Facile Synthesis of Block Copolymers by Tandem ROMP and eROP from Esters Precursors

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Facile Synthesis of Block Copolymers by Tandem ROMP and eROP from Esters Precursors

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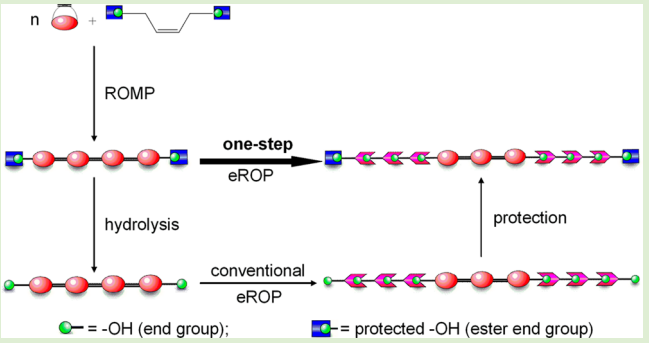
Supporting Information

ABSTRACT: In the present study, block copolymers were first synthesized through a tandem ring-opening metathesis polymerization (ROMP) and conventional enzymatic ring-opening polymerization (eROP) from hydroxyl initiator. Furthermore, a novel synthesis route, single-step eROP from ester precursor was successfully developed to synthesize targeted copolymers. The as-prepared polymers were analyzed by NMR, GPC, DSC, and MALDI-TOF-MS. There was no difference in the characteristic peaks of NMR between the end products obtained from these two synthetic routes. The GPC data showed that the copolymer obtained from single-step eROP was similar to the end product obtained from the traditional multistep synthesis method. Afterward, we used model compounds to carry out the conventional eROP and the single-step eROP. Finally, through the kinetic analysis and structural analysis of the resulting product, a reasonable initiation mechanism for this single-step eROP was elucidated.



INTRODUCTION

The increasing need of polymeric materials for various applications will dramatically require the construction of materials with tailor-made structures and properties, and thus, it will be necessary to develop novel catalysts or synthetic methods. In recent years, numerous chemical synthetic methods or catalytic systems have been developed for preparing polymeric materials, while most of these catalysts are highly specific and selective, which will limit the general application of a catalyst in multistep reactions.[1] This constraint of chemical methods can be overcome through the combination with other catalysts or methods, especially enzymatic polymerization. In the past two decades, enzymatic ring-opening polymerization (eROP) has rapidly developed and become an important synthetic method in polymer chemistry.[2−8] Compared with a conventional chemical route, enzymatic polymerization has many advantages,[4,5,9] including (1) mild reaction conditions, (2) high control of chemo- and regioselectivity, (3) recyclability of biocatalysts, (4) few byproducts, and (5) high efficiency to catalyze the ring-opening polymerization of macrocyclic lactones. By utilizing these advantages of enzymes, chemoenzymatic methods have been greatly developed for synthesizing new polymeric materials that are otherwise difficult to prepare. More importantly, chemoenzymatic polymerization could further increase the diversity and complexity of synthesizing macromolecules via multistep reactions and cascade reactions.[1] In the chemoenzymatic polymerization, the most prominent example is the combination of eROP of lactones with radical polymerization to construct the designed copolymers, for example, atom transfer radical polymerization (ATRP),[10−14] nitroxide mediated polymerization (NMP),[15] and reversible addition−fragmentation chain transfer (RAFT).[16] In the above chemoenzymatic polymerization, bifunctional initiators with hydroxyl groups were usually employed for the proceeding of these reactions.

In an attempt to expand this combination strategy to nonradical polymerization, ring-opening metathesis polymerization (ROMP) is undertaken to combine with eROP in the present research. Due to its versatility, effectiveness, and functional group tolerance, ROMP using Grubbs catalyst has been widely employed to construct functional polymers.[17,18] These ruthenium alkylidene catalysts could allow a variety of monomers bearing polar, apolar, and charged functional groups to be successfully polymerized.[19] To our knowledge, there were no previous reports on the combination of ROMP and eROP, while some research groups have realized the combination of ROMP and chemical ROP (cROP) to prepare copolymers.[20−33] Hillmyer once successfully synthesized hydroxyl-terminated polymers through the hydrolysis of acetoxy,[21,22] and then these hydroxyl-terminated precursors were used to initiate cROP, yielding block copolymers.[22−24] Jerome constructed the polymer through the ROMP of acetoxyl norbornene, and then

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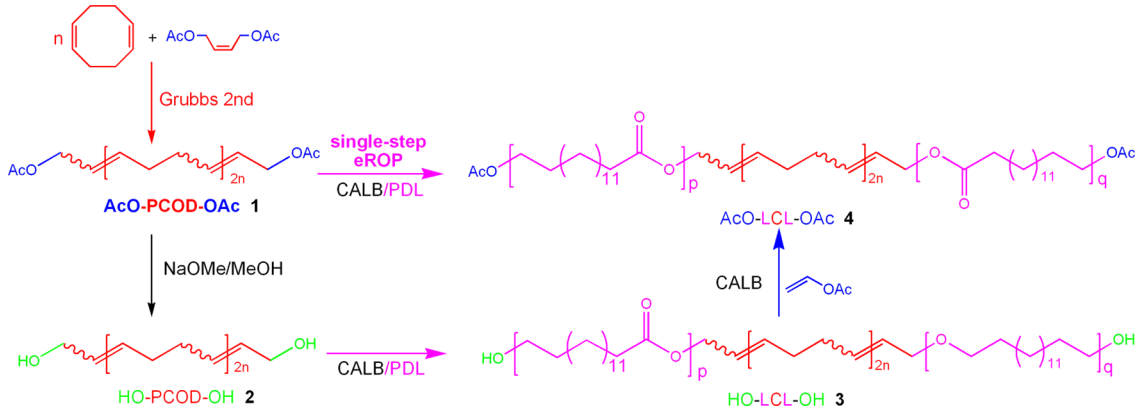
Scheme 1. Synthesis of Block Copolymers Using ROMP of COD Followed by eROP of PDL



the ester groups were hydrolyzed to hydroxyl groups, which could further initiate the cROP to prepare comb copolymers.[25] In these reactions, the nucleophilic hydroxyl group was used as initiators to trigger the cROP. However, hydroxyl group is not stable and can be easily oxidized to an aldehyde/ketone (CHO/CO) or a carboxylic acid group (COOH). In addition, it might coordinate into the metal catalytic center, which reduces the activity of catalysts or even deactivates the catalysts. It will be of great significance to develop new routes to avoid the tedious protection−deprotection procedure of hydroxyl group. Moreover, utilizing ROMP technique, end-functionalized macromolecular precursors are easily prepared, which could be used as initiators in the eROP for the synthesis of block copolymers under mild reaction conditions. Thus, the combination of these two techniques will be a simple and versatile tool for preparing block copolymers and also other polymeric materials with tailor-made structures and properties.

In this work, the combination of ROMP and eROP was first conducted to prepare the block copolymers. Based on the fact that lipases can catalyze the cleavage of ester groups, we used esters as the initiator of eROP to construct a unique single-step eROP. If esters precursor could be successfully applied to the initiation of eROP, it might solve the negative issues of active hydroxyl groups and simplify the procedure to avoid the hydrolysis procedure. Here, acetoxy-terminated polybutadiene (**1**) and hydroxyl-terminated polybutadiene (**2**) were prepared by ROMP, and then employed to initiate the eROP of ω-pentadecalactone (PDL) to construct block copolymers, respectively (Scheme 1). Subsequently, we used a small molecule 1,4-diacetoxy-2-butene as a model compound to carry out single-step eROP, and the precise structure of end groups of resulting product was confirmed. In addition, through the kinetic analysis and structural analysis of the resulting product, a reasonable mechanism for the single-step eROP using the esters precursor was elucidated.

EXPERIMENTAL SECTION

Materials. 1,5-Cyclooctadiene (COD, ≥99%, redistillation, without stabilizer), *cis*-1,4-diacetoxy-2-butene (**5**), *cis*-2-butene-1,4-diol (**6**), and poly(ethylene glycol) (PEG, M_n = 4000 Da) and ω-pentadecalactone (PDL) were purchased from Sigma-Aldrich, stored over P_2O_5 in a desiccator, and used without further purification. Novozym 435 (*Candida antarctica* lipase B immobilized on acrylic resin, CALB, Novozymes) was dried under vacuum before use. Toluene and vinyl acetate were purchased from Beijing Chemical Works. Toluene was freshly distilled before use from a purple Na/benzophenone ketyl solution.

Methods. The nuclear magnetic resonance (NMR) spectra were conducted on a Bruker Avance III NMR spectrometer with $CDCl_3$ as solvent, operating at 400 MHz for the corresponding ^1H nuclei. Chemical shifts (in ppm) were reported downfield using tetramethylsilane as internal standard. Gel permeation chromatography (GPC) was performed using a Shimadzu apparatus equipped with a refractive index detector and a Shim-pack GPC-803 column. Tetrahydrofuran (THF) was used as the eluent, at a flow rate of 1.0 mL/min at 40 °C. The detection was calibrated with polystyrene standards of narrow molecular weight distribution. The differential scanning calorimetric measurement (DSC) was performed using a PerkinElmer differential scanning calorimeter as follows: initial heating from −30 to 120 °C and then cooling from 120 to −30 °C, as well as the second heating from −30 to 120 °C at a rate of 10 °C/min. Matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements were performed on a Bruker Autoflex Speed TOF/TOF mass spectrometer in a linear mode. Dithranol (1,8-dihydroxy-9(10H)-anthracetone, ≥98.0%, Fluka) was used as matrix. The polymers were dissolved in THF and premixed with dithranol dissolved in THF. A volume of 0.9 μL was given onto the MALDI sample slide and allowed to dry at room temperature for measurement.

Synthesis of Precursors. The two kinds of precursors were synthesized by ROMP according to the previous report.[20] The synthesis of acetoxy-terminated poly(cyclooctadiene) (AcO-PCOD-OAc; **1**) was conducted using Grubbs second generation catalyst, COD (monomer) and **5** (chain transfer agent, CTA) in anhydrous toluene. Then **1** was hydrolyzed by sodium methoxide to obtain hydroxyl-terminated poly(cyclooctadiene) (HO-PCOD-OH; **2**). The products were precipitated in cooled methanol, and the polymers were separated by centrifugation, washed with CH_2Cl_2/CH_3OH for three times, and then dried under vacuum. The ^1H NMR spectra for AcO-PCOD-OAc and HO-PCOD-OH were shown in Figures S1 and S2.

Single-Step eROP Route. A total of 0.4 mmol acetoxy-terminated precursor (**1** or **5**), Novozym 435 (5 wt % of PDL), and anhydrous toluene (3 mL) were mixed in a 10 mL round reaction flask. Addition of 1 g PDL (4.17 mmol) triggered the eROP reaction that was allowed to run at 80 °C under magnetic stirring for 12 h. Reactions were stopped by filtrating the enzymes. The products were precipitated in cooled methanol, and the polymers were separated by centrifugation, washed with CH_2Cl_2/CH_3OH three times, and then dried under vacuum.

Conventional eROP Route and End-Capping Using Vinyl Acetate. A total of 0.4 mmol hydroxyl-terminated precursor (**2** or **6**), Novozym 435 (5 wt % of PDL), and anhydrous toluene (3 mL) were mixed in a 10 mL round reaction flask. A 1 g aliquot of PDL (4.17 mmol) was added to initiate the reaction at 80 °C under magnetic stirring. After 12 h, vinyl acetate (2.0 mmol) was added to the reaction flask, and the mixture was allowed to stir for an additional 2 h. After the reaction, the polymer was precipitated in cold methanol, and the acetoxy-terminated copolymer (AcO-LCL-OAc; **4**) was obtained. If the reaction was stopped before the addition of vinyl acetate, the

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hydroxyl-terminated copolymer (HO-LCL-OH; **3**) was obtained. The products were precipitated in cold methanol, and the polymers were separated by centrifugation, washed with CH_2Cl_2/CH_3OH three times, and dried under vacuum.

RESULTS AND DISCUSSION

Synthesis of Block Copolymers. As shown in Scheme 1, ROMP of COD and eROP of PDL were combined to prepare block copolymers through two synthetic procedures, namely, single-step eROP route and conventional eROP route. In the latter, **1** was efficiently synthesized by ROMP and then hydrolyzed to produce hydroxyl-terminated polymer **2**, as described in the classical method.[20] Then, the hydroxyl precursor initiated eROP to generate hydroxyl-terminated copolymer **3**. In order to identify the product of single-step route, **3** was end-capped using end-capping agent at the end of reaction to generate acetoxy-terminated copolymer **4**. In the single-step eROP route, eROP was carried out directly from ester precursor **1**. Thus, the resulting product **4** was prepared in a single step from **1** to **4**. Compared with the conventional eROP route, this route omitted the step of hydrolysis and end-capping.

NMR Analysis of Block Copolymers. The characteristic peaks of products in each step, for example, poly-COD and poly-PDL, were confirmed by ^{1}H NMR (Figure 1). For sample

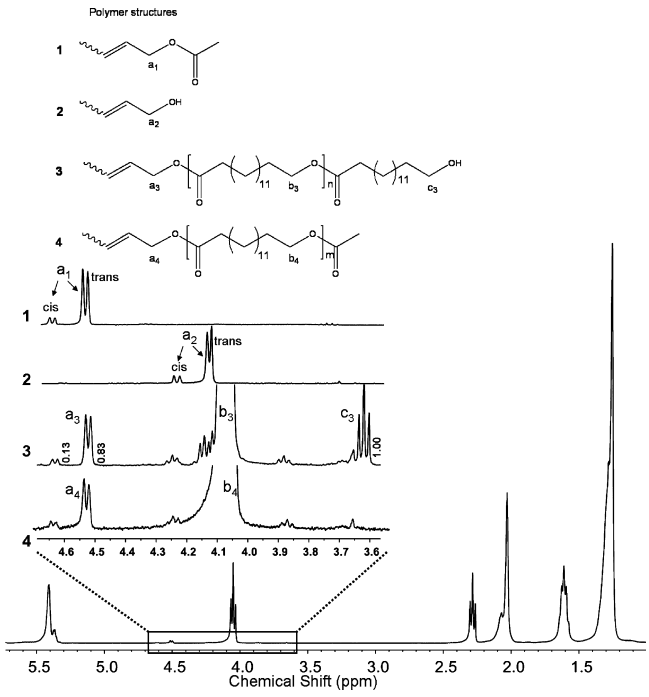

Figure 1. ^{1}H NMR spectra for telechelic PCOD homopolymer precursors and copolymer: **1**, AcO-PCOD-OAc; **2**, HO-PCOD-OH; **3**, HO-LCL-OH; **4**, AcO-LCL-OAc.

1, the chemical shifts of the end-group methylene protons adjacent to the carbon−carbon double bonds (-CH═CH-C$\underline{H}_2$-OAc) were assigned as peak a_1, which included two peaks, 4.61 ppm (cis) and 4.51 ppm (trans). The characteristic peaks of chemical structures were assigned as follows: -CH═CH-C$\underline{H}_2$-OH (peak a_2 in **2**); -CH═CH-C$\underline{H}_2$-OCOR (peak a_3 in **3**, and peak a_4 in **4**); -COO-C$\underline{H}_2$-R (peak b_3 in **3**); RCH_2-C$\underline{H}_2$-OH (peak c_3 in **3**). Other signals were assigned in Figures S1−S8 in the Supporting Information. In the conventional eROP route, the end-group methylene protons shifted upfield (peak a_1 to a_2) after the hydrolysis of **1**. Using the hydroxyl groups of **1** as initiating moieties, eROP of PDL would lead to a shift of the signal associated with the protons to δ = 4.5−4.7 ppm (peak a_3). An additional signal associated with the methylene protons on the PDL chain ends was present at δ = 3.6−3.7 ppm (peak c_3). The integration ratio of the methylene (peak a_3) and end-group methylene protons (peak c_3) was 0.96 (theoretically the ratio should be 1.0), consistent with the absence of significant PPDL homopolymer.

Whether HO-PCOD-OH fully participated in the reaction could be deduced by the disappearance of signals at δ = 4.1 ppm (peak a_2). Unfortunately, peak a_2 was overlapped with peak b_3, the characteristic peak of repeat units of PPDL (Figure 1). Thus, two-dimensional ^{1}H−^{1}H correlated spectroscopy (COSY) was conducted to further identify complete esterification of hydroxyl groups (Figure S9). The cross-peak of H_b (5.5−5.7 ppm) with H_a (4.5 ppm) was observed, whereas there was no cross-peak between H_d (5.6−5.8 ppm) and methylene protons H_c (4.1 ppm) adjacent to the carbon−carbon double bonds and hydroxyl group. Comparison of the COSY spectra for **3** and **2** indicated the absence of ═CH−CH_2−OH and a high initiation efficiency. Through these results, block copolymers with no trace homopolymer residues were successfully prepared, and then they could be used in the subsequent research.

The product **4** was obtained from the acetylation reaction of hydroxyl group at the end of copolymers **3**. As shown in Figure 1, the main characteristic peaks of product **4** were similar to **3**. The most obvious distinction in NMR was the disappearance of peak at 3.65 ppm (peak c_3), which suggested that their chemical structures were similar except for the end groups. Unfortunately, it was impossible to assign the spectra of this end group using ^{1}H NMR, because the end group resonances were overlapped by the repeat units of PCOD. Based on the acylation analysis of polyester terminals in eROP,[34] the chemical shifts of the end-group methyl protons (−COC$\underline{H}_3$) were at 2.0 ppm, which could be easy to deduce that the end groups were acetoxy groups. For the structure of **4** obtained from the single-step eROP, there were no differences in the characteristic peaks between the products **4** from single-step eROP and the conventional eROP route.

GPC Analysis. Different precursors were directly employed in the eROP without the step of acetylation, and the molecular weight of the precursors and block copolymers was determined by GPC. As shown in Table 1, the expected increase in molecular weight and decrease in polydispersity index (M_w/M_n) were obviously observed from the precursors to their corresponding block copolymers. The increase in M_n indicated the incorporation of PDL into the polymer chains. There was no shoulder peak in the block copolymers (Figure S10), which suggested the absence of homopolymer, consistent with the NMR analysis. For the precursor with the same main structure except for end groups, such as entries 1 and 3, their corresponding copolymers were similar in M_n and M_w/M_n, and the block copolymers **4** was slightly smaller than the block copolymers **3**. In addition, commercially available PEG with different end groups was utilized to initiate eROP, for example, entries 8 and 9 (Figure 2). The similar curves of GPC showed that this method was not confined to our products obtained from ROMP, and it could be extended to other chemo-enzymatic synthesis systems.

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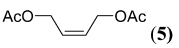
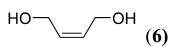
Table 1. Different Precursors were Carried out eROP of PDL Without the Step of Acetylation (80 °C, 12 h)

Entry	Precursor				[M]/[P][c]	Copolymer			Conv. of PDL[e] (%)
	Structure[a]	Mn[a]	Mn[b]	Mw/Mn[b]		Mn[d]	Mn[b]	Mw/Mn[b]	
1	HO-(PCOD)$_{30}$-OH	3200	6300	2.28	23	8700	14800	1.51	>99
2	HO-(PCOD)$_{15}$-OH	1600	3400	1.56	26	7800	11500	1.55	>99
3	AcO-(PCOD)$_{30}$-OAc	3400	6100	2.32	23	8900	12300	1.80	>99
4	AcO-(PCOD)$_{15}$-OAc	1800	4000	1.65	26	7900	9900	1.29	>99
5	AcO-(PCOD)$_{15}$-OAc	1800	4000	1.65	5.0	3000	6200	1.44	>99
6	 **(5)**	172	-	-	5.0	1300	3400	1.26	92
7	 **(6)**	88	-	-	5.0	1300	4100	1.24	>99
8	AcO-(PEG)$_{87}$-OAc	3900	6400	1.10	73	21200	23900	1.45	>99
9	HO-(PEG)$_{87}$-OH	3800	5900	1.12	73	21100	29100	1.56	>99

[a]Determined using the ratio of relative integration from repeat unit and end-group protons in the ^{1}H NMR spectrum, assuming the average number of functional groups per polymer chain is 2. [b]Determined using GPC with THF as the eluent at 40 °C. Values reported relative to polystyrene standards. [c]P = precursor, M = monomer. The ratio is in mol/mol. [d]Calculated by ^{1}H NMR spectroscopy using relative intensities of repeat unit signals at 4.05 (poly-PDL) to 5.35−5.45 (poly-COD). [e]Determined by ^{1}H NMR spectroscopy using signals at 4.14 (PDL) to 4.05 (poly-PDL).

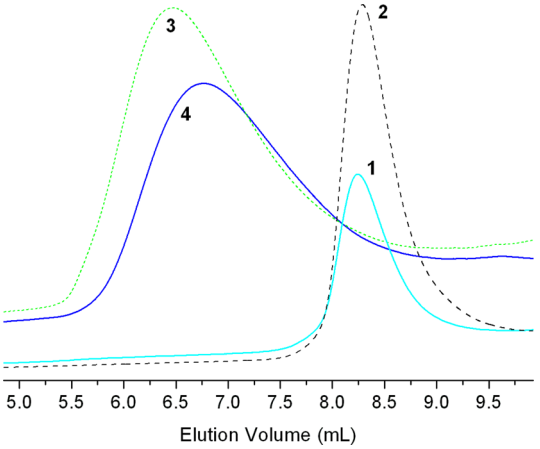


Figure 2. GPC chromatograms: (1) AcO-PEG-OAc, (2) HO-PEG-OH, (3) HO-PPDL-PEG-PPDL-OH, (4) AcO-PPDL-PEG-PPDL-OAc (obtained from the single-step eROP). These polymers were referred to the entries 8 and 9 in Table 1

Thermal Analysis. Samples of LCL (PPDL-PCOD-PPDL) were analyzed by DSC by first heating from −30 to 120 °C, cooling to −30 °C and reheating to 120 °C at 10 °C/min. As shown in Figure S11, an obvious endothermal peak was observed between 81 and 92 °C, which represented the melting temperature (T_m) of the samples. The T_m of PPDL synthesized by lipase catalysis was reported at 97 °C,[35] and the high trans PCOD exhibited a T_m between 20 and 25 °C.[21] From the DSC curves, it was observed that the T_m exhibited an increasing tendency with the increasing of PPDL blocks, which was probably caused by the successful construction of block copolymers. Meanwhile, the polymers PCOD and PPDL were both semicrystalline, and the block copolymers were of high crystallinity, mainly caused by the contribution of PPDL blocks.

Identification of End Groups. To further confirm the precise structure of end group of the resulting products by the single-step eROP, **5** and **6** were employed as model compounds for the termini of **1** and **2** in these two routes, respectively. It was recognized that the products of eROP initiated by hydroxyl precursor (including water) possessed a hydroxyl end group. In order to distinguish these two products, the conventional eROP procedure was conducted without the step of acetylation. According to our speculation, products of the single-step eROP were probably acetoxy-terminated polyester. As shown in Figure 3, there were two differences between the NMR spectra

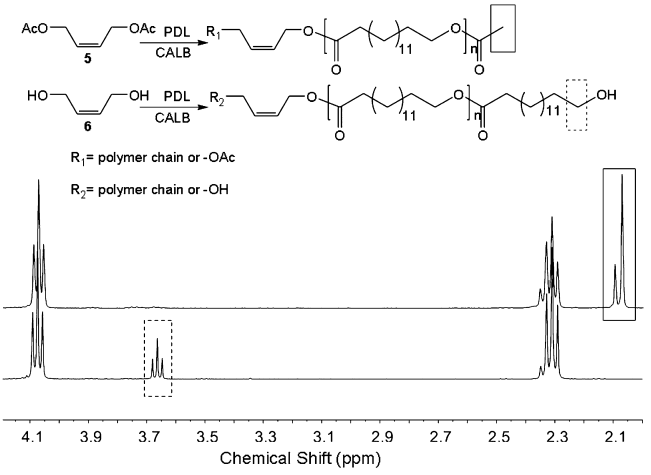


Figure 3. End group of the two kinds of PPDL: AcO-PPDL-OAc (obtained from precursor **5**, above) and HO-PPDL-OH (obtained from precursor **6**, below) were confirmed by ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$).

for AcO-PPDL-OAc and HO-PPDL-OH. First, the signal at 3.65 ppm of AcO-PPDL-OAc was very weak and easily merged by noises, which was the same as the results using macromolecular precursors. Second, AcO-PPDL-OAc exhibited a unique peak at 2.0 ppm assigned to the methyl protons of end group acetoxy. In the NMR spectra for **4**, this peak was overlapped by the repeat units of PCOD. These two points clearly confirmed the presence of the predesigned end group.

From MALDI-TOF-MS analysis, one main product distribution was observed, each with a repeating interval of 240 Da (the mass of one PDL monomer; Figure 4). The differences between the main products of the above and below were 84 Da,

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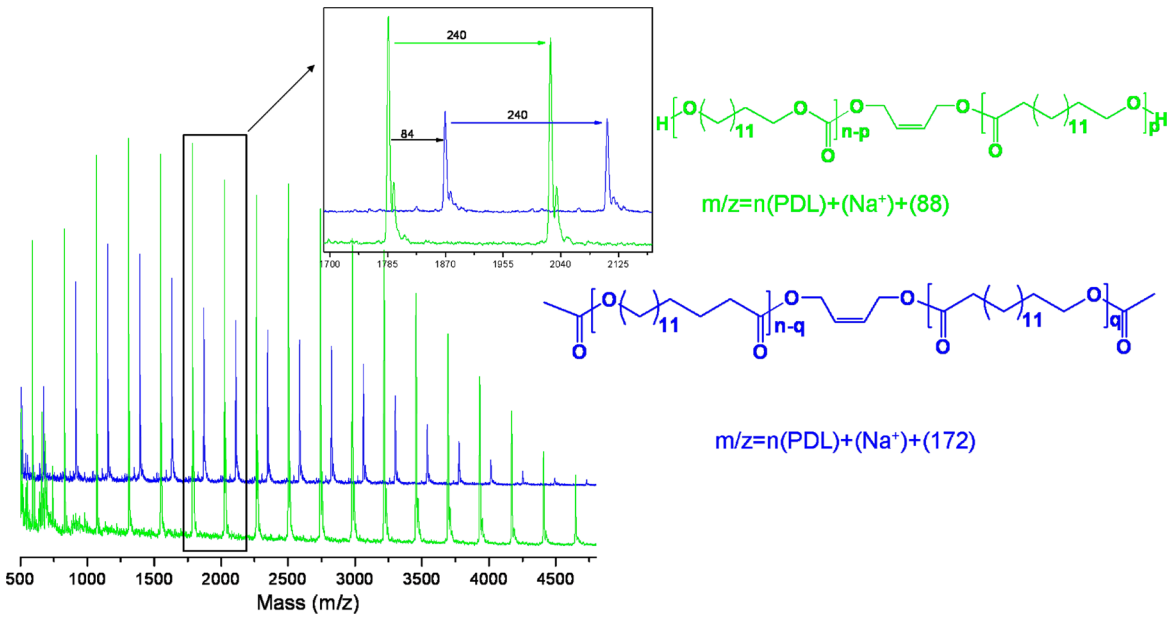

Figure 4. End group analysis of the two kinds of PPDL: AcO-PPDL-OAc (obtained from precursor **5**, blue) and HO-PPDL-OH (obtained from precursor **6**, green) confirmed by MALDI-TOF-MS.

whose half was corresponding to the mass difference between the acetoxyl and hydroxyl group. These results indicated that the end groups of the main products initiated by esters precursor and hydroxyl precursor were identified as ester and hydroxyl group, respectively. Minor signals in the spectra of AcO-PPDL-OAc were most likely caused by the macromolecules with hydroxyl or other chain ends. However, the population of these chains was the minor one. Thus, the consistent analysis for NMR and MALDI-TOF-MS confirmed that the end group of polyester by the single-step eROP from precursor **5** was the acetoxy group.

Kinetics and Mechanism Analysis for the Esters Precursor. In order to gain insight into the formation mechanism of the polyester capped with ester groups through eROP, kinetics of the single-step eROP were preliminarily studied. The conversion of monomer in eROP initiated by **5** and **6** was plotted as a function of time, as shown in Figure 5. For the calculation of PDL conversion, ^{1}H NMR signals at 4.14 (PDL) to 4.05 (poly-PDL) were used. Adopting the nucleophilic hydroxyl initiator **6**, most of the monomers were consumed in a short time. Nevertheless, it was evident that the polymerization rate of the eROP became very slow when the compound with cleavable ester groups was used, for example, the precursor **5**.

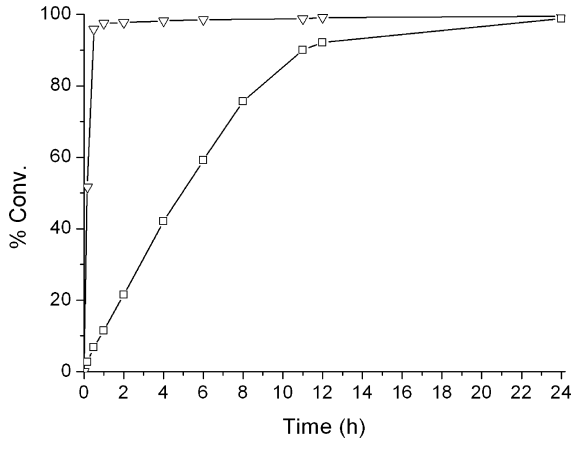

Figure 5. Conversion of the PDL with reaction time of CALB-catalyzed eROP using different precursors, *cis*-1,4-diacetoxy-2-butene (**5**, □) and *cis*-2-butene-1,4-diol (**6**, ∇).

Generally, the mechanism for eROP of lactones is accepted to be a monomer-activated process as follows:[36,37] the carbonyl group of lactones was activated by the nucleophilic attack of serine residue of the lipase, forming an acyl-enzyme intermediate; in the chain initiation, the nucleophilic attack of initiators (water or hydroxyl-terminated macromolecules) produced the ω-hydroxyl carboxylic acid or its derivative; then nucleophilic attack of ω-hydroxyl carboxylic acid would lead to the formation of one-unit-more elongated polymer chain. In the kinetics analysis, the true nucleophilic initiator hydroxyl group was produced from esters precursor catalyzed by CALB. In this system, low concentration of nucleophilic group led to the low reaction rate, compared with the hydroxyl initiator. Thus, the polymerization rate would be slow using esters precursor, and the technique was potential for realizing the control of polymerization.

Based on the above results, the formation mechanism for the polyester capped with ester group was elucidated (Scheme 2). In this reaction, lipase did not discriminate the carbonyl bonds of lactone monomer, polyester, the initiator or the precursor.[38] Thus, the esters precursor was activated by the nucleophilic attack of CALB, forming hydroxyl-terminated macromolecules. De Geus et al. once investigated the initiation for eROP and concluded that though water molecules dominated the initial initiation process, incorporation efficiency of alcohol initiators would be dramatically improved with the elongation of reaction time.[39] Similarly, almost no products with a hydroxyl end were detected using an ester precursor in the present research. Thus, the acyl-enzyme intermediate could be easily reacted with the terminal hydroxyl group to form polymers capped with the ester group, no need to be conducted at reduced pressure.

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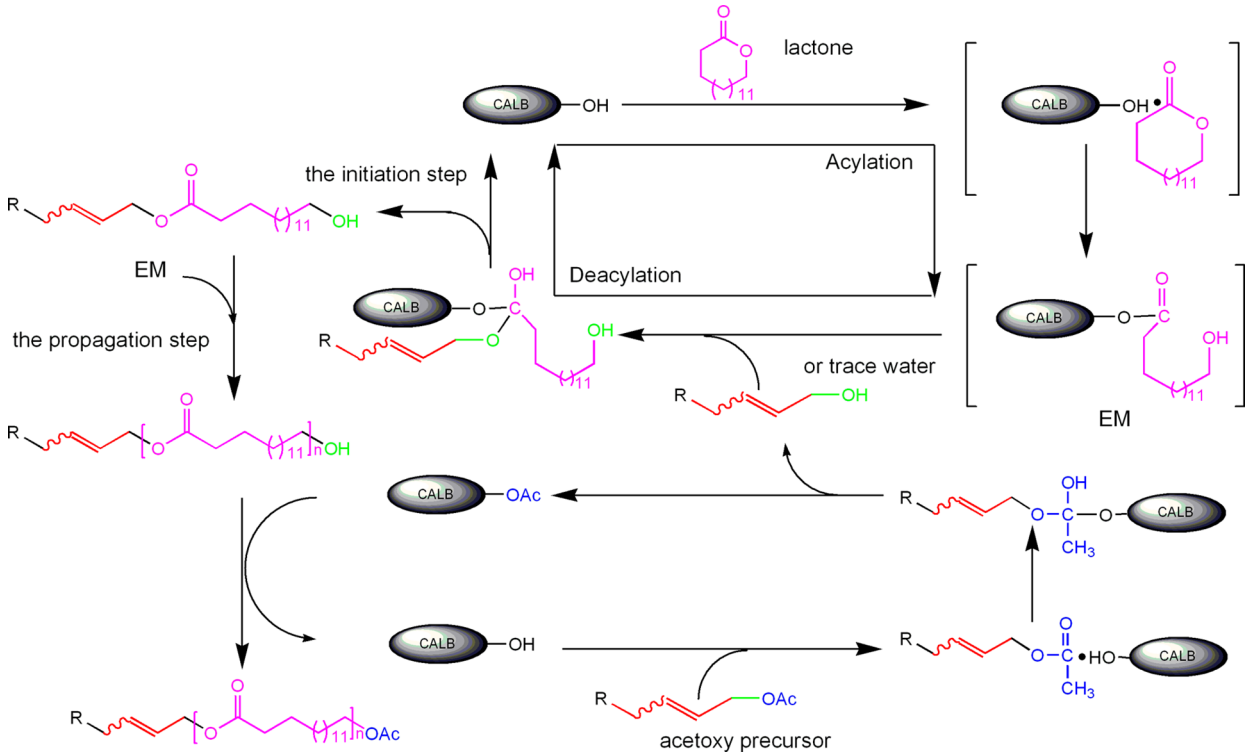
Scheme 2. Formation Mechanism of PPDL Capped with Ester Groups by eROP



CONCLUSIONS

In conclusion, this work reported the first combination of ROMP and eROP to synthesize block copolymers, and meanwhile, a novel synthesis route, single-step eROP of esters precursor was successfully constructed in our work. This single-step eROP without hydroxyl precursor simplified the process of synthesis, such as the protection and deprotection of hydroxyl group. In addition, the eROP and ROMP could be reacted in a one-pot consecutive manner, even simultaneously. The simple and controllable single-step eROP could also be extended to other chemoenzymatic synthesis systems. We believe that further theoretical and technical progress will make the chemoenzymatic synthesis a sustainable tool for the production of polymeric materials with tailor-made structures and properties in the future.

ASSOCIATED CONTENT

Supporting Information

Additional ^{1}H NMR for AcO-PCOD-OAc, HO-PCOD-OH, HO-LCL-OH, and AcO-LCL-OAc, AcO-PEG-OAc, HO-PEG-OH, HO-LEL-OH, and AcO-LEL-OAc. The COSY spectra for HO-LCL-OH and HO-PCOD-OH. GPC traces (refer to the data in Table 1). DSC curves for the block copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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