Poly(delta-gluconolactone) and Poly(delta-gluconolactone-\(\varepsilon\)-caprolactone) from delta-Gluconolactone and \(\varepsilon\)-Caprolactone by Ring-Opening Polymerization

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Poly(delta-gluconolactone) (PGL) and poly(delta-gluconolactone-\(\varepsilon\)-caprolactone) (P(GL-CL)) were synthesized through ring-opening polymerization (ROP) and characterized by FT-IR, NMR, XRD, intrinsic viscosity, GPC, DSC, and TGA. The crystallinity of P(GL-CL) with various d-GL/CL ratios (d-GL/CL = 5:5, 4:6, 3:7, 2:8, and 1:9) was 12.09 to 59.78% while PGL was amorphous. Melting temperature \(T_m\) of these polymers was 49.8 to 62.0°C and decomposition temperature was 282 to 489°C depending on the d-GL/CL ratios. In addition, all these polymers were degradable and the degradation rates could be controlled by adjusting d-GL/CL ratios. These results indicated that PGL and P(GL-CL) might be promising novel absorbable materials.

1. Introduction

Glucose is the most important energy source of living cells and intermediate materials of metabolism, which stored as a polymer, in plants as starch and in animals as glycogen [1]. Beside the function in biology, it is used as medicine, food additives, and chemicals [2]. Because of its huge storage in the celluloses, the glucose and its derivatives had a wide range of applications, such as calcium gluconate and zinc gluconate which are used as sequestrants, acidifiers, curing agents, pickling agents, or leavening agents [3, 4]. Although there are extensive researches and applications on the delta-gluconolactone (d-GL), the research on its further chemical reaction, derivatives, and synthesis polymers is relatively rare, especially on its ring-opening polymerization (ROP) reaction. This consequence is partly due to the presence of hydroxyl (–OH) on d-GL that is detrimental for ROP, as it leads to deactivation of the polymerization via undesirable side reaction, such as crosslinking-induced gelation [5, 6]. The polymerization of d-GL into poly(delta-gluconolactone) (PGL) suggested novel potential applications, like drug delivery system by introducing polar functionalities groups (–OH) as well as the functionalities group of the polymers, which can provide anchor for tissue regeneration through cell attachment, proliferation, control of inflammation, and healing.

PGL might be a good affinity for water while poly(\(\varepsilon\)-caprolactone) (PCL) is hydrophobic. Considering the similar cyclic structure between d-GL and \(\varepsilon\)-caprolactone (CL), copolymerization of d-GL with CL could overcome the drawbacks and induce new functionalities, to yield biobased polymers with possible industrial and medical applications [7, 8]. Such polymerization reactions can be accomplished by lipase biocatalysis, and d-GL can be copolymerized with \(\varepsilon\)-caprolactone (CL) and \(\beta\)-butyrolactone through immobilized lipases to form an aliphatic oligomer (best experiment \(m/z\) value 1587) in previous reports [7, 8]. The aim of present work is to obtain higher molecular weight polymers through chemical method.
To our knowledge, this is the first research in which PGL and P(GL-CL) with high molecular weight were successfully synthesis from d-GL and CL by chemical method. The aim of this work was to discuss synthesis, characterization, and in *vitro* degradation of PGL and P(GL-CL).

2. Materials and Methods

2.1. Materials. e-Caprolactone (CL, Xiya Reagent, 99.9%) was dried with CaH$_2$ (Aladdin Regent, 98.5%) for 24 hours at ambient temperature and by reduced pressure distillation prior to use [9–13]. delta-Gluconolactone (d-GL, Aladdin Reagent, 98%) was dried in vacuum at 80°C before use. The other reagents, Sn(Oct)$_2$, tetrabutyl titanate (TBT), dimethyl sulfoxide-d$_6$ (DMSO-d$_6$), monobutyltin oxide (MBTO), n-octane, methylbenzene, and diethylene glycol, purchasing from Aladdin Reagent Co., Ltd., were used without further purification. Other reagents from Shanghai Tengzhun Biotechnology Co., Ltd., were used according to the label instructions.

2.2. Synthesis PGL and PCL. In a typical experiment [11, 14], a Schlenk tube equipped with a magnetic stirrer was sequentially charged with catalyst (MBTO, 2 equiv), monomers (CL or d-GL, 1000 equiv), and initiator (diethylene glycol, 1 equiv) in n-octane followed by pumping vacuum and high pure dry nitrogen in turn for three times. Subsequently, the temperature was gradually raised to 160°C and then reaction was conducted at this temperature for assigned time to obtain PGL. PCL was synthesized through the same procedure except that the polymerization temperature was 140°C. After the reaction, the n-octane was removed in vacuum and then the target product was purified by dissolving in dichloromethane followed by precipitating in ethanol. In order to optimize the reaction condition, a series of polymerization reactions of PGL were performed at varying reaction time (4, 6, 8, and 12 h) and temperature (120, 130, 140, 150, 160, and 170°C) by some general catalysts by various initiator (diethylene glycol) and catalyst (MBTO, Sn(Oct)$_2$, TBT, Y[N(SiMe$_3$)$_2$]$_3$, Al complexes).

2.3. Synthesis of P(GL-CL) Copolymers. All these P(GL-CL) copolymers with various d-GL/CL ratios (d-GL/CL = 5:5, 4:6, 3:7, 2:8, 1:9) were obtained by one-pot-two-step process (Scheme 1). In short, a Schlenk tube equipped with a magnetic stirrer was charged sequentially with catalyst (MBTO, 2 equiv), initiator (diethylene glycol, 1 equiv), and CL in n-octane followed pumping vacuum and high pure dry nitrogen in turn for three times [15, 16]. Subsequently, the temperature was gradually raised to 140°C and kept for 4 hours and then d-GL was added to the flask and kept for another 4 hours. After that, the reaction temperature increased to 160°C and was kept for another 4 hours. After completion of this polymerization, the n-octane was removed in vacuum. The target product was purified and obtained by dissolving in dichloromethane, precipitating in ethanol and drying in vacuum to constant weight, sequentially.

2.4. *In Vitro* Degradation in PBS. An *in vitro* degradation study of P(GL-CL) was carried out in phosphate buffered saline (PBS). All the samples were shattered into particles (1100–2000 μm) and soaked in PBS with a weight-to-volume ratio of 1/30 (g mL$^{-1}$) at 37°C in a shaking water bath [17]. The incubation time was up to 10 weeks with PBS refreshment every week. The initial weight ($W_0$) of the particles was obtained after the samples were dried in vacuum. The weight ($W_t$) at certain time point was obtained by weighting the...
2.5.3. Intrinsic Viscosity and Gel Permeation Chromatography (GPC) of Polymers. The intrinsic viscosity measurement of each polymers was carried out in Dimethyl Sulphoxide (DMSO) at 30 °C by Cannon-Ubbelohde viscometer. The intrinsic viscosity values were obtained by a one-point method (the Solomon–Ciuta equation) as follows:

\[
\eta_{\text{int}} = \frac{\sqrt{2} (n_p - \ln n_r)}{c},
\]

where \( n_r \) = \( \eta / \eta_0 \), \( n_p = \eta / \eta_0 - 1 \), and \( c \) was polymer concentration in DMSO. And the number average (\( M_n \)) and polydispersity index (PDI) were measured using Water-2414 equipped with a Waters Styragel HT4 and using Dextran as standards with molecular weights from 1.0 × 10^3 to 2.7 × 10^5 g mol⁻¹. THF was used as mobile phase at a rate of 1 mL min⁻¹ and the column temperature was 30°C.

2.5.4. XRD of PGL and P(GL-CL). XRD (Philips X'pert Pro MPD) was used to study the crystalline characteristics of the polymers.

2.5.5. Differential Scanning Calorimetry Analysis (DSC) and Thermogravimetric Analysis (TGA). Differential scanning calorimetry analysis (DSC) was performed on a Perking-Elmer DSC-7 apparatus under nitrogen in the temperature ranging from 0 to 200°C at a heating rate of 10°C min⁻¹. The samples were first heated to 160°C and then cooled to 30°C by liquid nitrogen, followed by heating to 200°C at a heating rate of 10°C min⁻¹. The glass transition temperature \( (T_g) \) and melting point was recorded from the cooling flow and the second heating run, respectively. The thermogravimetric analysis (TGA) was conducted on PerkinElmer Pyris Diamond thermogravimetric/differential thermal analyser (TG/DTA) at 10°C min⁻¹ from 30 to 600°C.

3. Results

3.1. ROP of d-GL in Various Conditions. In this study, different reaction catalysts were investigated for ROP of d-GL, and the results are shown in Table 1. It was found that some general catalysts for polyester polymerization, like TBT, Sn(Oct)₂, some Al complexes (aluminium isopropoxide, aluminiumtriethyl, trisobutylaluminium) and the Rare Earth catalyst \( Y[N(SiMe_3)_2]_3 \) prepared as previous reported [18], failed for ROP of d-GL. When monobutyltin oxide (MBTO) was employed as catalyst and reflected in n-octane at 150°C for 8 hours under nitrogen, an off-white polymer (PGL) was precipitated from the solution. The obtained polymer was freely soluble in water and some polar solvents (e.g., THF, DMSO, and CHCl₃) but insoluble in alcohol, acetone, and methylbenzene. In addition, various reaction temperature (120, 130, 140, 150, 160, and 170°C) and reaction time (4, 6, 8, and 12 h) were also investigated in the MBTO catalytic system, summarized in Table 2. It was found that when the temperature was lower than 120°C, the reaction rate was lower, or the reaction could not proceed. And conversion failed for ROP of d-GL. When monobutyltin oxide (MBTO) was employed as catalyst and reflected in n-octane at 150°C for 8 hours under nitrogen, an off-white polymer (PGL) was precipitated from the solution. The obtained polymer was freely soluble in water and some polar solvents (e.g., THF, DMSO, and CHCl₃) but insoluble in alcohol, acetone, and methylbenzene. In addition, various reaction temperature (120, 130, 140, 150, 160, and 170°C) and reaction time (4, 6, 8, and 12 h) were also investigated in the MBTO catalytic system, summarized in Table 2. It was found that when the temperature was lower than 120°C, the reaction rate was lower, or the reaction could not proceed. And conversion

### Table 1: Catalysts, solvents and initiators were used for ROP of d-GL.

| Entry | Solvent | Catalyst | Initiator | Result |
|-------|---------|----------|-----------|--------|
| (1)   | THF     | MBTO     | Diethylene glycol | --- |
| (2)   | DMSO    | MBTO     | Diethylene glycol | --- |
| (3)   | CHCl₃   | MBTO     | Diethylene glycol | --- |
| (4)   | n-Octane | MBTO     | Diethylene glycol | Off-white |
| (5)   | n-Octane | Sn(Oct)₂ | Diethylene glycol | --- |
| (6)   | n-Octane | TBT      | Diethylene glycol | --- |
| (7)   | CL      | MBTO     | Diethylene glycol | --- |
| (8)   | Methylbenzene | MBTO     | Diethylene glycol | --- |
| (9)   | n-Octane | Y[N(SiMe₃)₂]₃ | Diethylene glycol | --- |
| (10)  | n-Octane | MBTO     | ---         | Off-white |
| (11)  | n-Octane | Al complexes | Diethylene glycol | --- |
| (12)  | Methylbenzene | MBTO     | Benzyl alcohol | Off-white |

--- reaction cannot carry out or cross-linking and gelation occur.
Table 2: ROP of d-GL with various time and temperature in MBTO catalytic system.

| Entry | Temperature/°C | Time/h | Conversion% |
|-------|----------------|--------|-------------|
| (1)   | 120            | 24     | ---         |
| (2)   | 130            | 8      | 48.2        |
| (3)   | 130            | 12     | 56.8        |
| (4)   | 140            | 4      | 51.3        |
| (5)   | 140            | 6      | 63         |
| (6)   | 140            | 8      | 61.7        |
| (7)   | 150            | 4      | 69         |
| (8)   | 150            | 6      | 78.3        |
| (9)   | 150            | 8      | 84.2        |
| (10)  | 160            | 4      | 91.6        |
| (11)  | 160            | 6      | 89.7        |
| (12)  | 170            | 4      | 78.3        |

*aAll reactions were performed in n-octane with MBTO, [d-GL]/[Cat] = 500:1, monomer:initiator = 1000:1. bCalculated by integration of methane resonances in 1H NMR of PGL (DMSO-d<sub>6</sub>, 600 MHz).

Table 3: The properties of polymers with varying d-GL/CL ratios.

| Entry | d-GL/CL ratio in the feed (mol) | Intrinsic viscosity (η<sub>intrinsic</sub>) | X<sub>c</sub> (%) | M<sub>n</sub>/g·mol<sup>-1</sup> | Polydispersity index<sup>b</sup> (PDI) |
|-------|---------------------------------|-------------------------------------------|----------------|--------------------------|-----------------------------------|
| (1)   | 10:0                            | 0.40                                      | ---            | 15814                    | 1.27                              |
| (2)   | 5:5                             | 0.46                                      | 12.09          | 18116                    | 1.16                              |
| (3)   | 4:6                             | 0.48                                      | 28.01          | 21675                    | 1.41                              |
| (4)   | 3:7                             | 0.56                                      | 33.42          | 22752                    | 1.33                              |
| (5)   | 2:8                             | 0.70                                      | 38.79          | 25524                    | 1.40                              |
| (6)   | 1:9                             | 0.87                                      | 40.51          | 28631                    | 1.35                              |
| (7)   | 0:10                            | 1.07                                      | 59.78          | 49901                    | 1.36                              |

*aThis PGL and P(GL-CL) were operated under the condition of MBTO as catalyst and diethylene glycol as initiator in n-octane. bThe viscosity of polymers was carried out in DMSO at 30°C by Ubbelohde viscometer. cDetermined by XRD spectra. dDetermined by GPC.

Increasing with rising the polymerization time when temperature was lower than 160°C. But coloration or decomposition of an aliphatic polyester could be manufactured, when the temperature was higher than 170°C.

3.2. FT-IR of PGL and P(GL-CL). As shown in Figure 2, the stretching vibration of hydroxyl associated with hydrogen bond shifted from (3468, 3392, 3277, and 3218 cm<sup>-1</sup>) of d-GL to an enlarged peak (3392 cm<sup>-1</sup>) in PGL. In addition, compared to d-GL, the deformation peak of hydroxyl shifted from 1719 to 1736 cm<sup>-1</sup> in PGL. Moreover, the sharp peaks corresponding to the C=O symmetric stretching vibration of ester linkage shifted from 1719 to 1736 cm<sup>-1</sup> in PGL, compared with d-GL.

Figure 2 showed the FT-IR spectra of copolymers with various d-GL/CL ratios. It was found that the FT-IR spectra of P(GL-CL) compared to PCL showed a broad-enlarged peak assigned to hydroxyl symmetric stretching vibration around 3526 cm<sup>-1</sup>. The enlarger hydroxyl peak of P(GL-CL) showed blue-shifted with d-GL/CL ratio increasing, as well as the peaks assigned to C=O symmetric stretching vibration from (1700 to 1750 cm<sup>-1</sup>).

3.3. NMR Spectra of PGL. To further investigate the structure of PGL, the 1H NMR was determined in DMSO-d<sub>6</sub> and D<sub>2</sub>O (Figure 3). The 1H NMR spectrum of PGL was reported as follows: 1H NMR (600 MHz, DMSO-d<sub>6</sub>, δ) 4.11 (d, J = 3.80 Hz, 1H), 4.0 (ddd, J = 2.35, 2.07, 2.18 Hz, 4H), 3.9 (dq, J = 3.51, 2.90 Hz, 1H), 3.65 (dd, J = 2.29, 2.32 Hz, 1H), 3.58–3.49 (m, 1H), 3.48 (m, 1H), and 3.35 (d, J = 5.56, 5.38 Hz, 1H). And the peak at δ = 4.0 in PGL/DMSO-d<sub>6</sub> disappeared in D<sub>2</sub>O. In Figure 2(b), 1H NMR results of PGL/D<sub>2</sub>O were listed as follows: 1H NMR (600 MHz, D<sub>2</sub>O, δ) 4.41 (d, J = 3.16 Hz, 1H), 4.26 (d, J = 4.07 Hz, 4H), 4.08–4.03 (m, 1H), 3.94 (dq, J = 3.51, 3.31 Hz, 4H), 3.75 (dd, J = 2.25, 2.21 Hz, 1H), 3.64 (dd, J = 2.34, 2.78 Hz, 4H), 3.61 (dd, J = 3.47, 2.83 Hz, 2H), 3.58 (dd, J = 2.5, 2.74 Hz, 8H), 3.55 (dd, J = 2.88, 4.99 Hz, 1H), and 3.47 (dd, J = 6.15, 5.51 Hz, 4H).

3.4. The Intrinsic Viscosity and GPC of Homo- and Copolymers. The intrinsic viscosities (η<sub>intrinsic</sub>) of polymers (Table 3) (d-GL/CL = 10:0, 5:5, 4:6, 3:7, 2:8, 1:9, and 0:10) were 0.40, 0.46, 0.48, 0.56, 0.70, 0.87, and 1.07, indicating that intrinsic viscosity decreased as d-GL proportion increasing. The molecular weight distributions (M<sub>n</sub>) measured by GPC were consistent with the intrinsic viscosities and ranged from 1.58 to 2.86 kDa. The molecular distribution of polymer was observed to be monomodal (Figure 4), and the molecular weight (M<sub>n</sub>) and PDI were summarized in Table 3.
3.5. XRD Curves of PGL and P(GL-CL). Figure 4(a) showed the XRD patterns of the novel polymer PGL was laight and diffuse, compared to its monomer d-GL. In Figure 4(b), obvious crystallinity peak of PCL appeared around 21.5 and 24°, and the intensity of P(GL-CL) decreased markedly as d-GL/CL ratio increasing. The degrees of crystallinity of P(GL-CL) copolymers (d-GL/CL = 5:5, 4:6, 3:7, 2:8, 1:9, and 0:10) were 12.09, 28.01, 33.42, 38.79, 40.51, and 59.78% (Table 3) obtained by X’pert HighScore software, respectively.

3.6. The Thermal Properties of PGL and P(GL-CL). In Figure 5(a), DSC data of PGL showed that no melting point could be observed during heating flow run and the glass transition temperature was 282 and 347°C, respectively. The glass transition temperature of the copolymer (d-GL/CL = 5:5) showed split-off peak at 49.8 and 55.8°C, and it showed continuous decline at higher temperature. And the first melting point of copolymers (d-GL/CL = 1:9, 2:8, 3:7, 4:6, and 5:5) were 54.0, 53.2, 53.1, 52.7, and 49.8°C, respectively.

In Figure 5(c), the TGA curves showed initiate and decomposition degradation temperatures of PGL were 222 and 299°C, respectively, while PCLs initiate and decomposition temperatures were 282 and 347°C. It can also be seen that a flight of double stages existed in the TGA curves of P(GL-CL) copolymers and it became more obvious as d-GL/CL ratio increases. In particular, the DSC curve of the copolymer (d-GL/CL = 5:5) showed split-off peak at 49.8 and 55.8°C and it showed continuous decline at higher temperature. And the first melting point of copolymers (d-GL/CL = 1:9, 2:8, 3:7, 4:6, and 5:5) were 54.0, 53.2, 53.1, 52.7, and 49.8°C, respectively.

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3.7. In Vitro Degradation. The weight loss of PGL and P(GL-CL) immersed in PBS solution over time was shown in Figure 6(a). It could be found that all the samples, except PCL, had a quick weight loss in the initial 2 weeks, followed by a slightly slow weight loss and PGL was easily dissolved in PBS. The weight loss of polymers (d-GL/CL = 0:10, 1:9, 2:8, 3:7, 4:6, and 5:5) were 0.4, 9.1, 19.7, 23.7, 33.6, and 56.2% in the first week and 6.8, 24.9, 35.7, 45.9, 52.3, and 73.5% at the end of the experiment, respectively. With d-GL content increasing in the main chain, the degradation of P(GL-CL) was significantly accelerated. And the degradation rate of copolymers gradually decreased as soaking time increasing; finally the rate of weight loss of copolymers was consistent with the PCL. Figure 6(b) expressed the pH changes of polymers (d-GL/CL = 0:10, 1:9, 2:8, 3:7, 4:6, 5:5) were 7.2, 5.9, 3.8, 2.4, and 2.1 at the first week, respectively, during soaking and the pH of PGL dissolved in PBS was 1.6. And the neutral pH of copolymers was achieved gradually at the end of the experiment.

4. Discussion

In this work, the d-GL was successfully catalyzed by MBTO into polymer without hydroxyl protection and deprotection and copolymerization with CL through one-pot-two-step process. But it was failed to polymerize d-GL into PCL through melt polymerization and by some general catalysts which could easily catalyst CL into PCL [14, 19, 20]. Noticed common polarity solvents, such as THF, DMSO, and CHCl3, caused crosslinking and gelation in the ROP process of d-GL into PGL (Table 1). The reason why P(GL-CL) copolymer could not synthesis through one-pot-one-steps process might be that the coloration or decomposition of polymer was induced by the polar dissolvability of CL. However, in the one-pot-two-step process, most of CL was catalyzed into PCL before d-GL was added to the reaction system, so it could be avoiding some side reaction of d-GL induced by the polar dissolvability of CL. Considering the effect of temperature (Table 2), the polymerization temperature of PGL was up to 130 to 170°C, because the melting point of d-GL was 151 to 155°C. When the temperature was lower than 120°C, the reaction rate was lower, or the reaction could not proceed. And coloration or decomposition of an aliphatic polyester could be manufactured [21], when the temperature was higher than 170°C. Thus, the favorable reaction temperature of PGL might be 150 to 160°C, and the reaction system should be limited to reflex in n-octane due to the boiling point of n-octane was 125°C. The favorable polymerization time might be 4–6 h in consideration of catalyst d-GL into PGL.

In Figure 1(a), it is obvious to observe that all bands ascribed to hydroxyl, for stretching vibration at 3392 cm⁻¹ and for deformation vibration at 1226 cm⁻¹, shifted to enlarged peaks in PGL, compared with d-GL, indicating that associated hydroxyl existed in PGLs structure after ROP. And the C=O vibration peak of PGL was band reshifted from 1719 to 1736 cm⁻¹, indicating C=O group was substituted with electron donating in ROP process (Scheme 2). From Figure 1(a), peak at δ = 4.0 (dd, J = 2.35, 2.07, 2.18 Hz, 4H) was observed as a steamed bun and tripeak, indicating the hydroxyl attached to three kinds of carbons (CH, CH₂, CH₂H), and it disappeared in D₂O due to hydroxyl exchange with solvent formed HDO [22], and it is easily observed PGL slow degradation into glucose acid in Figure 2(b). All these results are of FT-IR and ¹H NMR; it is most likely the desired product obtained was successful, and hydroxyl was protected in the whole synthesis process [6]. Along with d-GL/CL ratio increasing in P(GL-CL), the absorption peaks assigned hydroxyl of P(GL-CL) became more obvious and shifted to lower wavenumbers, indicating that hydroxyl was protected and undesirable reaction did not occur in the whole reaction. The same blue-shift phenomenon was observed at the peaks assigned C=O symmetric stretching vibration of P(GL-CL) and the GPC curves of all these P(GL-CL) were observed to be monomodal, demonstrating that the resulting products are a copolymer in nature not a mixture of PCL and PGL [23], so d-GL was copolymerized with CL successfully.

The mechanistic of ROP (Scheme 2) was hypothesized according to previously disclosed publication [18, 24–26],
Figure 1: FT-IR spectra of polymers and d-GL: (a) ((A) d-GL; (B) PGL); (b) ((A) PCL; (B)~(F) d-GL/CL = 1:9; 2:8; 3:7; 4:6; 5:5; (G) PGL).

Figure 2: 1H NMR spectrum of the PGL. This PGL was operated under the condition of MBTO as catalyst and diethylene glycol as initiator in n-octane, 160°C, 4 h ((a) DMSO-d6; (b) D2O).

Figure 3: GPC traces of polymers synthesized with varying d-GL/CL ratios.
Scheme 2: Proposed mechanism for the ROP of d-GL using diethylene glycol as initiator and MBTO as catalyst.

Figure 4: XRD of polymers and d-GL: (a) ((A) d-GL; (B) PGL); (b) polymers with various d-GL/CL ratio.
which follows typical coordination-insertion mechanism. At first, MBTO formed active species with initiator; then the active species ring-opening d-GL in the chain propagation step and dormant chain were formed by isolating MBTO segment in the chain growing process. As discussed in above-mentioned, it was the carbonyl oxygen rather than ether oxygen of d-GL that firstly coordinates with active species during the coordination polymerization, because C=O group substituted with electron donating in FT-IR spectrum of PGL (Figure 1(a)) [26]. And the possibility of primary hydroxyl of d-GL participating in the reaction process could not be excluded because the \(^1\)H NMR (Figure 2(a)) showed much clutter from 3.48 to 3.43 ppm. This hypothesis can be further confirmed by the experiment (Table 1, Entry (10)), which PGL also could be obtain in the reaction system without initiator. In that case, the primary hydroxyl of d-GL might be replacing hydroxyl of initiator in the reaction system. But in D\(_2\)O, PGL could be slowly degrading to glucose acid, indicating that some undesirable reaction did not occur in ROP of d-GL.

The copolymerization of d-GL with CL underwent a similar manner of ROP (Scheme 3). When CL monomer was consumed to some extent and PCL segment was long enough, d-GL could competitively replace CL to insert into the polymer chain, leading to block copolymer poly(GL-CL). In the PCL or PGL dominant component, the other less content unit as a defect existed in chain structure. This hypothesis block chain could be proved by TGA of P(GL-CL), which showed two kinds of stages.

From results of GPC (Figure 3, Table 3), the PDI of polymers was ranged from 1.16 to 1.41, indicating a narrow molecular weight distribution of the PGL. Compared to PCL, \(M_n\) of polymers was shown to be decreasing as the ratio of d-GL/CL increasing, which might be related to the fact that reactivity of d-GL’s six-membered ring structure was relatively lower than CL’s seven-membered structure [26]. All P(GL-CL)'s GPC curves were observed to be monomodal, demonstrating the resulting products were a copolymer instead of mixtures of PCL and PGL [23].
Scheme 3: Proposed mechanism for the copolymerization of d-GL and CL.

The DSC data (Figure 5(a)) of PGL showed that no melting point ($T_m$) was found in heating flow and XRD curves (Figure 4) of PGL was high and diffuse, indicating PGL belongs to amorphous structure. Likewise, the XRD curves (Figure 4) of P(GL-CL) became more high and diffuse as d-GL content increasing, showing lower crystallinity of P(GL-CL). And DSC curves of P(GL-CL) split-off more obvious as d-GL/CL ratio increasing at the slightly lower than pure PCL ($62.0^\circ$C) and showed continuous decline at higher temperature. These results could be caused by semicrystalline PCL that cannot form a eutectic with amorphous PGL and both homopolymer chain segments were long enough in block chain structure, which are two representatives of melting generated by each segment.

In Figure 5(c), below 222°C, the PGL loses ca.7% of its weight, suggested PGL crosslinking at high temperatures and low humidities was accompanied by a loss of water. And the backbone thermal degradation temperature of PGL...
was between 222 and 299°C. However, the decomposition temperature of P(GL-CL)s was higher than both PCL and PGL. The reason might be that endothermic of PGL segment thermal degradation at first and the PCL segment was protected from backbone thermal degradation. This phenomenon could be explained by the block copolymer structure, which segment with longer PGL start thermal degradation at first and thermal degradation endothermic process protected the shorter one, even leading a slowly continuous decline in TGA curves of P(GL-CL) (d-GL/CL = 5:5). The TGA results showed that both PGL and P(GL-CL) had good thermal stability. Because of pendant hydroxyl of d-GL, P(GL-CL) with more PGL segment could be continually hydrolyzed, resulting in quick hydrolysis and degradation. And the PGL segment in P(GL-CL) also reduced the molecular chain regularity, and this reinforces the short range hydration during the incubation in the PBS and enhanced the hydrophilic. As a result, the higher content of PGL segment in P(GL-CL) copolymers showed more degradation than that of PCL. The degradation of P(GL-CL) in the present research showed 6.8 to 73.5wt% in the 10-week soaking in PBS with deferent d-GL/CL proportion. This would greatly improve the degradation of the PCL and extend its application.

5. Conclusions

PGL and P(GL-CL) have been successfully synthesized without hydroxyl protection and deprotection. The obtained PGL was amorphous, had a good thermal stability and hydrophilic, and could degrade into glucose acid. Because the polar hydroxyl was introduced into P(GL-CL) copolymers, the hydrolytic degradation rate is significantly changed. Moreover, the eutectic cannot have form in P(GL-CL), resulting in the fact that the thermal properties have a tremendous change. Therefore, PGL and P(GL-CL) may be novel absorbable biomaterials because they have tunable biodegradability, as well as good physical and chemical properties, being worthy of being further evaluated in vivo and in vitro.

Conflicts of Interest

The authors declare that there are no conflicts of interest related to this paper.

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