Tetrahedron: *Asymmetry* 23 (2012) 867–875

Contents lists available at SciVerse ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

CAL-B catalyzed synthesis of chiral polyamides

Florent Poulhès [a,b], Dominique Mouysset [a,b], Gérard Gil [c,d,*], Michèle P. Bertrand [a,b,*], Stéphane Gastaldi [a,b,*]

[a] *Aix-Marseille Univ, Institut de Chimie Radicalaire UMR 7273, Equipe CMO, 13397 Cedex 20, Marseille, France*
[b] *CNRS, Institut de Chimie Radicalaire UMR 7273, Equipe CMO, 13397 Cedex 20, Marseille, France*
[c] *Aix-Marseille Univ, ISM2 UMR 7313, Equipe Chirosciences, 13397 Cedex 20, Marseille, France*
[d] *CNRS, ISM2 UMR 7313, Equipe Chirosciences, 13397 Cedex 20, Marseille, France*

ARTICLE INFO

Article history:
Received 19 April 2012
Accepted 22 May 2012

ABSTRACT

CAL-B (Novozym 435) plays a dual role in our approach to chiral polyamides. It is used to introduce the appropriate chirality in the synthesis of monomers (amino-esters and diamines) from racemic 12-methyldodecalactone and then to catalyze their polycondensation. The AB and AABB enzymatic polymerizations have been carried out under reduced pressure; they give rise to optically active polymers in good yield, with a good degree of polymerization, and a narrow polydispersity index. This approach demonstrates that the presence of a methyl group at the stereogenic center at the α-position relative to the nitrogen atom does not slow down the polymerization as compared with the polycondensation of a related achiral monomer.

1. Introduction

Polyamides are widely recognized for their excellent thermal, mechanical and chemical properties.[1] These interesting characteristics, which can be assigned to the polar amide bond, can be coupled with chiroptical effects resulting from the introduction of stereocenters all along the polymeric backbone. The combination of these two kinds of useful properties is very promising for the development of new materials equipped with unique features.[2–7] Indeed, some optically active polyamides can be used as materials for chiral separation membranes or as chiral stationary phases for high performance liquid chromatography, due to their chiral recognition abilities.[8,9] They may also be useful as chiral media for asymmetric synthesis, chiral liquid crystals in ferroelectric and non-linear optical devices.[10–12]

While a large amount of research dealing with the properties of conventional nylons has been performed,[13,14] little has been reported on with regard to optically active non-polypeptidic polyamides, in particular those bearing a stereocenter at the α-position relative to the nitrogen atom. Chiral moieties are usually either included in the main chain,[15,16] or as pendant groups with the aim of improving the hydrolytic degradation of the materials.[17–19] For example, carbohydrates are frequently employed as they provide varied functionalities, degradability, and chirality to the monomeric precursors.[17,20]

The main limitation is the necessity to select precursors from the chiral pool to synthesize optically active monomers, and being able to transmit their chiroptical properties to the polymeric chains. Moreover the monomer structure has to be suitable for the solubility and physical property requirements of the targeted polyamide. Classical experimental conditions used in polyamide syntheses are rather harsh (temperatures ranging from 200 to 300 °C, high pressure, etc)[21–23] and restrict the use of sophisticated monomers. All of these factors prompt the development of alternative strategies for the design of optically active monomers, starting from inexpensive and racemic materials, coupled with a non-racemizing polymerization procedure able to lead to chiral polymers with the intrinsic physical features of polyamides.

Following this guideline, enzymes can play a crucial role. In the last few years, we have been involved in the improvement of formation of the amide bond catalyzed by lipases and proteases (from amines bearing a stereocenter at the α-position relative to the nitrogen atom).[24–26] The ultimate goal was to make it compatible with the thiyl radical-promoted racemization of aliphatic amines in dynamic kinetic resolution processes.[27–31] Our aim was to approach the enzyme-catalyzed synthesis of chiral polyamides, by applying the successful strategy developed by Meijer and coworkers for the synthesis of chiral polyesters starting from racemic monomers.[32–34] To reach this goal, we have recently developed an efficient enzymatic polymerization using lipase B of *Candida Antarctica* (CAL-B).[35] These polymerization experiments were achieved on achiral monomers. It was therefore necessary to check the kinetic compatibility of the enzymatic procedure with an α-substituted optically active monomer.

* Corresponding authors.
E-mail addresses: gerard.gil@univ-amu.fr (G. Gil), michele.bertrand@univ-amu.fr (M.P. Bertrand), stephane.gastaldi@univ-amu.fr (S. Gastaldi).

0957-4166/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetasy.2012.05.021

Herein we report our results on the lipase-mediated synthesis of stereo-regular AB and AABB type polyamides based on an optically active amino-ester or a diamine as monomers. Both monomers were synthesized from racemic 12-methyldodecalactone (12-Me-DDL). The supported CAL-B [Novozym 435 (N435)] was first used to introduce chirality into the structure of the monomers via a kinetic resolution of the starting materials, and then to incorporate this chirality all along the polyamide chain *via* enzymatic polymerization.

2. Results and discussion

2.1. Monomers synthesis

In order to investigate both AB and AABB type polymerizations, optically active diamine (*R,R*)-**1**, aminoester (*R*)-**2** and diester **3** (Fig. 1) were synthesized.

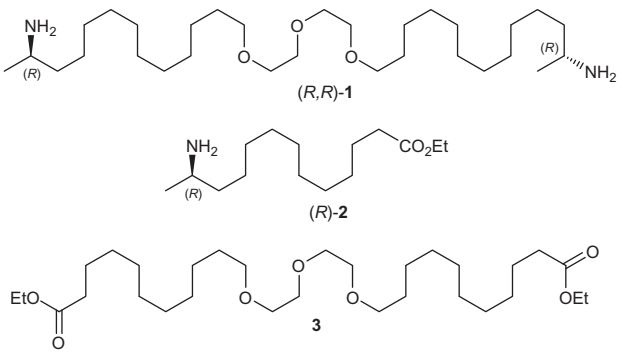


Figure 1. Structure of monomers (*R,R*)-**1**, (*R*)-**2** and **3**.

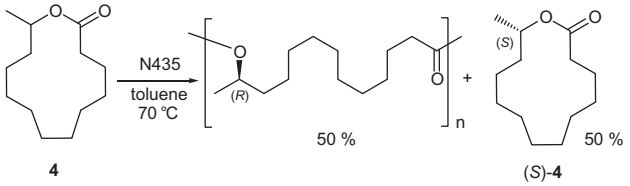
Both monomers **1** and **2** have stereocenters at the α-position relative to the amine function, and include long lipophilic chains to ensure good thermal properties in the resulting polymers and make their purification easier using a precipitation work-up. The configuration of the stereogenic centers has to be (*R*) to be fully consistent with the well-known selectivity of CAL-B in organic media[36] which should provide the targeted polymers with high yields. In the case of diamine **1**, a diethylene glycol moiety was inserted into the backbone of the molecule in order to optimize its solubility all along the polymerization process, and that of the resulting polyamides. This strategy has been used with success in our previous work,[35] for the coupling of diester **3**, with an oxygenated diamine in an AABB polymerization.

Regarding the synthesis of these monomers, the main constraint resides in full control of the configuration of their stereogenic centers, to reach optimal conversions during the enzymatic polymerization. A retrosynthetic route of monomers (*R,R*)-**1** and (*R*)-**2** is shown in Scheme 1.

In order to prepare diamine **1**, the synthesis of the corresponding diazido precursor could be envisaged as the result of a double Williamson etherification involving diethylene glycol and (*R*)-**9** as substrates. The latter could be derived from diol (*S*)-**5**, which presents the opposite configuration at the stereogenic center. This configuration is essential in order to obtain the required (*R*)-stereochemistry through the azidation step.[37] Compound **5** was prepared from the reduction of the optically active lactone (*S*)-**4**.

A similar pathway was followed for the synthesis of monomer **2**, involving the key-intermediate (*S*)-**11** obtained from the ring-opening of (*S*)-**4**. In this retrosynthetic strategy, the key-factor for the successful synthesis of these two monomers is the preparation of lactone (*S*)-**4** with a high enantiomeric excess.

To reach this goal, we chose to apply the strategy developed by Meijer et al. for the enantioselective ring-opening polymerization (ROP) of ω-methylated lactones, as shown in Scheme 2.[32]

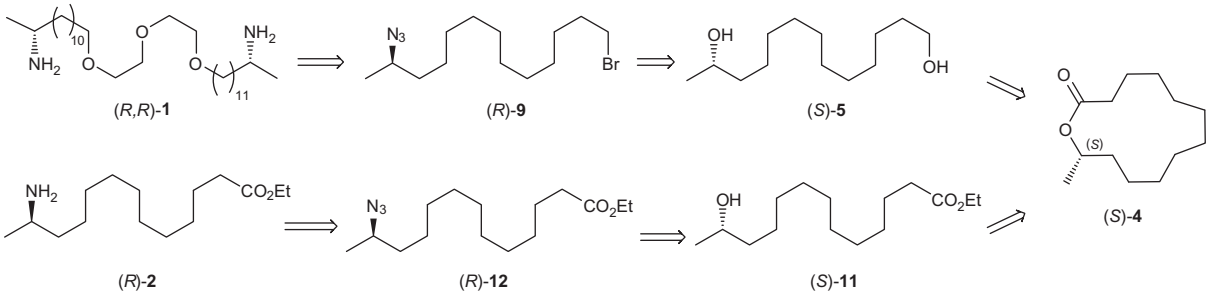


Scheme 2. Enzyme-mediated kinetic resolution polymerization of racemic methyldodecalactone.

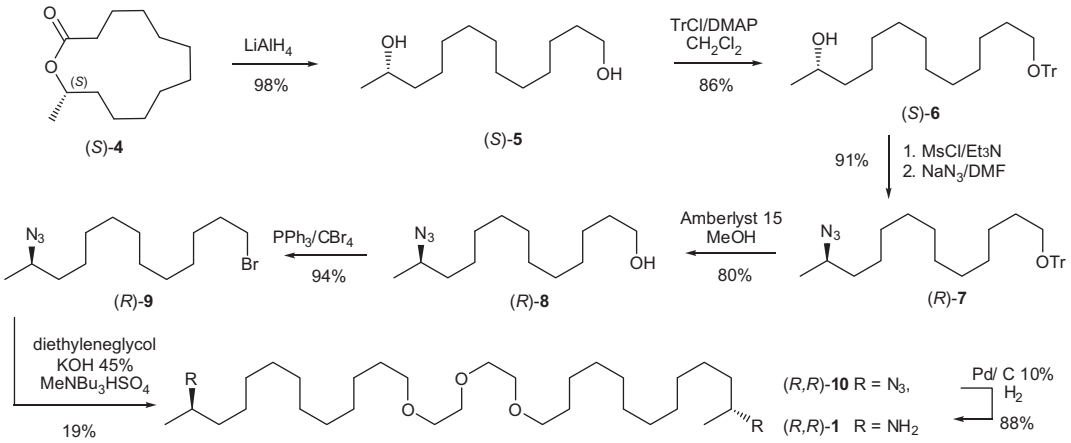
These authors have shown that the enantioselectivity of the enzymatic process depended on the ring-size of the ω-methylated lactones. This feature, assigned to the conformation of the ester bond of the lactone, has been used by the same group to synthesize enantiopure polyesters with excellent enantiomeric excess. When applied to 12-Me-DDL, this straightforward kinetic resolution polymerization allowed the isolation of the corresponding (*R*)-polyester with excellent enantiomeric excess (>99%), and the non-reactive enantiomer (*S*)-**4** in 50% yield with optimal ee (>99%).

The synthesis of diamine **1** could be achieved from lactone (*S*)-**4** (Scheme 3). The reduction of the lactone using lithium aluminium hydride afforded the linear diol (*S*)-**5**. Selective protection of the primary hydroxyl function with a trityl group was successfully completed. The functionalization of the remaining alcohol was achieved through a mesylation/azidation sequence. These last two steps proceeded in good yield, and with inversion of configuration at the stereogenic center.

After removal of the protecting group and bromination of the alcohol, the key intermediate (*R*)-**9** was used in a double Williamson reaction, in the presence of a phase-transfer catalyst.[38] This procedure gave (*R,R*)-**10**, with a modest yield (19%). The final step



Scheme 1. Retrosynthetic analysis of monomers (*R,R*)-**1** and (*R*)-**2**.



Scheme 3. Synthesis of (*R*,*R*)-**1**.

consisted of the reduction of the two azido functions, to give diamine (*R*,*R*)-**1** in 9.7% overall yield over 8 steps from lactone (*S*)-**4**.

The synthesis of aminoester (*R*)-**2** was performed from the same precursor, starting from lactone (*S*)-**4** via ring-opening in the presence of NaOEt (Scheme 4).

This reaction allowed the preparation of hydroxy-ester **11**, which was then transformed into azide **12**, using the mesylation/azidation sequence. Again, inversion of the configuration of the stereogenic center was achieved during the introduction of the azido group. The last step led to the targeted monomer, with the appropriate configuration for a lipase-promoted polymerization, in 37% overall yield over 4 steps.

2.2. Enzymatic polymerization

Monomers (*R*,*R*)-**1** and (*R*)-**2** were used in an enzymatic polymerization procedure. The experimental conditions were transposed from our previous work,[35] which involved diphenyl ether as the solvent. It has been previously demonstrated that this solvent, when used in small quantities, allowed to perform enzymatic polymerization in 'pseudo-bulk' conditions without any drawbacks due to viscosity and limited-diffusion of the reactive species.[39,40] Moreover, its high boiling point allowed the enzymatic reaction to be performed at 80 °C under a reduced pressure of 3 mbars, with continuous removal of the ethanol formed during the polymerization, in order to drive the reaction forward.

The AB and AABB polymerizations were then investigated, following this experimental procedure. In the case of the AABB reaction (Scheme 5), a 1:1 ratio of diamine **1** and diester **3** was used, as previous work had clearly demonstrated that this stoichiometry was well suited to the enzymatic polymerization.[41]

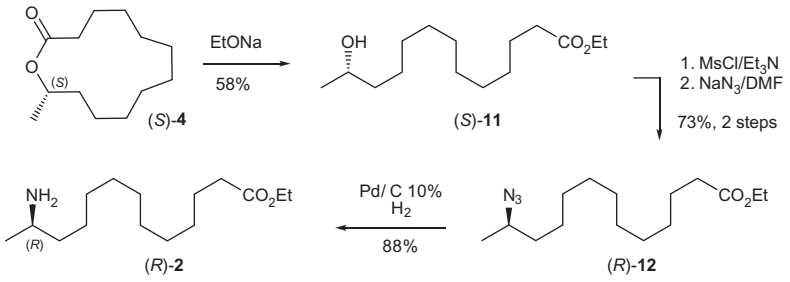
In both cases, the resulting oligomeric products were isolated by precipitation. The average molecular masses in number (M_n) and in weight (M_w) were determined by Size-Exclusion Chromatography (SEC) after isolation and drying of the product. The main results are shown in Table 1.

In the case of the AABB polymerization involving monomers **1** and **3** (Table 1, entry a), SEC analyses highlighted a very good value of the average degree of polymerization, close to sixteen units, which falls in the same range as the best results published in the field of lipase-assisted synthesis of polyamides.[35,42] The excellent value of the average degree of polymerization, due to the good yields in the isolated polymers, tends to prove that the presence of the methyl group at the α-position relative to the nitrogen atom did not hamper the progression of the reaction. The low value of the polydispersity index is in good agreement with the reported data.[35] These data confirmed the asset of the enzyme-mediated synthesis of polyamides. The specific rotation of polymer **P(1)** was found to be +11.7, thus confirming the chiral nature of the macromolecule. The low magnitude of this value could be easily explained by the symmetry in the structure of the monomers. Moreover, the flexibility endowed by the insertion of an oxyethylene moiety inside the polymeric backbone increases the number of available conformations for the polymer in solution.[2]

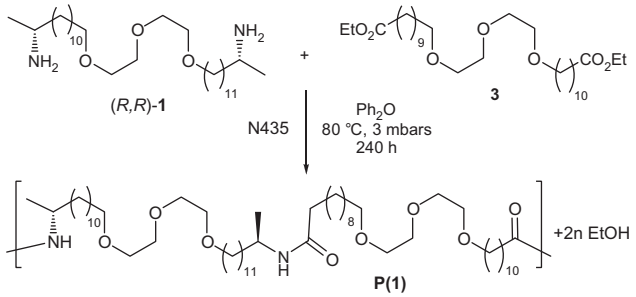
In the case of monomer **2** (entry c), SEC data were much more disappointing (Scheme 6). The reaction failed to reach a DPn higher than four units, which corresponds to an average molecular mass close to 700 daltons. Low yields and the recovery of a significant amount of the starting material isolated at the end of the reaction were observed.

It is worth noting, however, that in both cases, the polyamide synthesis did not proceed without a catalyst (Table 1, entries b and d), thus ruling out the possibility of a non-catalyzed reaction at this temperature.[42]

The efficiency of the polymerization involving monomers **1** and **3** proved that the poor *Mw* and *Mn* values obtained with amino-ester **2** probably did not result from the presence of the stereogenic center close to the reactive amine function. Since deactivation of



Scheme 4. Synthesis of (*R*)-**2**.

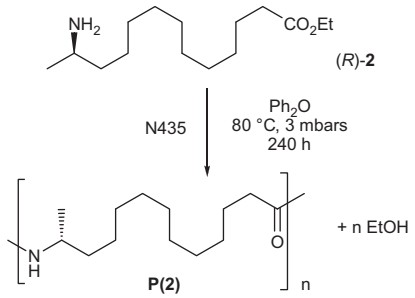


Scheme 5. Novozym 435-catalyzed polymerization of monomers (*R*,*R*)-**1** and **3**.

Table 1
Characterization of the optically active polyamides synthesized.

Entry	Monomer	Yield	M_n	M_w	PDI	DPn
a	**1** + **3**	87%	14718	19280	1.31	15.7
b[a]	**1** + **3**	nd[b]	1781	3757	2.11	1.9
c	**2**	64%	689	1316	1.91	3.3
d[a]	**2**	nd[b]	—[c]	—	—	—

[a] Blank experiments without N435.
[b] Not determined.
[c] The conversion value is lower than the limit of detection by NMR.



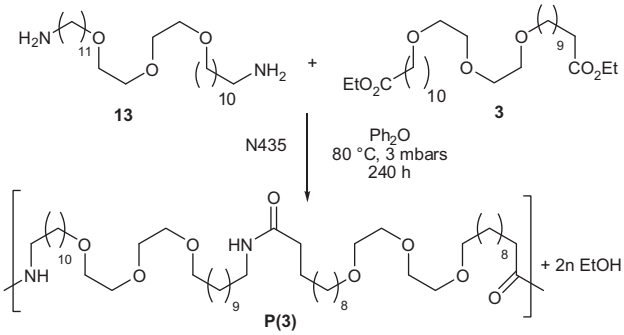
Scheme 6. Novozym 435-catalyzed polymerization of monomer (*R*)-**2**.

the catalyst could not be suspected at this temperature,[43] and as water-content was limited by using a drastic drying procedure,[44] the poor solubility of the monomer in diphenyl oxide, which is responsible for the early precipitation of oligomeric chains of low molecular masses, is the most likely explanation for these results (Table 1, entry c). It therefore impedes the propagation of the polymerization. This provides additional evidence for the advantage of inserting a diethylene glycol moiety into the backbone of monomers **1** and **3**, in order to overcome the solubility problem, and to optimize the polymerization procedure.

In order to fully evaluate the influence of the stereogenic center on the smooth progress of the reaction, the evolution of the conversion of diamine **1** during the reaction was monitored. This enabled us to draw a parallel with the conversion of diamine **13** in its copolymerization with diester **3** in the presence of Novozym 435 (Scheme 7).

This polymerization, already described,[35] has the advantage of proceeding under the same experimental conditions, that is, in diphenyl oxide under reduced pressure. Moreover, diamine **13** presents a backbone rather similar to that of diamine **1**, with long alkyl chains on both sides of a central diethylene glycol moiety. The evolution of the conversion of these diamines is shown in Table 2. The conversions were assessed by ^{1}H NMR spectroscopy.[33]

These results demonstrate that the presence of the stereogenic center α to the amino group generally did not notably influence the rate of the reaction during the polymerization. The progression of the polymerization involving the non-chiral diamine is faster than



Scheme 7. Novozym 435-catalyzed synthesis of model polymer **P(3)**.

Table 2
Evolution of the conversion (%) of diamine (***R*,*R***)-1 and 13 during the polymerization

Diamine	After 1 h[a]	After 45 h[a]	After 240 h[a]	DPn
13	57	77	94	16.7
1	48	75	93	15.7

[a] Conversion is based on the total conversion of amino groups.

that involving (*R*-*R*)-**1** during the first few hours of the reaction. After one hour of polymerization 57% of non-chiral diamine **13** was inserted inside the polymeric backbone versus only 48% for the chiral substrate. However, this slight imbalance is no longer observed after 45 h of reaction. At this stage, the conversion of **1** caught up the level of that of **13** with values close to 75% for both monomers. At the end of the reaction, the conversion levels were similar, which shows that the difference in propagation rate observed at the very beginning has no influence on the progression of the polymerization reaction, and as a result, on the average degree of polymerization of the isolated product.

2.3. Polymer characterization

Isolated polymer **P(1)** was then fully characterized and its ^{1}H NMR spectrum is shown in Fig. 2. It is important to note that this spectrum was recorded in $CDCl_3$, thus confirming the good solubility of the polymer obtained in this common organic solvent despite its high methylene content, the high crystallinity, and the low solubility often associated with polyamide backbones.[45]

In this spectrum, the characteristic signals of the ethyl carboxylate terminations are indicated ($CH_2C(O)OCH_2CH_3$). The characteristic signals of the amine terminations (CH_2NH_2), expected at 2.95 ppm, are hardly visible. The signals corresponding to the CH_2O groups are lettered **d**, **d'**, and **c**; those of the methylene protons at the α-position to the amide nitrogen atom are lettered **b**; the signals of the methylene protons at the α-position relative to the amide carbonyl group are lettered **e**; the other methylene group signals are indicated by letters **f**, **g**, and **h**; the amide group protons give rise to the broad singlets lettered **a**.

The FTIR spectrum (Fig. 3) shows the characteristic absorption of C=O stretching (amides band I) at 1639 cm^{-1}. The low frequency is in agreement with a hydrogen bonding association of the amido groups. The amide band II (N–H bending vibration) absorbs at 1553 cm^{-1}, whereas the N–H stretching vibrations absorb at 3292 cm^{-1}. The rather sharp characteristic anti-symmetric and symmetric elongations of methylene groups at 2933 and 2849 cm^{-1} also argue in favor of a spatial proximity between the alkyl chains due to van der Waals interactions.[46] This phenomenon has already been observed in non-chiral polyamide samples. It is a consequence of the introduction of long methylene chains into the backbone of monomers.

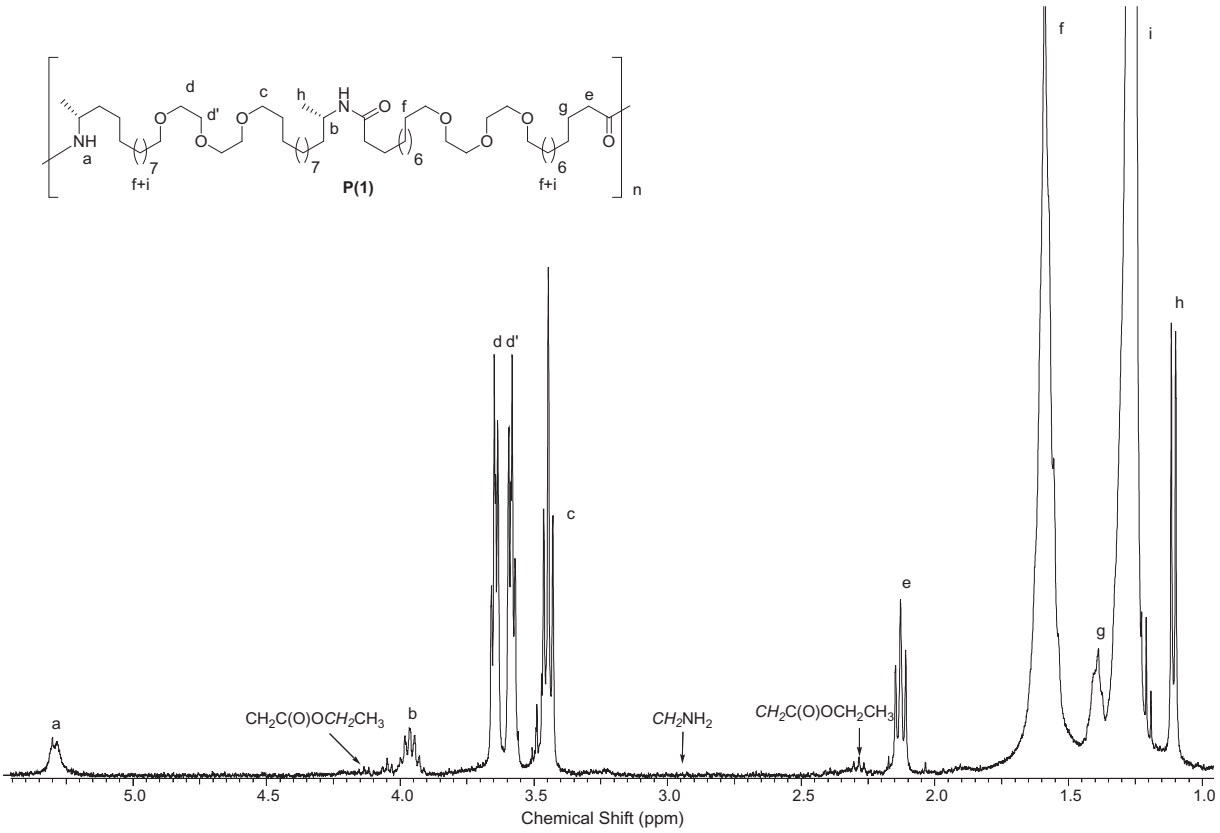


Figure 2. ^{1}H NMR spectrum of polymer **P(1)**.

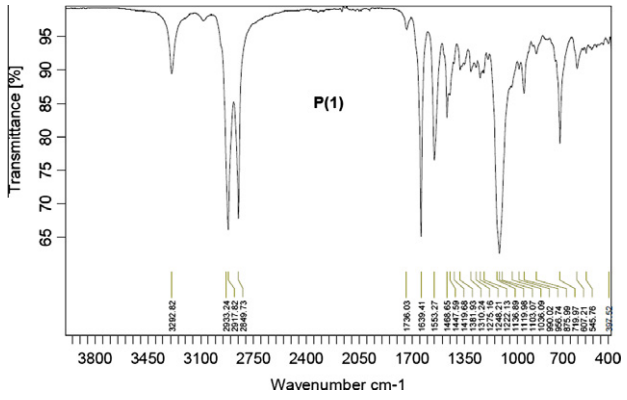


Figure 3. FTIR spectrum of polymer **P(1)**.

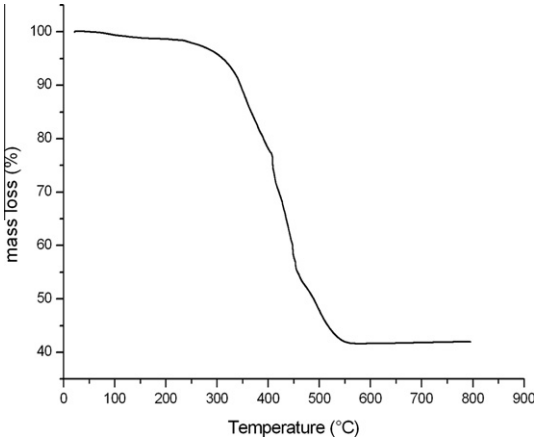


Figure 4. TGA of polymer **P(1)**.

2.4. Bulk properties

Polymer **P(1)** was subjected to a thermogravimetric analysis in order to evaluate its resistance to heat. The results are shown in Fig. 4.

This analysis clearly shows that the degradation of **P(1)** takes place in one straight stage spread between 310 and 520 °C. In this temperature range, the sample loses more than 50% of its weight. This simple behavior fits well with the good mass properties highlighted in Table 1, as a low value for the polydispersity index is often correlated with a good thermal resistance. The reported thermal behavior of polymer **P(3)** is in agreement with the known data corresponding to poly(ether)amides.[47,48]

A sharp melting endotherm at 95.4 °C was observed in the DSC analysis of **P(1)**, thus confirming the crystalline character of this polyamide (Fig. 5).

This supports the idea of supramolecular organization between polymeric chains, probably enhanced by the strong hydrogen bonding interactions already highlighted by FTIR.

In the WAXD spectrum of **P(1)** (Fig. 6), a rather large peak was observed, spread between the scattering angles of 18° and 25°. This could be assigned to the superimposed peaks of close values of scattering angles.[49] According to the literature, some crystalline polyetheramides exhibit a similar behavior. It is difficult to conclude whether the second peak (between 36° and 38°) indicates the presence of two superimposed crystal-like phases, due to the

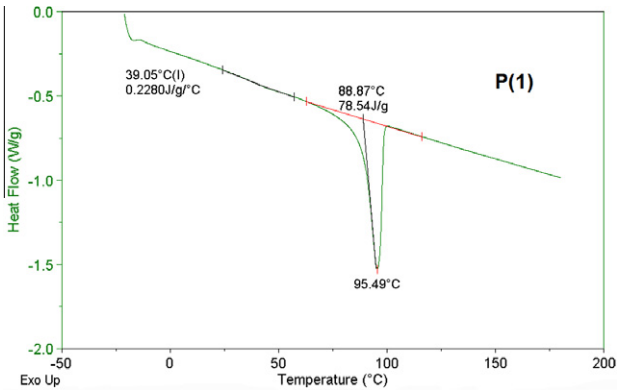


Figure 5. DSC data of polymer **P(1)**.

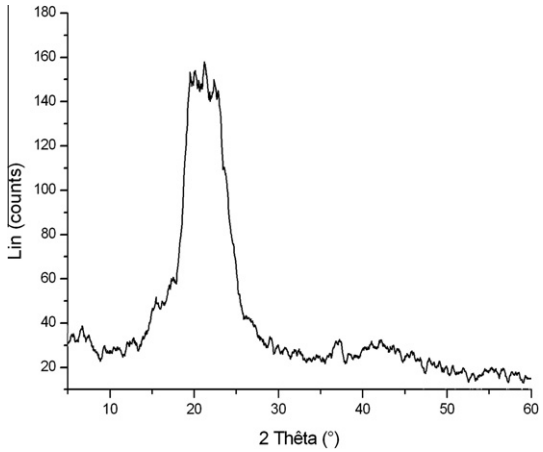


Figure 6. Wide angle X-ray diffraction analysis of polymer P(**1**).

lack of references for WAXD patterns for this type of structure, especially when dealing with optically active macromolecules.

3. Conclusion

Herein, we have reported the lipase-catalyzed synthesis of non-peptidic optically active polyamides. These polymers were prepared from chiral monomers with stereocenters that have the appropriate configuration to be fully compatible with the enzymatic procedure. The synthesis of the optically active monomers from racemic 12-methyldodecalactone is based on a lipase-mediated kinetic resolution polymerization, which enables the enantioselective formation of the targeted precursors. The AABB enzymatic polymerization was carried out under reduced pressure, and gave rise to an optically active polymer, obtained in a good yield, with a high degree of polymerization, and a narrow polydispersity index. This polyamide exhibits interesting physical properties. This work is an additional proof of the versatility of lipases as highly enantioselective catalysts that can be used to control both the stereospecific synthesis of chiral monomers from achiral starting materials, and to polymerize them in an efficient manner.

4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere. Solvents were degassed before use. The ^{1}H and ^{13}C NMR spectra were recorded at 400 or 300 MHz and 100 or 75 MHz, respectively. Chemical shifts (δ) are reported in ppm and coupling constants (J) are given in Hz. Ethyl 11-{2-[2-(10-ethoxycarbonyl-decyloxy)-ethoxy]-ethoxy}-undecanoate **3** and 11-{2-[2-(11-amino-undecyloxy)-ethoxy]-ethoxy}-undecylamine **13** were prepared according to literature procedures.[35]

4.2. Gel permeation chromatography analyses

The analyses and the monitoring of polymerization reactions were achieved by gel permeation chromatography (GPC) using Macherey-Nagel Nucleogel GPC 500, 100, and 50 (10 μm porosity; 300 × 7.7 mm) analytical columns fitted in series after a GPC (50 × 7.7 mm) pre-column. The system was piloted by Azur (Jasco©) software, and equipped with Waters 600 pump, a Varian oven (model 510), and a Waters differential diffractometer (model 410). Analyses used a 0.1 M solution of LiBr in *N,N*-dimethylacetamide (ACROS, HPLC grade, degassed and filtered on a Millipore membrane before use) as the solvent at 80 °C (0.6 mL/min rate of flow). Sample concentrations of 1–3 mg/mL and injection volumes of 200 μL were used. Toluene (500 μL/100 mL) was introduced in the mobile phase as an elution marker. System calibration data and relative molar mass calculations were acquired and processed using PSS WinGPC (Polymer laboratories) software. Narrow distribution polyethylene glycol standards (Varian) with *Mn* values of 106, 194, 430, 615, 1010, 1970, 3390, 7980, 12140, and 21030 Da were used to establish the calibration curves. Weight-average molecular weight (*Mw*), number-average molecular weight (*Mn*), and polydispersity index (PDI= *Mw*/*Mn*) were calculated from the chromatograms.

FTIR data were recorded with a Vertex 70 Bruker spectrometer. Attenuated Total Reflectance (ATR) analyses were performed with a cell centered on a germanium crystal. The acquisition of data was processed with EZ OMNIC 7.2a software. DSC analyses were effected with a Q200 DSC TA Instrument, the calorimeter under nitrogen (30 mL/min) connected to a cryostat from the same manufacturer. DSC scans were run at temperatures ranging from −150 to 150 °C with a heating rate of 5 °C/min. A controlled cooling rate of −10 °C was applied between heating runs. TGA analyses were recorded with TGA Q500 TA Instruments apparatus, under an air flux (60 mL/min). The measurements were carried out with a rate of 10 °C/min. WAXD spectrum was registered on powders with a Siemens D5000 XRD diffractometer using Cu (40 Kv 40 mA) Kα as source of radiations (λ = 1.54 Å) and a scintillator (θ–2θ). WAXD were obtained by setting a step size of 0.04 with a scattering angle 2θ ranging between 10° and 45 °.

4.2.1. (*S*)-Tridecane-1,12-diol 5

To a 0 °C solution of (*S*)-12-methyldodecalactone[32] **4** (1 g, 4.7 mmol) in Et_2O (25 mL) was added $LiAlH_4$ (182 mg, 4.8 mmol). The reaction mixture was allowed to warm slowly to room temperature and stirred overnight at rt. Next, $Na_2SO_4{\cdot}10\ H_2O$ (1.5 g, 4.8 mmol) was added and the resulting suspension was stirred for 5 h at rt. After drying over $MgSO_4$ and concentration, the crude material was subjected to column chromatography on silica gel (pentane/AcOEt 90/10 to 70/30) to give **5** (999 mg, 4.61 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): 3.80 (sext, J = 6.0, 1H), 3.63 (t, J = 6.6, 2H), 1.60–1.50 (m, 6H), 1.48–1.24 (m, 16H), 1.21 (d, J = 6.0, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 68.1 (CH), 63.0 (CH_2), 39.3 (CH_2), 32.8 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 ($CH_2 \times 2$), 25.7 (CH_2), 25.7 (CH_2), 23.4 (CH_3). IR (ATR, cm^{-1}): 3342, 2925, 2848, 1469, 1461, 1124, 1056, 657. $[\alpha]_D^{25} = +4.5$ (c 1.5, $CHCl_3$). HRMS ($[M+H]^+$, ESI): m/z calcd for $C_{13}H_{29}O_2$: 217.2162. Found: 217.2157.

4.2.2. (*S*)-13-(Trityloxy)tridecan-2-ol 6

A solution of diol **5** (664 mg, 3 mmol), triphenylmethane chloride (1.112 g, 3.98 mmol), and DMAP (50 mg, 0.4 mmol) in pyridine (6 mL) was stirred for 60 h at rt. After the addition of water (300 μl), the solution was concentrated. The crude material was diluted with water and extracted with dichloromethane (3 × 20 mL). The organic phase was then washed with 1 M aqueous HCl, water and brine, and dried over $MgSO_4$. After filtration and concentration, the crude material was subjected to column chromatography on silica gel (pentane/AcOEt 100/0 to 92/8) to give **6** (1.183 g, 2.58 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.48 (m, 6H), 7.38–7.22 (m, 9H), 3.81 (sext, *J* = 6.1, 1H), 3.08 (t, *J* = 6.5, 2H), 1.65 (quint, *J* = 6.5, 2H), 1.53–1.24 (m, 19H), 1.21 (d, *J* = 6.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.6 (C), 128.7 (CH), 127.7 (CH), 126.8 (CH), 86.3 (C), 68.2 (CH), 63.7 (CH_2), 39.4 (CH_2), 30.1 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2 × 3), 29.5 (CH_2), 26.3 (CH_2), 25.8 (CH_2), 23.5 (CH_3). IR (ATR, cm^{-1}): 3396, 3089, 3062, 3053, 2927, 2854, 1598, 1489, 1448, 1089, 1074, 1066, 1027, 761, 702, 634. $[\alpha]_{365}^{25} = +10.4$ (*c* 0.3, $CHCl_3$). HRMS ([M+Na]$^+$, ESI): *m/z* calcd for $C_{32}H_{42}O_2Na$: 481.3077. Found: 481.3075.

4.2.3. (*R*)-(12-Azidotridecyloxy)triphenylmethane 7

To a solution of alcohol **6** (3.15 g, 6.86 mmol) and triethylamine (1.17 g, 11.52 mmol) in dichloromethane (30 mL) was added at 0 °C methanesulfonyl chloride (1.10 g, 9.6 mmol). The reaction mixture was allowed to warm slowly to room temperature. After 30 min (TLC monitoring), the reaction mixture was diluted with water, washed with 1 M aqueous HCl and brine, and dried over $MgSO_4$. After filtration and concentration, the corresponding mesylate was obtained (1.05 g, 3.12 mmol, 81%) and used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): 7.44 (m, 6H), 7.32–7.19 (m, 9H), 4.78 (sext, *J* = 6.3, 1H), 3.03 (t, *J* = 6.6, 2H), 2.98 (s, 3H), 1.65–1.56 (m, 2H), 1.41 (d, *J* = 6.3, 3H), 1.40–1.21 (m, 18H). A solution of the freshly prepared mesylate and sodium azide (1.79 g, 27.44 mmol) in DMF (40 mL) was stirred overnight at 60 °C. The reaction mixture was diluted with water (400 mL) and extracted with AcOEt (3 × 50 mL). The organic phase was then washed with water and brine, and dried over $MgSO_4$. After filtration and concentration, the crude material was subjected to column chromatography on silica gel (pentane/AcOEt 100/0 to 95/5) to give **7** (2.94 g, 6.23 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.44 (m, 6H), 7.32–7.19 (m, 9H), 3.41 (sext, *J* = 6.3, 1H), 3.04 (t, *J* = 6.6, 2H), 1.61 (quint, *J* = 7.2, 2H), 1.52–1.21 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.6 (C), 128.8 (CH), 127.7 (CH), 126.8 (CH), 86.3 (C), 63.7 (CH_2), 58.1 (CH), 36.2 (CH_2), 30.1 (CH_2), 29.6 (CH_2 × 2), 29.6 (CH_2), 29.5 (CH_2 × 2), 29.4 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 19.5 (CH_3). IR (ATR, cm^{-1}): 3089, 3062, 3053, 2929, 2856, 2100, 1600, 1490, 1448, 1089, 1072, 1058, 744, 703, 632. $[\alpha]_{365}^{25} = -41.3$ (*c* 1.0, $CHCl_3$). HRMS ([M+Na]$^+$, ESI): *m/z* calcd for $C_{32}H_{41}N_3ONa$: 506.3142. Found: 506.3137.

4.2.4. (*R*)-12-Azidotridecan-1-ol 8

A solution of **7** (700 mg, 1.48 mmol) and Amberlyst 15 (600 mg) in methanol (20 ml) was stirred overnight at 45 °C. After filtration and concentration, the crude material was subjected to column chromatography on silica gel (pentane/AcOEt 100/0 to 90/10) to give **8** (286 mg, 1.18 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): 3.64 (t, *J* = 6.6, 2H), 3.41 (sext, *J* = 6.4, 1H), 1.57 (quint, *J* = 6.6, 2H), 1.51–1.26 (m, 19H), 1.24 (d, *J* = 6.4, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 63.0 (CH_2), 58.0 (CH), 36.2 (CH_2), 32.8 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.1 (CH_2), 25.7 (CH_2), 19.4 (CH_3). IR (ATR, cm^{-1}): 3375, 2929, 2854, 2102, 1467, 1062. $[\alpha]_{365}^{25} = -63.6$ (*c* 1.2, $CHCl_3$). HRMS ([M+NH_4]$^+$, ESI): *m/z* calcd for $C_{13}H_{31}N_4O$: 259.2492. Found: 259.2491.

4.2.5. (*R*)-12-Azido-1-bromotridecane 9

To a 0 °C solution of tetrabromomethane (3.592 g, 10.8 mmol) in dry THF (15 mL) was added triphenylphosphine (2.471 g, 9.4 mmol). After complete consumption of triphenylphosphine, alcohol **8** (1.137 g, 4.7 mmol) in dry THF (5 mL) was added at 0 °C. Next, the solution was stirred for 96 h at 30 °C. After concentration, the crude material was subjected to column chromatography on silica gel (pentane/AcOEt 100/0 to 90/10) to give **9** (1.35 g, 4.4 mmol, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): 3.42 (m, 1H), 3.41 (t, *J* = 6.8, 2H), 1.86 (quint, *J* = 6.8, 2H), 1.52–1.26 (m, 18H), 1.24 (d, *J* = 6.5, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 58.2 (CH), 36.3 (CH_2), 34.2 (CH_2), 33.0 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 28.9 (CH_2), 28.3 (CH_2), 29.3 (CH_2), 26.2 (CH_2), 19.6 (CH_3).

4.2.6. (*R*)-1-(2-(2-((*R*)-12-Azidotridecyloxy)ethoxy)ethoxy)-12-azidotridecane 10

A solution of **9** (1.35 g, 5.2 mmol), diethylene glycol (230 μl, 2.36 mmol), and NBu_4HSO_4 (160 mg, 0.5 mmol) was stirred vigorously, after which KOH 45% (1.3 mL) was added dropwise. The resulting solution was stirred for 48 h (TLC monitoring) at 70 °C. After dilution with CH_2Cl_2 (10 mL) and water (10 mL), the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic fractions were washed with brine and dried over $MgSO_4$. After concentration, the crude material was subjected to column chromatography on silica gel (pentane/AcOEt 100/0 to 95/5) to give **10** (247 mg, 0.44 mmol, 19%). ^{1}H NMR (400 MHz, $CDCl_3$): 3.68–3.56 (m, 8H), 3.47 (t, *J* = 6.8, 4H), 3.42 (sext, *J* = 6.4, 2H), 1.60 (quint, *J* = 7.1, 4H),1.52–1.28 (m, 36H), 1.24 (d, *J* = 6.4, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 70.6 (CH_2), 70.7 (CH_2), 70.1 (CH_2), 58.0 (CH), 36.2 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.1 (CH_2), 19.5 (CH_3). IR (ATR, cm^{-1}): 2927, 2854, 2102, 1465, 1122, 1066. $[\alpha]_{365}^{25} = -45.3$ (*c* 0.4, $CHCl_3$). HRMS ([M+NH_4]$^+$, ESI): *m/z* calcd for $C_{30}H_{64}N_7O_3$: 570.5065. Found: 570.5069.

4.2.7. (*R*)-13-(2-(2-((*R*)-12-Aminotridecyloxy)ethoxy)ethoxy)tridecan-2-amine 1

A solution of **10** (245 mg, 0.44 mmol), and Pd/C (10%) (50 mg) in EtOH (30 mL) was stirred overnight at rt under H_2 (8 bars). After filtration and concentration, **1** was obtained (194 mg, 0.39 mmol, 88%) and used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): 3.66–3.57 (m, 8H), 3.45 (t, *J* = 6.8, 4H), 2.87 (m, 2H), 1.57 (m, 8H), 1.34–1.24 (m, 36H), 1.06 (d, *J* = 6.3, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 71.6 (CH_2), 70.7 (CH_2), 70.1 (CH_2), 47.0 (CH), 40.2 (CH_2), 29.7 (CH_2), 29.6 (2 × CH_2), 29.6 (3 × CH_2), 29.5 (CH_2), 26.4 (CH_2), 26.1 (CH_2), 23.9 (CH_3). IR (ATR, cm^{-1}): 3326, 2919, 2850, 1591, 1469, 1143. $[\alpha]_{365}^{25} = -1.3$ (*c* 1.0, $CHCl_3$). HRMS ([M+H]$^+$, ESI): *m/z* calcd for $C_{30}H_{65}N_2O_3$: 501.4990. Found: 501.4977.

4.2.8. (*S*)-Ethyl 12-hydroxytridecanoate 11

A solution of (*S*)-12-methyldodecalactone (100 mg, 0.47 mmol) and EtONa (11 mg, 0.47 mmol) in ethanol (5 mL) was stirred for 6 h at reflux (TLC monitoring). After concentration, the crude mixture was diluted with AcOEt (15 mL) and washed successively with water (5 mL), 0.1 M HCl solution (5 mL) and brine (5 mL). After drying over $MgSO_4$ and concentration, **11** was obtained (71 mg, 0.27 mmol, 58%) and was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): 4.05 (q, *J* = 7.3, 2H), 3.70 (sext, *J* = 6.0, 1H), 2.21 (t, *J* = 7.5, 2H), 1.56–1.12 (m, 22H), 1.11 (d, *J* = 6.0, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 173.9 (CO), 68.1 (CH), 60.1 (CH_2), 39.3 (CH_2), 34.4 (CH_2), 29.6 (CH_2 × 2), 29.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 25.7 (CH_2), 25.0 (CH_3), 23.4 (CH_2), 14.2 (CH_3). IR (ATR, cm^{-1}): 3504, 2929, 2856, 1737, 1467, 1375, 1247,

1188, 1130, 1041. $[\alpha]_{Na}^{25} = +2.2$ (*c* 1.3, $CHCl_3$). HRMS ($[M+Na]^+$, ESI): *m/z* calcd for $C_{15}H_{30}O_3Na$: 281.2087. Found: 281.2084.

4.2.9. (*R*)-Ethyl 12-azidotridecanoate 12

To a solution of alcohol **11** (1 g, 3.87 mmol) and triethylamine (587 mg, 5.80 mmol) in dichloromethane (40 mL) was added at 0 °C methanesulfonyl chloride (554 mg, 4.84 mmol). The reaction mixture was then allowed to warm slowly to room temperature. After 3 h, triethylamine (587 mg, 5.80 mmol) and methanesulfonyl chloride (554 mg, 4.84 mmol) were added again. After 6 h, the reaction mixture was diluted with water, washed with 1 M aqueous HCl and brine, and dried over $MgSO_4$. After filtration and concentration, the corresponding mesylate was obtained (1.05 g, 3.12 mmol, 81%) and used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): 4.71 (sext, *J* = 6.3, 1H), 4.05 (q, *J* = 7.3, 2H), 2.93 (s, 3H), 2.21 (t, *J* = 7.5, 2H), 1.69–1.52 (m, 4H), 1.34–1.16 (m, 20H). A solution of the freshly prepared mesylate and sodium azide (1.26 g, 19.35 mmol) in DMF (30 mL) was stirred overnight at 60 °C. The reaction mixture was diluted with water (400 mL) and extracted with AcOEt (3 × 50 mL). The organic phase was then washed with water and brine, and dried over $MgSO_4$. After filtration and concentration, the crude material was subjected to column chromatography on silica gel (pentane/AcOEt 100/0 to 95/5) to give **12** (807 mg, 2.85 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): 4.05 (q, *J* = 7.3, 2H), 3.34 (sext, *J* = 6.8, 1H), 2.21 (t, *J* = 7.5, 2H), 1.56–1.16 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$): 173.9 (CO), 60.1 (CH_2), 58.0 (CH), 36.5 (CH_2), 36.1 (CH_2), 34.4 (CH_2), 31.4 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 26.1 (CH_2), 25.0 (CH_2), 19.4 (CH_3), 14.1 (CH_3). IR (ATR, cm^{-1}): 2929, 2856, 2102, 1737, 1467, 1378, 1253, 1186, 1120, 1047. $[\alpha]_{365}^{25} = -20.4$ (*c* 1.4, $CHCl_3$). HRMS ($[M+Na]^+$, ESI): *m/z* calcd for $C_{15}H_{29}N_3O_2Na$: 306.2151. Found: 306.2153.

4.2.10. (*R*)-Ethyl 12-aminotridecanoate 2

A solution of **12** (800 mg, 2.82 mmol), Pd/C (10%) (50 mg) in EtOH (60 mL) was stirred overnight at rt under H_2 (8 bars). After filtration and concentration, **2** was obtained (639 mg, 2.49 mmol, 88%) and used without further purification.^{1}H NMR (300 MHz, $CDCl_3$): 4.05 (q, *J* = 7.3, 2H), 2.80 (m, 1H), 2.21 (t, *J* = 7.3, 2H), 1.54 (quint, *J* = 7.0, 2H), 1.56 (m, 2H), 1.6–1.2 (m, 19H), 0.98 (d, *J* = 6.3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 173.1 (CO), 60.1 (CH_2), 46.9 (CH), 40.9 (CH_2), 34.4 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 26.4 (CH_2), 24.9 (CH_2), 23.8 (CH_3), 14.2 (CH_3). IR (ATR, cm^{-1}): 3413, 2927, 2856, 1737, 1596, 1467, 1375, 1186. $[\alpha]_{Na}^{25} = -0.6$ (*c* 1.4, $CHCl_3$). HRMS ($[M+H]^+$, ESI): *m/z* calcd for $C_{15}H_{32}NO_2$: 258.2427. Found: 258.2429.

4.2.11. Polyamide P(1)

A solution of diamine **1** (135 mg, 0.25 mmol) and diester **3** (132 mg, 0.25 mmol) in Ph_2O (515 mg) was stirred 15 min at rt, after which Novozym 435 (50 mg) was added. After filtration and concentration, **2** was obtained (639 mg, 2.49 mmol, 88%) and used without further purification. The mixture was then heated at 80 °C under 3 mbars for 240 h. After completion, the mixture was cooled to 60 °C and 10 mL of chloroform was added. The hot solution was filtered to remove the enzyme, the latter was washed with hot chloroform and the solution was concentrated up to 2 mL. The precipitate formed after the addition of methanol was filtered, and then washed with the same solvent. The polymer was recovered after drying at 40 °C under vacuum for 48 h (233 mg). ^{1}H NMR (400 MHz, $CDCl_3$): 5.3 (br s, NH), 4.13 (q, *J* = 7.3, OCH_2CH$_3$ terminations), 3.96 (pseudo quint, *J* = 6.5, CH_2CH(NH)CH_3), 3.67–3.56 (m, OCH_2CH_2OCH_2CH_2O), 3.45 (t, *J* = 6.8, CH_2OCH_2CH_2OCH_2CH_2OCH_2), 2.28 (t, *J* = 7.5, CH_2COOEt, terminations), 2.12 (t, *J* = 7.3, CH_2CONH), 1.71–1.49 (m, CH_2CH_2(OCH_2CH_2)$_2$OCH_2CH_2), 1.39 (m, CH_2CH_2NHCO), 1.27 (br s $(CH_2)_8$), 1.11 (d, *J* = 4.5, CH_2CH(NH)CH_3), 0.88 (t, *J* = 7.3, COOCH_2CH_3, terminations).^{13}C NMR (100 MHz, $CDCl_3$): 171.9 (CONH), 71.6 (CH_2), 70.7 (CH_2), 70.6 (CH_2), 70.1 (CH_2), 44.2 (CH_2), 39.0 (CH_2), 36.1 (CH_2), 31 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 26.9 (CH_2), 26.1 (CH_2), 20.2 (CH_3). IR (FTIR, cm^{-1}): 3292, 3233, 2849, 1639, 1553, 1468, 1119, 956, 719. $[\alpha]_{365}^{25} = +11.7$ (*c* 0.8, $CHCl_3$). No amine terminations were detected.

Acknowledgments

The authors thank: Dr Emmanuel Beaudoin and Dr Tran Phan for DSC measurements, Dr Jean-Valère Naubron for FTIR spectra, Dr Alain Garnier for WAXD analysis, and Dr Emilie Bloch for TGA measurements. A gift of Novozym 435 from Novozymes (Denmark) is gratefully acknowledged.

References

1. Lin, J.; Sherrington, D. C. *Adv. Polym. Sci.* **1994**, *111*, 179.
2. Wu, Z.; Huang, Y.; Zhang, C.; Zhu, D.; Bian, Z.; Ding, M.; Gao, L.; Yang, Z. *J. Appl. Polym. Sci.* **2010**, *117*, 3558.
3. Goto, H.; Zhang, H. Q.; Yashima, E. *J. Am. Chem. Soc.* **2003**, *125*, 2516.
4. Ikeuchi, Y.; Nakagawa, M.; Yoshida, H.; Sakurai, S. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *447*, 2530.
5. Okamura, A.; Hirai, T.; Tanihara, M.; Yamaoka, T. *Polymer* **2002**, *43*, 3549.
6. Mallakpour, S.; Taghavi, M. *Eur. Polym. J.* **2008**, *44*, 87.
7. Mallakpour, S.; Taghavi, M. *React. Funct. Polym.* **2009**, *69*, 206.
8. Nakano, T. *J. Chromatogr. A* **2001**, *906*, 205.
9. Okamoto, Y. *J. Polym. Sci. Part A Polym. Chem.* **2009**, *47*, 1731.
10. Song, N.; Qi, W.; Qiu, X.; Gao, L.; Ding, M. *J. Polym. Sci. Part A Polym. Chem.* **2004**, *42*, 4318.
11. Srinivasarao, M. *Curr. Opin. Colloid Interf. Sci.* **1999**, *4*, 370.
12. Zhou, J. L.; Chen, X. F.; Fan, X. H.; Lu, C. X.; Zhou, Q. F. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 6047.
13. Takadoro, H. *In Structure of Crystalline Polymers*; Wiley-Intersciences: New York, 1979.
14. Aharony, S. M. In *n-Nylons, their Synthesis, Structure, and Properties, J*; Wiley & Sons: New York, 1997.
15. Bueno, M.; Zamora, F.; Molina, I.; Orgueira, H. A.; Varela, O.; Galbis, J. A. *J. Polym. Sci. Part A: Polym. Chem.* **1997**, *35*, 3645.
16. Gomez, R. V.; Varela, O. *Tetrahedron: Asymmetry* **2007**, *18*, 2190.
17. Iribarren, J. J.; Martinez de Ilarduya, A.; Aleman, C.; Oraison, J. M.; Rodriguez-Galan, A.; Munoz-Guerra, S. *Polymer* **2000**, *41*, 4869.
18. Mallakpour, S.; Rafiee, Z. *Polym. Degrad. Stabil.* **2008**, *93*, 753.
19. Okada, M. *Prog. Polym. Sci.* **2002**, *27*, 87.
20. Gonsalves, K. E.; Mungara, P. M. *Trends Polym. Sci.* **1996**, *4*, 25.
21. Zimmerman, J.; Kohan, M. I. *J. Polym. Sci. Part. A. Polym. Chem.* **2001**, *39*, 2565.
22. Zimmerman, J. *J. Encycl. Polym. Sci. Eng.* **1988**, *11*, 315.
23. Welgos, R. *J. Encycl. Polym. Sci. Eng.* **1988**, *11*, 410.
24. Nechab, M.; Azzi, N.; Vanthuyne, N.; Bertrand, M.; Gastaldi, S.; Gil, G. *J. Org. Chem.* **2007**, *72*, 6918.
25. Nechab, M.; El Blidi, L.; Vanthuyne, N.; Gastaldi, S.; Bertrand, M. P.; Gil, G. *Org. Biomol. Chem.* **2008**, *6*, 3917.
26. Bottalla, A. L.; Queroy, S.; Azzi-Schue, N.; Vanthuyne, N.; Gastaldi, S.; Bertrand, M. P.; Gil, G. *Tetrahedron: Asymmetry* **2009**, *20*, 2823.
27. Gastaldi, S.; Escoubet, S.; Vanthuyne, N.; Gil, G.; Bertrand, M. P. *Org. Lett.* **2007**, *9*, 837.
28. El Blidi, L.; Nechab, M.; Vanthuyne, N.; Gastaldi, S.; Bertrand, M. P.; Gil, G. *J. Org. Chem.* **2009**, *74*, 2901.
29. El Blidi, L.; Vanthuyne, N.; Siri, D.; Gastaldi, S.; Bertrand, M. P.; Gil, G. *Org. Biomol. Chem.* **2010**, *8*, 4165.
30. Routaboul, L.; Vanthuyne, N.; Gastaldi, S.; Bertrand, M. P.; Gil, G. *J. Org. Chem.* **2008**, *73*, 364.
31. Poulhès, F.; Vanthuyne, N.; Bertrand, M. P.; Gastaldi, S.; Gil, G. *J. Org. Chem.* **2011**, *76*, 7281.
32. van Buijtenen, J.; van As, B. A. C.; Verbruggen, M.; Roumen, L.; Vekemans, J. A. J. M.; Pieterse, K.; Hilbers, P. A. J.; Hulshof, L.; Palmans, A. R. A.; Meijer, E. W. *J. Am. Chem. Soc.* **2007**, *129*, 7393.
33. van As, B. A. C.; van Buijtenen, J.; Mes, T.; Palmans, A. R. A.; Meijer, E. W. *Chem. Eur. J.* **2007**, *13*, 8325.
34. Kanca, U.; van Buijtenen, J.; van As, B. A. C.; Korevaar, P. A.; Vekemans, J. A. J. M.; Palmans, A. R. A.; Meijer, E. W. *J. Polym. Sci., Part A: Pol. Chem.* **2008**, *46*, 2721.
35. Poulhès, F.; Mouysset, D.; Gil, G.; Bertrand, M. P.; Gastaldi, S. *Polymer* **2012**, *53*, 1172.
36. Bornscheuer, U. T.; Kazlauskas, R. J. In *Hydrolases in Organic Synthesis, Regio- and Stereoselective Biotransformations*, 2nd ed.; Wiley-VCH: Weinheim, 2006; p 84. chapter 6.
37. Vos, J. N.; van Boom, J. H.; van Boeckel, J. H. H.; Beetz, T. *J. Carbohydr. Chem.* **1984**, *3*, 117.
38. Freedman, H. H.; Dubois, R. A. *Tetrahedron Lett.* **1975**, *38*, 3251.
39. Jiang, Z.; Liu, C.; Gross, R. A. *Macromolecules* **2008**, *41*, 4671.

40. Jiang, Z. *Biomacromolecules* **2008**, *9*, 3246.
41. Azim, A.; Azim, H.; Sahoo, B.; Gross, R. A. *Polym. Mater. Sci. Eng.* **2005**, *93*, 743.
42. Cheng, H. N.; Maslanka, W. W.; Gu Q. M. US6677427; 2004.
43. Kumar, A.; Gross, R. A. *Biomacromolecules* **2000**, *1*, 133.
44. de Geus, M.; Peeters, J.; Wolffs, M.; Hermans, T.; Palmans, A. R. A.; Koning, C. E.; Heise, A. *Macromolecules* **2005**, *38*, 4220.
45. Marot, G.; Lesec, J. *J. Liq. Chrom.* **1988**, *11*, 3305.
46. For similar observations on n-alkylthiol monolayers, see Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.
47. Cui, X.; Yan, D.; Xiao, D. *e-Polymers* **2004**, 068.
48. Preston, J. In *Encyclopedia of Polymer Science and Technology*; Bikales, N. M., Mark, H. F., Gaylord, N. G., Eds.; Interscience: New York, 1977; p 84. Vol. Sup. 2.
49. Sridhar, S.; Suryamurali, R.; Smitha, B.; Aminabhavi, T. M. *Colloids and Surfaces A: Physiochem. Engin. Aspects* **2007**, *297*, 267.