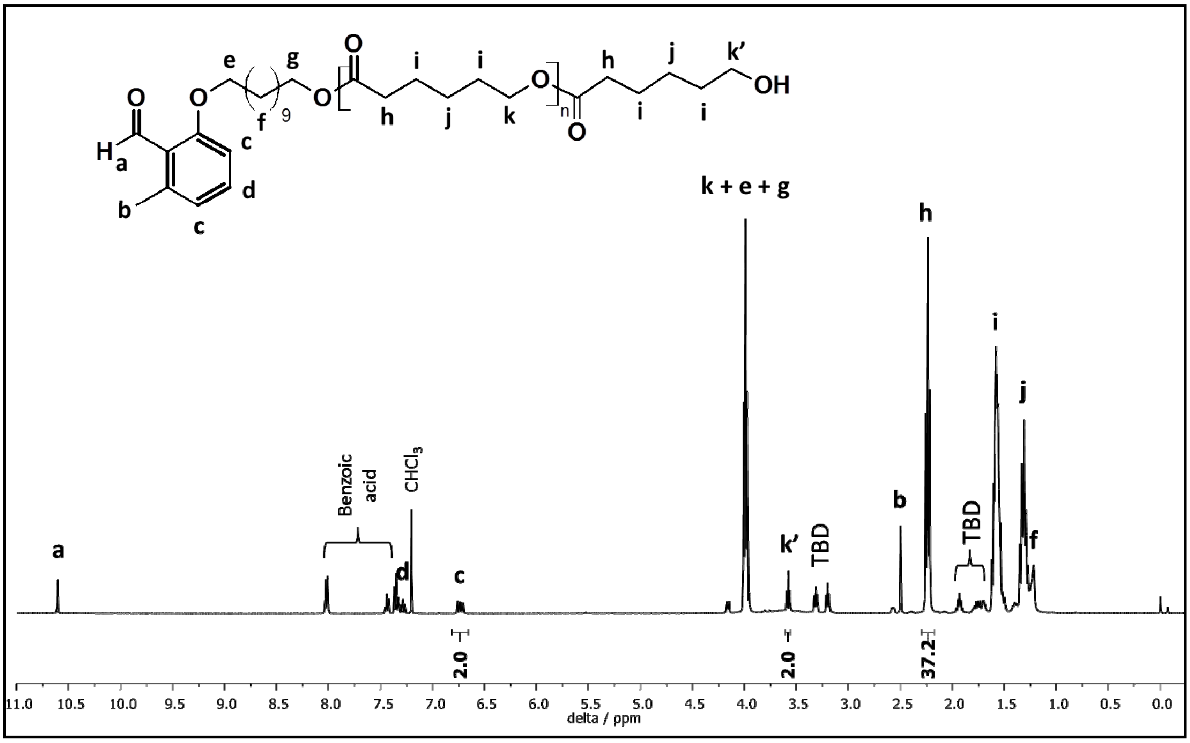


Figure S2. ^{1}H NMR spectrum of PCL **1** in $CDCl_3$.

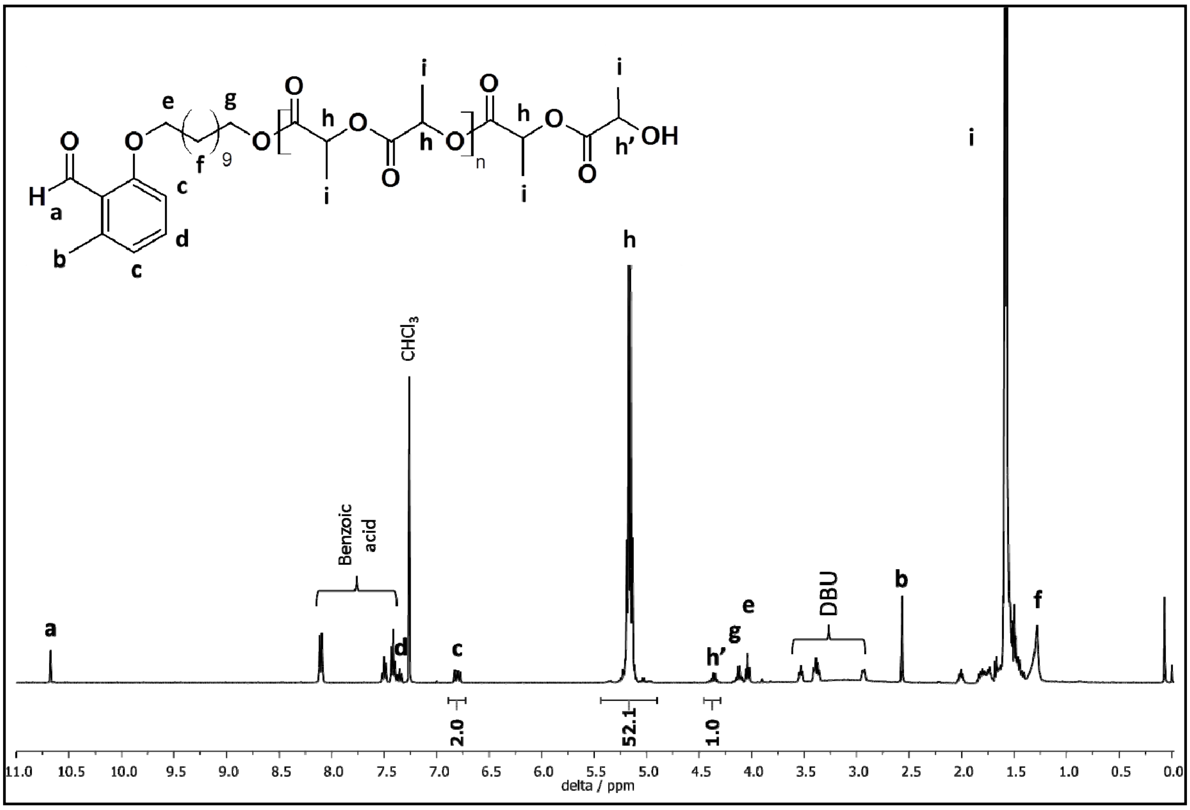


Figure S3. ^{1}H NMR spectrum of P(L-LA) **4** in $CDCl_3$.

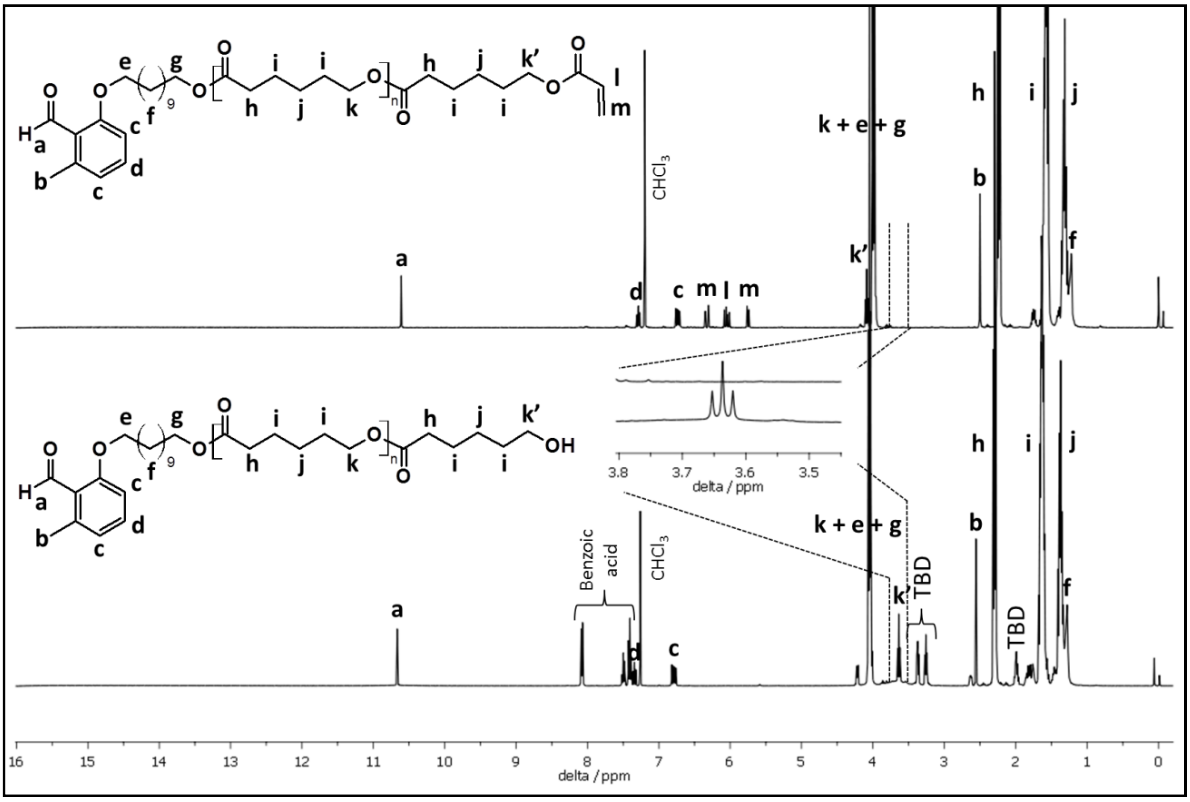


Figure S4. ^{1}H NMR spectra of PCLs **1** and **2** in CDCl$_3$. The expanded region shows the quantitative disappearance of the hydroxymethylene proton signal following the functionalization of the *ω*-hydroxyl end-group.

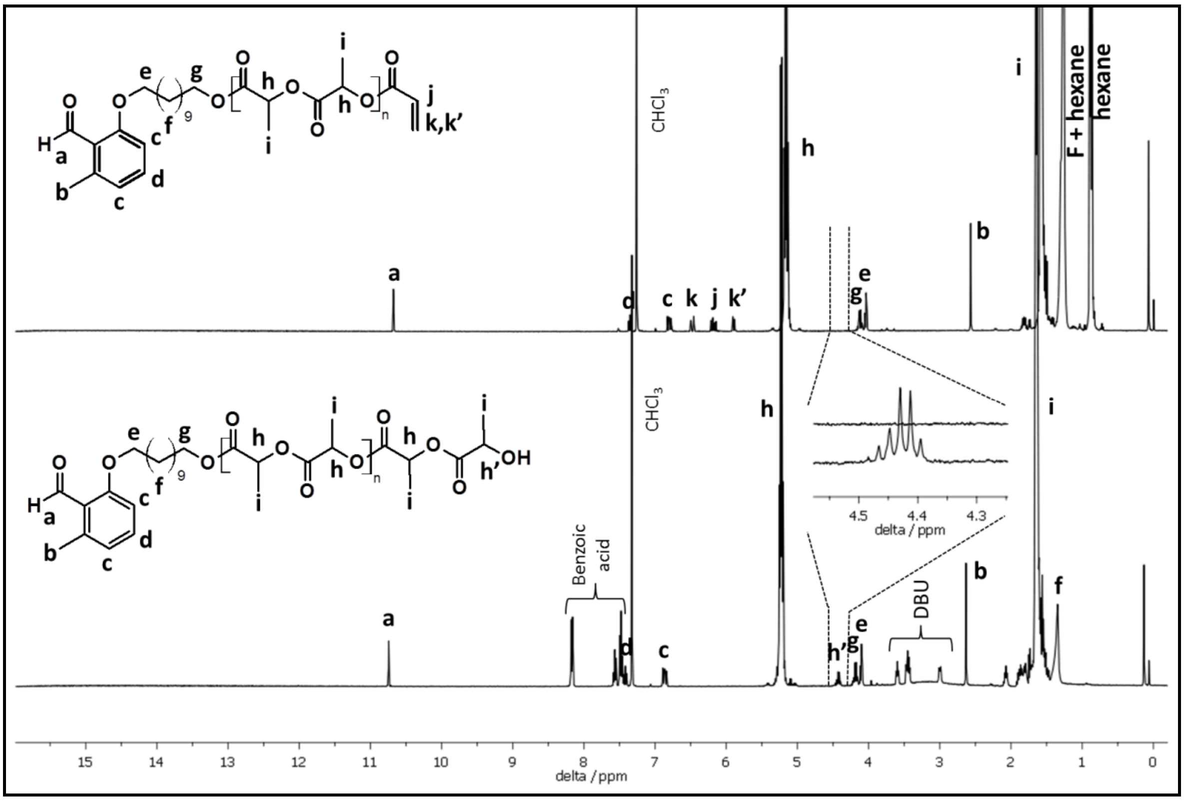


Figure S5. ^{1}H NMR spectra of P(L-LA)s **4** and **5** in $CDCl_3$. The expanded region shows the quantitative disappearance of the hydroxymethyne proton signal following the functionalization of the ω-hydroxyl end-group.

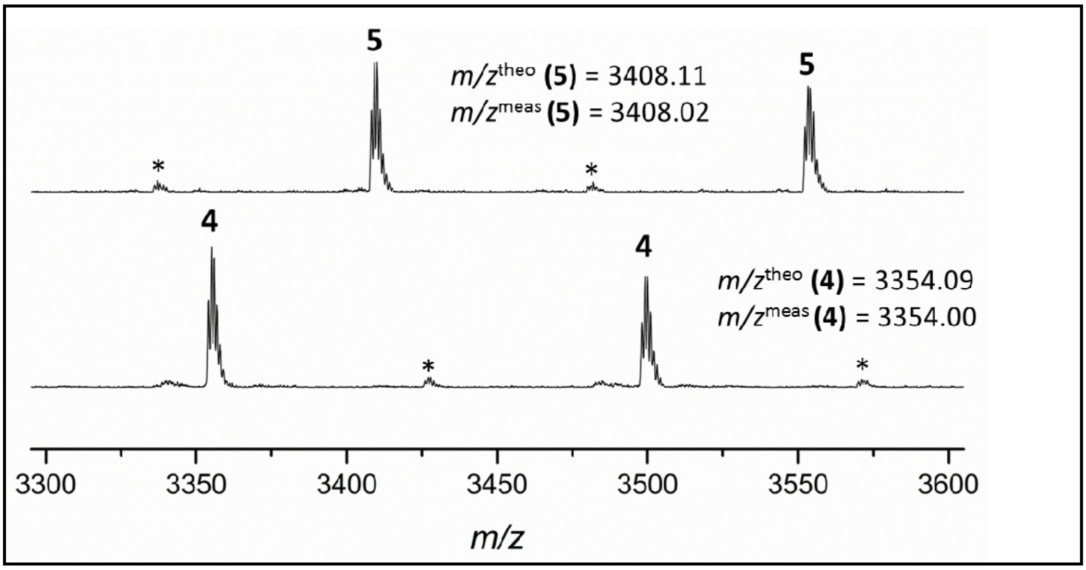


Figure S6. ESI-MS spectra of P(L-LA)s **4** and **5.** (*) refers to the transesterification reactions of lactide monomer units into lactoyl units.

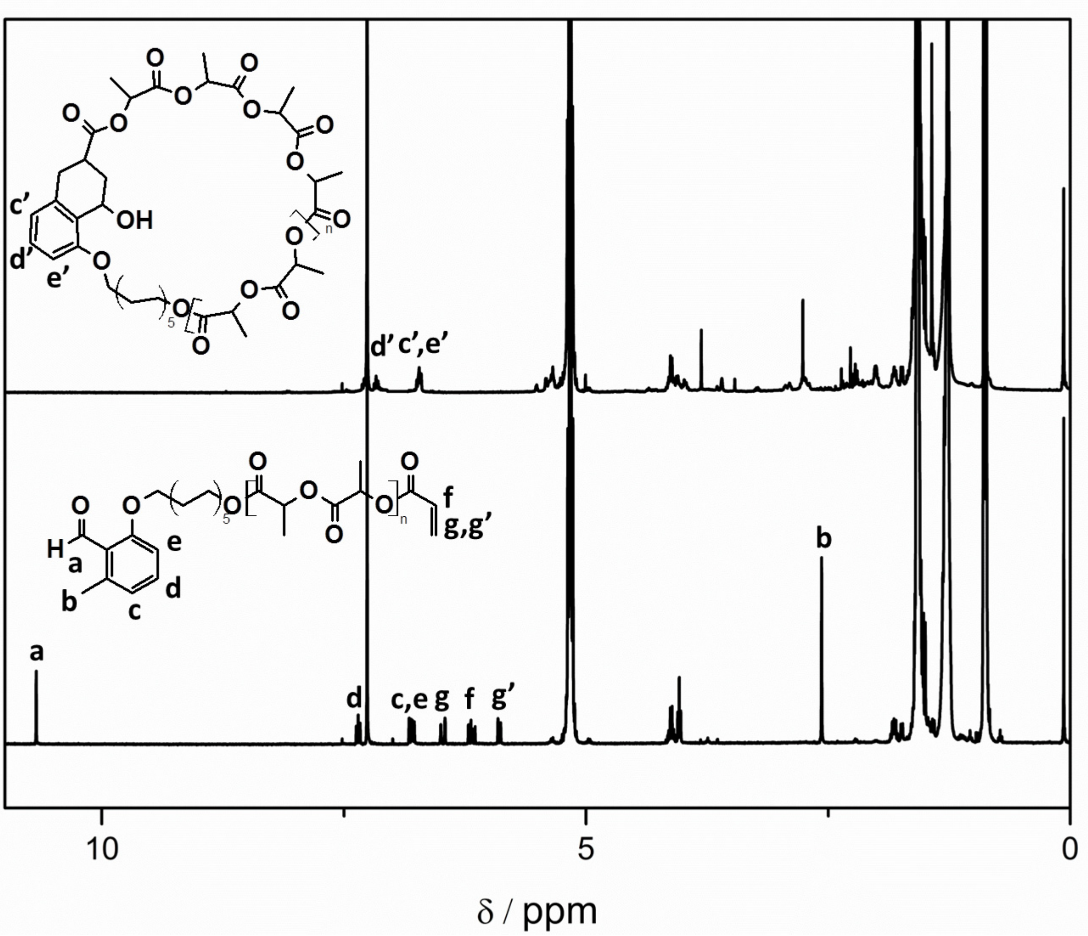


Figure S7. ^{1}H NMR spectra of (**5**) linear precursor, *α*-*o*-methylphenyl aldehyde-*ω*-acrylate-P(L-LA), and (**6**) cyclic P(L-LA) in $CDCl_3$.