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Novozym 435-catalyzed synthesis of polyetheramides from amino-esters, or diesters and diamines built on ethylene- and diethylene- glycol moieties

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

[a] Laboratoire Chimie Provence, LCP UMR 6264, Aix-Marseille Université, Faculté des Sciences St Jérôme, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France
[b] Laboratoire de Stéréochimie Dynamique et Chiralité, ISM2, UMR 6263, Aix-Marseille Université, Faculté des Sciences St Jérôme, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France

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ABSTRACT

The optimization of CAL-B-promoted (Novozym 435) A/B and AA/BB type polymerizations leading to polyetheramides, from amino ethylesters or diethyl esters and diamines based on ethylene- or diethylene-glycol moieties, is disclosed herein. From these preliminary experiments it became obvious that it is of prime importance: to avoid the presence of water by carefully drying the enzyme prior to use; to eliminate ethanol from the reaction medium, by working under reduced pressure in order to drive the amidation reaction forward; to select an appropriate high boiling solvent, the best choice being diphenyl ether. Under such experimental conditions, polyetheramides were obtained in 70–80% yield with an average degree of polymerization (DPn) up to 17.

1. Introduction

In automotive construction, the electrics/electronics sector and the packaging industry, users and developers particularly value the properties of polyamides. These include high mechanical and thermal stress resistance, excellent low-friction properties and abrasion resistance, good chemical stability, low stress crack resistance and good electrical insulating behavior [1]. These interesting properties result principally from hydrogen bonds induced by the planar amide function. These multiple interactions among adjacent strands are energetically strong due to the high dipolar moment of the amide group. The symmetrical and regular character of the backbone of the polyamide and the strength of interchain interactions lead often to highly crystalline polymers.

However, the low solubility associated to high melting and glass transition temperatures caused by the high crystallinity of the backbone lead to difficulties in synthesis, characterization and processing of polyamides. Practically, introduction of a flexible segment into the polymeric backbone is known to be effective in improving solubility and processability while maintaining the high thermal stability of the polymer [2]. The choice of an ether linkage is for example, a strategy commonly adopted to increase the solubility of aromatic polyamides [3,4].

Polyamides are usually prepared by direct amidation of diacids with diamines, self-condensation of aminoacids, or ring-opening of cyclic lactams, mediated by strong acids or metal-containing catalysts, at temperature ranging from 200 to 300 °C and pressure between 120 and 180 psi [5–7]. Moreover, it is often necessary to employ coupling agents and additional protection-deprotection steps to prevent the degradation of useful functionalities under such harsh reaction conditions [8].

To overcome these drawbacks, the bio-inspired synthesis of polymers is recognized as a powerful tool, mostly because enzymes react under mild conditions and provide sustainable chemical processes [9–13]. Polyesters are readily available from biocatalyzed lactones ring-opening, condensation of ω-hydroxyesters, or copolymerization of diesters with diols [9–15]. Comparatively, very few examples of enzymatic syntheses of polyamides have been reported [13,16–22], even though it is an attractive alternative to usual methodologies.

Regarding lipase-promoted lactam ring-opening strategy, only the unsubstituted β-lactam ring enables the formation of poly(β-alanine) [16]. However, this procedure affords oligomers with a DPn of 8. Polycondensations leading to Nylon 6,12 and Nylon 6,6 have been successfully achieved by Gross [18]. The influence of the carbon chain-length on the polymerization degree was

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

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emphasized in this study. The faster propagation of Nylon 6,12 chains as compared to Nylon 6,6 is in fair agreement with the chemical properties of lipases designed by nature for the hydrolysis of long chain fatty esters. Cheng and coworkers have also reported the lipase-catalyzed synthesis of polyamides, through an AA/BB strategy [19]. They coupled saturated diamines, heteroatom-containing diamines and even polyamines, with various diesters according to an enzymatic pathway. This study clearly demonstrated that the use of various lipases as polymerization catalysts led to the obtention of polymers with massic properties similar to those obtained by a chemical pathway at 180 °C, but with better polydispersity indexes. Moreover, the cationic resins derived from these products showed physical properties close to those of polymers obtained from chemical processes. Bio-catalyzed bulk polymerizations were expanded to the formation of polyamides and polyester/amides based on polydimethylsiloxane blocks [20,21], sometimes coupled with an aliphatic fluorinated backbone [22].

As evidenced from the above literature, most of these enzymatic polymerizations use immobilized *Candida antarctica* lipase B (Novozym 435) as the biocatalyst. Our group has been involved over the last five years in the improvement of the formation of amide bond catalyzed by lipases and proteases (from both rate and selectivity point of views) [23–25], with the goal to make it compatible with thiyl radical-promoted racemization of aliphatic amines [26–29]. At mean to long term, our aim was to approach the enzyme-catalyzed synthesis of chiral polyamides, applying the successful strategy developed by Meijer and coworkers for the synthesis of chiral polyesters [30–32]. However, the performance of an efficient oligomerization of either A/B or AA/BB type monomers was not straightforward.

One of the main difficulties in the synthesis of polyamides is their low solubility in most organic solvents, except the most polar aprotic ones [33], and the precipitation of low molecular weight oligomers which stops the propagation of the polymeric chains. We report hereafter the preliminary results obtained in the synthesis of oligomeric polyetheramides, from monomers built on ethylene glycol and diethylene glycol moieties (Fig. 1) to insure a better solubility of polymeric materials in organic solvents compatible with CAL-B catalysis.

2. Experimental

2.1. Materials

All of the chemicals were analytical grade and were used as received. Glyme was distilled before use from sodium/benzophenone ketyl. *Candida antartica* Lipase B (CAL-B) immobilized on macroporous acrylic resin (Novozym 435 (N435)) was a gift from Novozymes (Denmark).

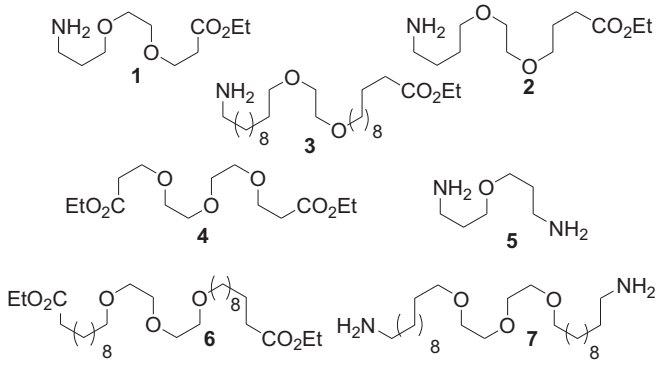

Fig. 1. Amino-esters, diamines and diesters structures.

2.2. General procedure for polymerization

2.2.1. A/B type polymerization under reduced pressure

In a typical experiment, ester **3** (133 mg, 0.3 mmol) in Ph_2O (300 mg) was introduced in a 10 mL flask. After stirring for 15 min, dried Novozym 435 (30 mg) was added. The mixture was then heated at 80 °C under 10 mbars for 240 h. After completion, the mixture was cooled at 60 °C, 10 mL of chloroform were 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. After addition of diethylether, the product was filtrated and washed with the same solvent. After drying under vacuum at 40 °C for 48 h the solid polymer was recovered (106 mg). ^{1}H NMR (300 MHz, $CDCl_3$): 5.60 (bs, NH), 4.05 (m, CH_3CH_2O, terminations), 3.57 (bs, OCH_2CH_2O), 3.45 (m, $CH_2OCH_2CH_2OCH_2$), 3.22 (m, CH_2NHCO), 2.88 (m, CH_2NH_2), 2.30 (m, CH_2COOEt, terminations), 2.15 (CH_2CONH), 1.76 (m, $CH_2CH_2CH_2O$), 1.59 (m, $CONHCH_2CH_2$), 1.48 (m, $EtOOCCH_2CH_2$, terminations), 1.29 (bs, $(CH_2)_7$), 1.10 (m, CH_3CH_2OCO, terminations). ^{13}C NMR (75 MHz, $CDCl_3$): 174.0 (CONH), 71.5 (CH_2), 70.1 (CH_2), 39.5 (CH_2), 36.9 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3(CH_2), 26.9 (CH_2), 26.1 (CH_2), 25.9 (CH_2). The characteristic signals of terminal groups could not be detected.

2.2.2. AA/BB type copolymerization of ***6*** and ***7*** under reduced pressure

In a typical experiment, **6** (151 mg, 0.34 mmol) and **7** (180 mg, 0.34 mmol) in Ph_2O (660 mg) were added in a 10 mL flask. After stirring for 15 min, dried Novozym 435 (60 mg) was added. The mixture was then heated at 80 °C under 10 mbars for 240 h. After completion, the mixture was cooled at 60 °C, 10 mL of chloroform were 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 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 (255 mg). ^{1}H NMR (300 MHz, $CDCl_3$): 5.5 (bs, NH), 4.16 (m, CH_3CH_2O, terminations), 3.61–3.48 (m, $OCH_2CH_2OCH_2CH_2O$), 3.38 (t, J = 6.6, $CH_2OCH_2CH_2OCH_2CH_2OCH_2$), 3.16 (dt, J = 6.6, 6.3, $CONHCH_2$), 2.77 (m, CH_2NH_2, terminations), 2.22 (t, J = 7.5, $EtOOCCH_2$, terminations), 2.07 (t, J = 7.5, CH_2CONH), 1.52 (m, $CH_2CH_2(OCH_2CH_2)_2OCH_2CH2$), 1.41 (m, $CONHCH_2CH_2$), 1.21 (bs, $(CH_2)_7$), 0.81 (m, CH_3CH_2O, terminations). ^{13}C NMR (75 MHz, $CDCl_3$): 173.2 (CONH), 71.5 (CH_2), 70.6 (CH_2), 70.1 (CH_2), 39.5 (CH_2), 36.9 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.9 (CH_2), 26.1 (CH_2), 25.8 (CH_2).

2.3. Characterization methods

2.3.1. 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 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 elution marker.

System calibration data and relative molar mass calculations were acquired and processed using PSS WinGPC (Polymer