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

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

You can find more information about Accepted Manuscripts in the Information for Authors.

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

Polymer Chemistry
Manuscript Accepted
Polymer
Page 1 of 13

45
40
35
30
25
20
15
10

lactide.

Daniela Pappalardo

their ability to promote stereoselective polymerization of

initiator. The obtained poly(6-
glycolide and lactides.

developed, that can afford products of predefined mole-

cular weights, narrow dispersities, controlled microstruc-

ture and end-

weights, narrow dispersities, controlled microstruc-

ture and end-

This journal is © The Royal Society of Chemistry [year]

Journal Name

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Ring-Opening Polymerization of ω–6-Hexadecenlactone by
Salicylaldiminato Aluminum Complex: a Route to Semicrystalline and
Functional Poly(ester)s

Tiziana Fuoco, a Angelo Meduri, b Marina Lamberti, a Vincenzo Venditto, a Claudio Pellecchia, a and
Daniela Pappalardo a b

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The controlled and pseudo-living ring-opening polymerization of a large ring size lactone, ω-6-
hexadecenlactone (6HDL), was achieved for the first time by a dimethyl(salicylaldiminato) aluminum
initiator. The obtained poly(6-ω-hexadecenlactone) was functionalized by thiol-ene coupling reaction. By
epoxidation of the double bond a poly(6,7-epoxy-ω-hexadecenlactone) was formed. The subsequent
opening of the epoxide by NaCNBH3 produced a poly(hydroxy-ω-hexadecanlactone) with occasional
inter and intra ether-type crosslinks. Modifications occurred without any change in the degree of
polymerization. The obtained polymeric samples were characterized by NMR, GPC and DSC and X-ray
diffraction analysis. The “polyethylene-like” orthorhombic crystal lattice of poly(ω-6-hexadecenlactone)
is deformed in the poly(6,7-epoxy-ω-hexadecanlactone) and it is replaced by a hexagonal packing when
the poly(ester) chains are hydroxylated. Furthermore copolymerization of 6HDL with smaller ω-
caprolactone produced random copolymers, with average sequence blocks lengths of 2, while the
sequential addition of 6HDL and ω-c-caprolactone or rac-lactide allowed the preparation of block-
copolymers. The block and random copolymers were also semicrystalline.

Introduction

The ring-opening polymerization (ROP) of cyclic esters, such as lactones and lactides, is the most efficient method for the
production of aliphatic polyesters, which have increasingly
important applications in agriculture, packaging and in the
biomedical field, due to their good mechanical properties,
hydrolyzability, biodegradability and biocompatibility.1

In recent years many research studies have been devoted to the
ROP of small (lactide, glycolide, butyrolactone, valerolactone) or
medium (ε-caprolactone) size cyclic esters: in these processes the
driving force is the relief of the ring-strain, an enthalpy-driven
process. In this regard, the ROP of cyclic esters catalyzed by
metal initiators, operating by a coordination-insertion mechanism,
is the elected method. A broad range of initiators have been
developed, that can afford products of predefined molecular
weights, narrow dispersions, controlled microstructure and end-
groups.2 Notable examples are the salen aluminum complexes for
their ability to promote stereoselective polymerization of rac-
lactide.3 The closely related phenoxy-imine based aluminum
complexes have been found able to promote the homo- and
copolymerization of various small and medium size lactones,
glycolide and lactides.4

On the contrary, the ROP of large cyclic esters, i.e. monomers
containing 12 or more atoms, is a far less explored and now
emerging field. These large lactones and macrolides were anticipated to have low polymerizability, due to the presence of
an unstrained ring.5 Anionic polymerization was explored and
produced linear polymers accompanied by cyclic oligomers.6 On
the other end, the enzymatic method of polymerization of these
large lactones proved to be successful. In particular, the lipase-
catalyzed polymerization of macrolides showed higher rates
affording high molecular weight products.7 However, low control
on the microstructures of the polymers was achieved, due to the
frequent transesterification reactions. Moreover, the production of
poly(hydroxyalkanoates) by enzymes is limited by the high costs,
compared to the costs associated with the chemical route.

The polymerization of large lactones by some traditional ROP
catalysts was explored, but it generally produced only low yields
and low molecular weight polymers, or required long
polymerization time.8 Organic catalysts were also used for the
polymerization of pentadecalactone and its copolymerization with ε-caprolactone, and they also produced low molecular weight polymers.9

In this contest, the pioneering work of Duchateau et al., with the
production of high molecular weight polyesters from
macrolactones by aluminum salen complexes, emerged as a
breakthrough.10 This result represented a very promising route to the production of degradable “polyethylene-like” materials from
renewable building blocks. Subsequently, few other single-site
metal complexes based on aluminum, zinc and calcium were
disclosed to homopolymerize the pentadecalactone to high
molecular weight polymer, and, in proper conditions, to
copolymerize it with ε-caprolactone to random or block
copolymers. Very recently, the “immortal” ROP of ε-pentadecalactone by magnesium based initiator was also reported. It is apparent, then, that in the literatur there is still a paucity of catalysts capable of efficiently polymerize macrolactones.

In the framework of our interest in the ROP of cyclic esters promoted by various metal complexes, we recently reported dimethyl(salicylaldiminato)aluminum compounds able to catalyze the homo- and copolymerization of lactide with ε-caprolactone and with glycolide to random, blocky or di-block copolymers. Such systems resulted highly efficient for the achievement of a controlled polymerization and very versatile for modulating the copolymers microstructure and the related thermal properties. In particular, it was shown that the imino substituents strongly affect the performance of the initiators, in some cases providing living catalysts with high initiation efficiency. These compounds, therefore, could represent promising candidate also for the ROP of large lactones. As a consequence, we have tested these compounds as precatalysts in the ROP of an unsaturated macrolactone, ω-6-hexadecen lactone (6HDL), and in its copolymerization with the smaller ε-caprolactone and rac-lactide.

The chosen macrolactone, 6HDL, is used in the fragrance industry with a worldwide volume of around 1.0 metric ton per year. On the contrary, its use as monomer in polymerization has been scarcely described. Similar large unsaturated lactones, such as ambrettolide and globalide, have been previously used in enzymatic polymerization. The globalide (11/12-pentadecen-15-olide) is a mixture of isomers with the double bond at the 11 or 12 position, whether the geometry of the double bond (E or Z isomers) is unclear. Ambrettolide, a natural occurring unsaturated macrolactone, presents the double bond in cis (Z) configuration. The selected macrolactone, 6HDL, instead, is commercially available as a single positional and geometric trans (E) isomer. By copolymerization with other cyclic esters, it could be useful to design and synthesize novel polyesters aimed to be functional and semicrystalline at the same time. Indeed, the presence of the unsaturation could provide a straightforward functionality for crosslinking and further chemical modifications of the obtained polymeric chains. As we learned from Nature, the presence of the double bonds in “trans” geometry would allow a better level of order and a good packaging of the polymeric chains than that achievable when double bonds are in “cis” geometry. Taking advantages of the double bonds, modifications of the polymeric chains by simple and effective reactions were ascertained. Furthermore, the feasibility of random and block copolymerization with the smaller ε-caprolactone and rac-lactide was studied. Thermal and structural properties of poly(ω-6-hexadecenlactone) and its derivatives were analyzed and described herein.

Materials and methods

Materials

Moisture and air-sensitive materials were manipulated under nitrogen using Schlenk techniques or a MBraun Labmaster glovebox. Toluene, xylene and methanol were refluxed over Na and distilled under nitrogen. Tetrahydrofuran (THF) was refluxed over Na and benzophenone and distilled under nitrogen. Monomers (Sigma-Aldrich) were purified prior to use: rac-lactide (rac-LA) was dried in vacuo with P2O5 for 72 h; ε-caprolactone (ε-CL) and 6-α-hexadecenlactone (6HDL) were distilled under vacuum on CaH2 and stored over 4 Å molecular sieves. meta-Chloroperoxybenzoic acid (mCPBA) was dissolved in CH2Cl2 and dried over Na2SO4, the solvent was evaporated in vacuo, then the acid was crystallized from hexane/Et2O 10/1 at -20 °C. CDCl3 and toluene-d8 were purchased from Eurisotop and used as received. The Al-salicylaldiminato complex was synthesized according to literature methodology. All other reagents and solvents were purchased from Aldrich and used without further purification.

Instruments and Measurements

NMR spectra of polymers were performed in CDCl3 at room temperature on Bruker Avance 300, 400 or 600 spectrometers (1H: 300.13, 400.13, 600.13 MHz; 13C: 75.47, 100.62, 150.92 MHz; respectively). The resonances are reported in ppm (δ) and coupling constants in Hz (J). Spectra recording was performed on Bruker TopSpin v2.1 software. Data processing was performed on TopSpin v2.1 or MestReNova v6.0.2 software.

2D DOSY PGSE NMR spectra of the block copolymers was performed on the Bruker Avance 400 spectrometer: 2 mg of polymer was dissolved in 0.5 mL of CDCl3 and the spectra were recorded at room temperature without spinning; parameters δ and Δ were kept constant during the experiments, whereas G was varied from 2 to 95 % in 25 steps, 64 scans each step.

Molecular weights (Mn and Mw) and molecular weight dispersions (Mw/Mn) were measured by gel permeation chromatography (GPC). The measurements were performed at 30 °C on a Waters 1525 binary system equipped with a Waters 2414 Refractive Index (RI) detector and a Waters 2487 Dual λ Absorption (UV, λabs = 220 nm) detector, using tetrahydrofuran as eluent (1.0 mL min⁻¹) and employing a system of four Styrage HR columns (7.8 x 300 mm; range 10^-3 - 10^-6 Å). Narrow polystyrene standards were used as reference and Waters Breeze v3.30 software for data processing.

MALDI-ToF-MS analysis was performed on a Waters Maldi Micro MX equipped with a 337 nm nitrogen laser. An acceleration voltage of 25 kV was applied. The polymer sample was dissolved in THF with Milli-Q water containing 0.1 % formic acid at a concentration of 0.8 mg mL⁻¹. The matrix used was 2,5-dihydroxybenzoic acid (DHB)(Pierce) and was dissolved in THF at a concentration of 30 mg mL⁻¹. Solution of matrix and polymer were mixed in a volume ratio of 1:1. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded in reflectron mode.

Glass transition temperatures (Tg), melting points (Tm) and enthalpy of fusion (ΔHm) of the polymer samples were measured by differential scanning calorimetry (DSC) using aluminum pans and a DSC 2920 TA Instruments apparatus, calibrated with indium. Measurements were performed in nitrogen flow with a heating rate of 10 °C min⁻¹ in the range of -80 to +220 °C. DSC data were processed with TA Universal Analysis v2.3 software and are reported for the second heating cycle. Infrared spectra of...
polymers were recorded on KBr disk samples by using a Bruker - Vertex 70 FT-IR spectrometer with a Globar (silicon carbide) light source.

X-ray diffraction measurements were performed on a Philips PW1710 powder diffractometer using a Ni-filtered CuKα radiation (λ = 1.5418 Å) at 40 kV and 20 mA. The scans were carried out, on as polymerized samples, in the 2θ range of 3 to 40° with a 0.05° step in 2θ and an acquisition time of 3 s. Data were processed with Origin 7.0 software.

Synthesis of poly(6-ω-hexadecenlactone)

A typical polymerization is described herein for the sample of run 5 in Table 1. A Schlenk tube was charged sequentially with the precatalyst (14.0 mg, 35 µmol), the monomer (883 mg, 3.5 mmol), xylenes (2.3 mL) and methanol (0.35 mL of a 0.1 M toluene solution, 35 µmol). The mixture was thermostated at 100 °C and magnetically stirred for 27 h, then cooled to room temperature. Volatiles were removed in vacuo, the product was dissolved in a minimal amount of CH3Cl, then added dropwise to rapidly stirring methanol. The precipitated polymer was recovered by filtration, washed with methanol and dried at 30 °C overnight in a vacuum oven. Yield = 60 %. 1H NMR (300 MHz, CDCl3, RT) δ 6.57 (bs, 2H; –H); 4.04 (t, J = 6.6 Hz, 2H; –CH(O)–), 3.66 (s, –OCH3), 3.63 (t, –CH(O)H), 2.28 (t, J = 7.4 Hz, 2H; –C(O)CH2–), 1.96 (bs, 4H; –CH2(CH3)=), 1.75–1.55 (m, 4H; 4H)

Epoxidation of poly(6,7-epoxy-hexadecenlactone)

The epoxidation procedure is based on a modification of a previously reported literature methodology. In a screw vial, poly(6-ω-hexadecenlactone) (obtained in run 1, 252 mg, 1.0 mmol alkene function) was dissolved in dry CHCl3 (5.0 mL) at room temperature. Then, mCPBA was added (260 mg, 1.5 mmol) at 0 °C. The mixture was stirred for 3 days at 20 °C. The epoxidized polymer was precipitated in methanol, recovered by filtration, washed with methanol and dried in vacuo at 20 °C. Yield = 95 %. Mw/Mn = 16.4 kDa. Mw/NMR = 15.6 kDa. Mw/GPC = 37.2 kDa. Mw/Mn = 1.9. 1H NMR (300 MHz, CDCl3, RT) δ 4.04 (t, J = 6.6 Hz, 2H; –CH(O)–), 3.66 (s, –OCH3), 3.63 (t, –CH(O)H), 2.65 (bs, 2H; –CHO–), 2.28 (t, J = 7.4 Hz, 2H; –C(O)CH2–), 1.75–1.55 (m, 4H; –C(O)CH2CH2– and –CH2CH2O–), 1.55–1.45 (m, 2H; –CH2CH(O)H) 1.45–1.15 (m, 14H; CH2).

Synthesis of poly[(6-ω-hexadecenlactone)-ran-(ε-caprolactone)]

A Schlenk tube was charged with precatalyst (14.0 mg, 35 µmol), 6HDL (442 mg, 1.75 mmol), ε-CL (200 mg, 1.75 mmol), xylenes (2.3 mL) and methanol (0.35 mL of a 0.1 M toluene solution, 35 µmol). The mixture was thermostated at 100 °C and magnetically stirred for 29 h, then cooled to room temperature. Product purification was attained by removal of xylenes under vacuum, followed by dropwise addition of the crude reaction mixture, dissolved in a minimal amount of CH2Cl2, to rapidly stirring methanol. The precipitated polymer was recovered by filtration, washed with methanol and dried at 30 °C overnight in a vacuum oven. Yield = 75 %. Composition ε-CL = 50 %; 6HDL = 50 %. Mn,θ = 15.0 kDa. Mw/NMR = 15.8 kDa. Mw/GPC = 36.0 kDa. Mw/Mn = 1.6. 1H NMR (300 MHz, CDCl3, RT) δ 5.37 (bs, 2H; –HCl) 4.05 (t, J = 6.3 Hz, 4H; –CH2OH), 3.66 (s, 3H; –OCH3), 3.63 (t, 2H; –CH2OH), 2.35–2.25 (m, 4H; –CH(O)CH2–), 1.96 (bs, 4H; –CH2CH(O)–), 1.75–1.55 (m, 8H; –C(O)CH2CH2– and –CH2CH2O–).
13C NMR (75 MHz, CDCl₃, RT) δ 174.15 (–C(O)O–; HDL-HDL), 174.1 (–C(O)O–; HDL*-CL), 173.8 (–C(O)O–; CL*-HDL), 173.7 (–C(O)O–; CL-CL), 130.6 (–CH=), 130.3 (–CH=), 124.6 (–C(O)OCH₂–; HDL*-CL), 124.6 (–C(O)OCH₂–; CL-CL), 124.6 (–CH(C)(O)C(O)–; HDL-HDL), 124.0 (–CH(C)(O)C(O)–; CL-CL), 123.9 (–CH(C)(O)C(O)–; CL-CL), 123.8 (–CH(C)(O)C(O)–; CL-CL), 123.7 (–CH(C)(O)C(O)–; HDL-HDL), 123.6 (–CH(C)(O)C(O)–; HDL-HDL), 123.5 (–CH(C)(O)C(O)–; HDL-HDL), 123.4 (–CH(C)(O)C(O)–; HDL-HDL), 123.3 (–CH(C)(O)C(O)–; HDL-HDL), 123.2 (–CH(C)(O)C(O)–; HDL-HDL), 123.1 (–CH(C)(O)C(O)–; CL-CL), 122.9 (–CH(C)(O)C(O)–; CL-CL), 122.8 (–CH(C)(O)C(O)–; CL-CL), 122.7 (–CH(C)(O)C(O)–; CL-CL), 122.6 (–CH(C)(O)C(O)–; CL-CL), 122.5 (–CH(C)(O)C(O)–; CL-CL), 122.4 (–CH(C)(O)C(O)–; CL-CL), 122.3 (–CH(C)(O)C(O)–; CL-CL), 122.2 (–CH(C)(O)C(O)–; CL-CL), 122.1 (–CH(C)(O)C(O)–; CL-CL), 122.0 (–CH(C)(O)C(O)–; CL-CL).

Synthesis of poly(6-o-hexadecenlactone)-block-poly(ε-caprolactone)

A Schlenk tube was charged with pre catalyst (14.0 mg, 35 μmol), HDL (442 mg, 1.75 mmol), xylene (0.7 mL) and methanol (0.35 mL of a 0.1 M toluene solution, 35 μmol). The mixture was thermostated at 100 °C and magnetically stirred. After 21 h, an aliquot was withdrawn from the reaction mixture, dissolved in CDCl₃, and analyzed by 1H NMR, the macro lactone conversion was 60%. Afterwards, ε-CL (515 mg, 4.50 mmol) was added and the reaction mixture was stirred for 20 h. Finally, the mixture was cooled to room temperature. Product purification was attained by removal of xylene under vacuum, followed by dropwise addition of the residue, dissolved in a minimal amount of CH₂Cl₂, to rapidly stirring methanol. The precipitated polymer was recovered by filtration, washed with methanol and dried at 30 °C overnight in a vacuum oven. Yield = 84%. Mₘ,θ = 22.3 kDa. Mₚ,GPC = 37.5 kDa. Mₚ/Mₘ = 1.7.

A lower molecular weight sample was prepared as above but adding 400 mg of ε-CL (3.50 mmol) and stirring the reaction for 1 h. Yield = 34%. Mₘ,θ = 7.9 kDa. Mₚ,GPC = 10.6 kDa. Mₚ/Mₘ = 1.4 (see Supporting Information).

1H NMR (300 MHz, CDCl₃, RT) δ 5.87 (bs, 2H; –CH₂–), 4.15 – 3.95 (m, 4H), 3.66 (s, 3H; –OC₃H₇), 3.63 (t, 2H; –CH₂–), 2.35 – 2.20 (m, 4H; –C(O)CH₂–), 1.96 (bs, 4H; –CH₂–), 1.75 – 1.55 (m, 8H; –C(O)CH₂–CH₂– and –CH₂–CH₂–O–), 1.45 – 1.25 (m, 16H; CH₂–).

13C NMR (75 MHz, CDCl₃, RT) δ 174.15 (–C(O)O–; HDL-HDL), 173.7 (–C(O)O–; CL-CL), 130.6 (–CH=), 130.3 (–CH=), 64.5 (–C(O)OCH₂–; HDL), 64.3 (–C(O)OCH₂–; HDL), 64.1 (–CH(C)(O)C(O)–; HDL), 34.25 (–CH(C)(O)C(O)–; CL-CL), 32.7 (–CH₂–HDL), 32.6 (–CH₂–HDL), 29.7 (–CH₂–HDL), 29.6 (–CH₂–HDL), 29.3 (–CH₂–HDL), 29.15 (–CH₂–HDL), 28.9 (–CH₂–HDL), 28.8 (–CH₂–HDL).

Synthesis of poly(6-o-hexadecenlactone)-block-poly(rac-lactide)

A Schlenk tube was charged with pre catalyst (14.0 mg, 35 μmol), HDL (442 mg, 1.75 mmol), ε-CL (200 mg, 1.75 mmol), xylene (2.3 mL) and methanol (0.35 mL of a 0.1 M toluene solution, 35 μmol). The mixture was thermostated at 100 °C and magnetically stirred for 24 h then rac-LA (252.2 mg, 1.75 mmol) was added and the reaction mixture was stirred for 23 h. Finally, the mixture was cooled to room temperature. Product purification was attained by dropwise addition of the reaction mixture, dissolved in CH₂Cl₂, to rapidly stirring n-hexane. The precipitated polymer was recovered by filtration, washed with n-hexane (x 3) and dried at 60 °C overnight in a vacuum oven. Yield = 48%. Mₘ,θ = 15.2 kDa. Mₚ,GPC = 29.1 kDa. Mₚ,Ν = 26.5 kDa. Mₚ/Mₘ = 2.0. Sequences block lengths, as evaluated by 1H NMR: I₉CGDLCL = 110; I₉CGCL = 58. Average sequence block lengths of the random HDL/CL block: I₉CGDL = 1.73; I₉CGCL = 2.93.

1H NMR (300 MHz, CDCl₃, RT) δ 5.87 (bs, 2H; –CH₂–), 4.15 – 3.95 (m, 4H), 3.66 (s, 3H; –OC₃H₇), 3.63 (t, 2H; –CH₂–), 2.28 (q, J = 7.4 Hz, 4H; –CH₂–).

Kinetic Experiments

In a Braun Labmaster glovebox, a Teflon-valved J. Young NMR...
tube was charged with a solution of the initiator, the monomer and dry methanol in toluene-d$_8$ (0.5 mL). The sample was thermostated at 80 °C. The polymerization reaction was monitored via $^1$H NMR analysis.

5 Results and discussion

Polymerization of $\omega$-$\omega$-$\omega$-$\omega$-6-hexadecenlactone

The polymerization of 6-$\omega$-hexadecenlactone (6HDL) by metal initiators is described herein for the first time.$^{12}$

The molecule is a large ring size unsaturated lactone, presenting a trans (E) geometry of the double bond. The configuration of the double bond of the monomer 6HDL was established by $^{13}$C NMR, showing a single couple of peaks (at 131.2 and 130.6 ppm) and by $^1$H NMR analysis, also in combination with homodecoupling experiments, which disclosed a $^3J$ value of 15.2 Hz, which is a typical value for the coupling of vicinal hydrogen atoms in trans alkenes (see Supporting Information).

The polymerization of the $\omega$-$\omega$-$\omega$-$\omega$-hexadecenlactone (6HDL) was performed in xylene solution, in the presence of complex I and one equivalent of methanol, under different conditions (Scheme 1). The obtained polymeric samples were characterized by $^1$H and $^{13}$C NMR spectroscopy, GPC and DSC. Illustrative results are shown in Table 1.

A typical $^1$H NMR spectrum of a poly(6-$\omega$-hexadecenlactone) (P6HDL) is shown in Fig. 1a. Besides the signals due to the methylenes of the main chain, signals due to the double bond appeared at $\delta = 5.37$ ppm. Conversely, inspection of the $^{13}$C NMR spectrum showed a couple of peaks with the same intensity at 130.6 and 130.3 ppm, corresponding to the trans configuration of the double bond. Obviously, the ROP process did not affect the configuration of the double bonds. Significantly, in the $^1$H NMR spectrum a signal attributable to the hydroxyl methylene end group ($\delta = 3.63$ ppm, -CH$_2$CH$_2$OH) and a singlet relative to the methyl ester end group ($\delta = 3.66$ ppm, -COOC$_3$H$_7$) were detected.

It is known from the literature that alkoxide initiators can be generated by alcoholysis of alkyl complexes with alcohols.$^{18}$ Thus, the methyl ester end group should be generated via insertion of the monomer unit into the Al-OC$_3$H$_7$ bond, formed in situ by reaction of the dimethylaluminum compound with MeOH, while the hydroxyl end group should be generated by hydrolysis of the growing chain.$^{19}$ Therefore, a “coordination-insertion” mechanism proceeding through acyl-oxygen cleavage should be operative in this system also for the ROP of the macrolactone.$^{20}$

The molecular weight of the samples was determined by NMR and GPC. The gel permeation chromatography (GPC) showed monomodal distribution with molecular dispersity of 1.6. It is worth noting that since the GPC analysis was run using THF as elution solvent vs polystyrene standards, and correction factors are not available in the literature for the polymers studied, the $M_{n,GPC}$ should be used with special care, while the $M_{n,NMR}$ values are more reliable. In detail, the $M_{n,NMR}$ was calculated from the integral ratio of the signal relative to the main chain methylene protons (4.04 ppm; -C$_3$H$_2$-OC(O)) and the singlet relative to the terminal -OCH$_3$ protons (3.66 ppm). The $M_{n,NMR}$ values are in good agreement with the theoretical molecular weight, $M_{n,th}$.
calculated on the basis of the monomer/catalyst feed ratio and the conversion (see Table 1). By increasing the [MeOH]/[Al] molar ratio in the feed, the experimental molecular weights $M_w$ decreased (See Table S1 in the Supporting Information). This observation would indicate that MeOH could also act as a chain transfer agent; however, a low degree of control on the molecular weight of the polymers was achieved, ostensibly due to the poor efficiency of the process.

A set of polymerization runs was carried out at increasing temperature (Table 1, runs 1-5). The molecular weights of polymers linearly increased with time and conversion (Fig. 2). Notably, the dispersity values were below 2 (see Table 1, $M_w/M_n = 1.6$) and remained constant during the reaction time. This “pseudo-living” character of the polymerization was previously discovered for the aluminum salen based catalysts, active in the ROP of pentadecalactone. However, in the latter case, the poly(pentadecalactone) obtained showed higher dispersities ($M_w/M_n \geq 2$). The values observed in the presence of compound 1, instead, compare well with those recently reported for the best performing catalyst in the ROP of macrolactones. Kinetic studies showed that the monomer conversion leveled off around 60 % (See Supporting Information). Indeed, due to the high viscosity of the medium, the diffusion of the monomer was hampered and full conversion was not achieved even after prolonged reaction time. By decreasing the monomer/catalyst ratio to the value of 20, and thus decreasing the viscosity of the reaction medium as a consequence of the lower molecular weight of the polymeric chains, almost full conversions were achieved with higher rates (See Supporting Information). The incomplete conversions may be also due to an equilibrium between cyclic oligomeric species and polymer, which is typical in the “entropy-driven” process of polymerization of macrolactones. This equilibrium would also affect the chain lengths and would also explain the observed dispersities. Indeed MALDI-ToF-MS analysis on a crude low molecular weight P6HDL sample showed the presence of cyclic oligomeric species, probably formed by “backbiting” side reactions, along with the major distribution of linear P6HDL chains, capped with methoxy groups (see Supporting Information). Cyclic oligomeric species have been previously observed in the ROP of various macrolactones promoted by anionic and organic initiators, as well as by metal complexes. A polymerization run was performed at a higher temperature (130 °C, Table 1, run 6) and afforded slightly lower yield and $M_n$ in comparison with the product obtained at 100 °C. By increasing the amount of the monomer (monomer/catalyst molar feed ratio = 250/1), a higher $M_n$ value was obtained (Table 1, run 8). The system is prone to polymerize the macrolactone to high molecular weight polymers, whose length could be simply modulated by the monomer/catalyst molar feed ratio. The effect of dilution of the polymerization mixture was also explored (Table 1, run 7). Lower conversion with lower $M_n$ were obtained, and slightly higher dispersity. It is well known, indeed, that for monomers having ring size higher than 14 atoms, the ring-opening polymerizations are usually entropy-driven, due to an increase of conformational freedom. Thus, the dilution will favor the monomer and the oligomeric cyclic species, while high concentration favors the polymeric product. However, this effect could be also merely a consequence of the decreased monomer concentration in the case of first-order kinetics of polymerization.

Indeed, more in-depth kinetics investigations were performed by $^1$H NMR at 80 °C in toluene-$d_8$ as solvent. To follow the progress of the 6HDL conversion by NMR, avoiding the viscosity problems depicted above, the initial monomer/initiator concentration ratio was reduced ([Cat] = 5.0 x 10^{-3} M; [6HDL]_0 = 1.0 M; [MeOH] = 5.0 x 10^{-2} M). The reaction kinetics featured a pseudo-first-order dependence in the 6HDL concentration, as reported in Fig. 3: the semilogarithmic plot of ln([6HDL]_0/[6HDL]) versus time was linear with a slope of 0.0047 min^{-1}. This value is lower than the polymerization rate of aluminum-salen based initiators.

### Table 1: Polymerization of ω-6-hexadecenlactone.

<table>
<thead>
<tr>
<th>Run</th>
<th>[6HDL]_0/[Cat]</th>
<th>$T$ (°C)</th>
<th>$t$ (h)</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
<th>$M_{n,th}$ (kDa)</th>
<th>$M_{n,GM}$ (kDa)</th>
<th>$M_{w,GM}$ (kDa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^a$</td>
<td>100</td>
<td>100</td>
<td>4</td>
<td>34</td>
<td>28</td>
<td>8.6</td>
<td>8.9</td>
<td>18.3</td>
</tr>
<tr>
<td>2$^a$</td>
<td>100</td>
<td>100</td>
<td>8</td>
<td>42</td>
<td>34</td>
<td>10.5</td>
<td>11.4</td>
<td>23.1</td>
</tr>
<tr>
<td>3$^a$</td>
<td>100</td>
<td>100</td>
<td>16</td>
<td>44</td>
<td>40</td>
<td>11.1</td>
<td>12.0</td>
<td>27.2</td>
</tr>
<tr>
<td>4$^a$</td>
<td>100</td>
<td>100</td>
<td>24</td>
<td>54</td>
<td>47</td>
<td>13.6</td>
<td>12.7</td>
<td>34.9</td>
</tr>
<tr>
<td>5$^a$</td>
<td>100</td>
<td>100</td>
<td>27</td>
<td>60</td>
<td>60</td>
<td>15.1</td>
<td>15.4</td>
<td>40.0</td>
</tr>
<tr>
<td>6$^a$</td>
<td>100</td>
<td>130</td>
<td>27</td>
<td>48</td>
<td>48</td>
<td>12.1</td>
<td>14.1</td>
<td>33.0</td>
</tr>
<tr>
<td>7$^b$</td>
<td>100</td>
<td>130</td>
<td>27</td>
<td>31</td>
<td>26</td>
<td>7.7</td>
<td>9.6</td>
<td>17.7</td>
</tr>
<tr>
<td>8$^b$</td>
<td>250</td>
<td>130</td>
<td>27</td>
<td>49</td>
<td>45</td>
<td>30.9</td>
<td>36.3</td>
<td>50.0</td>
</tr>
</tbody>
</table>

Polymerization conditions: $^a$Xylenes = 0.8 mL; precatalyst = 12 μmol; MeOH = 12 μmol (0.12 mL of a 0.1 M toluene solution). $^b$Xylenes = 2.3 mL; precatalyst = 35 μmol; MeOH = 35 μmol (0.35 mL of a 0.1 M toluene solution). $^c$Mol ratio of monomer to precatalyst in the feed. $^d$Determined by $^1$H NMR from the $\omega$-methylene resonances of monomer and obtained polymer. $^e$Calculated from monomer conversion. $^f$Determined by GPC vs polystyrene standards. $^g$Reaction performed in 5 mL of xylene.
Functionalization of the poly(6-o-hexadecenlactone) sample.

The double bond in the poly(6-o-hexadecenlactone) chains is a potential site for further chemical modification of the backbone, offering a wide range of possibilities to fabricate functional materials. Simple and effective reactions were selected to test the reactivity of the –ene groups embedded in the polymer (Scheme 2). The epoxidation of the –ene group performed on a P6HDL sample (Table 1, run 5) with meta-chloroperbenzoic acid (mCPBA) proceeded cleanly and with 95% of the yield (Scheme 2). In Fig. 1a and 1b the $^1$H NMR spectra of the native and of the obtained poly(6,7-epoxy-o-hexadecenlactone) are respectively shown. Interestingly, the disappearance of the signal relative to the double bond protons (at $\delta = 5.37$ ppm) and the appearance of a new signal (at $\delta = 2.65$ ppm) for the protons on the epoxide ring indicates that the modification was accomplished. 

Conversely, in the $^{13}$C spectrum the disappearance of signals at 130.6 and 130.3 ppm and the appearance of signals at 59.0 and 58.95 ppm were observed (see Supporting Information). The number of signals is compatible with the presence of a single couple of enantiomers, as expected for a non-enantioselective epoxidation mechanism proceeding with syn addition to the trans double bonds of the P6HDL.

Interestingly, the $M_n$ (15.6 kDa), evaluated from the integral ratio of the signal relative to the main chain methylene protons (4.04 ppm; $-\text{CH}_2\text{-OC(O)}$) and the singlet relative to the terminal –OCH$_3$ protons (3.66 ppm), was in good agreement with the theoretical molecular weight ($M_{\text{theo}} = 16.1$ kDa), calculated on the basis of the monomer/Al feed ratio and conversion, and assuming that all the double bonds were epoxidized. Notably, this value was close to the $M_n$ (15.4 kDa) of the native polymer. The GPC analysis disclosed monomodal molecular weight distribution, with a dispersity value of 1.9. Thus, the epoxidation of the double bond could be carried out quantitatively, without side reactions. The monomodal GPC curve and the perfect accord between the numerical molecular weight before and after the epoxidation were consistent with a non-degradative derivatization reaction.

Derivatization of the epoxy group of this sample was carried out in the presence of sodium cyanoborohydride as reducing agent and boron trifluoride (Scheme 2), following a literature procedure reported for the reduction of triepoxidized triglycerides to hydroxyl derivates. A white solid, insoluble in most common laboratory solvents, was produced, hampering the analysis by solution NMR and GPC. The same reaction was performed on a lower molecular weight epoxidized polymer sample (Table 1, run 7; $M_n$ = 9.6 kDa). The product resulted partially soluble in chloroform, thus the NMR analysis was in this case permitted. The $^1$H NMR spectrum of the soluble polymeric material showed the decrease of the epoxide signals of the starting material ($\delta = 2.65$ ppm), while new signals at $\delta = 3.57$ and 3.41 ppm appeared and were respectively attributed to the methine near an alcohol functionality [–CH–OH] and to vicinal ether protons [–CH–O–CH]. Formation of poly(hydroxy-o-hexadecenlactone) with occasional inter and intra ether-type crosslinks was hypothesized (structure c of Scheme 2). The ether-type crosslinks would probably be generated by the following mechanism: the hydride opens an epoxide group, generating an alkoxide species which, in turn, may act as a nucleophile for a close epoxide group. Analogous polyether bridges were also obtained through the ring-opening polymerization of epoxidized methyl oleate.

The FTIR characterization further supported this structure, showing broad bands for –OH around 3300 cm$^{-1}$ and ether cross-linkage bands at 1109 cm$^{-1}$ and 1023 cm$^{-1}$. Conversely, the epoxide bands at 886 cm$^{-1}$, observed in the FTIR spectrum of the epoxidized sample corresponding to the structure b are lowered (see Supporting Information).

Among the multiple reactions that have been accepted into the click chemistry realm, the addition of thiols to $\text{C}=$C bonds is one of the most applied, offering high yields and outstanding functional groups tolerance under simple reaction conditions. The feasibility of this reaction on the double bonds embedded in the polyester chains was previously described by Heise et al. on poly(globalide) samples obtained by enzimatic ROP. Following this procedure, we performed the reaction thermally, by using 2,2′-azobis(2-methylpropionitrile) (AIBN) as radical initiator in the presence of 6-mercapto-1-hexanol, which allowed the introduction of a primary alcohol terminated pendant group (Scheme 2, d).
The 1H NMR spectrum of the product (Fig. 4) showed a reduction in the intensity of the peak at 5.37 ppm corresponding to the double bond; conversely, a multiplet at 2.53 ppm corresponding to the methine bound to the S atom, belonging to polyesters main chain, and two triplets at 3.64 and 2.47 ppm, representative of methylenes adjacent to hydroxyl terminal group and thioether group respectively, belonging to the pendant chains, were observed.

The 13C NMR spectrum confirmed this attribution: the intensity of the signals due to the carbons of the double bonds (130.3 and 130.6 ppm) was around 20% of the initial value, while a new signal at 46.0 ppm appeared, and was attributed, also with the aid of a DEPT NMR experiment, to the methine bound to the S atom, of the pendant group. GPC data analysis revealed an increase in molecular weight (Mw,NMR = 36.6 kDa) with respect to the native polymer, which is compatible with the presence of the pendant group.

**Thermal and structural analysis of poly(6-o-hexadecenlactone) and its functionalized derivatives.**

The obtained poly(6-o-hexadecenlactone) and the functionalized derivatives (structures b, c, d, Scheme 2) were characterized by means of differential scanning calorimetry (DSC), in the temperature range of -80 to 150 °C, and powder X-ray diffraction analysis in the 2θ range from 3 to 40°.

In Fig. 5 second heating DSC runs (top image) and X-ray diffraction patterns (bottom image) of the native poly(6-o-hexadecenlactone) (a) and of its derivatives, poly(6,7-epoxy-o-hexadecenlactone) (b) and poly(hydroxy-o-hexadecanlactone) (c) samples, are reported.

The thermogram of the P6HDL sample (Table 1, run 5) showed a sharp endotherm, with a melting point Tm at 57.6 °C and an enthalpy of fusion ΔHm of 87.1 J/g, while the Tg was not detected in the scanned heating range (Fig. 5a, top). The Tm is slightly higher, while the ΔHm is very similar to that observed by Heise et al. for the poly(ambrettolide), a polyester obtained from an aliphatic long chain polyesters and of PE was previously reported for other polyesters obtained from saturated and unsaturated macrolactones.

In the X-ray spectrum of P6HDL (Fig. 5a, bottom), all the reflections (2θ = 4.4, 19.5, 21.5, 23.8, 29.4, 36.0 and 39.5 °) are in good agreement with those calculated by Scandola et al. for the pseudo-orthorhombic unit cell of poly(o-pentadecalactone) (PPDL), which is only slightly larger than those of PE. In detail, the reflection at 2θ = 4.4° can be attributed at the Miller index (001) of the pseudo-orthorhombic unit cell reported by these authors. On this basis, the resulting polymer chain periodicity, c = 20.2 Å, is very similar to that observed for the PPDL (c = 20.0 Å). Such periodicity was interpreted as the result of the inclusion of the ester groups into the polymer pseudo-orthorhombic crystal lattice, and in particular of their regular spacing along the chain axis. The close similarity observed in the polymer chain periodicity of P6HDL and PPDL suggests that, in addition to the ester groups, also the carbon-carbon double bonds are included into the polymer crystal lattice. Inclusion of trans double bonds was also observed in other “PE-like” polyesters.

The X-ray diffraction pattern of P6HDL (Fig. 5a, bottom), characterized by two strong reflections at 2θ = 21.5 and 23.8°, resembles that of polyethylene (PE). Similarity between the X-ray spectra of aliphatic long chain polyesters and of PE was...
87.9 J/g. The two very close melting peaks are probably due to a recrystallization process during which poorly-formed and small size crystals give rise to more ordered and large crystals.

The X-ray diffraction pattern (Fig. 5b, bottom) is very similar to that of P6HDL (curve a), except for the absence of the signals at 2θ = 4.4 and 19.5°. These signals were previously related to the indices 001 and 012, respectively, of the pseudo-orthorhombic unit cell of PPDL.27 The absence of these two signals indicates that the polymer chain periodicity is removed, due to the presence of epoxy groups not stereoregularly arranged along the chain. In addition, the observed small differences in 2θ reflect the position that the parameters a and b of the crystal lattice are slightly distorted respect to the P6HDL ones. In conclusion, the poly(6,7-epoxy-ω-caprolactone) chains are presumably arranged in the crystal lattice ab plane, in a pseudo-orthorhombic packing with a and b parameters similar to those of the P6HDL unit cell, while the polymer chain periodicity along the c axis is absent.

In spite of the absence of the polymer chain periodicity along the c axis, the Tm of poly(6,7-epoxy-ω-hexadecenlactone) is higher than that of P6HDL. This behavior can be rationalized considering that polymer chains containing double bonds are more flexible than chains containing bulkier epoxy groups. It is well known, indeed, that flexible semicrystalline polymers have higher melting entropy and therefore lower Tm than rigid polymers, provided that they have similar enthalpy of fusion. DSC analysis of the poly(hydroxy-ω-hexadecenlactone) sample (c) (Fig. 5c, top) showed a melting point Tm at 65.8 °C and an enthalpy of fusion of 61.7 J/g.

The X-ray diffraction pattern (Fig. 5c, bottom) showed a single well defined peak at 2θ = 20.9°. This pattern is compatible with a hexagonal crystalline structure. Hexagonal crystal structures have been proposed for ethylene/vinyl alcohol copolymers, when the ethylene molar content is in the range 14 - 27%. For the poly(hydroxy-o-hexadecenlactone) a percentage of hydroxyl groups of about 15 % can be calculated on the basis of the molecular formula. Moreover, in the ethylene/vinyl alcohol copolymers described by Namakae et al. the strong equatorial 20 peak around 2θ = 4.25 Å, which is very similar to that observed for poly(hydroxy-o-hexadecenlactone) sample (c) (d = 4.24 Å).31 Hexagonal and pseudo-hexagonal structures were observed in ethylene/propylene (EP) copolymers32 and ethylene/1,5-hexadiene copolymers.33 In detail, in the EP copolymers, with the increase of propylene molar content, the PE orthorhombic unit cell is gradually distorted, and it is replaced by a pseudo-hexagonal structure when the propylene content is in the range 15-35 %.32

The inclusion of hydroxyl units in the crystal structure of poly(hydroxy-o-hexadecenlactone) sample and the presence of strong hydrogen bonds,33 could also justify that the Tm is not very different from that of poly(6,7-epoxy-o-hexadecenlactone).34 DSC analysis of the polymer sample (d) bearing 6-mercapto-1-hexanol pendant groups did not show a melting transition (see Supporting Information), thus indicating that the native crystalline structure is disrupted by the presence of the mercapto side chains. An amorphous material was obtained, with a Tg of -61 °C.

Copolymerization of ω-(6-hexadecenol)c copolymer was performed in conditions analogous to those used for the homopolymerization (xylene solution, 100 °C). The copolymer composition (50/50 in the two monomers) nicely reflected the feed, as evidenced by the 1H NMR analysis.

A detailed microstructure characterization of the copolymeric chain was achieved through inspection of the 13C NMR spectrum. Indeed, the chemical shifts of the carbonyl, α-methylene, β-methylene and α-methylene carbons are very sensitive to the chemical environment. By comparison with the spectra of the corresponding homopolymers, the resonance due to the hetero-sequences have been recognized and assigned. The significant 13C NMR spectra regions of a poly[(6-ω-hexadecenlactone)-ran-(ω-caprolactone)] sample and, for comparison, of a poly(6-ω-hexadecenlactone) are shown, respectively, in Fig. 6a and 6b.

The average lengths of the hexadecenlactoyl (Lcalc0) and caproyl (Lcalc1) sequences were calculated from the 13C NMR data by using previously reported equations. Interestingly, the average blocks lengths (Lcalc0 = 2.17; Lcalc1 = 1.85) were close to the value of 2, as expected for a random copolymer prepared with 50/50 feed.

The molecular weight of the copolymer calculated from the 1H NMR data, (Mw(NMR) = 15.8 kDa) was in excellent agreement with the theoretical one (Mw (θ) = 15.0 kDa). The experimental GPC value (Mw(GPC) = 36.0 kDa) resulted to be higher, but the above considerations hold also in this case. However, the GPC trace was monomodal, with dispersions Mw/Mn = 1.6.

DSC analysis evidenced a melting peak at Tm = 44.1 °C, with an enthalpy of fusion ΔHf of 80.7 J/g. The high crystallinity of this random copolymer sample is not surprising, in fact analogous random copolymers of ω-pentadecanolc and ε-caprolactone have been reported to be crystalline over the whole composition range. The X-ray diffraction pattern (see Supporting Information) shows that the observed crystallinity is due to a polyethylene-like packaging. This result, as already reported by
Scandola and Gross for ε-pentadecalactone/ε-caprolactone copolymers,\textsuperscript{25} is the consequence of the co-crystallization of CL and 6HDL units into a crystalline structure in which, the chain packing is substantially similar to that of the polyethylene and the homopolymers, while the chain periodicity, for a composition 50/50, is lost due to the random distribution of the ester groups in polymer chains.

To further explore the ability of the catalyst in the production of copolymeric materials, the synthesis of the diblock copolymer was attempted by sequential addition of different monomers. The obtained block copolymers have been characterized by \textsuperscript{1}H and \textsuperscript{13}C NMR, GPC, DSC and 2D NMR experiments (Supporting Information). The poly(6-o-hexadecenlactone)-block-poly(ε-caprolactone) copolymer was prepared in the presence of 1 by sequential addition of the two monomers in xylenes. When the 6HDL conversion reached its maximum (60%), a large excess of ε-CL was added. The \textsuperscript{1}H NMR spectrum, in addition to the resonances of the main signals due to two blocks (see Supporting Information), showed peaks corresponding to the methyl ester end group at 3.66 ppm deriving from the insertion of the macrolactone monomer in the Al-OMe bond, and hydroxyl methylene group at 3.63 ppm deriving from the hydrolysis of the growing chains. From these data it was possible to calculate the length of each block. In the \textsuperscript{13}C NMR spectrum (see Fig. 6c) the heterodiads were not observed, thus indicating that transesterification reactions were absent.

To confirm the formation of the copolymer, a lower molecular weight sample having a short PCL block was prepared. The \textsuperscript{13}C NMR spectrum of this sample (see Supporting Information) showed, besides the signals relative to the two blocks (CL*-CL and HDL*-HDL), other signals, with low intensity, attributable to the junction sequence. Indeed, in the carbonyl region, the signal at 173.8 ppm, relative to the caprolactone carbonyl group flanking an HDL unit (CL*-HDL) was observed. Moreover, the signals relative to methylene in α position respect to the CL carbonyl carbon, and that of the methylene bound to the oxygen (-CH₂-O-) of the 6HDL next to the CL carbonyl were respectively observed at 34.3 and 64.6 ppm. Assignments were performed by comparison with the spectra of the PCL and 6HDL homopolymers and with that of the poly[(6-o-hexadecenlactone)-ran-(ε-caprolactone)] sample. Significantly, signals relative to the reverse junction (i.e. signals relative to the 6HDL carbonyl flanking a CL unit), were not observed, thus indicating that a perfect di-block copolymer was obtained. The absence of a random block of the two monomers can be explained taking into account that in the used experimental conditions the CL monomer was present in large excess respect to the residual amount of 6HDL, and that the CL polymerization is faster than the 6HDL polymerization and of the CL/6HDL random copolymerization. DSC analysis, (see Supporting Information) showed a single melting peak \( T_m \) at 55.6 °C, with an enthalpy of fusion \( \Delta H_m \) of 78.4 J/g. The X-ray diffraction pattern of this sample (see Supporting Information) shows that the observed crystallinity is due to the long caprolactone sequences. The observed \( T_m \) is similar to that of the poly(ε-caprolactone) homopolymer obtained in the same conditions (\( T_m = 56 °C, \Delta H_m = 76.6 \) J/g, see Supporting Information). These data can be rationalized by considering that the inclusion of 6HDL units in the crystalline PCL blocks probably occurs, as well as in ε-pentadecalactone/ε-caprolactone copolymers the PDL units are included in the PCL crystal phase.\textsuperscript{9,10c,35} The absence of the crystalline phase of P6HDL blocks is not surprising, in fact it is generally accepted that the crystallization of semicrystalline block copolymers is strictly dependent on the copolymer composition\textsuperscript{36} and it preferentially occurs when comparable fractions of each copolymer components are present.\textsuperscript{36a,6}

Copolymerization of the macrolactone with the rac-lactide was also attempted. However, when the two monomers were mixed together in the presence of the catalyst, only poly(lactide) was obtained. This behavior is probably due to the higher coordination ability of the diester lactide, in comparison to that of the macrolactone. Moreover, a computational study showed that the insertion of a macrolactone into a metal secondary alkoxide group is dramatically hampered for steric reason.\textsuperscript{10f} A similar effect should also be significant in our system.

The poly(6-o-hexadecenlactone)-block-poly(rac-lactide) copolymer was prepared in the presence of the aluminum complex by sequential addition of macrolactone and rac-LA in xylenes. As above, \textsuperscript{1}H and \textsuperscript{13}C NMR analysis disclosed the presence of the two blocks, while heterosequences were not detected. Interestingly, the observed end groups were the methyl ester end group at 3.66 ppm, deriving from the insertion of the macrolactone into the Al-OCH\textsubscript{3} bond, and the hydroxyl methine at 4.35 ppm due to the hydrolysis of the growing chain ending with a lactide unit. For the PHDL-block-PLA, tacticity of the PLA block was also studied by homodecoupled \textsuperscript{1}H NMR analysis, leading to a substantially atactic PLA, with \( P_m \) value of 0.55, in agreement with what previously observed for the poly(rac-lactide)s obtained in toluene solution with similar salicylaldiminato aluminum catalysts.\textsuperscript{46} DSC analysis of the poly(6-o-hexadecenlactone)-block-poly(rac-lactide) copolymer showed a melting peak at 49.3 °C (\( \Delta H_m = 37.2 \) J/g, see Supporting Information). The crystallinity is due to the crystallizable P6HDL block, while, of course, the stereoirregular LA sequences do not crystallize. The observed decrease of \( T_m \) and \( \Delta H_m \) with respect to the P6HDL homopolymer could be due to the greater difficulty of 6HDL units to crystallize in the presence of long LA blocks.

The assignment of the signals corresponding to the chain end groups allowed to determine the molecular weights of both the copolymers by integration of the named signals and the determination of the blocks lengths (see Supporting Information). GPC analysis was performed for the products of these copolymerization reactions. It is worth of noting that chromatograms were unimodal and the dispersity indices were 1.9 and 1.5 respectively, in line with the presence of one kind of macromolecular chains, i.e. the expected diblock copolymers.
The achievement of the described diblock copolymers is a further indication of the pseudo-living nature of ROP catalyzed by this system. Taking advantage of this feature, we attempted to synthesize a diblock copolymer of the type poly[(6-o-hexadecenlactone)-ran-(ε-caprolactone)]-block-poly(rac-lactide) by first copolymerizing 6HDL and ε-CL, and subsequently adding rac-LA. The first random block was obtained by polymerization of the 6HDL and ε-CL (50/50) in xylene at 100 °C for one day. Subsequently, 50 equivalents of rac-LA were added, and after 3 days a conversion of 93% of lactide was observed. Also in this case, GPC analysis confirmed the diblock nature of this copolymer, showing a monomodal peak and a dispersity index of 2.0.

DSC analysis of this sample (see Supporting Information) showed a single melting peak $T_m$ of 38.8 °C, and an enthalpy of fusion $\Delta H_m$ of 46.9 J/g. Also in this case the stereoirregular LA sequences do not crystallize, therefore the crystallinity is due to recrystallization of random sequences of monomers 6HDL and ε-CL. The observed decrease of $T_m$ with respect to the poly[(6-o-hexadecenlactone)-ran-(ε-caprolactone)] ($T_m$ = 44.1 °C), could be due to the greater difficulty of random 6HDL/ε-CL block to crystallize in the presence of the LA block.

GPC showed monomodal distribution for all the copolymers, which is a clear indication that the samples were block copolymers, and not mechanical mixtures of homopolymers. Moreover, the same conclusion can be derived from the 2D DOSY NMR carried out on all the copolymers (see Supporting Information). This experiment, indeed, provides diffusion coefficients of molecules related to hydrodynamic radius and molecular weight. DOSY NMR experiments (see Fig. 7 and Supporting Information) of all the described copolymers showed that the signals of the first block and those of the second block lied at the same diffusion coefficient, and therefore belonged to the same polymeric chains, thus confirming the diblock nature. Notably, most of the reported catalytic systems (enzymatic, organic, and metal-based) active in the polymerization of macrolactones, undergo intra- and inter-molecular transterification reactions preventing the formation of diblock copolymers. In particular, several aluminum based complexes have been explored in the sequential polymerization of macroide and small lactones. Actually, when the copolymers were allowed to react for longer time, they showed an increased randomness with increasing reaction time. On the contrary, only two catalysts able to produce poly(PHDL)-block-poly(CL) copolymers have been reported in the literature. The salicylaldiminato aluminum compound represents the first example of aluminum based catalyst able to produce perfect block copolymers with the desired composition even if the reaction is carried out for prolonged reaction times.

**Conclusions**

Dimethyl(salicylaldiminato) aluminum compound resulted active catalysts for the ROP of α-6-hexadecenlactone to high molecular weight polymer. The used catalyst offered narrower dispersities and better control in comparison to the enzymatic and/or metal based traditional macrolactone catalysts. Since the ROP process does not affect the unsaturation of the main chain, this functionality was used for further chemical modifications. Thiol-ene coupling reaction and epoxidation of the double bond occurred without any change in the degree of polymerization. In the presence of hydrides, the epoxides were opened and alcohol-substituted poly(ester) chains with occasional inter and intra ether-type crosslinks were formed. Thermal and structural characterization showed that not only the poly(α-6-hexadecenlactone) itself, but also the epoxy-functionalized and the hydroxylated derivatives are semicrystalline. While the poly(α-6-hexadecenlactone) has a crystal structure very similar to that of orthorhombic PE, in the presence of more bulky and stereoirregularly arranged epoxy groups the structure is deformed and the periodicity along the chain axis is lost. Conversely, the polymer chains containing the randomly arranged hydroxyl groups are packaged into a hexagonal crystal lattice.

The used chemical approach thus allowed the preparation of functional and semicrystalline aliphatic polyesters, with a high control of the chain microstructure. Copolymerization of the macrolactone with the smaller ring size ε-caprolactone produced a random semicrystalline copolymer, having both the monomers included in the crystal lattice. The “pseudo-living” behavior of the catalytic system allowed the preparation of linear block copolymers of 6HDL with ε-CL and/or rac-LA by sequential addition of the monomers. These block copolymers were also semicrystalline.

In conclusion, we demonstrated the high versatility of the salicylaldiminato aluminum complexes in mediating the homo and copolymerization of the α-6-hexadecenlactone with smaller ring size cyclic esters to block and random copolymers. Moreover we proposed the poly(α-6-hexadecenlactone) as a potential starting material for the preparation of functional and semicrystalline, thermoplastic polyesters.
Acknowledgements
The authors thank Dr. Patrizia Oliva for NMR technical assistance, Dr. Ilaria D’Auria for GPC technical assistance and Prof. Agostino Casapullo for MALDI-ToF-MS analysis. This work was supported by the Italian Ministry of University and Research (PRIN 2010-2011: Nanostructured polymeric materials with tailored molecular and crystalline structures, for advanced technologies and for the environment) and by Università del Sannio (FAR2012).

Notes and references

1. **a** Dipartimento di Chimica e Biologia, Università di Salerno, via Giovanni Paolo II 132, 84084 Fisciano, Salerno (Italy).
2. **b** Dipartimento di Scienze e Tecnologie, Università del Sannio, via dei Mulini 59/A, 82100 Benevento (Italy). Fax: 0039 0824 323623; Tel: 0039 0824 323632 E-mail: pappalardo@unisannio.it
3. **c** Electronic Supplementary Information (ESI) available: NMR, DSC and X ray diffraction analysis of the polymers .See DOI: 10.1039/b000000x/

10 The same end groups should be generated also by “activated monomer” mechanisms. To discriminate between the “coordination-insertion” and the “activated monomer” mechanisms, both resulting in the same end groups, the aluminum dimethyl complex was mixed together with 1 equiv
of MeOH and 1 equiv of 6HDL in toluene-$d_8$ (See Scheme S1 in Supporting Information). The reaction was monitored by $^1$H NMR at 70 °C. Although a mixture of products was observed, the 6HDL signals remained unmodified and formation of methane (signal at 0.16 ppm) was observed, suggesting the alcoholysis of the aluminum–methyl bond, ruling out the “activated monomer” mechanism. Analogous results have been previously obtained for closely related systems.\(^{20}\)

The concentration of 6HDL in all the runs of Table 1 is above the critical monomer concentration, i.e. the concentration of monomer up to which only cyclic chains are formed (0.2 M), as recently reported.\(^{10}\) Thus, in the experimental conditions of Table 1, the equilibrium is shifted versus the linear polymers.


In ethylene/vinyl alcohol copolymers, the $T_m$ is increased, compared to that of PE, due to the presence of strong hydrogen bonds between the hydroxyl groups. See: Y. Mori., H. Sumi, T. Hirabayashi, Y. Ynai, K. Yokota, *Macromolecules*, 1999, **32**, 5860–5871.
