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Effects of Introduction of L-Lactide on Microstructures, Thermal Properties and *In vitro* Degradation of Poly(glycolide-co-ε-caprolactone) Block Copolymer

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Abstract: In this study, poly(glycolide-co-ε-caprolactone) (PGCL) block copolymers, which have an ABA block structure, were prepared by a two-step polymerization process, and their microstructures, thermal properties and *in vitro* degradation properties according to introducing a small amount of L-lactide as a comonomer in the first step of the polymerization process were systematically investigated. Through our study, it was confirmed that the introduction of L-lactide in the first step of the polymerization process had a great effect on the microstructure of the random PGCL prepolymer (B block) as well as the final PGCL block copolymer (ABA block). Specifically, with the introduction of L-lactide, the average sequence length of glycolide segments on the PGCL prepolymer decreased from 3.32 to 2.40. In addition, it was observed that there is a relatively large difference in the average sequence length of glycolide segments in the final PGCL block copolymers. As a result, these microstructural changes of the PGCL prepolymer originated from the L-lactide comonomer affected significantly the thermal properties and *in vitro* degradation properties on the final PGCL block copolymers. Compared with the PGCL block copolymer without L-lactide, melting temperature and crystallization temperature of the PGCL block copolymer with L-lactide decreased, as well as their thermal degradation temperature. In addition, the introduction of a small amount of L-lactide comonomer accelerated the hydrolytic degradation of the PGCL block copolymer. Overall, by introducing L-lactide copolymer in the first step of the two-step manufacturing process for the PGCL block copolymer, changes of various properties on the PGCL block copolymer originated from the changes in the microstructure of random PGCL prepolymer were confirmed.

Keywords: PGCL block copolymer, L-lactide as a comonomer, Microstructures, Thermal properties, In vitro degradation

Introduction

Poly(glycolide) (PGA) is an aliphatic polyester with an extremely simple structural unit (-O-CH_2-CO-), and various studies on PGA are being conducted in the medical field, including surgical sutures, because of the absorption and degradation properties of the polymeric material [1-4]. In particular, a monofilament manufactured using PGA can be used as a high-strength suture. However, it is known to be unsuitable for use as a monofilament suture owing to its relatively high rigidity and faster degradation rate [5]. To solve these problems, methods for controlling the degradation rate and physical properties through polymer blending or copolymerization have been proposed and applied [6-8]. Poly(glycolide-co-ε-caprolactone) (PGCL) is the most representative material meeting this purpose [9].

PGCL, which is generally used as a monofilament for sutures, is known to be prepared through a two-step polymerization process. During the first step, a random PGCL prepolymer (B block) is prepared through the copolymerizing of glycolide and ε-caprolactone used as monomers (glycolide:ε-caprolactone, 55:45), and during the second step, glycolide (A block) is added for the final preparation of a PGCL block copolymer (glycolide:ε-caprolactone, 75:25) having an ABA-type block structure [10,11]. The random PGCL prepolymer prepared through the first step mainly acts as an amorphous component providing flexibility to the final PGCL block copolymer. In addition, the A block composed mainly of glycolide acts as a crystalline component and influences the mechanical properties of the final PGCL block copolymer and their suture [9]. Therefore, in the PGCL block copolymer system, the glycolide content and average sequence length must be important factors that can influence the physical properties of the entire block copolymer.

Our previous study clearly showed that, under the reaction condition of having the same composition of glycolide and ε-caprolactone, the microstructures of the random PGCL prepolymer was affected by reaction temperature and catalyst feed ratio [12,13]. In addition, it was concluded that the structural characteristics of the PGCL prepolymer have significant influences on thermal properties and crystallization behavior of the final PGCL block copolymer. In other words, these results indicate that it is possible to fabricate final PGCL block copolymers with various physical and chemical properties through controlling the microstructures

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on the random PGCL prepolymer, especially the microstructure of glycolide, even when the same amounts of monomers are applied. Nevertheless, there is a limit to controlling the microstructure of the random PGCL prepolymer only by adjusting the reaction conditions under the same amount of monomer. This is because the reaction temperature and catalyst concentration outside a certain level can cause serious problems on a processability such as melt-spinning and post-processing of the final PGCL block copolymer. Therefore, to develop various biodegradable sutures or polymer materials centering on the ABA-type PGCL block copolymer, it is necessary to systematically study a manufacturing method for the random PGCL prepolymer or B block composed of various microstructures, and thus the changes of characteristics of the final PGCL block copolymer.

In this study, in order to prepare PGCL block copolymers having various microstructures at the same reaction conditions, a method for introducing a comonomer into the polymerization process was proposed. More specifically, a small amount of L-lactide was introduced as a comonomer in the first step of the polymerization process consisting of two steps for the PGCL block copolymer, and the effect of the L-lactide comonomer on the microstructure of the PGCL at each step and thus the changes of the properties on the final PGCL block copolymer was systematically investigated.

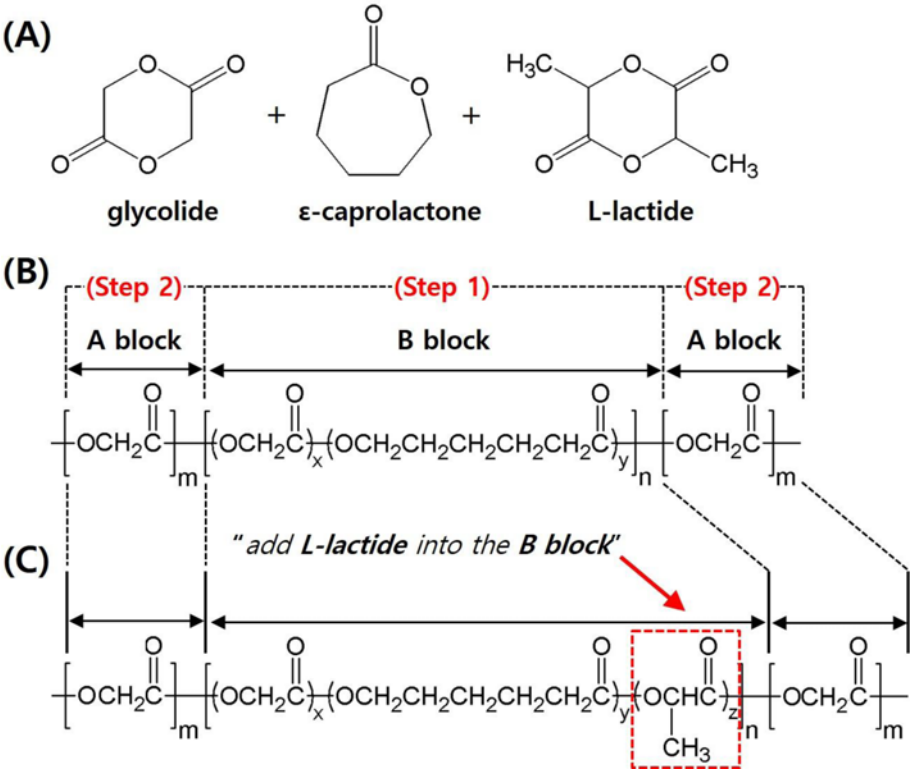
Experimental

Materials

In this study, glycolide, ε-caprolactone, and L-lactide, obtained from Boehringer-Ingelheim and Daicel, were used as monomers for the preparation of the PGCL prepolymers and block copolymers. Each chemical structure including monomers and copolymers is shown in Scheme 1. Stannous octoate and diethylene glycol (DEG) were applied as a catalyst and an initiator, respectively, for a bulk ring-opening polymerization. Deuterated dimethyl sulfoxide-d_6 (DMSO-d_6) was used as a solvent for an ^{1}H-NMR analysis. All reagents used in this study except for the monomers were purchased from Aldrich and used without further purification.

Synthesis of PGCL Prepolymers and its Block Copolymers

It is known that PGCL block copolymer, which is generally used for suture purposes, is prepared as an ABA-type block copolymer by a two-step process [9]. As shown in Scheme 1(B), a random PGCL prepolymer (B block) is prepared by ring-opening polymerization of glycolide and ε-caprolactone in the first step process, and in the second step process, glycolide is added (A block) to finally complete a PGCL block copolymer having an ABA-type structure. In this study, a small amount of L-lactide was additionally



Scheme 1. Monomers used in this study (A) and chemical structures for the PGCL block copolymers (B and C) obtained from glycolide, ε-caprolactone and L-lactide.

Table 1. Changes in composition and structural characteristics of the PGCL prepolymers and its block copolymers

Sample code		Molar ratio in feed (GG/C/LL)	Molar ratio (GG/C/LL)	L_G	L_C	L_L	I.V
Random PGCL prepolymer (B block)	r-PGCL-1	55/45/-	55.1/44.9/-	3.32	1.16	-	0.99
	r-PGCL-2	55/30/15	55.3/28.6/16.1	2.40	1.14	2.88	1.01
PGCL block copolymer (ABA block)	PGCL-1	75/25/-	75.4/ 24.6/-	7.84	1.30	-	1.70
	PGCL-2	75/16.7/8.3	76.4/14.4/9.2	4.92	1.16	1.61	1.68

GG: glycolide, C: ε-caprolactone, LL: L-lactide, L_G: average length of glycolyl sequences, L_C: average length of caproyl sequences, L_L: average length of lactyl sequences, and I.V: inherent viscosity.

introduced as a third monomer in the first-step process for the random PGCL prepolymer (Scheme 1(C)). The experimental details for the synthesis of the PGCL prepolymer and thus its block copolymers in this study are as follows. In the first step process, glycolide and ε-caprolactone, L-lactide as monomers were added in a molar ratio of 55:45:0 (r-PGCL-1) or 55:30:15 (r-PGCL-2), respectively, and stannous octoate dispersed in DEG and toluene was added as a catalyst to proceed with the reaction. The total amount of initiator and catalyst were added at a ratio of 1250:1 (monomer:initiator) and 40,000:1 (monomer:catalyst), respectively. Before a bulk ring-opening polymerization was applied, a vacuum-nitrogen purge was conducted three times for 20 min each to remove oxygen and toluene in the reactor. To maintain the consistency of the process, the polymerization was applied by setting the reaction time based on the target reaction temperature 190 °C to 6 hours as the basic conditions with a heating time of 60 min and a stirring speed of 50 rpm. In the second step reaction, glycolide was added to adjust the molar ratio of the final copolymer to be 75:25 (PGCL-1) or 75:16.7:8.3 (PGCL-2). In the second step, the reaction was performed at 210 °C for 2 hours and 30 minutes. As a result, the composition ratio of each PGCL prepolymer and its block copolymer prepared was relatively well matched with the molar ratio in feed, and uniform viscosity results were obtained, as shown in Table 1. Based on this, it was confirmed that the PGCL prepolymer and its block copolymer on each step were well synthesized within the experimental error range.

Characterization

Nuclear magnetic resonance spectroscopy (500 MHz NMR Spectroscopy, Bruker) was used to analyze the microstructure of the PGCL prepolymer and its block copolymer. Based on the ^{1}H-NMR spectrum, the average sequence length and composition of the PGCL prepolymer and its block copolymer for each step were obtained. Furthermore, during the synthesis process of the PGCL prepolymer, a transesterification reaction that occurs when the end group of each activated monomer attacks the glycolidyl (GG) or lactidyl (LL) unit is expected. For example, through this transesterification reaction, bond cleavage occurs in glycolidyl to form CGC and LGL sequences, and in the case of lactidyl, CLC and GLG sequences are formed. In general, because the ring-opening of a glycolide monomer produces GG units, which are even-numbered G blocks, it can be seen that odd-numbered G units are generated through this transesterification reaction. In this way, a total of eight sequences including CGC can be predicted. However, considering the effect of the average sequence length by the transesterification, it is expected to occur focused on the glycolide and L-lactide monomers, which have a high initial reactivity, CGC, CLC, LGL, and GLG sequences were mainly used with a transesterification coefficient in this study. For instance, the transesterification coefficient of glycolidyl unit by an activated caproyl end group can be calculated using equation (1) [14-16].

$$T_{II}^{CGC} = [CGC]/[CGC]_R \quad (1)$$

Here, $[CGC]$ is the experimental concentration value of the CGC sequence obtained through ^{1}H-NMR, and $[CGC]_R$ indicates the concentration of a completely randomized chain. In this way, a total of four transesterification coefficients, e.g., T_{II}^{CLC} T_{II}^{LGL}, and T_{II}^{GLG} can be obtained.

Considering melt spinning and post-processing, changes in thermal properties and hydrolytic degradation properties due to the introduction of L-lactide were evaluated focusing on the final PGCL block copolymer. The thermal properties of the final PGCL block copolymer were measured using a differential scanning calorimeter (DSC 2910, TA Instruments) over a temperature range of 30-240 ℃ at a heating rate of 20 ℃/min. The thermal degradation of the final PGCL block copolymers were examined using a TGA-7 (Perkin Elmer) from 30 ℃ to 600 ℃ at a heating rate of 20 ℃/min under a nitrogen atmosphere. The hydrolytic degradation behavior of the final PGCL block copolymers was evaluated by placing a PGCL film prepared by hot-press with a size of 1.5×1.5 cm^2 in a phosphate buffer solution (PBS) at pH 7.4. The temperature of the PBS solution was set to 37 ℃. The weight loss of the final PGCL block copolymers due to hydrolytic degradation was calculated as follows.

$$\text{Weight loss (\%)} = \frac{W_0 - W_d}{W_0} \times 100$$

Here, W_0 is the weight of the sample before degradation,

and W_d is the weight of the sample after degradation. The morphological features of the final PGCL block copolymers according to the hydrolytic degradation were characterized using field emission scanning electron microscopy (FESEM, JEOL, JSM-7000F).

Results and Discussion

Microstructure Analysis of PGCL Prepolymers and its Block Copolymers

Figure 1 shows the ^{1}H-NMR spectrum of a random PGCL prepolymer containing L-lactide as a comonomer. In the case of the G and L units, it is divided into four peaks showing triad sequences GGG, GGZ, ZGG, ZGZ and LLL, LLY, YLL, YLY, respectively, and the C unit shows a dyad sequence (CC, CX). Because the polarity is large in order of L > G > C, the L unit is located relatively downfield. For instance, when an L unit is attached to another L unit, it moves downfield, and when a G unit is attached, it moves up-field. The peak positions corresponding to each sequence of the random PGCL prepolymer are summarized in Table 2.

The average sequence length and composition of the random PGCL prepolymer (B block) and the final PGCL block copolymer (ABA-type) prepared in each step were calculated using the method used in previous studies [12,13] based on the ^{1}H-NMR analysis, and are summarized in Table 1. As can be seen in Figure 2(A), it is confirmed that the introduction of L-lactide as a comonomer had great influences on the microstructures of the random PGCL prepolymer prepared in the first step. Specifically, with the introduction of L-lactide, the average sequence length of glycolide segments on the PGCL prepolymer decreased from 3.32 (r-PGCL-1) to 2.40 (r-PGCL-2).

According to our previous our studies, it can be considered that the average sequence length of glycolide segments on random PGCL copolymer (or random PGCL prepolymer in this study), which consists of only glycolide and ε-caprolactone, is significantly affected by transesterification reaction originated from an activated ε-caprolactone sequences

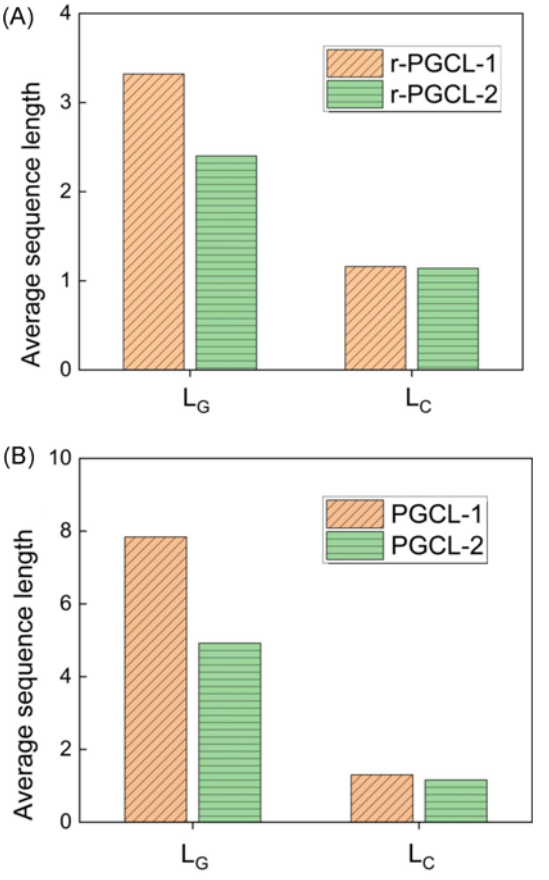


Figure 2. Relative comparison of average sequence length in (A) PGCL prepolymer and (B) PGCL block copolymer (L_G: average length of glycolyl sequences, L_C: average length of caproyl sequences).

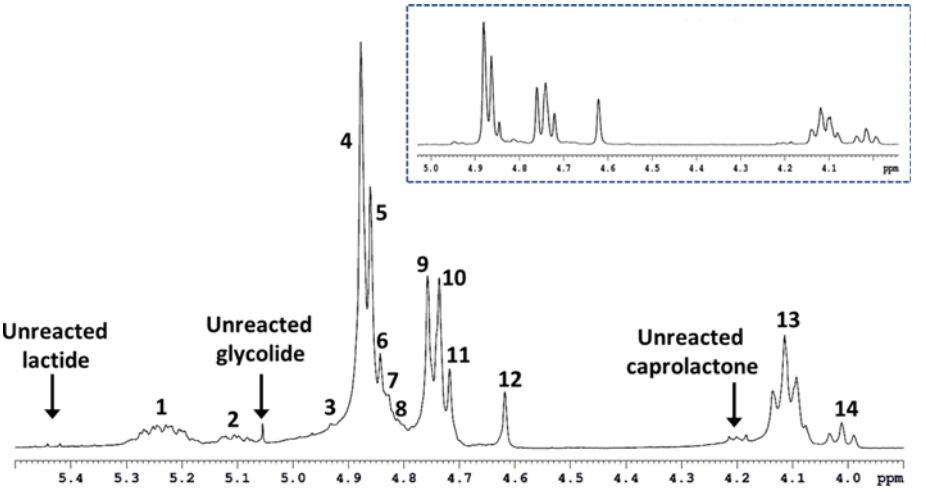


Figure 1. ^{1}H-NMR spectra of a random PGCL copolymer with L-lactide and a random PGCL copolymer without L-lactide (inset figure).

Table 2. Peak position of the random PGCL copolymer obtained from ^{1}H-NMR spectrum

Number	Sequence	δ (ppm)
1	LLLL	5.20
2	LLGG+LLC+CLL+GGLL	5.10
3	CLC+GLG	5.00
4	GGGG	4.88
5	CGGGG+GGGGC	4.86
6	GGL+LGG	4.85
7	CGGGC	4.84
8	LGL	4.83
9	GGGC	4.76
10	CGGGG+CGGGC	4.74
11	CGGC	4.72
12	CGC	4.62
13	GC+LC	4.13
14	CC	4.03

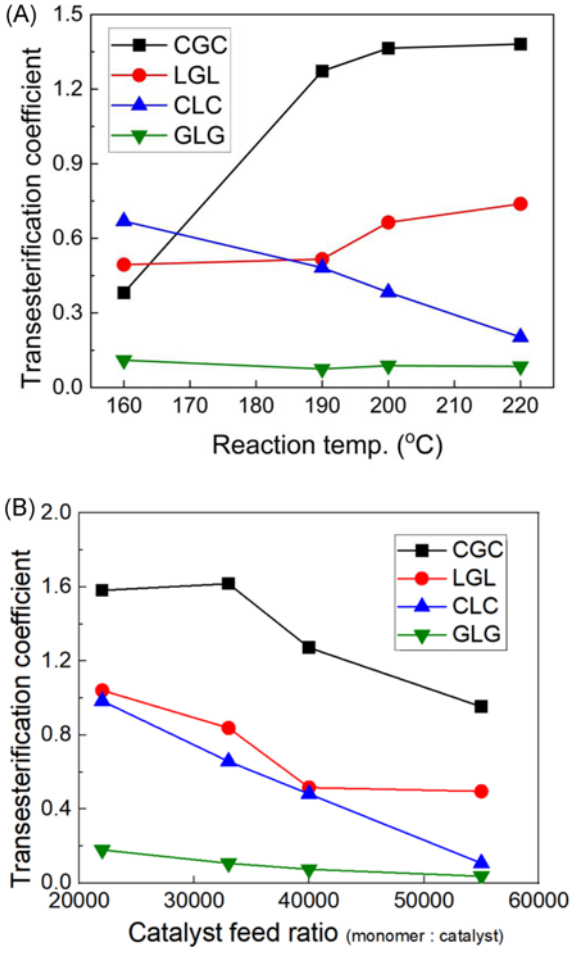


Figure 3. Changes in coefficient of transesterification with various reaction temperatures (A) and catalyst feed ratio (B).

in the growth of glycolide segments. This means that, as a result of transesterification reaction due to the activated ε-caprolactone sequences, the average sequence length of the glycolide segments becomes smaller. In addition, the transesterification reaction on the random PGCL prepolymer varies according to various reaction conditions such as reaction temperature, catalyst feed ratio. In this study, to observe changes of the transesterification reaction according to the introduction of L-lactide comonomer, various reaction conditions such as reaction temperatures and catalyst feed ratios were conducted on synthesis of the random PGCL prepolymer. As can be seen in Figure 3, it was found that in addition to activated ε-caprolactone sequences, a transesterification reaction by activated L-lactide sequences was also very active on the entire reaction condition. Thus, it can be seen that the relatively low average sequence length of the glycolide segments on the random PGCL prepolymer with the L-lactide was obtained as a result of a more accelerated transesterification reaction by the activated both ε-caprolactone and L-lactide sequences in the growth of glycolide segments.

Interestingly, as shown in Figure 2(b), it can be observed that there is a relatively large difference in the average sequence length of glycolide segment in the final PGCL block copolymers (ABA block structure). The average sequence length of the glycolide segments for PGCL-1 was 7.84, whereas the average sequence length of the glycolide segment for PGCL-2 introduced with L-lactide was evaluated to be 4.92, which is relatively low compared to the PGCL-1. However, further investigation is needed as to whether the decrease in the average sequence length of the glycolide segments on the final PGCL block copolymer is due to the transesterification reaction or obtained arithmetically by the microstructure determined in the PGCL prepolymer. On the other hand, it was observed that there were no notable changes in the average sequence length of the ε-caprolactone segments in the entire process including the first and second steps. Therefore, even though these two PGCL block copolymers have the same ABA-type structure and the same glycolide content as a main component, it can be concluded that the PGCL-2 with a small amount of L-lactide has more random B blocks (Figure 4), as well as A blocks with relatively short crystalline glycolide sequences.

In general, it is well known that the B block (or random

Figure 4. Schematic model of PGCL block copolymer with different sequence lengths at the same glycolide content.

PGCL prepolymer) mainly acts as an amorphous component to give flexibility to the final PGCL block copolymer, and the A block composed mainly of glycolide segments acts as a crystalline component and thus influences the physical properties of the final block copolymer. As a result, the changes on the microstructure of the PGCL prepolymer and its block copolymer induced by a small amount of L-lactide is expected to have a significant impact on the final thermal properties and decomposition behavior of the PGCL block copolymers.

Thermal Properties of PGCL Block Copolymers

Figure 5 shows DSC curves of the PGCL block copolymers, and the detailed analysis results are summarized in Table 3. To exclude the thermal history of each sample, DSC curves obtained from second heating process were used in this study. In general, it is well known that, the addition of a comonomer within a crystallizable polymer influences the formation of crystal structure, crystallinity, and melting temperature for the polymeric materials. In particular, a decrease in the average sequence length of a major component (glycolide or A block in this study) increases the free energetic barrier and prevents rearranging and packing of the major component. Since the temperature at which the crystal formed from the polymer melts is defined as the melting temperature, the melting temperature of the final polymers can be affected by the amount and shape of the crystal produced. Of course, this crystal is also closely related to the average length of the crystalline major component. Based on this point of view, it is expected that, considering the changes of the average sequence length of crystalline glycolide segments (A block) with the L-lactide, the introduction of L-lactide in the PGCL block copolymers influences thermal properties of the block copolymers. As can be seen in Figure 5(A), PGCL-2 with L-lactide has a lower melting temperature compared to PGCL-1, and the crystallization temperature of the PGCL-2 decreased as well (Figure 5(B)). Considering the amount of glycolide contents present in PGCL-1 and PGCL-2 is the same, it can be seen that the decrease in the melting temperature of the PGCL-2 by the introduction of the L-lactide is due to the decrease in the average length of the crystallizable glycolide segments. Furthermore, it is found that the PGCL-2 has a larger value of degree of supercooling than the PGCL-1. Since the degree of supercooling can be interpreted as a thermodynamic driving force for crystallization of a polymer, it can be considered that a larger degree of supercooling requires a greater driving force for crystallization and consequently the PGCL-2 with L-lactide is difficult to crystallize compared with the PGCL-1. However, the crystallization behavior may also be influenced by molecular weight of a polymer, so it is necessary to confirm the molecular weight of each random PGCL prepolymer and its block copolymer. For random PGCL prepolymers, the value of the measured inherent viscosity was 0.99, 1.01 dl/g, respectively, and was evaluated at 1.70 and 1.68 dl/g for the final PGCL block copolymers, as listed in Table 1. As a result, since molecular weight between each of the samples is similar to each other, it is reasonable to conclude that the difference in the thermal properties of these two PGCL block copolymer is due to changes of the microstructures on the PGCL prepolymer and thus block copolymer according to the introduction of L-Lactide as a comonomer.

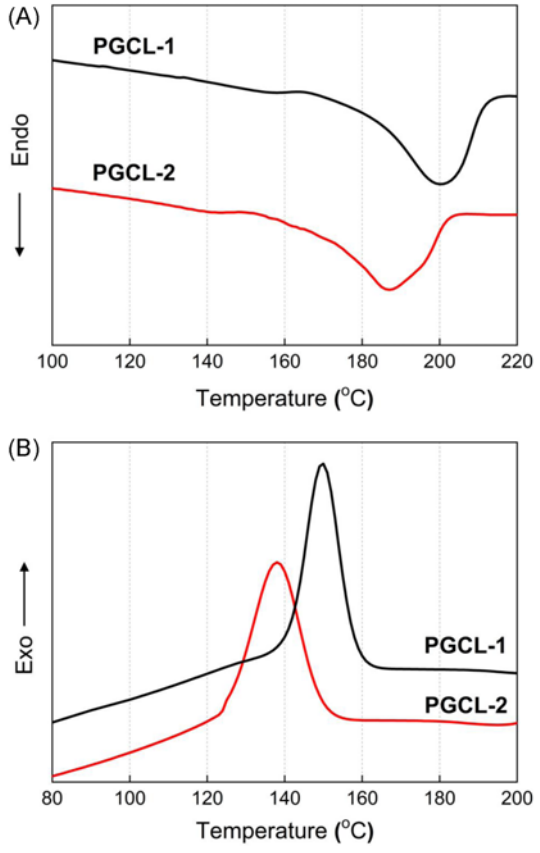


Figure 5. DSC heating (A) and cooling (B) thermogram of the PGCL block copolymers.

Table 3. Thermal properties of the PGCL block copolymers

Sample code	T_m (°C)	ΔH_m (J/g)	T_{mc} (°C)	ΔH_{mc} (J/g)	ΔT^a (°C)
PGCL-1	200.1	27.6	149.9	27.1	50.2
PGCL-2	187.8	20.39	133.7	24.9	54.1

[a]Degree of supercooling, $\Delta T = T_m - T_{mc}$.

Thermal Degradation Properties of PGCL Block Copolymers

TGA thermogram was obtained to investigate the thermal degradation property of the PGCL block copolymers according to the introduction of L-lactide comonomer.

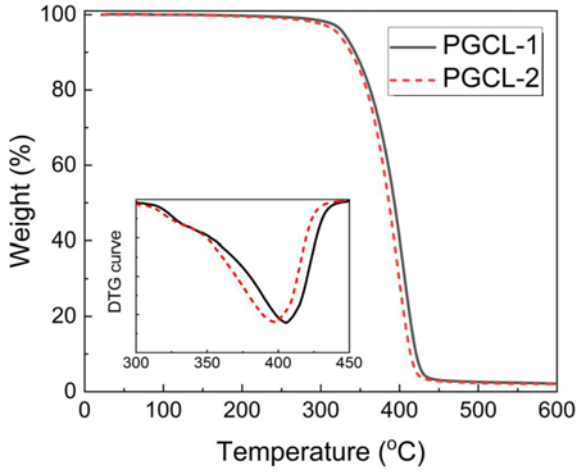


Figure 6. TGA thermogram and the corresponding DTG curves (inset figure) of the PGCL block copolymers up to 600 °C under nitrogen atmosphere.

Figure 6 shows the weight changes and the corresponding DTG curves (inset figure) of the PGCL block copolymers up to 600 °C under nitrogen atmosphere. The temperature on the weight loss value of 5 %, ($T_{5\,\%}$), was chosen as the reasonable criterion to evaluate the onset of the thermal degradation of each block copolymer. As can be seen in the Figure, $T_{5\,\%}$ for the PGCL-1 was evaluated to be about 329.4 °C. On the other hand, $T_{5\,\%}$ of PGCL-2 with L-lactide was measured at 321.8 °C, which is about 8 °C lower than that of PGCL-1. Moreover, the maximum degradation temperature, T_{max}, has decreased from 404.3 °C (PGCL-1) to 396.1 °C (PGCL-2). These results indicate that the thermal stability of the PGCL block copolymer has somewhat degraded with introduction of L-lactide. In general, it is known that the thermal decomposition temperatures of poly(ε-caprolactone), and poly(glycolide), and poly(lactide) are 402 °C, 360 °C, and 295 °C, respectively [17]. Based on these results, it can be expected that the thermal stability of the PGCL block copolymers decreased gradually with introducing L-lactide segment, because the L-lactide segments presented into the PGCL block copolymer reduces the thermal stability of the entire block copolymer by causing its intramolecular ester interchange mechanism during thermal decomposition.

In vitro Degradation Properties of PGCL Block Copolymers

As mentioned above, since the PGCL block copolymer is used as the main material for sutures, it is very important to evaluate the *in vitro* degradation characteristics of the block copolymer according to the changes of its microstructure. To determine the effect of L-lactide on the hydrolytic degradation behavior of the PGCL block copolymers, PGCL-1 and PGCL-2 film prepared with a size of 1.5×1.5 cm^2 were immersed in pH 7.4 phosphate buffer solution. The hydrolytic

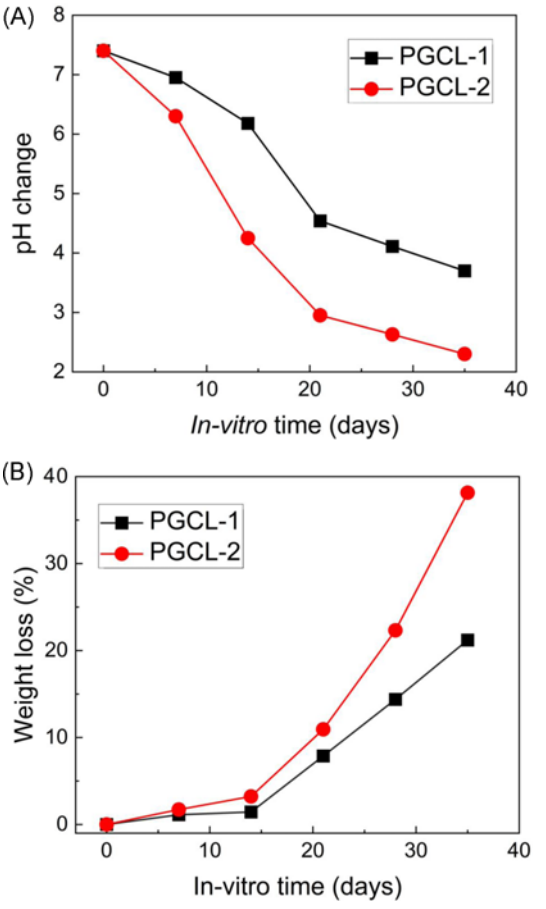


Figure 7. Changes in pH (A) and weight loss (B) of the PGCL block copolymers at 37 °C.

degradation of the PGCL block copolymers was then determined as a function of the degradation time and characterized by changes in pH and weight loss. The morphological characterization of the PGCL block copolymers during the hydrolytic degradation was analyzed using FE-SEM. Figure 7 shows the changes in pH (A) and the weight loss (B) of the PGCL block copolymers at 37 °C. As can be seen from the figure, the PGCL-2 containing L-lactide exhibits a lower pH value generally than the PGCL-1. In addition, the time taken for the PGCL-2 to reach pH 4.0 at 37°C was 15 days, whereas the PGCL-1 reached pH 4.0 in 30 days. Furthermore, the PGCL-2 lost their weight of 38.1 % after 5 weeks, while the PGCL-1 recorded a weight loss of 21.2 % at the same time point. The pH and weight reduction results according to these time changes clearly indicate that the hydrolytic degradation rate of PGCL-2 with L-lactide is faster than that of PGCL-1. These results can also be confirmed through the morphological analysis of the PGCL block copolymers. Figure 8 shows FE-SEM images of both PGCL-1 and PGCL-2 films at 37 °C according to time change. As can be seen from the figure, many cracks

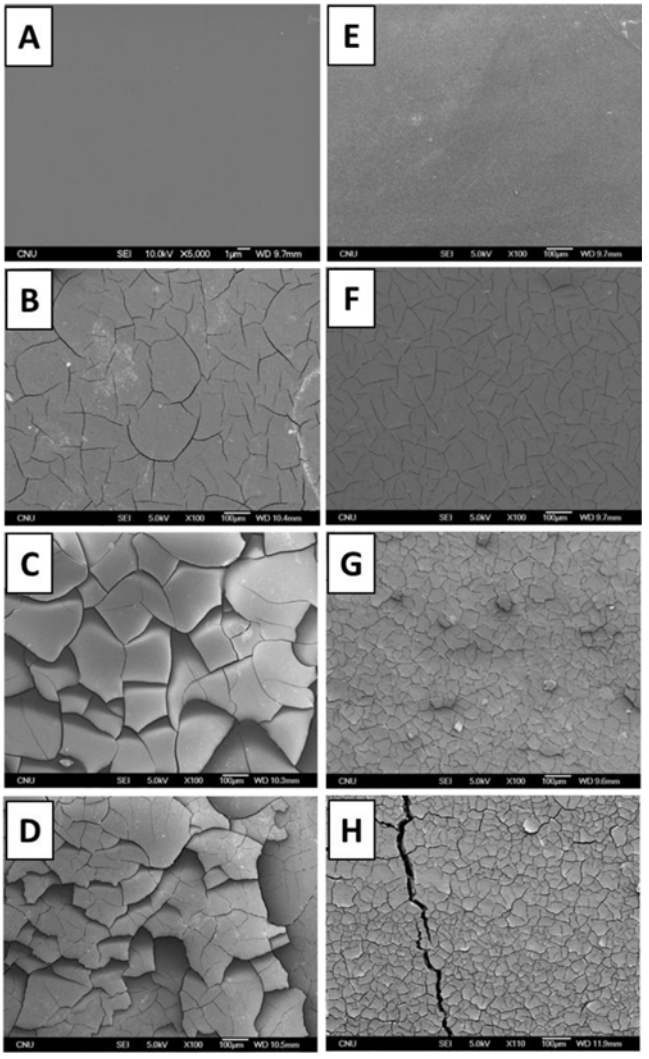


Figure 8. FE-SEM images of PGCL-1 (A-D) and PGCL-2 (E-H) with various degradation time (0 week (A, E), after 1 week (B, F), 3 week (C, G) and 5 week (D, H)) at 37 °C.

start to occur on the surface of the film of the PGCL block copolymers after 1 week. In particular, it can be observed that more cracks occurred in PGCL-2 compared with PGCL-1. The morphological features obtained from the FE-SEM analysis support the results observed in changes in pH and weight loss of both PGCL-1 and PGCL-2 films. According to the hydrolysis mechanism of biodegradable polyesters, it is generally known that the hydrolysis of the polymers proceeds rapidly in the initial stage in the amorphous region where water molecules can penetrate relatively easily. Thus, based on the results of this study, the average sequence length of glycolide on the PGCL block copolymer decreased with the introduction of L-lactide, and it can be fully expected that it affects the microstructure such as the randomness of PGCL as well as the expansion of the amorphous region. As a result, considering that there is no significant difference in the molecular weight of the two block copolymers, it is reasonable to conclude that these results in the hydrolytic degradation behavior are due to the microstructural changes of the PGCL block copolymer caused by the introduction of L-lactide.

Conclusion

In this study, a method for introducing a comonomer into the polymerization process was proposed in order to prepare PGCL block copolymers having various microstructures. For this purpose, a small amount of L-lactide was introduced as a comonomer in the first step of the polymerization process consisting of two steps for the PGCL block copolymer, and the effect of the L-lactide comonomer on the microstructure of the PGCL at each step and thus the changes of the properties on the final PGCL block copolymer was systematically investigated. Through our studies, it was found that the introduction of L-lactide in the first step of the polymerization process had a great effect on the micro-structures of the random PGCL prepolymer (B block) as well as the final PGCL block copolymer (ABA block). Also, it was identified that the relatively low average sequence length of the glycolide segments on the random PGCL prepolymer with the L-lactide was obtained as a result of a more accelerated transesterification reaction by the activated both ε-caprolactone and L-lactide sequences in the growth of glycolide segments. As results of the structural changes, melting temperature and crystallization temperature of the PGCL block copolymer with L-lactide decreased, as well as their thermal degradation temperature. In addition, the introduction of a small amount of L-lactide comonomer accelerated the hydrolytic degradation of the PGCL block copolymer. Overall, by introducing L-lactide comonomer in the first step of the two-step manufacturing process of the PGCL block copolymer, significant changes of various properties on the PGCL block copolymer were confirmed. Furthermore, we are also confident that this study conducted on finding suitable method to control the microstructures of the PGCL prepolymer will serve as an academic foundation for expanding the application field of the final PGCL block copolymer.

Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this article.

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