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Review

A review on enzymatic polymerization to produce polycondensation polymers: The case of aliphatic polyesters, polyamides and polyesteramides

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ABSTRACT

Enzymatic polymerization represents today an effective and preferable alternative to conventional chemically-catalyzed processes. It offers significant advantages, summarized in the applied mild reaction conditions mainly in terms of temperature and toxicity, and high selectivity of enzymes, avoiding protection-deprotection strategies and resulting in improved quality/performance of end products. Especially for polycondensation polymers, biocatalyzed synthetic routes have been under research for the last thirty years, including homo- and copolymerization of a significant number of monomers. Aliphatic polyesters, polyamides and at a much lower extent polyesteramides, represent the core of the pertinent studies, and are systematically discussed in the current review. Emphasis is given on polycondensates with biodegradability properties, derived from bio-based monomers such as succinic acid, 1,3- propanediol and lactide/lactic acid.

Free or immobilized lipases and cutinases are the predominant biocatalysts in the relevant polymer families, being used in polycondensation as well as in ring-opening reaction schemes. The efficiency of the different biocatalytic processes is herein correlated to important process parameters, such as the enzyme and monomer type, the reaction temperature and time, the polymerization technique (solution or solvent-free), as well as the by-product removal method, e.g., application of vacuum, water absorption by molecular sieves, azeotropic distillation.

Abbreviations: AYL, type AY from *Candida cylindracea*; BDO, 1,4-butanediol; [C4mim][BF4], 1-butyl-3-methylimidazolium tetrafluoroborate; [C4mim][NTf2], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide; [C4mim][PF6], 1-butyl-3-methylimidazolium hexafluorophosphate; CALB, *Candida antarctica* lipase B; 1,4-CHDM, 1,4-cyclohexanedimethanol; CLEA, cross-linked enzyme aggregates; CLL, *Camalica* lipolytic lipase; COOH, carboxyl groups; DADD, 1,12-diaminododecane; DAO, 1,8-diaminooctane; DBTO, di-butyl tin oxide; DEA, diethyl adipate; DDL, dodecanolactone; DES, diethyl sebacate; DLA, DD-lactide; DP, polymerization degree; EAM, enzyme activated monomer; EAPC, enzyme – activated polymer chain; e-ROP FDCA, enzymatic ring opening polymerization 2,5-furandicarboxylic acid; GADE, L-glutamic acid diethyl ester; HDL, hexadecanolactone; HiC, cutinase from *Humicola insolens*; HLE, hog liver esterase; ^{1}H NMR, H- Nuclear magnetic resonance spectroscopy; ILs, ionic liquids; IM-PC, *Pseudomonas cepacia* lipase immobilized in ceramics; K, equilibrium constant; k, reaction rate constant; Lipase A, *Aspergillus niger* lipase; Lipase CC, *Candida cylindracea lipase*; Lipase CR, *Candida rugose* lipase; Lipase G, *Penicillium camemberti* lipase; Lipase MM, *Mucor miehei* lipase; Lipase PA, *Pseudomonas aeroginosa* lipase; Lipase PC, *Pseudomonas cepacia* lipase; Lipase PF, *Pseudomonas fluorescens* lipase; Lipase RD, *Rhizopus delemer* lipase; Lipase RJ, *Rhizopus japonicus* lipase; Lipase RM, *Rhizomucor miehei* lipase; LLA, LL-lactide; L-MA, L-malic acid; 12-Me-DDL, methyldodelactone; M_n, number-average molecular weight; M_w, weight-average molecular weight; MW, molecular weight; MWD, molecular weight distribution; N435, immobilized *Candida antarctica* lipase B (Novozym 435); OH, hydroxyl groups; 8-OL, 8-octanolide; PA(s), polyamide(s); PBS, poly(butylene succinate); PCL, poly(ε-caprolactone); PD, 15-pentadecanolide; PDI, polydispersion index; PDL, pentadecanolactone; PDO, 1,3-propanediol; PE 4.4, poly(butylene succinate) – PBS; PEA(s), polyesteramide(s); PE(s), polyester(s); PEG, poly(ethylene glycol); PEL, expansion *Penicillium* lipase; PHA, polyhydroxyalkanoates; PHB, polyhydroxybutyrate; PLA, poly(lactic acid); PPL, porcine pancreatic lipase; PSA, *Pseudomonas aeruginosa*; PSAI, *Pseudomonas aeruginosa* S.P.I lipase; PSAII, *Pseudomonas aeruginosa* S.P.II lipase; PTC, phase-transfer catalytic; RSM, response surface methodology; ROP, ring – opening polymerization; SA, succinic acid; $scCO_2$, supercritical CO_2; SSP, solid state polymerization; T, temperature; T_b, boiling temperature; *t*-BuOH, *tert*-butyl alcohol; T_g, glass transition temperature; TGA, themogravimetric analysis; THF, tetrahydrofuran; T_m, melting temperature; TSAS, transition – state analogue substrate; UDL, undecanolactone; δ-VL, δ-valerolactone; ε-CL, ε-caprolactone; [η], intrinsic viscosity; ω-carboxyl OA, 1,18-*cis*-9-octadecenedioic acid; ω-carboxyl SA, 1,18-*cis*-9,10-epoxy-octadecanedioic acid; ω-HA, ω-hydroxyalkanoic acid.

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Contents

1. Introduction

1.1. Principles of polycondensation reactions – targeted polymers

Polycondensation (step-growth) method and reactions have been investigated in a profusion of work [1–16], favored by the variety of possible monomers and the respective range of reaction schemes. Typical classes of polycondensates are polyesters (PEs), polyamides (PAs), polyurethanes, polyureas, polysiloxanes, polysulfides and polyethers with a number of these polymers being bio-based and/or biodegradable and promoting thus the sustainability of the relevant production schemes.

During a polycondensation process, the main reaction involves the interaction of two functional groups of different or same type of molecules, resulting in the formation of a "new" intermolecular bond. Based on the equal reactivity principle, this combination of two reacting molecules, such as monomers, oligomers or short-chain polymers, results in the formation of one higher-molecular-weight molecule, and is often accompanied by the extraction of a by-product (condensate), such as water in the case of PAs and PEs. Regarding kinetics, polycondensation reactions are equilibrium systems: the reverse reaction is the depolymerization of a polymer molecule, the rate of which is mainly determined by the equilibrium constant K. At moderate K values, the reversibility of the polycondensation becomes essential and reaction may proceed under either equilibrium or nonequilibrium conditions. In order to achieve equilibrium regime, it is necessary to remove slowly enough the by-product from the reaction zone, while a reversible polycondensation will proceed under nonequilibrium regime, when the rate of the by-product removal is high enough and comparable with that of its formation.

The current review focuses on the enzymatic synthesis of aliphatic polyesters (PE X.Y) and polyamides (PA X.Y) (Fig. 1), including their copolymers (polyesteramides, PEA X/Xo.Y). X and Y denote the number of carbon atoms in the diol/diamine and the diacid, respectively, in the polyester or polyamide repeating unit. In the case of polyesteramides, X and Xo denote the number of the carbon atoms of the diamine and diol, respectively. The relevant polymers may be used in a variety of applications across industries such as packaging, automotive, medicine, electrical & electronics, machinery, consumer goods, textiles, films & coatings, and others [17–23].

In particular, aliphatic PEs, such as poly(ε-caprolactone)-PCL (e.g., Tone® Series, Dow Chemicals Co.), poly(lactic acid)-PLA (e.g., Ingeo™ Series, NatureWork), poly(butylene succinate)-PE 4.4/PBS (e.g., Bionolle™ Series, Showa High-Polymer Co.), polyhydroxybutyrate-PHB, are increasingly produced [24–28] due to legislation on the development of environmentally and economically viable manufacturing and recycling of polymers. They own a leading position in biodegradable materials, since their hydrolytic and enzymatic degradation products can be naturally metabolized into non-toxic substances. In parallel, they exhibit balanced thermal and mechanical properties, being dependent on the repeating unit. For example, for long-chain PEs, such as PE 8.10, PE 8.12 and PE 8.14, the melting point (T_m) has been found to increase with the number of diacid carbon atoms (Y) (Fig. 2a): ester bonds are considered to act as defects along the polymer backbone, and as the distance between ester groups increases the number of defects decreases and consequently T_m raises [18,29,30]. Note that this family of long-chain PEs is named after "polyethylene-like polyesters", and is designed to couple the biodegradability with chemical and physical properties close to those of the mostly used polymer, polyethylene.

Amongst short-chain PEs, PE 4.4 (also referred as PBS) is excluded from the aforementioned rule, and shows significantly high T_m probably due to its rigid and symmetric short repeating unit. PE 4.4 is a bio-based and biodegradable PE with crystallization behavior and mechanical properties similar to polyethylene, and an easier melt processability ($T_g = -32\,^\circ C$) compared to PLA ($T_g > 50\,^\circ C$). PE 4.4 is stable at temperatures below 220 °C, with the rate of mass loss reaching a maximum at ca. 390 °C [31–33], presenting higher stability than PLA (max at 365–368 °C) (Fig. 2b). Its potential is also strenghtened by the bio-based origin of its monomers, with succinic acid (SA) being classified in the TOP 10 "building block molecules" that can be produced industrially from renewable resources [34–38]. For the same reasons, aliphatic PEs based on 1,3-propanediol (PDO) currently exhibit also increasing shares in open literature, due to the fact that more attractive processes have been developed for the production of commercial high-quality bio-based PDO with low cost [39].

Concerning polyamides, PAs have been available commercially since the first half of the 20th century; their improved properties originate from the strong intermolecular hydrogen bonds formed