

# Ring opening precipitation polymerization for preparing polylactide particles with tunable size and porous structure and their application as chiral material



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## ABSTRACT

Poly lactide (PLA) particles become increasingly important for practical applications as typical sustainable polymeric materials; however, their preparation still remains as a big challenge due to lacking effective preparation method directly starting from monomer lactide (LA) and lactic acid. In this study, we established an unprecedented strategy for preparing PLA particles in a high yield (>90 wt%) — precipitation polymerization of LA in ethyl acetate at 0 °C. The method provides PLA particles with narrowly distributed size. Phase separation occurred in the course of precipitation polymerization and endowed the PLA particles with interesting porous structures. The particles and their formation process were investigated by SEM, CD, XRD and DSC analyses. Noticeably, the size of PLA particles and the porous structure can be tuned through controlling the crystallization of PLA by adding D-LA in the polymerization system of L-LA. We further explored chiral recognition ability of the PLLA particles. The established strategy provides promising approaches for preparing novel PLA-based materials.

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## 1. Introduction

Sustainable polymers become increasingly important nowadays [1,2]. Polylactide (PLA) has constituted the most important synthetic sustainable polymeric materials. Due to its biocompatibility, biodegradability, nontoxicity and good mechanical properties [3], PLA has found practical applications as packaging [4], medical [5], tissue engineering materials [6] and in other fields [7–9]. PLA has been approved by FDA for clinical use, which further promotes the progress in PLA biomaterials. Among PLA-based biomaterials, PLA particles have been intensively investigated as drug carriers [10]. Such particles are generally prepared by nanoprecipitation [11], emulsification [12], and spray drying techniques [13], all using pre-obtained polymers rather than starting from monomer. The methods show some limitations. The preparation processes are quite tedious, generally comprising several major steps: to prepare PLA, emulsify it, and then to evaporate the solvent, freeze-dry, or to precipitate the polymer for preparing polymer particles. Dispersion

polymerization also can provide PLA particles, however it requires the use of dispersing agent which leads to another trouble task, i.e. to completely exclude the dispersing agent from the resulting particles [14]. Accordingly, simple and efficient methods for preparing PLA particles from LA are complement to existing techniques, in view of the significant importance of PLA as promising biomaterials. In the context above, we created a new strategy for preparing PLLA particles from L-LA (L-lactide) by precipitation polymerization.

Internal structure and surface morphology of polymer particles are important factors affecting their performance and actual uses [15]. A tunable pore structure is especially desirable [16]. The traditional strategies for constructing PLA porous structures mainly include thermal-induced phase separation [17], non-solvent induced phase separation [18], and gradual precipitation [19]. The porous structures formed in these processes are highly related to phase separation [19–21]. The formation of porous structure in these cases is limited to phase separation necessarily occurring in good solvents of pre-formed PLA. Especially, most of the as-established architectures assume fibrous form. The present study establishes a novel methodology to regulate the pore structure of PLLA particles by controlling the phase separation process in the

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course of polymerization.

Our strategy is illustratively presented in Fig. 1. Precipitation polymerization is a convenient method for preparing clean polymeric particles featuring narrow size distribution and simple posttreatment [22]. In the precipitation polymerization systems, we took advantage of the phase separation in the course of polymerization to endow the particles with a lot of slit pores. The preparation conditions, structural features, and the formation process of PLA particles were investigated in detail. We further used D-LA to control the crystallization of PLLA to regulate the particles size and pore structures. We then performed enantioselective crystallization and adsorption experiments to investigate the chiral recognition ability of the PLLA particles.

## 2. Experimental section

### 2.1. Materials

Ethyl acetate and ethylene glycol were purchased from Beijing Chemical Reagents Company (China) and purified by distillation under reduced pressure. L- and D-lactide were purchased from TCI and purified by recrystallizing twice from ethyl acetate. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from J&K and used without further purification.

### 2.2. Measurements

FT-IR spectra were measured with a Nicolet NEXUS 870 infrared spectrometer (KBr tablet). Molecular weights of polylactide were recorded by gel permeation chromatography (GPC, Waters 150C) calibrated using polystyrenes as standard and tetrahydrofuran (THF) as eluent (Waters Styragel HT6E-HT5-HT3, in series at 35 °C, flow rate of 1.0 mL/min). The surface morphology of the particles was observed with scanning electron microscopy (SEM, Hitachi S-4800). Differential scanning calorimetry (DSC) measurements were conducted using a Netzsch DSC204F1 instrument under a flow of nitrogen at a heating rate of 10 °C/min. Samples were heated from 30 to 200 °C and the measurements were taken from the first heating scan. Powder X-ray diffraction (XRD) patterns were obtained using a D/max2500 VB2+/PC X-ray diffractometer (Rigaku) using Cu K $\alpha$  radiation. Circular dichroism (CD) and UV-vis

absorption spectra were recorded using a JASCO J-810 spectropolarimeter.

### 2.3. Preparation of PLLA particles

We selected DBU as a catalyst for polymerizing L-LA and ethylene glycol as an initiator to control PLLA molecular weight. A typical procedure for polymerization is briefly stated below. First, 0.4 g lactide (LA, L-LA or D-LA) was added in a tube. The tube was exhausted and recharged with nitrogen to make sure the subsequent polymerization to occur in N<sub>2</sub> atmosphere without water and oxygen. 0.4 mL ethyl acetate was added in the tube to dissolve the monomer. Given amounts of initiator and catalyst (monomer/initiator/DBU ratio, 70/1/1, in mol) were added in 0.5 mL ethyl acetate and dissolved for 3 min. After complete dissolution, the initiator and catalyst solution was injected into the tube containing monomer and then extra ethyl acetate was added to achieve a certain monomer concentration (0.4 g/mL). The polymerization occurred at 0 °C and lasted for 2 h at the temperature. After filtration, the product from precipitation polymerization was dried at 45 °C in vacuum. Yield of particles was determined by gravimetric method.

### 2.4. Adsorption experiments

(R)-(+)-/(S)-(–)-1-PEA and Boc-L-/Boc-D-phenylalanine were chosen as adsorbate. All the chiral adsorption experiments were performed by dispersing a certain amount of particles in adsorbate solution at room temperature. The major experiment procedure is stated as follows.

A certain amount of the adsorbate is dissolved in deionized water to form 0.5 mg/mL solution. 50 mg of PLLA particles was dispersed in 5 mL adsorbate solution. All experiments were carried out at room temperature for 24 h. The initial concentration ( $c_0$ , mg/mL) and residual concentration ( $c$ , mg/mL) of adsorbate solution were calculated by UV measurement. The absorbency ( $q$ , mg/g) was calculated according to the following equation:  $q = V(c_0 - c)/m$ , where  $m$  is the mass of particles (g) and  $V$  (mL) is the volume of adsorbate solution. For racemic samples, the ellipticity of residual solution ( $\theta_1$ , mdeg) was measured by CD measurement. The enantiomeric excess (e.e.) of residual solution was calculated according

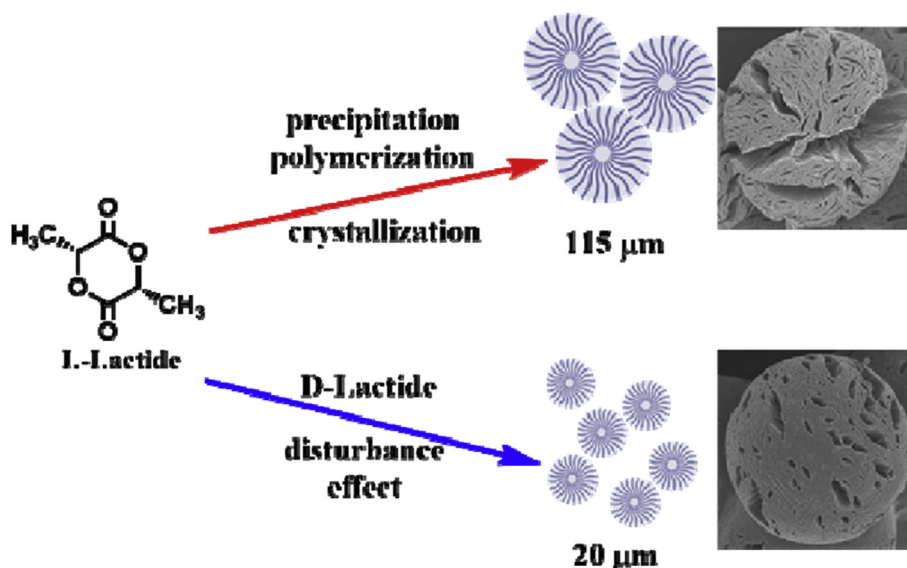


Fig. 1. Strategies for preparing PLLA particles by precipitation polymerization of L-LA and for regulating the morphology of particles by adding D-LA.

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