

Biocatalytic synthesis of polymeric materials for biomedical applications

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Polymeric materials have been widely used in biomedical fields such as tissue engineering scaffolds and drug/gene delivery systems. In comparison to conventional chemical routes, enzymatic polymerization has shown great potential in the synthesis of polymeric materials owing to its mild reaction conditions, high enantio-, chemo- and regio-selectivity, and no residue of metallic catalysts and low toxicity. Meanwhile, it could be used to obtain polymeric materials with unique structures and properties which are difficult to be synthesized in a chemical route. However, there are still several problems to be solved in enzymatic polymerization including low activity and stability of enzymes during the reactions, limited structural scope of polymers and high production cost.

To solve these issues, enzymatic polymerization has been systematically studied from three aspects in our laboratory. First, we explored thermophilic esterases with high activity and stability from extreme conditions and constructed enzyme-MOF nanocomplexes using biomimetic mineralization, and these catalysts have been successfully applied in the polymer synthesis with favorable catalytic activity and stability. Second, enzymatic polymerization has been combined with chemical routes (e.g., ATRP and ROMP) for the synthesis of novel block and grafting copolymers in a one-pot or cascade manner. Finally, a series of cationic polymers have been developed via enzymatic polymerization and could be applied in the efficient and targeted delivery of therapeutic genes and oligonucleotides, which could achieve the inhibition of proliferation, migration and invasion of tumors both *in vitro* and *in vivo*. Overall, enzymatic polymerization has provided a green and sustainable route for constructing polymeric materials and facilitated their applications in biomedical fields.

Keywords: Enzymatic polymerization; Biomedical polymers; thermophilic enzyme; Chemoenzymatic polymerization; Gene delivery