



Research review paper

Chemoenzymatic synthesis of polymeric materials using lipases as catalysts: A review



Yan Yang^{a,b,c}, Jianxu Zhang^{a,c}, Di Wu^{a,c}, Zhen Xing^{a,c}, Yulin Zhou^{a,b,c}, Wei Shi^{a,b,c,*}, Quanshun Li^{a,b,c,*}

^a Key Laboratory for Molecular Enzymology and Engineering, The Ministry of Education, Jilin University, Changchun 130012, China

^b National Engineering Laboratory for AIDS Vaccine, Jilin University, Changchun 130012, China

^c School of Life Sciences, Jilin University, Changchun 130012, China

ARTICLE INFO

Article history:

Received 26 August 2013

Received in revised form 17 April 2014

Accepted 19 April 2014

Available online 25 April 2014

Keywords:

Lipase

Chemoenzymatic polymerization

ATRP

Kinetic resolution

RAFT

Click reaction

Carbene chemistry

ABSTRACT

In the past two decades, enzymatic polymerization has rapidly developed and become an important polymer synthesis technique. However, the range of polymers resulting from enzymatic polymerization could be further expanded through combination with chemical methods. This review systematically introduces recent developments in the combination of lipase-catalyzed polymerization with atom transfer radical polymerization (ATRP), kinetic resolution, reversible addition–fragmentation chain transfer (RAFT), click reaction and carbene chemistry to construct polymeric materials like block, brush, comb and graft copolymers, hyperbranched and chiral polymers. Moreover, it presents a thorough and descriptive evaluation of future trends and perspectives concerning chemoenzymatic polymerization. It is expected that combining enzymatic polymerization with multiple chemical methods will be an efficient tool for producing more highly advanced polymeric materials.

© 2014 Elsevier Inc. All rights reserved.

Contents

Introduction	642
Combination of enzymatic polymerization with radical polymerization	643
Chemoenzymatic synthesis of polymers via bifunctional initiators	643
Chemoenzymatic synthesis of polymers by a simple alcohol-initiated route	645
Combination of enzymatic acryloylation or transacylation with free radical polymerization	646
Combination of enzymatic polymerization with kinetic resolution	646
Combination of enzymatic polymerization with other reactions	647
Concluding remarks	649
Acknowledgments	650
References	650

Introduction

Polymeric materials, both natural and artificial, play important roles in modern society. They are widely used as highly advanced materials in many sectors, e.g., electronics, machinery, communications, pharmacy

and transportation. The increasing need of polymeric materials for various applications will require the construction of more structurally and functionally diverse materials. Thus it will be necessary to develop novel catalysts or synthetic methods.

To date, chemists have developed numerous synthetic methods or catalytic systems for preparing polymeric materials with tailor-made structures and properties. For the chemical conversion they catalyze, most catalysts are highly specific and selective, while this characteristic will limit the general application of a catalyst in multistep reactions (Heise and Palmans, 2010). In contrast to chemical conversion,

* Corresponding author at: Key Laboratory for Molecular Enzymology and Engineering, the Ministry of Education, Jilin University, Changchun 130012, China. Tel.: +86 431 85155216; fax: +86 431 85155200.

E-mail addresses: shiw@jlu.edu.cn (W. Shi), quanshun@jlu.edu.cn (Q. Li).

concurrent action of several enzymes in tandem reactions like multi-enzyme systems in nature, can easily be realized with many advantages, e.g., permitting a reversible process to become irreversible, reducing the product inhibition or substrate shortage, and further increasing the approaches' control and diversity for building complex catalytic systems (Lopez-Gallego and Schmidt-Dannert, 2010; Oroz-Guinea and Garcia-Junceda, 2013). Thus, this constraint of chemical methods can be overcome through combination with other catalysts or methods, e.g., enzymatic polymerization. In the past two decades, enzymatic polymerization, particularly using lipases as catalysts, has rapidly developed and become an important synthetic method in polymer chemistry (Albertsson and Srivastava, 2008; Gross et al., 2001, 2010; Idris and Bukhari, 2012; Kadokawa and Kobayashi, 2010; Kobayashi, 2009, 2010; Kobayashi and Makino, 2009; Kobayashi et al., 2001; Park et al., 1994; Uyama and Kobayashi, 2002; Varma et al., 2005; Veld and Palmans, 2010; Yang et al., 2011; Yu et al., 2012). Compared with a conventional chemical route, enzymatic polymerization has many advantages, including: (1) mild reaction conditions, (2) high control of enantio-, chemo-, and regioselectivity, (3) recyclability of biocatalysts, and (4) ability to catalyze the ring-opening polymerization of macrocyclic lactones, which is difficult to achieve through chemical catalysis except for metal-based catalysts developed by Duchateau and colleagues, e.g., aluminum-salen complexes (Bouyahy and Duchateau, 2014; Jasinska-Walc et al., 2014; Pepels et al., 2013; Van der Meulen et al., 2011). Thus, this method is considered an environmentally friendly synthetic process for polymeric materials. Accordingly, the process has proven efficient for producing diverse polymers via ring-opening polymerization or polycondensation reactions. However, not all chemical conversions can be replaced by this biocatalytic route, and a typical shortcoming of enzymatic polymerization is the lack of control over the polymer structure, prohibiting the synthesis of complex molecular architectures like block and graft copolymers (Heise and Palmans, 2010).

Full exploitation of multistep strategies for polymer synthesis will require the development of novel organic and biosynthetic methods called chemoenzymatic procedures. Catalysis by chemical and enzymatic methods differs in function and mechanism, but both methods are mutually compatible and can occur concurrently in the same system if their combination is desirable (Kobayashi, 2009). By utilizing the advantages of enzymes, chemoenzymatic methods have recently been developed for synthesizing new polymeric materials that are otherwise difficult to prepare. More importantly, chemoenzymatic polymerization could further increase the diversity and complexity of synthesized macromolecules via multistep reactions and cascade reactions (the combination of two different, consecutive polymerization reactions),

e.g., the construction of chiral block polymers using the catalytic complexity of a chemical route and the enantioselectivity of enzymatic polymerization.

In this paper, recent developments and future trends in chemoenzymatic polymerization using lipases as catalysts via multistep and cascade reactions are systematically reviewed.

Combination of enzymatic polymerization with radical polymerization

Among the chemical routes, atom transfer radical polymerization (ATRP) is the most widely used technique to be combined with lipase-catalyzed polymerization. The success of this strategy is highly attributed to enzymatic synthesis of end-functionalized polyesters. There are two methods for constructing these polyesters, initiator and terminator method, as illustrated in Fig. 1. In the initiator method, a nucleophile (alcohol, amine or sugar) induces the enzymatic polymerization which produces the end-functionalized polyesters (Uyama et al., 1998). For the terminator method, vinyl esters (usually vinyl methacrylic acid and divinyl sebacate) are used as terminators, and the nature of reaction is a single-step acylation of a hydroxyl end-group of polyester (Uyama et al., 1995). As yield and product molecular weight will dramatically decrease with increasing terminator concentration, the terminator method is less efficient and thus has attracted less attention.

Chemoenzymatic synthesis of polymers via bifunctional initiators

Enzymatic polymerization with ATRP can be achieved in a stepwise or cascade manner by including designed bifunctional initiators. Typical bifunctional initiators, which have been widely used to prepare block copolymers via chemoenzymatic polymerization, are shown in Fig. 2. These initiators possess a functional group capable of initiating the enzymatic polymerization (the hydroxyl) and another group that induces the ATRP (e.g., Br). As trace water molecules in the reaction system are essential to retain the activity and stability of enzymes (Klibanov, 2001) and can also initiate the enzymatic polymerization, the incorporation ratio of these initiators is highly dependent on their structure and the control of reaction conditions (De Geus et al., 2008).

General reaction routes using a designed bifunctional initiator to construct block copolymers are shown in Fig. 3. This approach has the advantage of avoiding any polymer-analogous end-group modifications (Heise and Palmans, 2010). However, bifunctional initiators should be used in excess during enzymatic polymerization to obtain a high yield of incorporation. Meyer et al. (2002) successfully synthesized block copolymers in a one-pot mode using a bifunctional initiator that contained

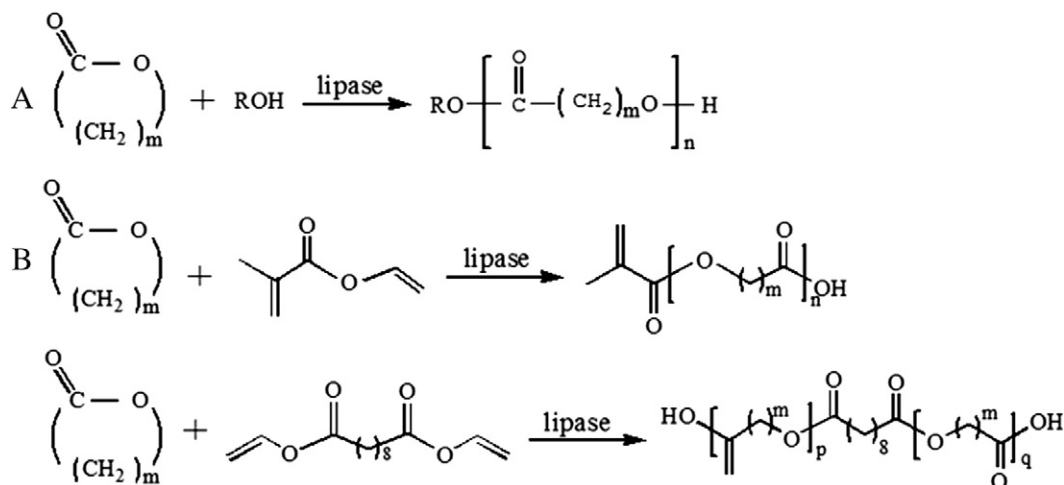


Fig. 1. Enzymatic synthesis of end-functionalized polyesters via the initiator (A) and terminator (B) methods.

Download English Version:

<https://daneshyari.com/en/article/10231544>

Download Persian Version:

<https://daneshyari.com/article/10231544>

[Daneshyari.com](https://daneshyari.com)