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# Kinetics and mechanism of the ring opening polymerization of (*R*,*S*)-β-butyrolactone initiated with dibutylmagnesium

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**Abstract**

Ring opening polymerization (ROP) of (*R*,*S*)-β-butyrolactone (BL) using dibutylmagnesium ($Bu_2Mg$) as initiator was investigated both in bulk and in solution. The synthetic poly-3-hydroxybutyrates (P3HB) were characterized by $^1H$ NMR, $^{13}C$ NMR, FT-IR and GPC. Effects of molar ratio of initiator to monomer, reaction temperature and time on the monomer conversion and the polymer molecular weight and its distribution were discussed. The kinetics of the solution polymerization of BL was examined and showed a first order both in monomer concentration and initiator concentration. The end groups analysis suggested that the monomer inserted into the growing chain proceeding through the coordination-insertion mechanism based on the acyl–oxygen bond scission rather than the alkyl–oxygen bond cleavage of the BL ring. Furthermore, a possible mechanism for the initiation and propagation procedures of P3HB synthesized from BL with $Bu_2Mg$ was proposed.
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*Keywords:* β-Butyrolactone; Poly-3-hydroxybutyrate; Dibutylmagnesium; Kinetics; Mechanism

## 1. Introduction

Poly(R)-3-hydroxybutyrate, P(R)3HB, produced by a wide variety of microorganisms, serves as an intracellular carbon and energy storage material [1,2]. P(R)3HB is becoming one of the most attractive biomedical materials because of its good biocompatibility, biodegradability, and other physical properties. However, the stiffness and brittleness of bacterial P(R)3HB due to high isotacticity and crystallinity have limited its practical applications.

Chemical synthesis of poly 3-hydroxyalkanoates is another attractive strategy which relies upon the ring opening polymerization (ROP) of racemic (*R*,*S*)-β-butyrolactone (BL) in the presence of organometallic compounds. One approach is anionic ROP of BL initiated with sodium or potassium alkoxides. The anionic polymerization of BL proceeds via alkoxide anions, and these anions are basic enough to deprotonate the monomer [3,4]. The problems associated with the anionic polymerization are chain transfer to the monomer and the extensive back-biting, and in some cases only low molecular weight polyesters are achieved [5,6]. Nonetheless they could be used as drug delivery

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carrier where extreme high molecular weights are always unnecessary, or even undesirable.

Zhang et al. [7] confirmed that the ring opening polymerization of BL with diethyl zinc ($ZnEt_2$/$H_2O$) initiator (1/0.6) proceeds by an acyl–oxygen cleavage with retention of configuration, indicating an inability to cause stereoregulation during the polymerization. In contrast, aluminum-based initiators trigger the ring opening through either acyl–oxygen bond cleavage or alkyl–oxygen bond cleavage, depending on the methods used for the catalyst preparation [8]. A mixture of predominantly isotactic P3HB and amorphous atactic P3HB was obtained by ROP of BL initiated with $AlEt_3/H_2O$ [9]. The BL polymerization initiated with $AI(O^iPr)_3$ proceeded through coordination-insertion mechanism by acyl–oxygen bond scission.

Almost Sn(IV) alkoxides are quite effective initiators for the ring opening polymerization of BL. Kricheldorf et al. [10] firstly demonstrated that tributyltin methoxide is very active in the polymerization of lactones. Subsequently, several research groups, such as Kricheldorf [11,12], Kemnitzer [13], Hori [14,15] and co-workers have published many papers on ROP of BL initiated with Sn(IV) compounds as initiators which gave preferentially syndiotactic polyesters. Recently, P3HB with high yield (almost 100%) and high molecular weight (>1,000,000 Da) can be easily prepared via ROP of BL using some well-designed tin initiators, such as, distannoxane [14–17], spirocyclic tin [18,19] and cyclic tin alkoxide [20], which possess the high reactivity on initiating ROP of BL even at low temperature. Mechanism studies carried out by these workers indicated that the lactones polymerizations proceed by coordination-insertion mechanism.

However, from the biomedical point of view, the synthetic P3HB without any toxic heavy metal ions is reasonably desirable. Magnesium ions are required by the metabolism of living organism, including human body, therefore, the magnesium compounds are a potential substitute for tin compounds because of its nontoxicity. Moreover, dibutylmagnesium ($Bu_2Mg$) was reported as the initiator for the ring opening polymerization of lactide [21] and adipic anhydride [22], however, its initiation mechanism remains unclearly since few papers on this subject. Also, there is no report on the ROP of BL initiated with $Bu_2Mg$ to the best of our knowledge.

In this study, we synthesized poly 3-hydroxyalkanoates (P3HB), for medical and pharmaceutical applications, by the ring opening polymerization (ROP) of (*R*,*S*)-β-butyrolactone (BL) initiated with dibutylmagnesium ($Bu_2Mg$), investigated the action of the initiator in toluene by kinetic experiments and polymer end groups analysis in detail, and proposed a possible mechanism for the initiation and propagation procedures of P3HB using $Bu_2Mg$ as initiator.

## 2. Experimental

### 2.1. Materials

(*R*,*S*)-β-Butyrolactone (BL) was purchased from Tokyo Kasei Kogyo Co. Ltd., then dried over $CaH_2$ by stirring, distilled under reduced pressure and stored under nitrogen atmosphere for further use. Dibutylmagnesium ($Bu_2Mg$) solution (in heptane, 1 M) was purchased from Aldrich Chemical Co. Ltd. Toluene was dried over $CaH_2$ by stirring and distilled prior to use under nitrogen atmosphere. All other reagents were used as received.

### 2.2. Polymerization

Bulk polymerization of (*R*,*S*)-β-butyrolactone (BL) was carried out in a previously flamed and nitrogen purged glass reactor equipped with magnetic stirrer. Desired amount of $Bu_2Mg$ was added to the flask using a syringe. The reaction vessel was then immersed into a thermostated oil bath at 100 °C for 24 h under nitrogen atmosphere. The products were dissolved in chloroform and then precipitated in an acidic mixture of 50/50 hexane and diethyl ether (by volume). The crude products were dried up to constant weight in vacuum at room temperature.

Solution polymerization of BL was carried out following a procedure similar to the bulk polymerization except that desired amount of solvent was transferred into the flask. $^1H$ NMR and GPC samples, for the kinetic investigation, were withdrawn from the reaction mixture at various intervals and quenched immediately into and stored in liquid nitrogen until analyses.

### 2.3. Analytical procedures

All molecular weights of the polymer were determined by GPC-220 (Polymer Laboratories Co., UK), equipped with ultrastyragel column connected (PL gel, mixtec, 5 μm) and Shodex RI-71 model refractive index detector at 40 °C. Tetrahydrofuran

was used as eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve of polymers was obtained with polystyrene standards of low polydispersity.

$^1$H NMR spectra were recorded on a Bruker DRX 400 spectrometer at 400 MHz. The sample concentrations were ca. 1% (w/v) polymer in $CDCl_3$ at 25 °C, pulse width 30°, 32 K data points, relaxation delay 2.5 s, and 8–16 transients, tetramethylsilane as the internal reference. The monomer conversion was calculated from the relative intensity of the resonance peaks for the monomer (4.70 ppm) and the polymer methine protons (5.25 ppm).

$^{13}$C NMR were recorded on a Bruker DRX 400 spectrometer at 100 MHz. The polymer spectral acquisitions were conducted as ca. 5% (w/v) $CDCl_3$ solutions with TMS as the internal reference using the following parameters: temperature 25 °C, pulse width 30°, 32 K data points, relaxation delay 2.5 s, and 1024 or 2048 transients.

FT-IR spectra in the range of 4000–400 $cm^{-1}$ were recorded on a Nicolet 5DX spectrometer, with a resolution of 2 $cm^{-1}$ using film samples cast on a KBr plate from 5 wt.% $CHCl_3$ solution.

## 3. Results and discussion

### 3.1. BL bulk polymerization

The melt bulk polymerization of (*R*,*S*)-β-butyrolactone (BL) using dibutylmagnesium ($Bu_2Mg$) as initiator has been conducted at 100 °C for 24 h. The results are summarized in Table 1. The experimental molecular weights of the formed polymers after precipitated in an acidic mixture of hexane and diethyl ether were measured by $^1$H NMR and GPC. The absolute number-average molecular weights ($M_{n(H\ NMR)}$), determined by $^1$H NMR, were calculated from the ratio between the *n*-butyl end group peak and the methine proton peak in the polymer chains (see Fig. 7 in Section 3.3 as an example).

The molecular weight ($M_{n(GPC)}$) measured by GPC was larger than the $M_{n(H\ NMR)}$. This result is consistent with some pervious reports that GPC measurements calibrated with polystyrene overestimate the real molecular weights of aliphatic polyesters by 50–100% [23–25], probably because of the increased difference in hydrodynamic volume of the higher molecular weight polymers. Such fractionation also influenced the polymer molecular weight distribution values ($M_w/M_n$); a slightly narrower distribution than actual was determined for the lower molecular weight samples. Therefore, the GPC results were only used as a semiquantitative tool to check the peak shape, molecular weight distribution, and the increase in molecular weight during kinetic experiments [23].

The theoretical molecular weight ($M_{n(Theor)}$) is calculated as

$$M_{n(Theor)} = [M]/[I] \times MW_{(BL)} \times X/100 \quad (1)$$

where [M]/[I] is the monomer to initiator molar ratio in feed; $MW_{(BL)}$, molecular weight of the BL monomer being 86; *X*, monomer conversion (%). Table 1 showed that the molecular weight is lower than the theoretical value and does not particularly depend on the monomer/initiator ([M]/[I]). It could be ascribed to the competition between propagation and intermolecular or intramolecular transesterifications, and the chain transfer reactions, which yields cyclic BL oligomers, control the molecular weight and monomer conversion [26].

### 3.2. Kinetics of BL solution polymerization

To understand the mechanism of $Bu_2Mg$-initiated BL ring opening polymerization, the kinetic

Table 1
Bulk polymerization of BL initiated with $Bu_2Mg$ at 100 °C for 24 h

| Polymer no. | Ratio of monomer to initiator ([M]/[I]) | Conversion[a] (%) | $M_{n(Theor)}$[b] | $M_{n(H\ NMR)}$[c] | $M_{n(GPC)}$[d] | $M_w/M_n$[d] |
|---|---|---|---|---|---|---|
| P3HB1 | 10 | 100 | 900 | 950 | 2100 | 1.26 |
| P3HB2 | 50 | 96 | 4100 | 4300 | 6800 | 1.32 |
| P3HB3 | 100 | 91 | 7800 | 7000 | 11,500 | 1.36 |
| P3HB4 | 200 | 83 | 14,300 | 7800 | 13,000 | 1.38 |
| P3HB5 | 400 | 75 | 25,800 | 7500 | 12,400 | 1.44 |

[a] Calculated from $^1$H NMR on the crude reaction mixture.
[b] Theoretical molecular weight calculated as Eq. (1).
[c] Determined by $^1$H NMR analysis.
[d] Measured by GPC analysis with polystyrene standard calibration.

behaviors of the $Bu_2Mg$ initiator were carefully investigated. A series of polymerization reactions were carried out in toluene solvent at 80 °C for monomer to initiator molar ratios ([M]/[I]) at 25/1, 50/1, and 100/1. The polymerization reaction progress was monitored by $^1H$ NMR analysis to determine the monomer conversion.

Fig. 1 shows the semilogarithmic plot of $\ln([M]_0/[M]_t)$ versus the reaction time, $t$, for the polymerization of BL using $Bu_2Mg$ as initiator ($[M]_0$ is the initial monomer concentration and $[M]_t$ is the concentration of the unreacted monomer at time $t$). Although there appears a short induction period, all of our kinetic analyses gave similar linear relationships. Ignoring the initiation process and using the generally accepted kinetic form for the polymerization of BL with $Bu_2Mg$, the linearity of these plots is consistent with polymerization process that is first order in BL and the kinetic equation can be described as follows:

$$-d[M]/dt = k_{abs}[P^*][M] \quad (2)$$

where $k_{abs}$ is the absolute polymerization rate constant, $[P^*]$ is the number of propagating chains, and [M] is the unreacted monomer concentration. The linearity of the plot of $\ln([M]_0/[M]_t)$ versus the reaction time was systematically observed, and it illustrates that no termination reactions occurred during polymerization; i.e., $[P^*]$ remained constant throughout the polymerization reaction [23]. However, potential aggregation of $[P^*]$ to an inactive form, that is, polymerization proceeds with reversible aggregation (temporary termination), a situation observed in many other polymerizations using aluminum alkoxide, complicates the determination of $[P^*]$ (i.e. $[P^*] \neq [Bu_2Mg]_0$). The evaluation of $k_{abs}$ is not straightforward due to a change of proportions of aggregated and nonaggregated species. For ease of comparison we define the apparent rate constant $k_{app} = k_{abs}[P^*]$ in Eq. (2), then,

$$-d[M]/dt = k_{app}[M] \quad (3)$$

The apparent rate constants, $k_{app} = \ln([M]_t/[M]_0)/t$, determined from the slope of the linear dependence in Fig. 1, range from $2.01 \times 10^{-4}$ min$^{-1}$ ([M]/[I] = 100), $4.05 \times 10^{-4}$ min$^{-1}$ ([M]/[I] = 50), up to $7.12 \times 10^{-4}$ min$^{-1}$ ([M]/[I] = 25) for the different initiator concentrations, $[I]_0$. If the polymerization is concluded to be first order in initiator, the $k_{app}/[I]$ ratio must be constant as long as the number of active sites is independent of the initiator concentration. This assumption is easily supported by the slope of the $k_{app}$ versus $[I]_0$ plot in Fig. 2.

$$k_{abs} = \ln([M]_0/[M]_t)/t/[I] = k_{app}/[I]_0 \quad (4)$$

Then, the absolute polymerization rate constant at 80 °C, $k_{abs(80)}$, is $8.9 \times 10^{-2}$ L mol$^{-1}$ min$^{-1}$ calculated from Fig. 2 in our experimental conditions.

Moreover, the effect of temperature was also studied and found that increasing the temperature does not change the overall polymerization kinetics reported in toluene. Fig. 3 illustrates that the apparent rate constant $k_{app}$, i.e., the slope of the linear $\ln([M]_0/[M]_t)$ versus time plots, is ca. six times as

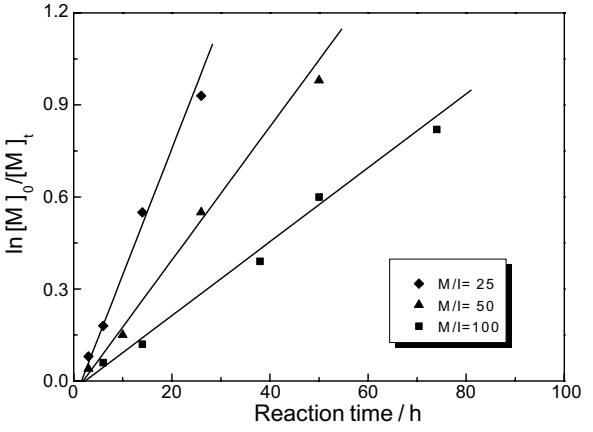


Fig. 1. Semilogarithmic plots of the monomer conversion expressed as $\ln[M]_0/[M]_t$ versus the reaction time for the solution polymerization of BL initiated with $Bu_2Mg$ in toluene at different initiator concentrations, M/I = 25 (◆), 50 (▲) and 100 (■) ($[M]_0 = 2$ mol L$^{-1}$, 80 °C).

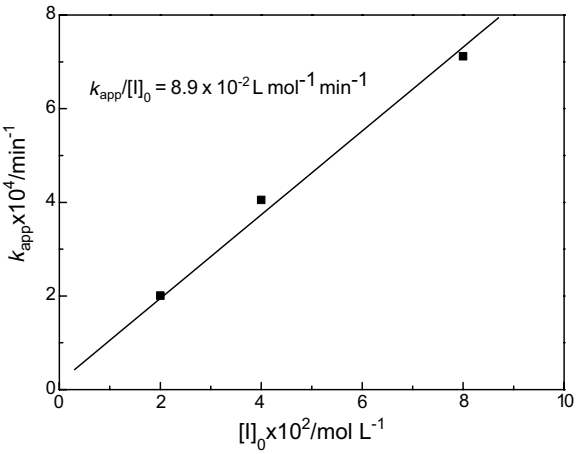


Fig. 2. Dependence of the apparent rate constant, $k_{app}$, on the initiator concentration, $[I]_0$. Polymerizations were conducted at 80 °C, and initial monomer concentration of 2 mol L$^{-1}$ was used.

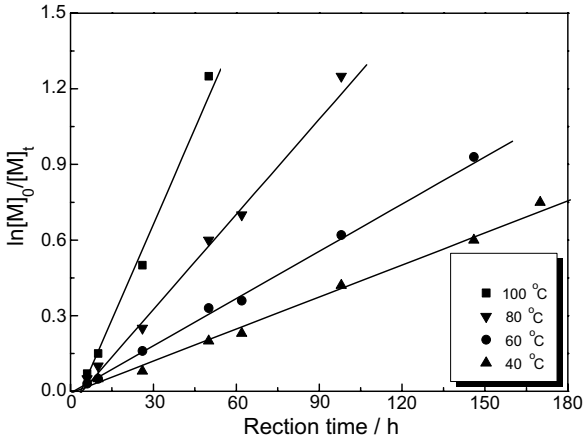


Fig. 3. Semilogarithmic plots of BL monomer conversion expressed as $\ln[M]_0/[M]_t$ versus the reaction time for the solution polymerization of BL initiated with $Bu_2Mg$ in toluene ($[M]_0 = 2$ mol $L^{-1}$, $[M]/[I] = 100$) at various temperatures: (■) 100 °C, (▼) 80 °C, (●) 60 °C, (▲) 40 °C.

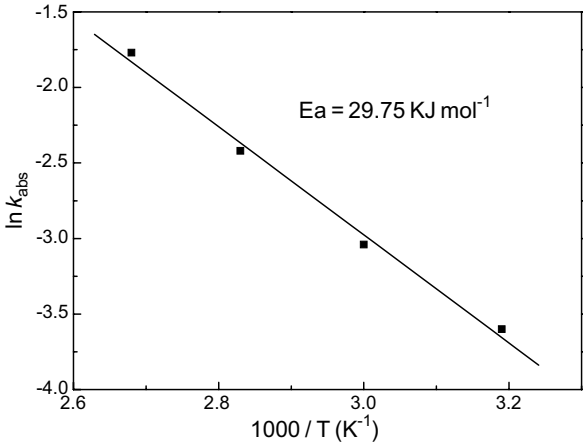


Fig. 4. Determination of the energy of activation for the solution polymerization of BL initiated with $Bu_2Mg$ in toluene ($[M]_0 = 2$ mol $L^{-1}$, $[M]/[I] = 100$) at various temperatures.

high at 100 °C compared with 40 °C. Due to the propagating chains reactive species [$P^*$] remained constant during the polymerization reaction, the $k_{abs}$ values at various temperatures, calculated according to the method previously described, were summarized in Table 2. And an Arrhenius analysis revealed that the relationship between $k_{abs}$ and polymerization temperature is consistent with the following equation:

$$k_{abs} = A\exp(-E_a/RT) \quad (5)$$

where $A$ is the Arrhenius coefficient, $R$ is the molar gas constant, $T$ is the temperature. Fig. 4 is the related Arrhensius plot that allows the activation energy to be calculated. The activation energy ($E_a$) obtained for $Bu_2Mg$-initiated BL polymerization (29.75 kJ/mol) is ca. three times, however, on the same order of magnitude as the values for ε-caprolactone initiated with aluminum alkoxides previously reported by Dubois et al. [27].

Table 2
Kinetics data of BL polymerization initiated with $Bu_2Mg$ in toluene at various temperatures[a]

| Temperature (°C) | $k_{app} \times 10^4$ ($min^{-1}$) | $k_{abs} \times 10^2$ (L $mol^{-1}$ $min^{-1}$) |
|---|---|---|
| 100 | 4.21 | 17.0 |
| 80 | 2.01 | 8.9 |
| 60 | 1.04 | 4.9 |
| 40 | 0.71 | 2.7 |

[a] Reaction was conducted at $[M]/[I] = 100$, an initial monomer concentration of 2 mol $L^{-1}$ was used.

In addition, the influence of monomer conversion on the number-average molecular weight ($M_n$) and molecular weight distribution (MWD) was determined by and GPC during the polymerization process. The analyses were performed on the crude reaction mixture; no precipitation or deactivation was executed in order to avoid the influence of these additional processes such as fractionation of the samples. However, it should be noted that some deactivation, i.e., hydrolysis, might take place during preparation of the polymer/tetrahydrofuran mixture subsequently subjected to GPC analysis [23].

Fig. 5 shows the influence of monomer conversion on $M_n$ and MWD for the solution polymerization of BL initiated with $Bu_2Mg$ in toluene ($[M]_0 = 2$ mol $L^{-1}$, $[M]/[I] = 100$, 80 °C) as an example. It reveals that the $M_n$ determined by GPC gradually increases with the monomer conversion and follows a linear relationship even at high conversion. The MWD remains quite narrow though the reaction is very slow throughout the polymerization process. The MWD broadens when the conversion is over 80% due to the completive depolymerization and transesterification reaction, which is suppressed under low conversion. This is generally observed in systems propagating in a living manner, e.g., ε-caprolactone initiated with aluminum isopropoxide [28]. Short induction period was observed in our polymerization reactions, which is different to previously reported that either no induction period or long induction period for many other metal alkoxide initiator systems. This indicated that the active species were formed rapidly under the actual experimental

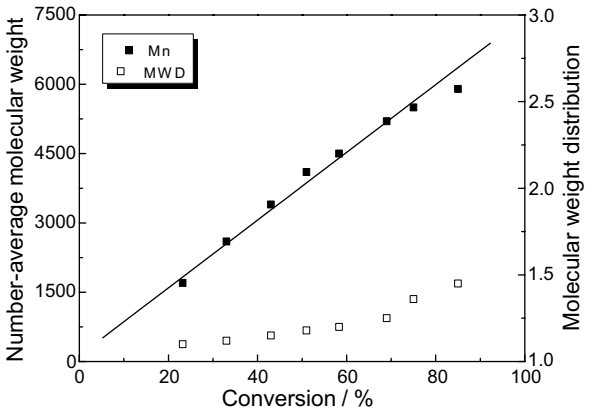


Fig. 5. Relationships between the number-average molecular weight (■), molecular weight distribution (□) and the monomer conversion for the solution polymerization of BL initiated with $Bu_2Mg$ in toluene ($[M]_0 = 2$ mol $L^{-1}$, $[M]/[I] = 100$, 80 °C).

conditions; the initiator rearranged to become reactive and initiate polymerization.

### 3.3. Polymer end groups analysis

With the purpose of clarifying the ring opening polymerization mechanism of BL initiated with $Bu_2Mg$, the P3HB sample with low molecular weight was prepared from the molar ratio of BL to $Bu_2Mg$ were equal to 10/1 at 100 °C, acidically deactivated, and finally characterized by FT-IR, $^1H$ NMR and $^{13}C$ NMR to analysis its end groups.

FT-IR spectrum (Fig. 6) shows the absorption band at 1815 $cm^{-1}$, characteristic of the lactone carbonyl function, completely disappeared with the formation of a new absorption band at 1735 $cm^{-1}$, which is typical of the ester carbonyl group of the polymer. In addition, the absorption at 3500 $cm^{-1}$ combined with the absence of a band at 1700 $cm^{-1}$, characteristic of carboxylic acid, is in agreement with the formation of hydroxyl end groups. Furthermore, the bands in the region of 1645 $cm^{-1}$ and 925 $cm^{-1}$ are attributed to carbon–carbon double band (C=C).

Signals of the synthetic P3HB in the $^1H$ NMR spectrum were assigned in Fig. 7. The signals of the methyl, methylene, and methine protons of the 3-hydroxybutyrate (3HB) units were detected at $\delta$ 1.28 ppm (a), 2.43–2.64 ppm (c), and 5.25 ppm (b), respectively. It is worth noting that the signals (d–g) corresponding to *n*-butyl end groups ($\delta[CH_3CH_2CH_2CH_2CO–] = 0.93$, 1.23, 1.58 and 2.34 ppm), derived from the initiator, were also detected in the $^1H$ NMR spectrum.

The downfield shift of the methine signal from $\delta$ 4.20 ppm (b″) to $\delta$ 5.50 ppm (b‴) as shown in the expanded $^1H$ NMR spectrum (Fig. 7 upper left) after reacting the polymer with an excess of trifluoroacetic anhydride (TFA) also supported the presence of hydroxyl terminal groups. The absence of any acidic signal at >10 ppm verified the formation of hydroxyl end groups. In addition, two peaks at $\delta$ 5.85 (c′) and 7.05 ppm (b′), characteristic of carbon–carbon double band, together its methyl at $\delta$ 1.80 ppm (a′) in the $^1H$ NMR spectrum (Fig. 7) gave evidence for crotonate end groups, which were firstly reported by Kricheldorf and Scharnagl [3], and commonly observed by Kurcok et al. [5,8] and Chen et al. [29,30].

Furthermore, the signals in $^1H$ NMR spectrum are also observed in the $^{13}C$ NMR spectrum (Fig. 8), which supports the same conclusion

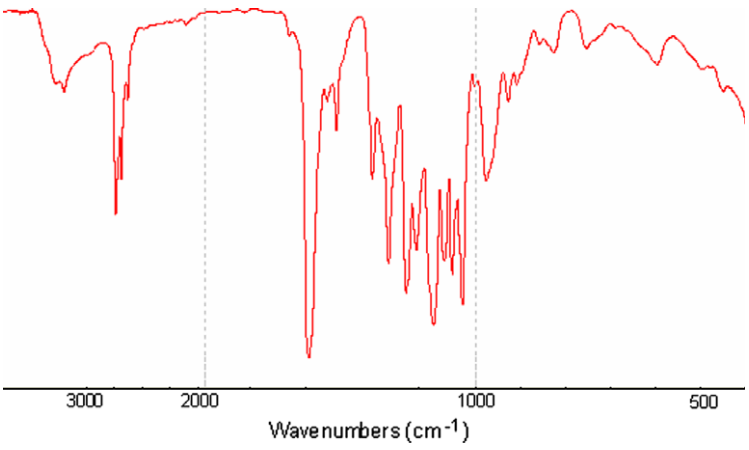


Fig. 6. FT-IR spectrum of P3HB as recovered after hydrolysis of the oligopolyester initiated with $Bu_2Mg$ ($[M]/[I] = 10$, 100 °C).

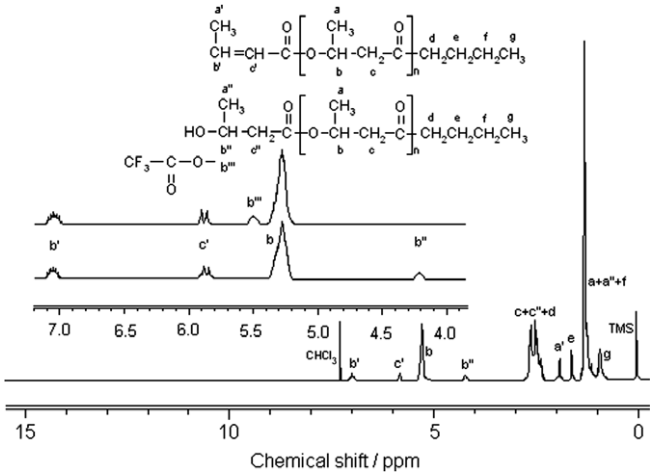


Fig. 7. 400 MHz $^{1}$H NMR spectrum (below) of P3HB oligopolyester ([M]/[I] = 10, 100 °C) and an expanded spectrum (upper) of its reaction product with an excess of trifluoroacetic anhydride.

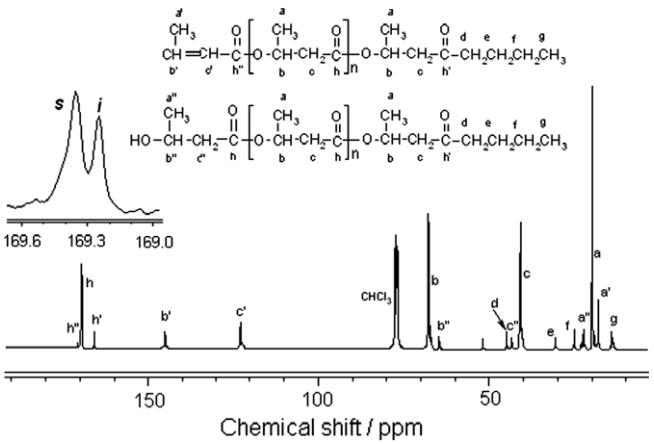


Fig. 8. 100 MHz $^{13}$C NMR spectrum (below) of P3HB oligopolyester ([M]/[I] = 10, 100 °C) and its expanded spectrum (upper) of the carbonyl carbon region.

obtained from $^{1}$H NMR. The carbon signals due to the methyl, methylene, methine and carbonyl carbons of the 3HB units are detected around $\delta$ 19.7 (a), 40.8 (c), 67.6 (b), and 169 ppm (h), respectively. In addition, the small signals of the 3HB end groups were detected and assigned in Fig. 8, respectively. It is noteworthy that the signals at $\delta$ 145.0 ppm (c′) and 122.8 ppm (b′) which were characteristic of the crotonic C═C, indicated the sample possess the crotonate end groups.

The carbonyl signal at $\delta$ being 169.1–169.3 ppm was split into two peaks due to the syndiotactic (*s*) and isotactic (*i*) diad sequences of (*R*)- and (*S*)-3HB units (Fig. 8, upper). The diad sequence distributions analysis of the P3HB samples revealed that the syndiotactic diad fraction was ca. 0.6. Therefore, the above P3HB prepared by $Bu_2Mg$ as initiator have only slightly preferentially syndiotactic sequence comparing with the dominating syndiotactic P3HB using tin compounds [17,20].

### 3.4. Mechanistic aspects

Kricheldorf and Lee [21] reported several experimental observes that contradict an anionic polymerization mechanism and it seemed that $Bu_2Mg$-initiated polymerization of L-lactide follows a coordinative-insertion mechanism. Recently Li et al.

[22] verified that ROP of adipic anhydride (AA) initiated with $Bu_2Mg$ proceed through the coordination-insertion mechanism based on the acyl–oxygen cleavage of the AA ring. However, it turned out that $Bu_2Mg$-initiated polymerization of the lactones is more complex and remains still unclearly as far as the mechanism of this reaction is concerned. We attempted to explain the BL polymerization mechanism with $Bu_2Mg$ as the initiator in this section.

The above results of polymer end groups analysis in Section 3.3 strongly confirmed that P3HB is quantitatively capped by *n*-butyl group of the initiator at one end, and either a hydroxyl or crotonate group at the other, which results from the hydrolysis of the growing species or the elimination reaction, respectively. It should be noted that the presence of unsaturated and hydroxyl end groups was also simultaneously observed in FT-IR, $^1$H NMR and $^{13}$C NMR spectra of all the P3HB samples even with high molecular weight prepared at lower polymerization temperatures. The aforementioned results have now demonstrated that the propagation procedure is unambiguous, which the monomer inserts into the growing chains with the acyl–oxygen bond scission rather than the break of alkyl–oxygen bond.

The initiation process is yet ambiguous, as mentioned in Section 1. Based on the α-proton of lactide is highly acidic and deprotonation may occur even with rather weak bases, Kricheldorf postulated that deprotonation of the monomer is clearly the first step and the resulting lactide magnesium complex somehow initiates the polymerization [21]. However, other monomers may differ in the initiation process due to they are undeprotonated. The fact that *n*-butyl end groups are clearly detected by $^1$H NMR concludes that *n*-butyl group of the initiator incorporated to polymer chains during initiation step. And the induction period could well be explained that a complex between the initiator and the monomer firstly forms prior to the ring opening polymerization of the monomer BL.

These observed crotonate end groups clearly indicate that an elimination reaction occurs, probably with formation of magnesium hydroxide, which also could initiate further polymerization confirmed in our experiments. This type of elimination reaction has been reported in the case of BL polymerization initiated by alkali metal alkoxides [5] and with tin derivatives [28]. Four distinct mechanisms have been proposed to account for this elimination reaction in relation to the experimental condition [31].

It is worth noting that the relative ratio of protons in the crotonic CH=CH group, the hydroxyl

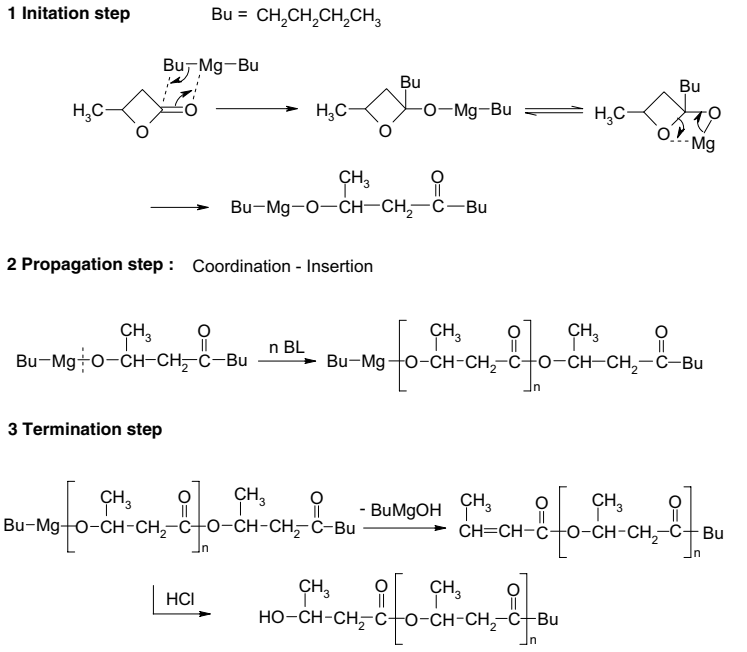


Fig. 9. Proposed mechanism for the ring opening polymerization of BL initiated with $Bu_2Mg$.

CHOH endgroup and *n*-butyl groups is ca. 1.2:1:2 calculated from Fig. 7, so the total amount of hydroxyl and crotonic end groups is slightly higher than the amount of *n*-butyl capping the second chain end. This discrepancy might result from thermal degradation reactions in higher temperature leading to carbon–carbon double bond formation. Consequently, we presumed that crotonate is introduced into the growing chain occurring at the termination stage.

According to discussions hereinbefore and mechanism previously reported [15,17,22], we indicate that the mechanism of the present ring opening polymerization of BL initiated with $Bu_2Mg$ is shown in Fig. 9. In initiation step, the carbonyl group of BL coordinates with the Mg atom center to form the alkoxide of 3-hydroxybutyrate. The ligand exchange not only aids the monomer's coordination, but also stimulates the nucleophilic attack of the alkoxide toward the carbonyl group. Then alkoxy groups attack the activated carbonyl carbon of BL. The propagation, which proceeds through the insertion of the BL monomer into the Mg–O bond of the initiator by the acyl–oxygen bond scission rather than the alkyl–oxygen bond break of the lactones, occurs to afford the polymer. The poly-3-hydroxybutyrates with hydroxyl-terminated by acidic deactivation as well as carbon–carbon double bond end groups due to the elimination of butyl magnesium hydroxide are formed in termination step.

## 4. Conclusions

Ring opening polymerizations of (*R*,*S*)-β-butyrolactone (BL) initiated with dibutylmagnesium ($Bu_2Mg$) were carried out both in solution and in bulk. The results of kinetics indicate that a first order in both monomer concentration and initiator concentration. The value of activation energy obtained for $Bu_2Mg$-initiated BL polymerization is ca. 29.75 kJ/mol. The end group analysis by $^1H$ NMR and $^{13}C$ NMR clearly revealed that the polymerization of BL proceeded through the coordinative-insertion mechanism based on the acyl–oxygen cleavage of BL ring.

## References

[1] Doi Y. Microbial polyesters. New York: VCH Publishers; 1990.
[2] Sudesh K, Abe H, Doi Y. Prog Polym Sci 2000;25:1503–55.
[3] Kricheldorf HR, Scharnagl NJ. Macromol Sci Chem 1989;A26:951–68.
[4] Jedlinski Z, Kowalczuk M, Kurcok P. Macromolecules 1991;24:1218–9.
[5] Kurcok P, Kowalczuk M, Hennek K, et al. Macromolecules 1992;25:2017–20.
[6] Jedlinski Z, Kowalczuk M, Kurcok P, et al. Macromolecules 1996;29:3773–7.
[7] Zhang Y, Gross RA, Lenz RW. Macromolecules 1990;23:3206–12.
[8] Kurcok P, Duboist P, Jereme R. Polym Int 1996;41:479–85.
[9] Jaimes C, Couve J, Crbtte S, et al. Eur Polym J 1996;32:1175–81.
[10] Kricheldorf HR, Berl M, Scharnagl N. Macromolecules 1988;21:286–93.
[11] Kricheldorf HR, Lee S-R. Macromol Chem Phys 1994;195:2299–306.
[12] Kricheldorf HR, Eggerstedt S. Macromolecules 1997;30:5693–7.
[13] Kemnitzer JE, McCarthy SP, Gross RA. Macromolecules 1993;26:1221–9.
[14] Hori Y, Suzuki M, Yamaguchi A. Macromolecules 1993;26:5533–4.
[15] Hori Y, Hagiwara T. Int J Biol Macromol 1999;25:237–45.
[16] Arcana M, Giani-Beaune O, Schue F, et al. Polym Int 2000;49:1348–55.
[17] Hiki S, Miyamoto M, Kimura Y. Polymer 2000;41:7369–79.
[18] Kricheldorf HR, Fechner B. Biomacromolecules 2002;3(4):691–5.
[19] Kricheldorf HR. J Polym Sci Part A: Polym Chem 2004;42:4723–42.
[20] Wei ZY, Liu L, Qi M. React Funct Polym 2006;66:1411–9.
[21] Kricheldorf HR, Lee S-R. Polymer 1995;36:2995–3003.
[22] Li Z, Hao JY, Yuan ML, et al. Eur Polym J 2003;39:313–7.
[23] Stridsberg K, Ryner M, Albertsson A-C. Macromolecules 2000;33:2862–9.
[24] Save M, Schappacher M, Soum A. Macromol Chem Phys 2002;203:889–99.
[25] Kricheldorf HR, Rost S. Polymer 2005;46:3248–56.
[26] Kurcok P, Dubois P, Sikorska W, et al. Macromolecules 1997;30:5591–5.
[27] Dubois Ph, Ropson N, Jerome R, et al. Macromolecules 1996;29:1965–75.
[28] Barakat I, Dubois Ph, Jerome R, et al. Macromolecules 1991;24:6542–5.
[29] Chen C, Yu CH, Cheng YC, et al. Biomaterials 2006;27:4804–14.
[30] Chen C, Yu CH, Cheng YC, et al. Eur Polym J 2006;42:2211–20.
[31] Kricheldorf HR, Scharnad N, Jedlinski Z. Polymer 1996;37:1405–11.