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Ionic liquid coated lipase: Green synthesis of high molecular weight poly(1,4-dioxan-2-one)

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ABSTRACT

The ring-opening polymerization (ROP) of 1,4-dioxan-2-one (PDO) catalyzed by ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) coated lipase was investigated for the first time. By coating Novozym 435 with 10 wt% ionic liquid [BMIM][PF_6] (based on PDO) for 6 h, poly(1,4-dioxan-2-one) (PPDO) with a maximum molecular weight (M_w) of 182,100 g mol^{-1} was obtained. In order to demonstrate the efficiency of this method, [BMIM][PF_6] was also employed as a solvent for Novozym 435 catalyzed ROP of PDO. The results achieved using ionic liquid coated Novozym 435 were much superior to that with ionic liquid as a solvent. The probable mechanism of ionic liquid-coated Novozym 435 catalyzed the ROP of PDO was investigated by SEM, FT-IR, GPC and MALDI-TOF. All the results showed that ionic liquid coated lipase was an efficient and green catalyst for the ROP of PDO.

1. Introduction

As a new trend in polymer science, in particular, in the enzyme-catalyzed the ROP of lactones, cyclic carbonates, and other cyclic monomers, enzymatic catalysis with high selectivity and mild reaction conditions has aroused increasing interests in the past decades [1–4]. As an aliphatic polyester, poly(1,4-dioxan-2-one) (PPDO) has received a great deal of attention due to its excellent biocompatibility, bioabsorbability and flexibility, usually synthesized by many organometallic catalysts [5–9]. Due to the harmful effects of metallic residues in the synthesis of PPDO, lipase-catalyzed ring-opening polymerization (ROP) of 1,4-dioxan-2-one (PDO) in bulk has been investigated by few researchers [10,11]. Nishida et al. tested twelve enzymes for the polymerization of PDO and found that immobilized lipase CA, derived from *Candida antarctica*, showed especially high catalytic activity. In their experiments, PPDO with a maximum molecular weight (M_w) of 41,000 g mol^{-1} was obtained [10]. Chen et al. obtained PPDO with a maximum viscosity–average molecular weight (M_v) of 58,000 g mol^{-1} by adding 1,1,2,2-tetrachloroethane and molecular sieve to the polymerization system of PDO [11]. However, the molecular weight of PPDO obtained in the presence of enzyme was rather low compared to that obtained using organic metal catalyst. The enzymatic synthesis of PPDO can only be feasible if the molecular weight of the products can be increased significantly. Herein, we introduced a new green and efficient enzymatic method for the synthesis of high molecular weight PPDO.

Usually, in enzyme catalyzed reactions, organic solvents are the most common reaction media [12,13]. However, with the requirements of sustainable development and environmental protection, ionic liquids (ILs) whose properties can be adjusted by altering cation and anion have been reported as an interesting alternative to organic solvents due to their significant advantages, including nonexistent vapor pressure, high thermal stability, and excellent ability to dissolve organic, inorganic compounds and polymers [14,15]. Besides this, it was found that enzymes can keep high thermal and operational stability in some ionic liquids. Some organic reactions catalyzed by enzyme using ionic liquid as an solvent can even achieve excellent selectivity including substrate, regio- and enantioselectivity [16].

Besides acting as a reaction media, ionic liquid also can be used to pre-treat enzyme. Some literatures revealed that the enzyme activity and stability was enhanced by coating it with ILs which had been used for small molecule's transesterification, esterfication and hydrolysis reaction with higher enantioselecticity and yields [17–19]. However, there are no reports on this IL coated enzyme used for polymer synthesis.

In this manuscript, it was found for the first time that this IL coated Novozym 435 was an efficient catalyst for the ROP of PDO. PPDO with a maximum molecular weight (M_w) of 182,100 was obtained in the presence of [BMIM][PF_6] coated Novozym

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435. In order to demonstrate it clearly, a series of ROP of PDO were carried out in the presence of Novozym 435 using [BMIM][PF_6] as a solvent or [BMIM][PF_6] coated Novozym 435. The probable mechanism of ionic liquid-coated lipase catalyzed the ROP of PDO was also suggested. This feasible and efficient method can also be used for lipase-catalyzed the ROP of other lactones.

2. Materials and methods

2.1. Materials

1,4-Dioxan-2-one (PDO) was provided by the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China), and was distilled twice in vacuum immediately before use. The purity of PDO of 99.9% was determined by Gas Chromatography, and the water content in PDO was less than 200 ppm, as measured by 831 KF Coulometer (Metrohm, Switzerland). Novozym 435, lipase *Candida antarctica* B (CALB) immobilized on methacrylate macroporous resin, was purchased from Novo Nordisk Bioindustrials, Inc., in China and dried in vacuum at 50 °C for 20 h before use. Ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), purchased from Cheng Jie Chemical Co., Ltd. (Shanghai, China) with a purity of 99%, was dried in vacuum at 70 °C for 7 h before use. Other reagents such as phenol, 1,1,2,2-tetrachloroethane and methanol were all of A.R. grade and were used as received.

2.2. Characterization

^{1}H NMR spectra of PPDO were recorded in $CDCl_3$ on a Varian Germini 400 MHz NMR spectrometer using TMS as an internal standard. The matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) were conducted with a Bruker Ultraflex mass spectrometer equipped with a nitrogen laser emitting at $\lambda = 355$ nm. The samples were dissolved in chloroform ($CHCl_3$) and mixed with the matrix 2,5-dihydroxybenzoic acid (DHB) at a mass ratio of 1:5. The M_w, M_n and polydispersity index (PDI) of PPDO were measured by gel permeation chromatography (GPC) at 30 °C on a Waters HPLC system equipped with a model 2414 refractive-index detector. Chloroform was used as an eluent at a flow rate of 1 mL/min. The calibration curves for GPC analysis were obtained using polystyrene standards with different molecular weights and low polydispersity. Intrinsic viscosities ([η]) were measured at 30 °C with $C = 1$ mg/mL in phenol/1,1,2,2-tetrachloroethane (v/v = 1:1) using Ubbelohde viscosimeter. The M_v of PPDO was calculated from the intrinsic viscosity according to Mark–Houwink equation ($[\eta] = KM_v^{\alpha}$, where $\alpha = 0.63$ and $K = 7.9 \times 10^{-4}$ cm^3/g) [20]. The infrared absorption spectra were performed on a Nicolet FTIR 170SX infrared spectrometer using KBr pellets of samples. The scanning electron microscopy (SEM) images were recorded with a FEI Inspect F instrument operated at 20 kV, and all fracture surfaces of Novozym 435 were coated with gold prior to examination.

2.3. General procedure for the ROP of PDO

Method A: Novozym 435 catalyzed ROP of PDO using [BMIM][PF_6] as a solvent. Typically, 10 wt% [BMIM][PF_6] ionic liquid (0.62 g, based on PDO) and 5 wt% Novozym 435 (0.31 g, based on PDO) were added in a 10 mL round bottom flask. After the reactor was evacuated and filled with N_2 several times, PDO (6.2 g, 60.8 mmol) was immediately injected into the flask with a syringe under N_2 atmosphere and a homogeneous solution was obtained. Then the flask was immersed in an oil bath at the predetermined temperature for a period of time. At the end of the reaction, the flask was immediately immersed into ice water. Finally, the crude solid product was dissolved in phenol/1,1,2,2-tetrachloroethane and Novozym 435 was obtained by filtration. Afterwards the filtrate was poured into a large amount of methanol, and the product was obtained by filtration. The obtained product was dried at 60 °C under vacuum for 24 h. The monomer conversion was determined gravimetrically. The ionic liquid was recycled by vacuum distillation of the filtrate.

Method B: Ionic liquid-coated Novozym 435 used as a catalyst without solvent. Before the addition of PDO, 5 wt% Novozym 435 (0.31 g, based on PDO) was pre-incubated in 10 wt% [BMIM][PF_6] (0.62 g, based on PDO) for 2–8 h in N_2. After that, the same amount of PDO (6.2 g, 60.8 mmol) like method A was injected into the flask with a syringe under N_2 atmosphere. The subsequent procedures were the same as method A.

^{1}H NMR ($CDCl_3$, δ, ppm) of PPDO: 4.18 ppm (s, 2H, —OCH_2COO—), 4.36 ppm (t, 2H, —OCH_2CH_2OCO—), 3.80 ppm (t, 2H, —OCH_2CH_2OCO—), which were the same as that of PPDO synthesized by using chemical catalysts [6].

3. Results and discussion

In order to determine the best ionic liquid amount for the ROP of PDO conducted with method A, 10–50 wt% ionic liquid (based on PDO) was used. The result shows (Supplementary material) that both monomer conversion and viscosity–average molecular weight (M_v) of PPDO increased with the increase of ionic liquid concentration from 10 wt% to 20 wt%. And then they were decreased with the further increase of ionic liquid concentrations. We think the excessive ionic liquid amount would limit the lipase contact with monomer, therefore, the monomer conversions and the molecular weight of PPDO will be lowered. In addition, the difference of M_v and monomer conversion obtained using 10 wt% and 20 wt% ionic liquid as solvent was relative small. At the same time, considering the cost of ionic liquid, we chose 10 wt% ionic liquid as the optimum amount for the following experiments.

3.1. Effect of temperature on the ROP of PDO

It is well known that the activity and stability of lipase highly depends on the reaction temperature. A series of experiments were conducted using the above two methods at different temperatures. Fig. 1 shows the effect of the reaction temperature on the molecular weight of PPDO and monomer conversion.

Just as the results in Fig. 1 show, temperature had great influence on the polymerization of PDO regardless of which method was adopted. The molecular weight (M_w) and monomer conversion increased with the increase of reaction temperature up to 70 °C at which both of them reached their maximum values. For example, the maximum M_w and monomer conversion was 90,600 g mol^{-1} and 63%, respectively, using ionic liquid-coated Novozym 435 as a catalyst. However, these values decreased to 12,500 g mol^{-1} and 61%, respectively, when only Novozym 435 was used as a catalyst and [BMIM][PF_6] as a solvent. When the reaction temperature increased to 80 °C, the molecular weight of PPDO and monomer conversion sharply decreased whatever method used. This means the activity of Novozym 435 was inhibited greatly at 80 °C. Therefore, 70 °C was the optimum reaction temperature for Novozym 435 catalyzed ROP of PDO.

Comparing methods A and B, we found that the M_w of PPDO obtained by using ionic liquid-coated Novozym 435 as a catalyst was much higher than that obtained by using ionic liquid as a solvent, especially at the best reaction temperature (70 °C).

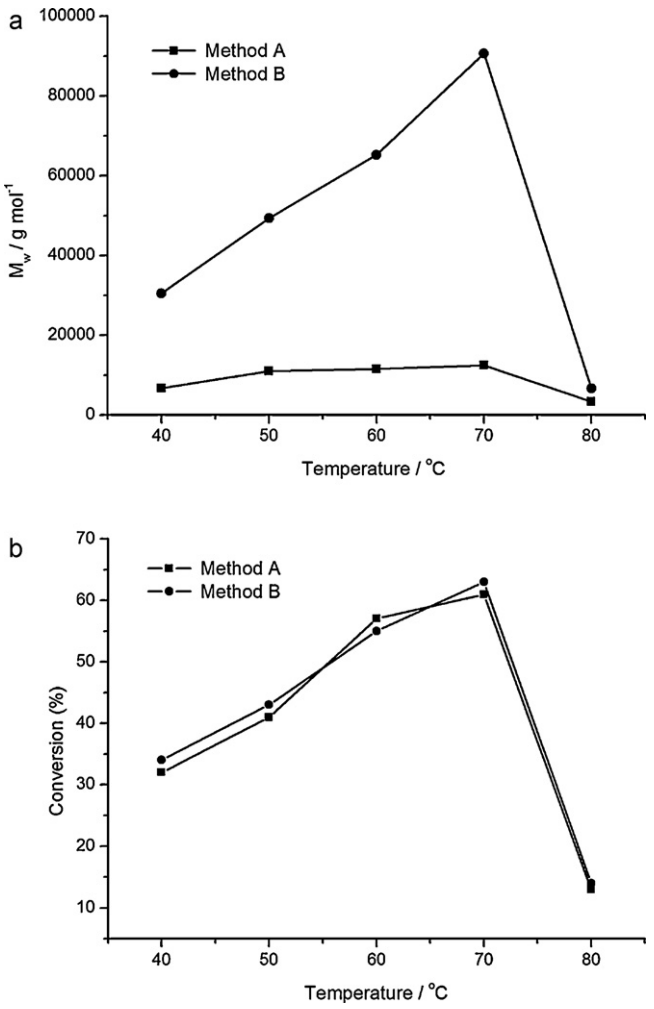


Fig. 1. Effect of reaction temperature on M_w (A) and monomer conversion (B) of PPDO under different catalyst system.

However, the monomer conversion of PDO was almost invariable at the same reaction temperature using these two methods (Fig. 1(b)). This phenomenon indicated that method B was much in favor of obtaining high molecular weight PPDO. In terms of the monomer conversion, method A had no advantage. As we know, a monomer conversion has great relationships with catalyst amount. For both of methods A and B, the content of Novozym 435 fixed at 5 wt% (based on PDO), therefore, they had no difference on monomer conversions.

3.2. Effect of enzyme pre-incubation time on the ROP of PDO at 70 °C

In order to discuss the effect of enzyme pre-incubation time on polymerization, a series of experiments were carried out and the results were shown in Fig. 2.

Interestingly, it was found that the molecular weight of PPDO increased significantly with the increase of enzyme pre-incubation time from 2 h to 6 h while the monomer conversion kept nearly invariant (about 60%). By putting PDO monomer, Novozym 435 and [BMIM][PF_6] together immediately instead of pre-incubating Novozym 435 in [BMIM][PF_6], PPDO with M_w of 52,400 g mol^{-1} was obtained after 20 h. By introducing PDO after pre-incubating Novozym 435 in [BMIM][PF_6] for 6 h, the molecular weight of PPDO reached 99,900 g mol^{-1}. This illustrated that the pre-incubation

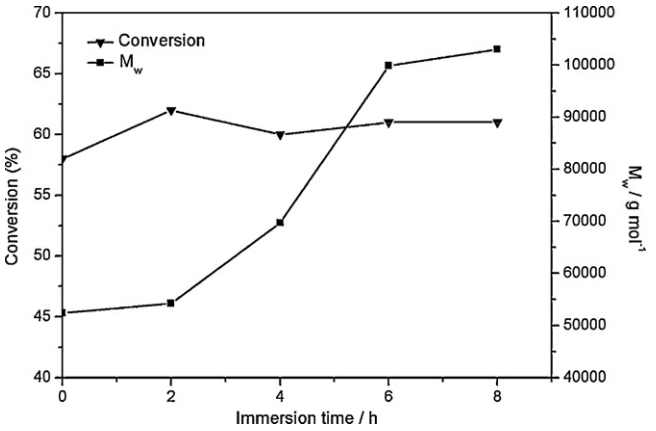


Fig. 2. Effect of enzyme pre-incubation time on the polymerization of PDO catalyzed by ionic liquid-coated Novozym 435.

of Novozym 435 in [BMIM][PF_6] can improve the catalytic activity of Novozym 435, and subsequently the molecular weight of the obtained PPDO was increased. By further extending the enzyme pre-incubation time to 8 h, however, the molecular

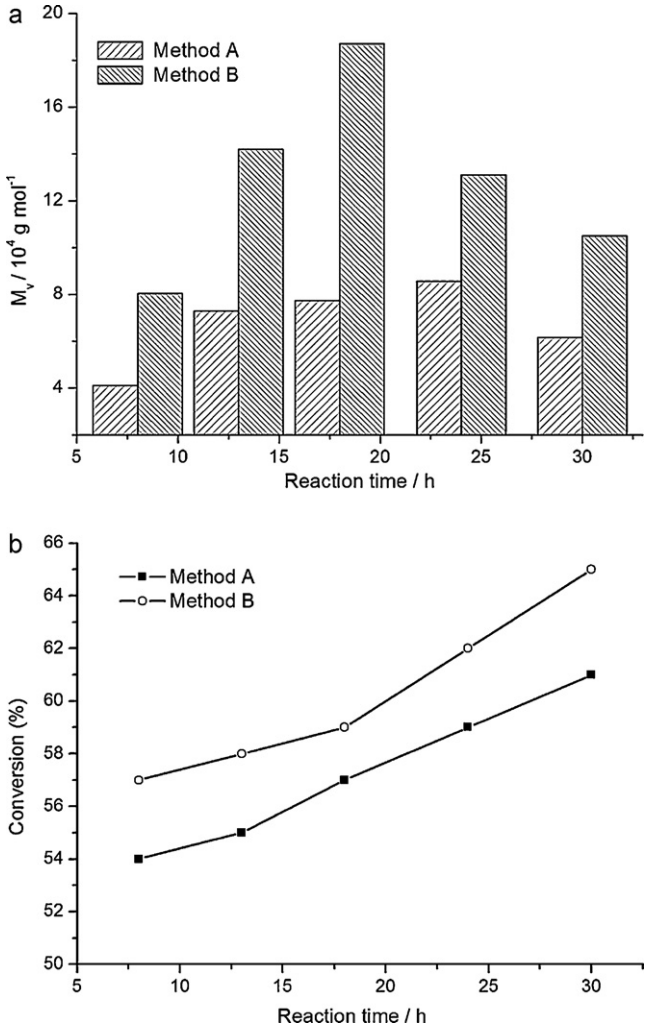


Fig. 3. Effect of reaction time on the polymerization of PDO catalyzed by two methods.

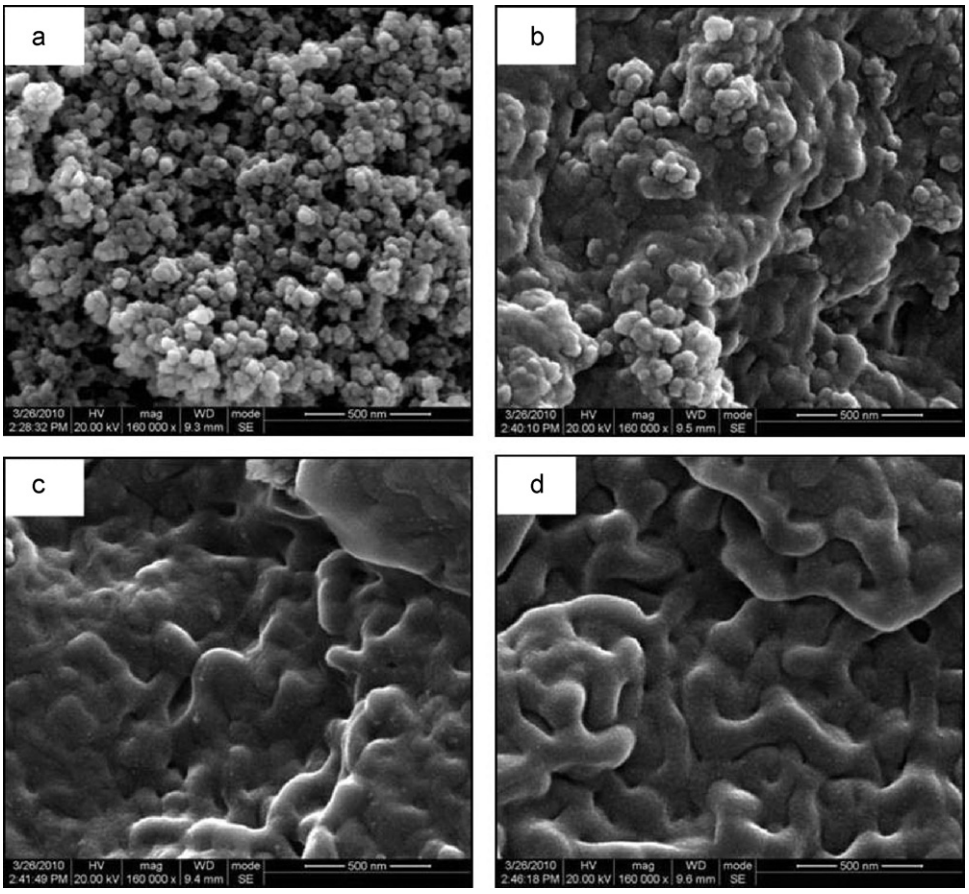


Fig. 4. SEM images of Novozym 435 and pre-incubated Novozym 435. (a) Novozym 435, (b) Novozym 435 pre-incubated in [BMIM][PF_6] for 2 h, (c) Novozym 435 pre-incubated in [BMIM][PF_6] for 6 h, and (d) Novozym 435 pre-incubated in [BMIM][PF_6] for 8 h.

weight increased slightly. Considering the reaction efficiency, the enzyme pre-incubation time was fixed at 6 h in the following experiments.

3.3. Effect of reaction time on the polymerization

The effect of reaction time on the polymerization of PDO with these two methods was investigated, and the corresponding results were plotted in Fig. 3. Fig. 3(a) shows that the molecular weight of PPDO obtained by these two methods increased with the increase of reaction time from 8 h to 18 h. And then they gradually decreased with the further increase of reaction time to 30 h. For example, with ionic liquid-coated Novozym 435 as a catalyst, the molecular weight reached its maximum value of 182,100 g mol^{-1} after 18 h, and then decreased to 84,100 g mol^{-1} after 30 h. With method A, the corresponding maximum value was found at 48,300 g mol^{-1} after 24 h and then decreased to 27,700 g mol^{-1} after 30 h. These results revealed that the optimal reaction time for method A and method B was 24 h and 18 h, respectively.

Further increasing the reaction time caused some side reactions such as inter- and intra-transesterification. Fig. 3(b) shows that the monomer conversion increased very slowly with the increase of reaction time from 8 h to 30 h illustrating that the polymerization of PDO had almost reached their thermodynamic equilibrium after 8 h [6]. Comparing the results of the ROP of PDO obtained by these two catalyst systems, the PPDO molecular weight increase was more notable when using ionic liquid-coated Novozym 435 as a catalyst. However, as far as monomer conversion is concerned, no significant difference was found with these two methods. This phenomenon demonstrated again that method B had more advantages in obtaining high molecular weight PPDO. This enhancement of the catalytic activity of Novozym 435 was due to the fact that the bound water layer surrounding the lipase was protected by immersing Novozym 435 in [BMIM][PF_6] [21]. And the catalytic activity of enzyme had great relationship with the bound water. A detailed analysis on [BMIM][PF_6] coated Novozym 435 and the catalyzed mechanism of the ROP of PDO will be covered in the later section.

3.4. Interaction analysis of Novozym 435 and [BMIM][PF_6]

Now there are two questions about this experiment. The first is whether the ionic liquid [BMIM][PF_6] could catalyze the ring-opening polymerization of PDO. To answer this question, a series of the ROP of PDO were conducted in [BMIM][PF_6] without using lipase. However, with the increase of reaction time, only a little oligomer was obtained after 72 h. It was therefore demonstrated that [BMIM][PF_6] was not a catalyst for the ROP of PDO.

Another question is how [BMIM][PF_6] and lipase worked synergically in the system. The following experiment was carried out in order to illuminate this issue. 0.62 g [BMIM][PF_6] and 0.31 g Novozym 435 were mixed together by stirring at room temperature for different time, and then Novozym 435 was filtered out. The inside morphology of the original Novozym 435

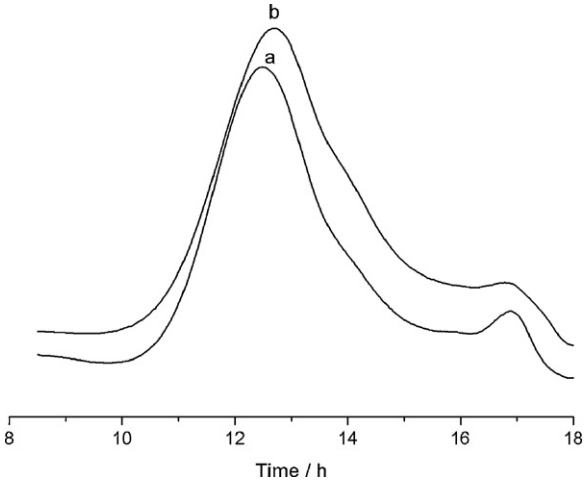


Fig. 5. GPC traces of PPDO obtained by different methods (a) Novozym 435 as a catalyst and [BMIM][PF_6] as a solvent (b) ionic liquid-coated Novozym 435 as a catalyst.

and the pre-incubated Novozym 435 was observed by scanning electron microscopy (Fig. 4). Obviously, there were many interspaces between the polyacrylate beads in the original Novozym 435 (Fig. 4(a)). However, these interspaces vanished gradually with the increase of pre-incubation time. For example, when the pre-incubation time was 6 h or 8 h (Fig. 4(c) and (d)), the spacing was vanished and some liquid layers even could be on the surface of polyacrylate beads. This indicated that Novozym 435 was coated by [BMIM][PF_6].

Furthermore, in order to investigate whether [BMIM][PF_6] was absorbed or had some reactions with lipase, the coated Novozym 435 was washed using methanol for several times. The washed Novozym 435 and the original Novozym 435 were characterized by FT-IR. No differences were found between their FT-IR spectra (not shown here). This further illustrated that Novozym 435 was only coated by [BMIM][PF_6] due to the absorption of the macroporous structure of polyacrylate substrate [19,22]. Via this treatment the activity of Novozym 435 was increased because the bound water layer surrounding the lipase was protected by [BMIM][PF_6]. Other researchers also found these bound or "essential" water molecules acted as lubricants, providing enzyme molecules with the flexibility, which is necessary for enzyme catalysis [23,24].

During the investigation, it was found that the polydispersity indices (PDI) of PPDO obtained in the presence of Novozym 435 were relatively broad. From their GPC profiles (Fig. 5), the multimodal molecular weight distributions were typically shown whatever method was used. It was deduced that besides the linear PPDO (main product), specific oligomers or cyclic species were obtained simultaneously using Novozym 435 as a catalyst. In order to demonstrate this, MALDI-TOF MS spectrograph of PPDO was investigated.

Fig. 6 was the MALDI-TOF spectra of PPDO catalyzed by ionic liquid coated Novozym 435. In the expanded view for the 1000–3000 and 3000–5000 m/z fragments, PPDO with two different structures were found. A series of peaks at m/z 1352, 1454, 1658, 1862 were ascribed to the cyclic PPDO. The other series of peaks at m/z 3006, 3312, 3414, 3619, 3823 were belonged to the linear PPDO. The value increment of these peaks for both series was 102, which was the molecular weight of PDO monomer. The results further demonstrated that cyclic species were obtained simultaneously using Novozym 435 as a catalyst for the ROP of PDO. This illustrated that during the last stage of the ROP, there were some side reactions such as inter- and intra-molecular transesterification, end-to-end condensation, backbiting of the terminal OH group onto the activated carbonyl group, etc. Some literatures also reported this phenomenon during enzyme catalyzed synthesizing other aliphatic polyesters [25–28].

Based on the above results, it was deduced that besides the traditional steps such as initiation, propagation, chain-end [29,30], adsorption and monomer activation were involved in ionic liquid coated Novozym 435 catalyzed the ROP of PDO. The deduced step-wise reaction was shown in Scheme 1. That is to say, during the ROP of PDO, ionic liquid was firstly absorbed by Novozym 435 to form the ionic liquid coated lipase, and then the ionic liquid coated lipase nucleophilically attacked the monomer PDO to form an enzyme activated monomer complex (EAM). EAM reacted with the bound water of lipase to produce ω-hydroxyl carboxylic acid which would nucleophilically attacked EAM to produce PPDO with long chain during the propagation stage. It was thought that the monomer activation and especially the initiation step were the key steps for ionic liquid coated Novozym 435 catalyzed the ROP of PDO.

Because of the activation and the initiation steps, an equilibrium reaction, was easy to produce ω-hydroxyl carboxylic acid. Therefore, during the propagation process, the longer PPDO chain was achieved comparing with that obtained by pure enzyme without coating. Besides these steps, during the polymerization of PDO, there were some side reactions including inter-, intra-transesterification, polycondensation, etc., which were demonstrated by GPC and MALDI-TOF results. The detailed activation mechanism of lipase being coated with ionic liquid still needs further investigations.

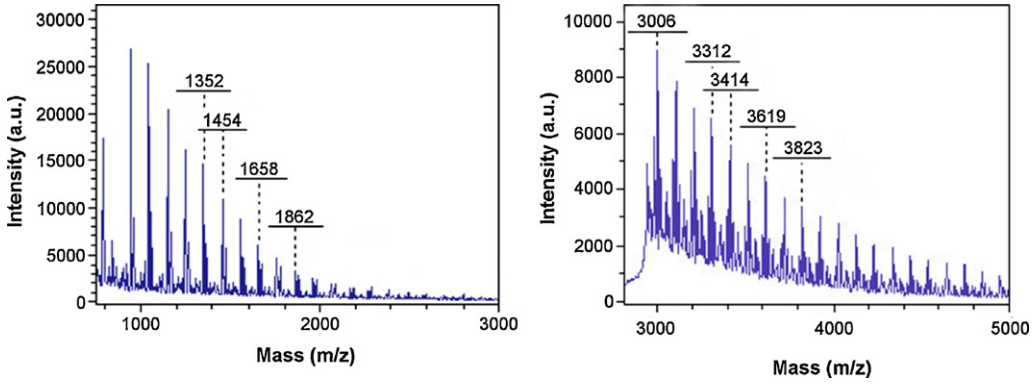
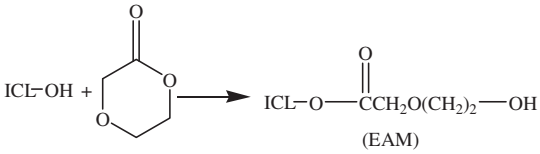


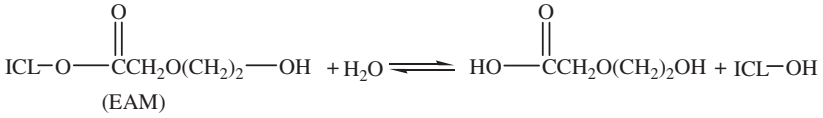
Fig. 6. MALDI-TOF spectra of PPDO catalyzed by ionic liquid coated Novozym 435.

Adsorption:

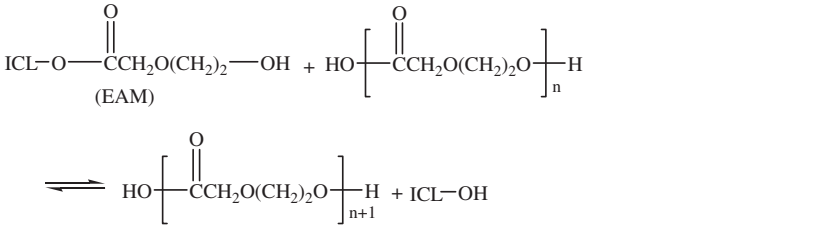
Monomer Activation:



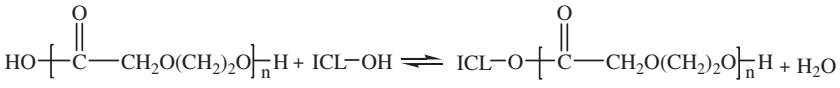
Initiation:



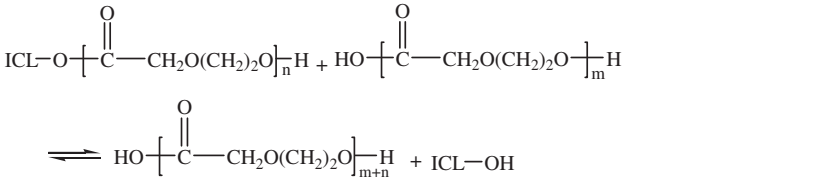
Propagation:



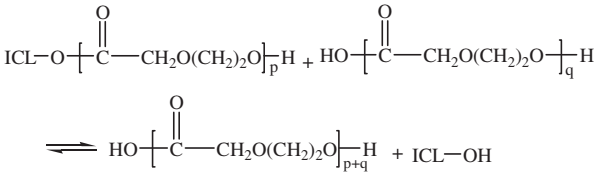
Chain-End Activation:



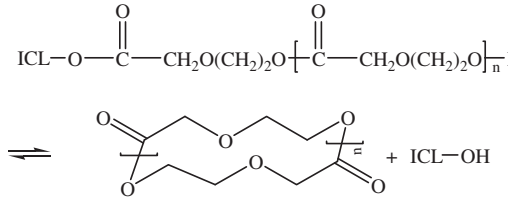
Polycondensation:



Inter-transesterification:



Intra-transesterification:



Scheme 1. Proposed mechanism of ionic liquid-coated Novozym 435 catalyzed the ROP of PDO.

4. Conclusion

Two methods were adopted for the ROP of PDO in the presence of [BMIM][PF_6] and Novozym 435. It was found that pre-incubating Novozym 435 in [BMIM][PF_6] for several hours before use was a novel and efficient method for obtaining PPDO with high molecular weight. PPDO with a high molecular weight (M_w = 182,100 g mol^{-1}) was obtained by keeping at 70 °C for 18 h with 5 wt% Novozym 435 (based on PDO) pre-incubated in 10 wt% ionic liquid (based on PDO) for 6 h. Via this treatment, the catalytic activity of Novozym 435 was increased, because the bound water layer surrounding the lipase was protected by [BMIM][PF_6]. The protected bound water of lipase made the monomer activation and initiation steps of the ROP of PDO easy to progress. It was expected that this feasible method would provide a new way for lipase-catalyzed the ROP of lactones. The synthesis of other aliphatic polyester via this method is still going on.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcatb.2012.01.006.

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