Polymer Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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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

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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 $NaCNBH_3$ 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-hexadecenlactone) and it is replaced by a hexagonal packing when the poly(ester) chains are hydroxylated. Furthermore copolymerization of 6HDL with smaller ε-caprolactone produced random copolymers, with average sequence blocks lengths of 2, while the sequential addition of 6HDL and ε -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 dispersities, 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(hydroxyalkanoate)s 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.[10a] 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.[10b-d] Very recently, the “immortal” ROP of ω-pentadecalactone by magnesium based initiator was also reported.[10e] It is apparent, then, that in the literature 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,[11] we recently reported dimethyl(salicylaldiminato)aluminum compounds able to catalyze the homo- and copolymerization of lactide with ε-caprolactone[4e] and with glycolide[4h] 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.[4d-f] 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-hexadecenlactone (6HDL), and in its copolymerization with the smaller ε-caprolactone and *rac*-lactide.

The chosen macrocycle, 6HDL, is used in the fragrance industry with a worldwide volume of around 1.0 metric ton per year.[12a] On the contrary, its use as monomer in polymerization has been scarcely described.[12b] Similar large unsaturated lactones, such as ambrettolide and globalide, have been previously used in enzymatic polymerization.[7g] 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.[5c] Ambrettolide, a natural occurring unsaturated macrolactone, presents the double bond in *cis* (*Z*) configuration.[5c] 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[13] and/or 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.[14] Taking advantages of the double bonds, modifications of the polymer 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, xylenes 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 P_2O_5 for 72 h; ε-caprolactone (ε-CL) and 6-ω-hexadecenlactone (6HDL) were distilled under vacuum on CaH_2 and stored over 4 Å molecular sieves. *meta*-Chloroperoxybenzoic acid (mCPBA) was dissolved in CH_2Cl_2 and dried over Na_2SO_4, the solvent was evaporated in vacuo, then the acid was crystallized from *n*-hexane/Et_2O 10/1 at -20 °C. $CDCl_3$ and toluene-d_8 were purchased from Eurisotop and used as received. The Al-salicylaldiminato complex was synthesized according to literature methodology.[15] All other reagents and solvents were purchased from Aldrich and used without further purification.

Instruments and Measurements

NMR spectra of polymers were performed in $CDCl_3$ at room temperature on Bruker Avance 300, 400 or 600 spectrometers (^{1}H: 300.13, 400.13, 600.13 MHz; ^{13}C: 75.47, 100.62, 150.92 MHz; respectively). The resonances are reported in ppm (δ) and coupling constants in Hz (*J*), and they are referenced to the residual solvent peak versus $Si(CH_3)_4$: at δ 7.26 (^{1}H) and δ 77.16 (^{13}C). Spectra recording was performed on BrukerTopSpin 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 were dissolved in 0.5 mL of $CDCl_3$ 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 (M_n and M_w) and molecular weight dispersities (M_w/M_n) 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 Absorbtion (UV, λ_{abs} = 220 nm) detector, using tetrahydrofuran as eluent (1.0 mL min^{-1}) and employing a system of four Styragel 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 (DHBA)(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 (T_g), melting points (T_m) and enthalpy of fusion (ΔH_m) 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

Cite this: DOI: 10.1039/c0xx00000x

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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 CH_2Cl_2, 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 %. ^{1}H NMR (300 MHz, $CDCl_3$, RT) δ 5.37 (bs, 2H; –C(H)=), 4.04 (t, J = 6.6 Hz, 2H; $–CH_2O–$), 3.66 (s, $–OCH_3$), 3.63 (t, $–\mathit{CH}_2OH$), 2.28 (t, J = 7.4 Hz, 2H; $–C(O)CH_2–$), 1.96 (bs, 4H; $–\mathit{CH}_2C(H)=$), 1.75–1.55 (m, 4H; $–C(O)CH_2\mathit{CH}_2–$ and $–\mathit{CH}_2CH_2O–$), 1.45–1.25 (m, 14H; CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, RT) δ 174.15 (–C(O)O–), 130.6 (–CH=), 130.3 (–CH=), 64.5 ($–C(O)O\mathit{CH}_2–$), 34.5 ($–\mathit{CH}_2C(O)O–$), 32.7, 32.6, 29.7 and 29.6 (CH_2), 29.3 (2 C; CH_2), 29.15 ($–\mathit{CH}_2CH=$), 28.9 ($–\mathit{CH}_2CH=$), 28.8, 25.95 and 25.15 (CH_2).

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

The epoxidation procedure is based on a modification of previously reported literature methodologies.[16] In a screw vial, poly(6-ω-hexadecenlactone) (obtained in run 1, 252 mg, 1.0 mmol alkene function) was dissolved in dry $CHCl_3$ (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 %. $M_{n,th}$ = 16.4 kDa. $M_{n,NMR}$ = 15.6 kDa. $M_{n,GPC}$ = 37.2 kDa. M_n/M_w = 1.9. ^{1}H NMR (300 MHz, $CDCl_3$, RT) δ 4.04 (t, J = 6.6 Hz, 2H; $–CH_2O–$), 3.66 (s, $–OCH_3$), 3.63 (t, $–\mathit{CH}_2OH$), 2.65 (bs, 2H; –CHO–), 2.28 (t, J = 7.4 Hz, 2H; $–C(O)CH_2–$), 1.75–1.55 (m, 4H; $–C(O)CH_2\mathit{CH}_2–$ and $–\mathit{CH}_2CH_2O–$), 1.55–1.45 (m, 2H; $\mathit{CH}_2CHO–$) 1.45–1.15 (m, 14H; CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, RT) δ 174.15 (–C(O)O–), 64.5 ($–C(O)O\mathit{CH}_2–$), 59.0 (–CHO–), 58.95 (–CHO–), 34.45 ($–\mathit{CH}_2C(O)O–$), 32.2, 32.15, 29.4 and 29.3 (CH_2), 29.2 (2C; CH_2), 28.65 (CH_2), 26.15 and 26.1 ($–\mathit{CH}_2CHO–$), 25.95 and 25.05 (CH_2).

Reaction of poly(6,7-epoxy-ω-hexadecenlactone) with $NaCNBH_3$

The reaction procedure is based on a modification of a literature methodology.[17] In a Schlenk flask, the poly(6,7-epoxy-ω-hexadecenlactone) described above (88 mg, 0.33 mmol epoxy function) was dissolved in dry THF (33.0 mL) at room temperature. Then, $NaCNBH_3$ (82.5 mg, 1.3 mmol) and BF_3•ether (82.0 μL, 0.66 mmol) were added at 0 °C. The mixture was stirred for 8 h at 20 °C. The polymer was recovered by filtration, washed with methanol five times and dried in vacuum at 20 °C. Yield = 69 %. The same procedure was performed on a lower molecular weight epoxidized sample (Table 1, Run 3). ^{1}H NMR (300 MHz, $CDCl_3$, RT) δ 4.04 (t, J = 6.6 Hz, 2H; $–CH_2O–$), 3.57 (bs, 1H; C*H*OH), 3.41 (bs, 2H; –C*H*–O–C*H*–), 2.28 (t, J = 7.4 Hz, 2H; $–C(O)CH_2–$), 1.75–1.50 (m, 8H; $–CH_2–$), 1.50–1.15 (m, 16H; CH_2).

Reaction of poly(6-ω-hexadecenlactone) with 6-mercapto-1-hexanol

In a screw vial, 6-mercapto-1-hexanol (250 mg, 2.1 mmol) and 2,2'-azobis(2-methylproprionitrile) (5 mg) were added under N_2 atmosphere to poly(6-ω-hexadecenlactone) (104 mg of the sample of run 2, Table 1, $M_{n,NMR}$ = 14.1 kDa), dissolved in dry THF (1.0 mL). The mixture was stirred for 24 h at 80 °C. The product was precipitated in methanol, recovered by filtration, washed with methanol and dried in vacuum at 20 °C. Yield = 62 %. $M_{n,NMR}$ = 21.5 kDa. $M_{n,GPC}$ = 36.6 kDa. M_n/M_w = 1.8. ^{1}H NMR (400 MHz, $CDCl_3$, RT) δ 4.05 (t, J = 6.4 Hz, 2H; $–CH_2O–$), 3.64 (t, J = 6.8 Hz, 2H; $–CH_2OH$), 2.54-2.51 (m, 1H; –CHS–),2.47 (t, J = 7.2 Hz, 2H; $–CH_2S–$), 2.29 (t, J = 7.2 Hz, 2H; $–C(O)CH_2–$), 1.68–1.46 (m, 14H; $–CH_2–$), 1.46–1.20 (m, 18H; $–CH_2–$). ^{13}C NMR (100 MHz, $CDCl_3$, RT) δ 174.2 (–C(O)O–), 64.5 ($–C(O)O\mathit{CH}_2–$) 63.0 ($–CH_2OH$), 46.0 (–CS–),35.0 (–CS–), 34.5 ($–\mathit{CH}_2C(O)O–$), 32.8, 30.4, 30.0, 29.7, 29.6 and 29.5 (CH_2), 29.4 (2C; CH_2), 29.3, 28.9, 28.8, 26.9, 26.85, 26.0, 25.6 and 25.1(CH_2).

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 CH_2Cl_2, 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 %. $M_{n,th}$ = 15.0 kDa. $M_{n,NMR}$ = 15.8 kDa. $M_{n,GPC}$ = 36.0 kDa. M_n/M_w = 1.6. ^{1}H NMR (300 MHz, $CDCl_3$, RT) δ 5.37 (bs, 2H; –C(H)=), 4.05 (t, J = 6.3 Hz, 4H; $–CH_2O–$), 3.66 (s, 3H; $–OCH_3$), 3.63 (t, 2H; $–\mathit{CH}_2OH$), 2.35–2.25 (m, 4H; $–C(O)CH_2–$), 1.96 (bs, 4H; $–\mathit{CH}_2CH=$), 1.75 – 1.55 (m, 8H; $–C(O)CH_2\mathit{CH}_2–$ and $–\mathit{CH}_2CH_2O–$

), 1.45 – 1.25 (m, 16 H; CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$, 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=), 64.6 (–C(O)O*C*H$_2$–; HDL*-CL), 64.5 (–C(O)O*C*H$_2$–; HDL-HDL), 64.3 (–C(O)O*C*H$_2$–; CL-CL), 64.2 (CL*-HDL), 34.5 (–*C*H$_2$C(O)O–; HDL-HDL), 34.45 (–*C*H$_2$C(O)O–; HDL*-CL), 34.3 (–*C*H$_2$C(O)O–; CL*-HDL), 34.25 (–*C*H$_2$C(O)O–; CL-CL), 32.7, 32.6, 29.7 and 29.6 (CH$_2$, HDL), 29.3 (2C; CH$_2$, HDL), 29.15 (–*C*H$_2$CH=), 28.9 (–*C*H$_2$CH=), 28.8 (CH$_2$, HDL), 28.5 (–C(O)OCH$_2$*C*H$_2$–), 25.95 (CH$_2$, HDL), 25.7 (–*C*H$_2$CH$_2$CH$_2$C(O)O–, CL), 25.15 (*C*H$_2$CH$_2$C(O)O–; HDL-HDL), 25.1 (*C*H$_2$CH$_2$C(O)O–; HDL*-CL), 24.75 (*C*H$_2$CH$_2$C(O)O–; CL*-HDL), 24.7 (*C*H$_2$CH$_2$C(O)O–; CL-CL).

Synthesis of poly(6-ω-hexadecenlactone)-*block*-poly(ε-caprolactone)

A Schlenk tube was charged with precatalyst (14.0 mg, 35 μmol), 6HDL (442 mg, 1.75 mmol), xylenes (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 CDCl$_3$ and analyzed by ^{1}H NMR, the macrolactone 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 xylenes under vacuum, followed by dropwise addition of the residue, dissolved in a minimal amount of CH$_2$Cl$_2$, 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 %. $M_{n,th}$ = 22.4 kDa. $M_{n,NMR}$ = 22.3 kDa. $M_{n,GPC}$ = 37.5 kDa. M_n/M_w = 1.9.

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 %. $M_{n,th}$ = 7.9 kDa. $M_{n,NMR}$ = 10.6 kDa. $M_{n,GPC}$ = 19.1 kDa. M_n/M_w = 2.4 (see Supporting Information).

^{1}H NMR (300 MHz, CDCl$_3$, RT) δ 5.37 (bs, 2H; –C(H)=), 4.15 – 3.95 (m, 4H), 3.66 (s, 3H; –OCH$_3$), 3.63 (t, 2H; –C*H*$_2$OH), 2.35 – 2.20 (m, 4H; –C(O)CH$_2$–), 1.96 (bs, 4H; –C*H*$_2$C(H)=), 1.75–1.55 (m, 8H; –C(O)CH$_2$C*H*$_2$– and –C*H*$_2$CH$_2$O–), 1.45–1.25 (m, 16H; CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$, RT) δ 174.15 (–C(O)O–, HDL), 173.7 (–C(O)O–, CL), 130.6 (–C(H)=), 130.3 (–C(H)=), 64.5 (–C(O)O*C*H$_2$–, HDL), 64.3 (–C(O)O*C*H$_2$–, CL), 34.5 (–*C*H$_2$C(O)O–, HDL), 34.25 (–*C*H$_2$C(O)O–, CL), 32.7 (CH$_2$, HDL), 32.6 (CH$_2$, HDL), 29.7 (CH$_2$, HDL), 29.6 (CH$_2$, HDL), 29.3 (2C; CH$_2$, HDL), 29.15 (–*C*H$_2$CH=), 28.9 (–*C*H$_2$CH=), 28.8 (CH$_2$, HDL), 28.5 (CH$_2$, CL), 25.95 (CH$_2$, HDL), 25.7 (CH$_2$, CL), 25.15 (CH$_2$, HDL), 24.75 (CH$_2$, CL).

Synthesis of poly(6-ω-hexadecenlactone)-*block*-poly(*rac*-lactide)

A Schlenk tube was charged with precatalyst (14.0 mg, 35 μmol), 6HDL (442 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 24 h. Then, an aliquot was withdrawn, dissolved in CDCl$_3$ and analyzed by ^{1}H NMR, resulting in a macrolactone conversion of 50 %. Afterwards, *rac*-LA (252.2 mg, 1.75 mmol) was added and the reaction mixture was stirred for other 17 h (*rac*-LA conversion = 95 %). Finally, the mixture was cooled to room temperature. Product purification was attained by dropwise addition of the reaction mixture, dissolved in CH$_2$Cl$_2$, to rapidly stirring *n*-hexane. The precipitated polymer was recovered by filtration, washed with *n*-hexane and dried at 60 °C overnight in a vacuum oven. Yield = 51 %. $M_{n,th}$ = 16.9 kDa. $M_{n,NMR}$ = 28.4 kDa. $M_{n,GPC}$ = 24.3 kDa. M_n/M_w = 1.5. ^{1}H NMR (300 MHz, CDCl$_3$, RT) δ 5.37 (bs, 2H; –CH=), 5.30 – 5.05 (m, 1H; –C*H*CH$_3$–), 4.04 (t, *J* = 6.6 Hz, 2H; –CH$_2$O–), 3.66 (s, 3H; –OCH$_3$), 3.63 (t, 2H; –C*H*$_2$OH), 2.28 (t, *J* = 7.4 Hz, 2H; –C(O)CH$_2$–), 1.96 (bs, 4H; –C*H*$_2$CH=), 1.75 – 1.55 (m, 7H; –C(O)CH$_2$C*H*$_2$–, –C*H*$_2$CH$_2$O– and –CH$_3$), 1.45 – 1.20 (m, 14 H; CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$, RT) δ 174.15 (–C(O)O–, HDL-HDL), 169.8, 169.6, 169.55, 169.5 and 169.3 (–C(O)O–, LA-LA), 130.6 (–C(H)=), 130.3 (–CH=), 69.3 and 69.15 (–C(O)O*C*H–), 64.5 (–C(O)O*C*H$_2$–), 34.5 (–*C*H$_2$C(O)O–), 32.7, 32.6, 29.7 and 29.6 (CH$_2$), 29.3 (2C; CH$_2$) , 29.15 (–*C*H$_2$CH=), 28.9 (–*C*H$_2$CH=), 28.8, 25.95 and 25.15 (CH$_2$), 16.9 and 16.8 (C(O)OCH*C*H$_3$–).

Synthesis of poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)]-*block*-poly(*rac*-lactide)

A Schlenk tube was charged sequentially with precatalyst (14.0 mg, 35 μmol), HDL (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 Schlenk tube 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 CH$_2$Cl$_2$, 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 %. $M_{n,th}$ = 15.2 kDa. $M_{n,GPC}$ = 29.1 kDa. $M_{n,NMR}$ = 26.5 kDa. M_n/M_w = 2.0. Sequences block lengths, as evaluated by ^{1}H NMR: $L_{(HDL\text{-}ran\text{-}CL)}$ = 110; L_{LL} = 58. Average sequence block lengths of the random HDL/CL block: L_{HDL} = 1.73; L_{CL} = 2.93. ^{1}H NMR (300 MHz, CDCl$_3$, RT) δ 5.37 (bs, 2H; –CH=), 5.30 – 5.05 (m, 1H; –C*H*CH$_3$–), 4.04 (t, *J* = 5.7 Hz, 2H; –CH$_2$O–), 3.66 (s, 3H; –OCH$_3$), 3.63 (t, 2H; –C*H*$_2$OH), 2.28 (q, *J* = 7.4 Hz, 4H; –C(O)CH$_2$–), 1.96 (bs, 4H; –C*H*$_2$CH=), 1.75 – 1.45 (m, 11H, –C(O)CH$_2$C*H*$_2$–, –C*H*$_2$CH$_2$O– and –CHC*H*$_3$–), 1.45 – 1.15 (m, 16H, CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$, 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), 169.8, 169.6, 169.55, 169.5 and 169.3 (–C(O)O–, LA-LA), 130.6 (–CH=), 130.3 (–CH=), 69.3 and 69.15 (–C(O)O*C*H–, LA), 64.6 (–C(O)O*C*H$_2$–; HDL*-CL), 64.5 (–C(O)O*C*H$_2$–; HDL-HDL), 64.3 (–C(O)O*C*H$_2$–; CL-CL), 64.2 (CL*-HDL), 34.5 (–*C*H$_2$C(O)O–; HDL-HDL), 34.45 (–*C*H$_2$C(O)O–; HDL*-CL), 34.3 (–*C*H$_2$C(O)O–; CL*-HDL), 34.25 (–*C*H$_2$C(O)O–; CL-CL), 32.7, 32.6, 29.7 and 29.6 (CH$_2$, HDL), 29.3 (2C; CH$_2$, HDL), 29.15 (–*C*H$_2$CH=), 28.9 (–*C*H$_2$CH=), 28.8 (CH$_2$, HDL), 28.5 (–C(O)OCH$_2$*C*H$_2$–), 25.95 (CH$_2$, HDL), 25.7 (–*C*H$_2$CH$_2$CH$_2$C(O)O–, CL), 25.15 (*C*H$_2$CH$_2$C(O)O–; HDL-HDL), 25.1 (*C*H$_2$CH$_2$C(O)O–; HDL*-CL), 24.75 (*C*H$_2$CH$_2$C(O)O–; CL-CL), 24.7 (*C*H$_2$CH$_2$C(O)O–; CL*-HDL), 16.9 and 16.8 (C(O)OCH(*C*H$_3$)–).

Kinetic Experiments

In a Braun Labmaster glovebox, a Teflon-valved J. Young NMR

Cite this: DOI: 10.1039/c0xx00000x

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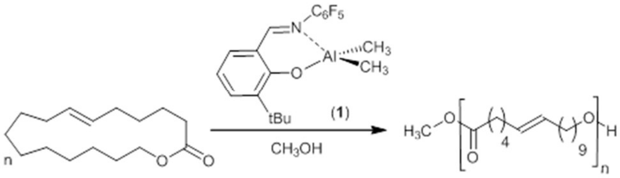
ARTICLE TYPE

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.

Results and discussion

Polymerization of ω-6-hexadecenlactone

The polymerization of 6-ω-hexadecenlactone (6HDL) by metal initiators is described herein for the first time.[12]



Scheme 1 ROP of ω-6-hexadecenlactone by compound (**1**).

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 ω-6-hexadecenlactone (6HDL) was performed in xylenes solution, in the presence of complex **1** 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-ω-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 δ = 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 (δ = 3.63 ppm, $–CH_2CH_2OH$) and a singlet relative to the methyl ester end group (δ = 3.66 ppm, $-COOCH_3$) 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 $Al-OCH_3$ 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.[4e]

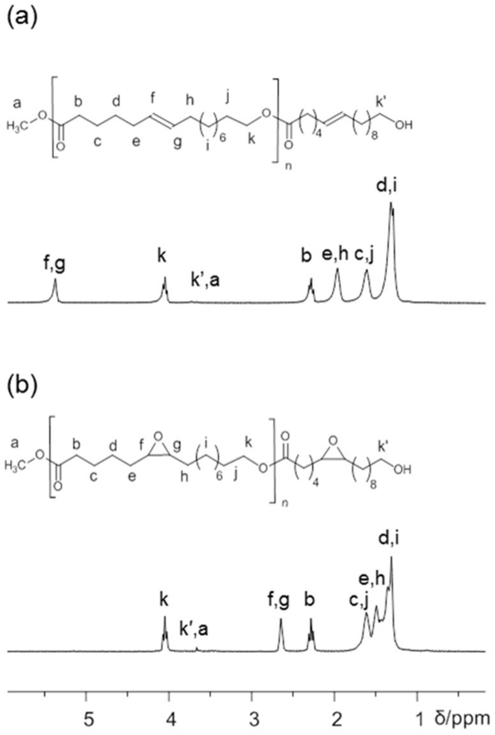


Fig. 1^{1}H NMR (300 MHz, $CDCl_3$, RT) of: (a) poly(6-ω-hexadecenlactone); (b) poly(6,7-epoxy-ω-hexadecenlactone).

The molecular weight of the samples was determined by NMR and GPC. The gel permeation cromatography (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; $-CH_2-OC(O)$) 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, $M_{n,th}$

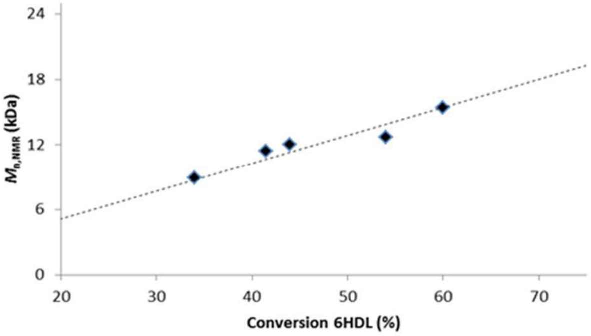


Fig. 2 $M_{n,NMR}$ versus conversion plot for P6HDL (Table 1, runs 1-5).

Table 1 Polymerization of ω-6-hexadecenlactone.

Run	$[6HDL]_0/[Cat]^c$	T (°C)	t (h)	Conv $(\%)^d$	Yield (%)	$M_{n,th}^e$ (kDa)	$M_{n,NMR}$ (kDa)	$M_{n,GPC}^f$ (kDa)	M_w/M_n^f
1^a	100	100	4	34	28	8.6	8.9	18.3	1.6
2^a	100	100	8	42	34	10.5	11.4	23.1	1.6
3^a	100	100	16	44	40	11.1	12.0	27.2	1.6
4^a	100	100	24	54	47	13.6	12.7	34.9	1.6
5^b	100	100	27	60	60	15.1	15.4	40.0	1.6
6^b	100	130	27	48	48	12.1	14.1	33.0	1.5
$7^{b,g}$	100	130	27	31	26	7.7	9.6	17.7	1.7
8^b	250	130	27	49	45	30.9	36.3	50.0	1.6

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 ^1H NMR from the ω-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 xylenes.

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 $M_{n,NMR}$ 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 time (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 ($M_w/M_n \geq 2$).[10a,b,f] 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 macrolactone.[10d]

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 Informations). 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.[5] This equilibrium would also affect the chain lengths and would also explain the observed dispersities.[5a] 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, endcapped with methoxy groups (see Supporting Information). Cyclic oligomeric species have been previously observed in the ROP of various macrolactones promoted by anionic[6] and organic initiators,[9] as well as by metal complexes.[10a,d-g]

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.[5] Thus, the dilution will favor the monomer and the oligomeric cyclic species, while high concentration favors the polymeric product.[20] 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 ^1H 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 ($[Cat] = 5.0 \times 10^{-2}$ M; $[6HDL]_0 = 1.0$ M; $[MeOH] = 5.0 \times 10^{-2}$ M). The reaction kinetics featured a pseudo-first-order dependence in the 6HDL concentration, as reported in Fig. 3: the semilogarithmic plot of $\ln([6HDL]_0/[6HDL]_t)$ 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.[10a]

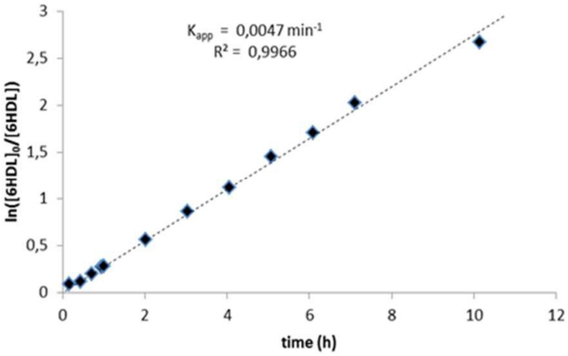


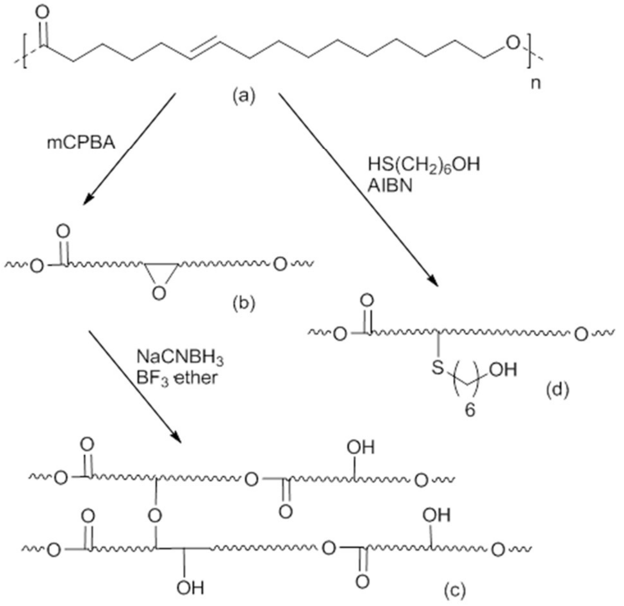
Fig. 3 Pseudo first-order kinetic plot for ROP of 6-ω-hexadecenlactone determined by ^{1}H NMR spectra. [Cat] = 5.0 x 10^{-2} M; $[6HDL]_0$ = 1.0 M; [MeOH] = 5.0 x 10^{-2} M; T = 80 °C; toluene-d_8 as a solvent.

Functionalyzation of the poly(6-ω-hexadecenlactone) sample.

The double bond in the poly(6-ω-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-ω-hexadecenlactone) are respectively shown. Interestingly, the disappearance of the signal relative to the double bond protons (at δ = 5.37 ppm) and the appearance of a new signal (at δ = 2.65 ppm) for the protons on the epoxide ring indicates that the modification was accomplished.[16b,21] 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 $M_{n,NMR}$ (15.6 kDa), evaluated from the integral ratio of the signal relative to the main chain methylene protons (4.04 ppm; -CH_2-OC(O)) and the singlet relative to the terminal –OCH_3 protons (3.66 ppm), was in good agreement with the theoretical molecular weight ($M_{n,th}$ = 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 $M_{n,NMR}$ (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 numeral molecular weight before and after the epoxidation were consistent with a non-degradative derivatization reaction.[16a]

Derivatization of the epoxide 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 triepoxided triglycerides to hydroxyl derivates.[17] 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; $M_{n,NMR}$ = 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 (δ= 2.65 ppm), while new signals at δ = 3.57 and 3.41 ppm appeared and were respectively attributed to the methine near an alcohol functionality [-C*H*-OH] and to vicinal ether protons [-C*H*-O-C*H*-].[22] Formation of poly(hydroxy-ω-hexadecanlactone) 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.[23]



Scheme 2 Modification of poly(ω–hexadecenlactone).

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).[24]

Among the multiple reactions that have been accepted into the click chemistry realm, the addition of thiols to C=C bonds is one of the most applied, offering high yields and outstanding functional groups tolerance under simple reaction conditions.[25] 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.[26] 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***).

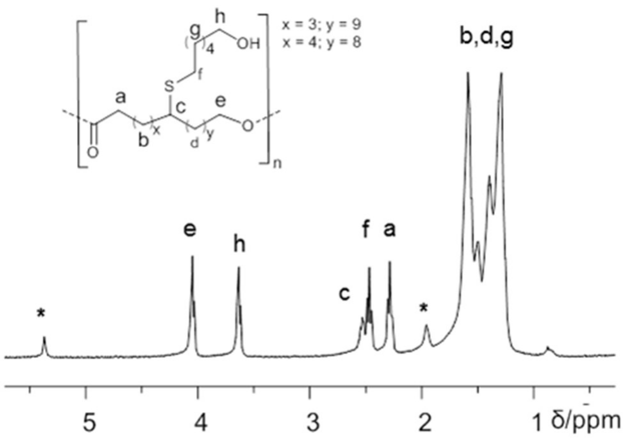


Fig. 4 ^{1}H NMR ($CDCl_3$, RT) of poly(ω-hexadecalactone) with 6-mercapto-1-hexanol pendant group. *: traces of starting poly(6-ω-hexadecenlactone).

The ^{1}H 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 ^{13}C 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 ($M_{\mathrm{n,NMR}}$ = 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-ω-hexadecenlactone) and its functionalized derivatives.

The obtained poly(6-ω-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 rangeo f 3 to 40°.

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

The thermogram of the P6HDL sample (Table 1, run 5) showed a sharp endotherm, with a melting point T_m at 57.6 °C and an enthalpy of fusion ΔH_m of 87.1 J/g, while the T_g was not detected in the scanned heating range (Fig. 5a, top). The T_m is slightly higher, while the ΔH_m is very similar to that observed by Heise *et al*. for the poly(ambrettolide), a polyester obtained from an isomer of 6HDL.[7g,13]

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 previously reported for other polyesters obtained from saturated and unsaturated macrolactones.[7g,27]

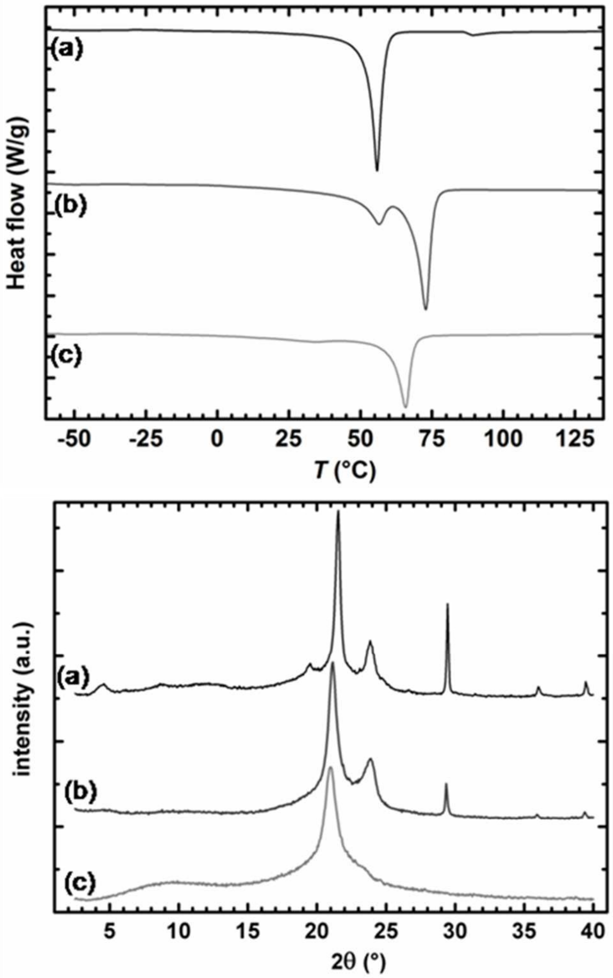


Fig. 5 DSC scans for the second heating runs (top) and X-ray diffraction pattern (bottom) of: (**a**) poly(6-ω-hexadecenlactone); (**b**) poly(6,7-epoxy-ω-hexadecenlactone); (**c**) and poly(hydroxy-ω-hexadecanlactone).

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(ω-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-orthorombic unit cell reported by these authors.[28] 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-orthorombic crystal lattice, and in particular of their regular spacing along the chain axis.[28] 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.[28]

The DSC thermogram of poly(6,7-epoxy-ω-hexadecenlactone) (Fig. 5b, top) showed a large endotherm with two close melting transitions at 56.3 and 72.9 °C and an enthalpy of fusion ΔH_m of

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-orthorombic unit cell of PPDL.[27b] 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 reflection positions indicate 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-hexadecenlactone) chains are presumably arranged in the crystal lattice *ab* plane, in a pseudo-orthorhombic packaging 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 T_m 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 T_m than rigid polymers, provided that they have similar enthalpy of fusion.[29]

DSC analysis of the poly(hydroxy-ω-hexadecanlactone) sample (***c***) (Fig. 5c, top) showed a melting point T_m 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 = 20.94°. 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%.[30] For the poly(hydroxy-ω-hexadecalactone) 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 2θ peak around 20° corresponds to an interplanar distance d=4.25 Å, which is very similar to that observed for poly(hydroxy-ω-hexadecanlactone) sample (**c**) (d = 4.24 Å).[31] Hexagonal and pseudo-hexagonal structures were observed in ethylene/propylene (EP) copolymers[32] 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-ω-hexadecalactone) sample and the presence of strong hydrogen bonds,[33] could also justify that the T_m is not very different from that of poly(6,7-epoxy-ω-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 T_g of -61 °C.

Copolymerization of ω-6-hexadecenlactone with small and medium size lactones.

Copolymerization of ω-6-HDL with ε-CL was performed in conditions analogous to those used for the homopolymerization (xylenes solution, 100 °C). The copolymer composition (50/50 in the two monomers) nicely reflected the feed, as evidenced by the ^{1}H NMR analysis.

A detailed microstructure characterization of the copolymeric chain was achieved through inspection of the ^{13}C NMR spectrum. Indeed, the chemical shifts of the carbonyl, α-methylene, ß-methylene and ω-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 ^{13}C NMR spectra regions of a poly[(6-ω-hexadecenlactone)-*ran*-(ε-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 (L_{HDL}) and caproyl (L_{CL}) sequences were calculated from the ^{13}C NMR data by using previously reported equations.[10c] Interestingly, the average blocks lengths (L_{HDL} = 2.17; L_{CL} = 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 ^{1}H NMR data, ($M_{n,NMR}$ = 15.8 kDa) was in excellent agreement with the theoretical one ($M_{n,th}$ = 15.0 kDa). The experimental GPC value ($M_{n,GPC}$ = 36.0 kDa) resulted to be higher, but the above considerations hold also in this case. However, the GPC trace was monomodal, with dispersities M_w/M_n = 1.6.

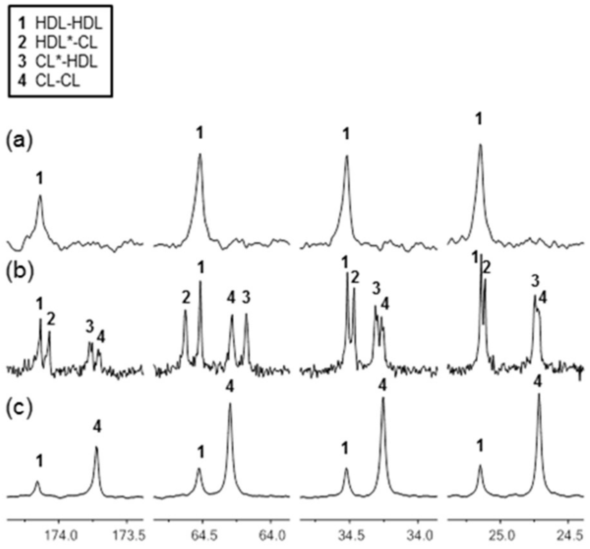


Fig. 6 ^{13}C NMR (300 MHz, $CDCl_3$, RT) spectra of: (a) poly(6-ω-hexadecenlactone); (b) poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)]; (c) poly(6-ω-hexadecenlactone)-*block*-poly(ε-caprolactone).

DSC analysis evidenced a melting peak at T_m = 44.1 °C, with an enthalpy of fusion ΔH_m of 80.7 J/g. The high crystallinity of this random copolymer sample is not surprising, in fact analogous random copolymers of ω-pentadecalactone and ε-caprolactone have been reported to be crystalline over the whole composition range.[10c,35] 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 ω-pentadecalactone/ε-caprolactone copolymers,[35] 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 ^{1}H and ^{13}C NMR, GPC, DSC and 2D NMR experiments (Supporting Information). The poly(6-ω-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 ^{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 ^{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 ^{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 carbon 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 ($-CH_2O-$) of the 6HDL next to the CL carbonyl were respectively observed at 34.3 and 64.6 ppm. Attributions were performed by comparison with the spectra of the PCL and P(6HDL) homopolymers and with that of the poly[(6-ω-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 ΔH_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, ΔH_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 ω-pentadecalactone/ε-caprolactone copolymers the PDL units are included in the PCL crystal phase.[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[36] and it preferentially occurs when comparable fractions of each copolymer components are present.[36a,c]

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 alkoxy group is dramatically hampered for steric reason.[10f] A similar effect should also be significant in our system.

The poly(6-ω-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, ^{1}H and ^{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 $Al-OCH_3$ 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 ^{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.[4e] DSC analysis of the poly(6-ω-hexadecenlactone)-*block*-poly(*rac*-lactide) copolymer showed a melting peak at 49.3 °C (ΔH_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 ΔH_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.

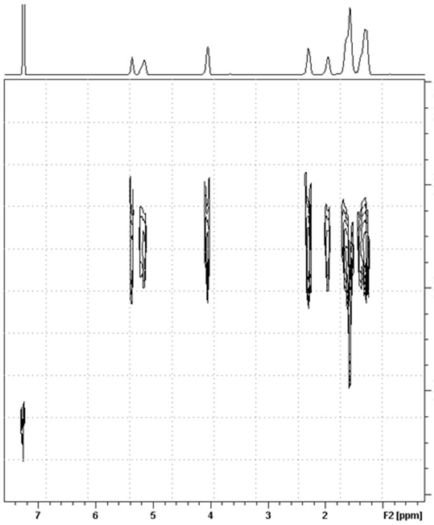


Fig. 7. 2D DOSY NMR (400 MHz, $CDCl_3$, RT) of poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)]-*block*-poly(*rac*-lactide), recorded employing δ = 1000 μs and Δ = 0.8 s. Signals at 7.26 and 1.56 ppm are relative to deuterated solvent residual protic signal ($CHCl_3$) and to adventitious water, respectively.

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-ω-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 εCL (50/ 50) in xylenes 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 at 38.8 °C, and an enthalpy of fusion ΔH_m of 46.9 J/g.

Also in this case the stereoirregular LA sequences do not crystallize, therefore the crystallinity is due to cocrystallization of random sequences of monomers 6HDL and ε-CL. The observed decrease of T_m with respect to the poly[(6-ω-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.[37]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 transesterification reactions preventing the formation of diblock copolymers. In particular, several aluminum based complexes have been explored in the sequential polymerization of macrolide and small lactones.[10c,d] 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.[10d] The salicylaldiminato aluminium 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 ω-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(ω-6-hexadecenlactone) itself, but also the epoxy-functionalized and the hydroxylated derivatives are semicrystalline. While the poly(ω-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 ω-6-hexadecenlactone with smaller ring size cyclic esters to block and random copolymers. Moreover we proposed the poly(ω-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

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† Electronic Supplementary Information (ESI) available: NMR, DSC and X ray diffraction analysis of the polymers .See DOI: 10.1039/b000000x/

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19 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 togheter 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.[4f]

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.[10g] Thus, in the experimental conditions of Table 1, the equilibrium is shifted versus the linear polymers.

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