

# Microstructural analysis and structure-property relationship of poly(glycolide-co-1,3-trimethylene carbonate)

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## Abstract

A series of linear copolymers of glycolide and 1,3-trimethylene carbonate were synthesized by bulk ring-opening polymerization. The copolymers were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, viscometry, and differential scanning calorimetry (DSC). The dependency of reaction temperature, reaction time, and the feed composition on the microstructure of the copolymers was examined by <sup>13</sup>C NMR analysis. The microstructural analysis using <sup>13</sup>C NMR was useful to calculate the average block length of the glycolyl ( $L_G$ ) and trimethylene carbonyl ( $L_T$ ) sequence. The structural change such as transesterification, which was assigned by TGT sequence, was reflected in the average block length and the sequence of each monomeric unit in the copolymer. The average length of glycolyl sequence ( $L_G$ ) was much longer than that of trimethylene carbonyl sequence ( $L_T$ ) in polymerization temperature of 100–150 °C. Upon further increasing the polymerization temperature, the  $L_G$  decreased, but the change of  $L_T$  was insignificant. During the polymerization, transesterification did not occur at 100 °C, but it was observed at a polymerization temperature range of 130–200 °C resulting in the decrease in  $L_G$ . As the composition of trimethylene carbonate increased,  $L_G$  decreased, but  $L_T$  do not show remarkable change. DSC results showed a close relationship between crystallinity and nature of microstructural sequence. The crystallinity of block copolymers was mainly decided by the average length of the glycolyl block. © 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Poly(glycolide-co-1,3-trimethylene carbonate); Microstructure; Transesterification

## 1. Introduction

Biodegradable synthetic polymers including aliphatic polyesters and polycarbonates have been of great interest due to their usefulness especially in medicine and biotechnology [1–12]. In particular, polyglycolide and its copolymers have found versatile application fields such as a surgical suture, scaffolds in tissue engineering, and controlled drug delivery systems [13–15]. In addition to their macrostructural characterization and application-driven studies, the detailed analysis of microstructure is also important in that it can significantly affect thermal and mechanical properties, biodegradability, and so on [16,17]. The microstructural analyses of block copolymers including

sequence analysis of each monomer unit have been performed by NMR spectroscopy [16,17]. Especially, <sup>13</sup>C NMR spectroscopy has been successfully applied to the elucidation of microstructure of various copolyamides and copolyesters [16–24]. For instance, Kricheldorf et al. reported on the sequence analysis of copolymers of polyglycolide and poly( $\epsilon$ -caprolactone) by using <sup>13</sup>C NMR spectroscopy and correlated it with the reaction mechanism and properties such as solubility and crystallinity [16]. Dobrzynski et al. studied intensively the relationship between the microstructure and thermal or degradation properties of glycolide/ $\epsilon$ -caprolactone and glycolide/L-lactide copolymers [17–19]. In this paper, we describe microstructural analysis of linear copolymers of glycolide and 1,3-trimethylene carbonate. The copolymerization of glycolide and 1,3-trimethylene carbonate may provide promising bioabsorbable materials such as the surgical suture and the scaffold for tissue engineering since their appropriate combination can produce useful materials with controlled strength, flexibility, and biodegradability. To date, most of copolymers prepared from glycolide and

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1,3-trimethylene carbonate have been mainly tailored to the specific application, whereas understanding of the microstructure is still lacking [25]. The microstructure of the glycolide/1,3-trimethylene carbonate block copolymer appears to affect both thermal properties and biodegradation of the copolymer. Thus, microstructural analysis of the copolymer is important to predict the final properties of the copolymer.

In this work, the linear copolymers of glycolide and 1,3-trimethylene carbonate were synthesized, and their microstructures were analyzed by  $^{13}\text{C}$  NMR spectroscopy. The effects of reaction variables, such as polymerization time and temperature, and the feed comonomer ratio on the sequence and average block length of each monomer unit in the copolymers were investigated. In addition, the relationship between the average block length and the thermal properties of copolymers was discussed.

## 2. Experimental section

### 2.1. Materials

Glycolide (Boehringer Ingelheim) was recrystallized two times from ethyl acetate and sublimed prior to use. 1,3-Propanediol was purchased from Aldrich Co. (Milwaukee, WI) and was vacuum distilled over calcium hydride. Diethyl carbonate was purchased from Aldrich Co. (Milwaukee, WI) and was distilled over calcium chloride. Stannous octoate ( $\text{Sn}(\text{Oct})_2$ ) from Sigma Co. (St Louis, MO) and 1,1,1,3,3,3-hexafluoro-2-propanol from Aldrich Co. (Milwaukee, WI) were used as received. Benzene and diethyl ether were of the reagent grade and used without further purification.

### 2.2. Synthesis of 1,3-trimethylene carbonate

1,3-Trimethylene carbonate was synthesized following a literature procedure [12]. In brief, 1,3-propanediol (76 g, 1 mol), diethyl carbonate (141 g, 1.19 mol), and sodium metal (0.1 g) were refluxed at 140 °C for 4 h. Ethanol and residual diethyl carbonate were distilled off, and the residue was dissolved in benzene, washed with water, and dried over calcium chloride. After removal of solvent, the crude product was obtained by vacuum distillation, then purified by recrystallization from diethyl ether, and dried for 24 h in vacuum at 30 °C.

### 2.3. Synthesis of poly(glycolide-co-1,3-trimethylene carbonate)

The copolymerization of glycolide and 1,3-trimethylene carbonate was conducted in bulk. As an example, copolymer 3, which was 7:3 feed ratio of glycolide and 1,3-trimethylene carbonate was prepared by a following procedure. Glycolide (0.725 g, 6.2 mmol), 1,3-trimethylene

carbonate (0.273 g, 2.7 mmol), and  $\text{Sn}(\text{Oct})_2$  ( $1.34 \times 10^{-4}$  M) in toluene (48  $\mu\text{L}$ ) were placed in 20 mL glass ampoule. The toluene was evaporated under vacuum in glass ampoule. The vent and purge with nitrogen were repeated five times. The glass ampoule was sealed using flame under vacuum. The reaction mixture was stirred and heated up to 150 °C. The reaction was maintained for 20 h. The copolymer was recovered, and dried for 24 h in vacuum at 40 °C. Other linear copolymers with various feed ratios, polymerization temperatures, and polymerization times were synthesized in an identical manner.

### 2.4. NMR analysis

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC 250 spectrometer in hexafluoroacetone-*d*-6 ( $\text{CF}_3\text{COCF}_3 \cdot \text{D}_2\text{O}$ ) (Cambridge isotope laboratories) at 250 and 63 MHz, respectively. The copolymer composition and the microstructure of the copolymer chain were estimated, respectively, by  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses.

### 2.5. DSC measurements

Melting temperatures ( $T_m$ ) and glass transition temperatures ( $T_g$ ) of the copolymers were measured using a Perkin-Elmer DSC7. The copolymer sample (6 mg) was placed in a hermetically sealed aluminum pan. The thermograms were recorded at a heating rate of 10 °C/min. Calibration of the system was performed using gallium and indium standards.

### 2.6. Viscometry

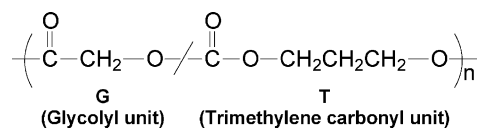
The inherent viscosity was measured in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) at 25 °C using an Ubbelohde viscometer. The concentration of the solution was 0.5 g/dL.

## 3. Results and discussion

### 3.1. Synthesis and characterization of copolymers

The linear copolymers of glycolide and 1,3-trimethylene carbonate (Scheme 1) were synthesized with various reaction variables such as polymerization temperature, polymerization time, and the feed composition ratio.

The block compositions of copolymers were determined by analysis of  $^1\text{H}$  NMR spectra. The  $^1\text{H}$  NMR spectrum of



Scheme 1. Chemical structure of glycolide/1,3-trimethylene carbonate copolymer.

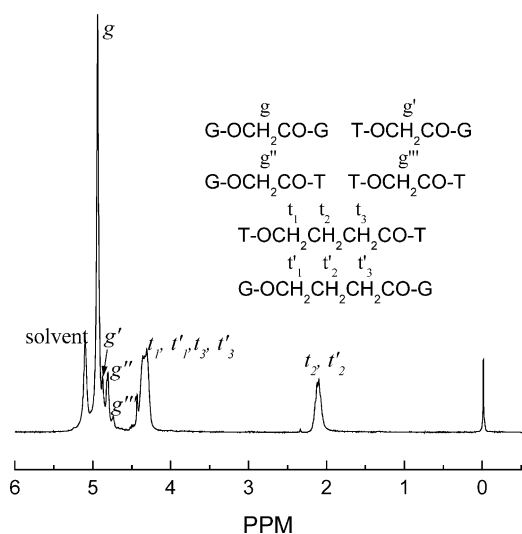


Fig. 1.  $^1\text{H}$  NMR spectrum of polymer 3.

polymer 3 in Fig. 1, as a representative example, shows characteristic resonance peaks of copolymers.

The chemical shift of protons of glycolide and 1,3-trimethylene carbonate units was sensitive to adjacent each monomer unit as assigned in Fig. 1. The composition ratios of block copolymers were determined by peak integration ratios of total methylene protons of glycolide assigned as  $g$ ,  $g'$ ,  $g''$ , and  $g'''$  and methylene protons of 1,3-trimethylene carbonate assigned as  $t_2$  and  $t_2'$ . The properties of copolymers which have the 7:3 molar feed ratio of glycolide ([GG]) to trimethylene carbonate ([T]), synthesized at various polymerization temperatures, are summarized in Table 1. The composition ratio of the copolymers was consistent with the feed ratios of the comonomers at the reaction temperature range of 100–150 °C, where yields were almost 100%, but above 170 °C of polymerization temperature, the [GG]/[T] composition ratio was rather lower than its feed ratio. As listed in Table 1, at the polymerization temperature of 100–150 °C, highly crystalline copolymers are obtained, and the inherent viscosity increases with increasing the polymerization temperature.

On the other hand, when the reaction temperature was

higher than 150 °C, the molecular weight and crystallinity of copolymers decreased, and the copolymer synthesized at 200 °C became amorphous. Table 2 shows that the inherent viscosity increases as the reaction time increases to 20 h, and the reaction over 20 h did not contribute to the increase of the molecular weight of copolymers.

In Table 3, the properties of copolymers with various block compositions are summarized. The yields of the copolymers were nearly 100%, and the composition ratios of all copolymers were in good accordance with the feed molar ratios of glycolide and 1,3-trimethylene carbonate.

As the composition of 1,3-trimethylene carbonate increases, the melting and glass transition temperatures decreased due to the low crystallinity and glass transition temperature of poly(1,3-trimethylene carbonate) [25].

The copolymers had low solubility in THF, chloroform, dichloromethane, and benzene, although poly(1,3-trimethylene carbonate) is soluble in those solvents. The solubility of the copolymers was dependent on the block composition. In case the content of poly(1,3-trimethylene carbonate) was much higher than polyglycolide such as polymer 14 ([GG]:[T]=3:7), the copolymer was soluble in DMSO. However, most of copolymers studied in this study had the higher content of glycolide. Only HFIP and hexafluoroacetone solubilized the copolymers of all compositions. Thus, HFIP or trifluoroacetone was useful for processing these copolymers and was used for viscometry and NMR experiments, respectively.

Wettability of the copolymer is closely related to the hydrophobicity or hydrophilicity of the materials. The contact angle of polymer 3 with the 7:3 composition ratio was compared with that of poly(1,3-trimethylene carbonate). Our preliminary study showed that the contact angle of the poly(1,3-trimethylene carbonate) homopolymer is around  $61 \pm 2^\circ$ , and the contact angle of polymer 3 became lower but showed little change (ca.  $55 \pm 2^\circ$ ). This result seems unreasonable since glycolide is more hydrophilic than trimethylene carbonate. Although the hydrophilicity of the copolymer may decrease by increasing the glycolide content, the crystallinity of the copolymers increased due to the high crystallinity of polyglycolide. Normally, high

Table 1  
Properties of glycolide/trimethylene carbonate linear copolymers with various polymerization temperature for 20 h

Polymer	Feed ratio <sup>a</sup> ([GG]:[T])	Temp <sup>b</sup> (°C)	$T_m$ (°C)	$T_g$ (°C)	Composition ratio <sup>c</sup>	Avg. block length <sup>d</sup>		I.V. <sup>e</sup> (dl/g)
						$L_G$	$L_T$	
1	7:3	100	192	20	7.3:2.7	15.6	2.1	0.63
2	7:3	130	193	17	7.1:2.9	8.1	2.5	0.74
3	7:3	150	214	23	7.1:2.9	7.6	2.0	0.92
4	7:3	170	110	13	6.1:3.9	2.0	2.8	0.53
5	7:3	200	–	6	6.2:3.8	1.5	2.3	0.41

<sup>a</sup> Feed ratio of glycolide (two G units)/trimethylene carbonate (one T unit).

<sup>b</sup> Polymerization temperature.

<sup>c</sup> Estimated by  $^1\text{H}$  NMR spectra.

<sup>d</sup> Calculated by  $^{13}\text{C}$  NMR spectra.

<sup>e</sup> Inherent viscosity in HFIP at 0.5 g/dl at 25 °C.

Table 2  
Properties of glycolide/trimethylene carbonate linear copolymers with various polymerization time at 150 °C

Polymer	Feed ratio <sup>a</sup> ([GG]:[T])	Time <sup>b</sup> (h)	$T_m$ (°C)	$T_g$ (°C)	Composition ratio <sup>c</sup>	Avg. block length <sup>d</sup>		I.V. <sup>e</sup> (dl/g)
						$L_G$	$L_T$	
6	7:3	5	191	12	6.8:3.2	5.9	1.8	0.65
7	7:3	10	202	16	6.9:3.1	6.4	1.6	0.71
8	7:3	15	205	17	7.0:3.0	6.8	1.9	0.85
3	7:3	20	214	23	7.1:2.9	7.6	2.0	0.92
9	7:3	30	203	21	7.2:2.8	7.8	1.6	0.90

<sup>a</sup> Feed ratio of glycolide (two G units)/trimethylene carbonate (one T unit).

<sup>b</sup> Polymerization time.

<sup>c</sup> Estimated by <sup>1</sup>H NMR spectra.

<sup>d</sup> Calculated by <sup>13</sup>C NMR spectra.

<sup>e</sup> Inherent viscosity in HFIP at 0.5 g/dl at 25 °C.

crystallinity of the polymer hinders water diffusing into the bulk body of the copolymers. Thus, almost no difference in terms of contact angle is well understood.

### 3.2. Microstructural analysis of the block copolymers

The microstructural characterization of copolymers was performed by the analysis of the block sequence and average block length using <sup>13</sup>C NMR spectroscopy. In this work, the analysis of the block sequence and average block length is based on the method of Kricheldorf et al. [16]. It is general characteristics for <sup>13</sup>C NMR spectra that C=O resonance signals are more sensitive to sequence effects than O–CH<sub>2</sub> signals [16–21]. Besides, resonance signals of other carbon such as O=C–CH<sub>2</sub> are rather insensitive to the sequence [17]. Scheme 2 shows the nature of possible sequence effects in the copolymer chains. The influence of sequence effects on the <sup>13</sup>C NMR signals of glycolyl and trimethylene carbonyl unit are demonstrated. Particularly, the triad effect for C=O signals in glycolyl units and the dyad effect for C=O signals in trimethylene carbonyl units are well demonstrated and used in calculation of the average block length of glycolyl ( $L_G$ ) and trimethylene carbonyl ( $L_T$ ) sequence.

In Fig. 2, the <sup>13</sup>C NMR spectrum of polymer 3 shows characteristic resonance peaks of copolymers.

Each average block length of glycolyl and trimethylene carbonyl was calculated according to a literature method [16].

$$L_G = \frac{I_{GGG} + I_{TGG}}{I_{GGT} + I_{TGT}} + 1 \quad (1)$$

$$L_T = \frac{I_{TT}}{I_{TG}} + 1 \quad (2)$$

In Eq. (1),  $I_{GGG}$ ,  $I_{GGT}$ ,  $I_{TGG}$ , and  $I_{TGT}$  are intensities ascribed to triad sequence effect of glycolyl unit, which are assigned as  $x$ ,  $x'$ ,  $x''$ , and  $x'''$  in <sup>13</sup>C NMR spectrum, respectively. The peaks assigned as  $x$ ,  $x'$ ,  $x''$ , and  $x'''$  are ascribed to the carbon signal in the carbonyl group of the one glycolyl unit. The peak environment for the resonance by the external magnetic field are all the same for the C=O signals in glycolyl units. Thus, the intensities estimated by the peak height are dependent on the content of the each sequence in the copolymer and can be used to calculate the average block length. In Eq. (2), the intensities of trimethylene carbonyl unit,  $I_{TT}$  and  $I_{TG}$  or  $I_{GT}$  caused by dyad sequence effect were assigned as  $y$  and  $y'$ , respectively.

Table 3  
Properties of glycolide/trimethylene carbonate linear copolymers with various comonomer compositions (reaction temp = 150 °C, reaction time = 20 h)

Polymer	Feed ratio <sup>a</sup> ([GG]:[T])	$T_m$ (°C)	$T_g$ (°C)	Composition ratio <sup>b</sup>	Avg. block length <sup>c</sup>		I.V. <sup>d</sup> (dl/g)
					$L_G$	$L_T$	
10	10:0	220	43	10:0	∞	0	<sup>e</sup>
11	8:2	212	31	8.3:1.7	13.1	1.7	1.01
3	7:3	214	23	7.1:2.9	7.6	2.0	0.92
12	6:4	208	19	6.1:3.9	4.5	2.0	0.90
13	5:5	200	11	5.3:4.7	3.5	1.9	0.84
14	3:7	200	–8	3.2:6.8	2.8	2.7	0.62
15	0:10	43	–14	0:10	0	∞	0.40

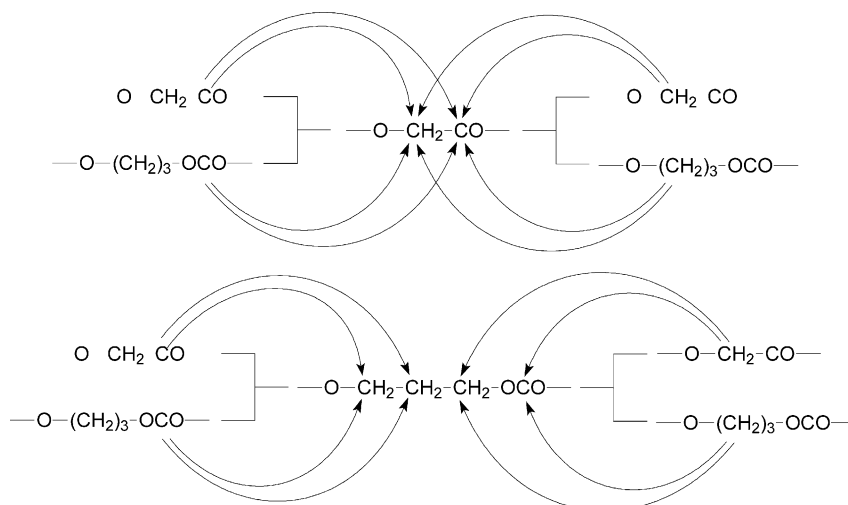
<sup>a</sup> Feed ratio of glycolide (two G units)/trimethylene carbonate (one T unit).

<sup>b</sup> Estimated by <sup>1</sup>H NMR spectra.

<sup>c</sup> Calculated by <sup>13</sup>C NMR spectra.

<sup>d</sup> Inherent viscosity in HFIP at 0.5 g/dl at 25 °C.

<sup>e</sup> Insoluble in HFIP.



Scheme 2. Influence of triad and dyad sequences on the  $^{13}\text{C}$  NMR signals of glycolyl and trimethylene carbonyl units.

### 3.2.1. Influence of the reaction temperature on microstructure

In Table 1, the average block length of glycolyl unit ( $L_G$ ) and trimethylene carbonyl unit ( $L_T$ ) of copolymers, synthesized at various temperature, are listed, where the feed ratio of glycolide to and 1,3-trimethylene carbonyl and reaction time are fixed. It is interesting to note that  $L_G$  is longer than  $L_T$  up to 150 °C of polymerization temperature, but above 170 °C of polymerization temperature, the difference between  $L_G$  and  $L_T$  is not remarkable. In copolymerization of glycolide and 1,3-trimethylene carbonate, the reactivity ratio of glycolide was reported much higher than that of 1,3-trimethylene carbonate [25]. Therefore, the longer  $L_G$  was caused by high reactivity of glycolide at reaction temperature of 100–150 °C. However,  $L_G$  underwent dramatic decrease at reaction temperature above 170 °C. This reflects that some other process such as transesterification is the main contributor to decide the microstructure and the sequence of the copolymer. At the reaction temperature higher than 170 °C, the product becomes dark brown, and copolymers with the high

molecular weight were not obtained. Thus, it can be assumed that the difference of the average block length for the copolymers obtained in the different temperature is caused by various rate of transesterification during the reaction.

The ring-opening polymerization of glycolide resulted in two G units (GG), but undergo, at a specific reaction condition of copolymerization, chain cleavage leading to the transesterification. In this study, transesterification process leads to formation of the triad TGT sequence with an odd number of the G unit. Fig. 3 shows the  $^{13}\text{C}$  NMR spectra of polymer 1 and polymer 3. For polymer 1 synthesized at 100 °C, triad sequence peak TGT assigned as  $x'''$  is not detected, which proves the absence of transesterification during the polymerization. On the other hand, the peak of TGT at 173.1 ppm can be assigned for the copolymer synthesized at 170 °C. The  $^{13}\text{C}$  NMR spectra of copolymers showed that the transesterification was also observed in the copolymer polymerized at 130, 150, and 200 °C (data not shown). This contributed to the increase of TGT sequence in the copolymer and consequently

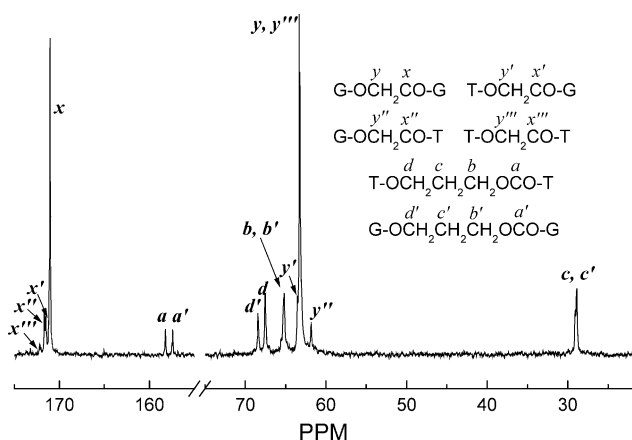


Fig. 2.  $^{13}\text{C}$  NMR spectrum of polymer 3.

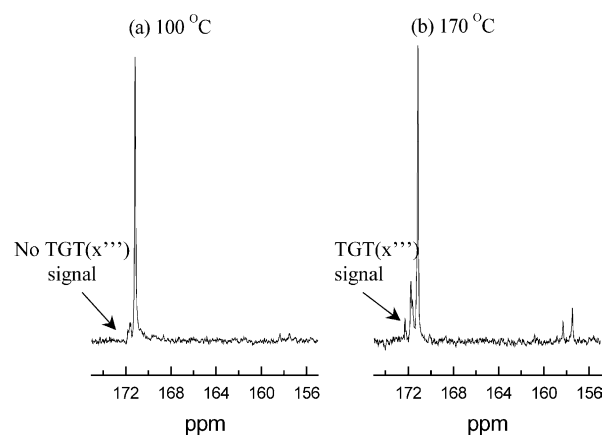


Fig. 3. Carbonyl signals in the  $^{13}\text{C}$  NMR spectra of (a) polymer 1 and (b) polymer 3.

decreased  $L_G$ . The  $L_G$  of polymer 1 is obviously longer than those of polymer 2–5 since the transesterification does not occur at 100 °C of polymerization temperature. Table 1 shows that high melting temperatures at around 200 °C ascribing to the crystalline polyglycolide domain are detected for polymer 1–3 consisting of relatively longer  $L_G$ . On the other hand, the polymer 4 with relatively short  $L_G$  (2.0) shows the melting endotherm at 110 °C. It is noteworthy that the polymer 5 with  $L_G$  of 1.5 and  $L_T$  (2.0) showed no crystalline melting.

### 3.2.2. Influence of the reaction time on microstructure

The dependency of the microstructure on the reaction time was examined at fixed reaction temperature and the comonomer feed ratio. As listed in Table 2, the copolymer with long  $L_G$  can be obtained in 5 h due to high reactivity of glycolide. As the reaction time increases,  $L_G$  shows a gradual increase and becomes constant at around 20 h. On the other hand, the change in  $L_T$  is negligible.

### 3.2.3. Influence of the comonomer composition on microstructure

To observe the effect of block composition on the block sequence and average block length, copolymers with various block compositions were synthesized at fixed reaction temperature (150 °C) and time (20 h). As summarized in Table 3, as the composition of 1,3-trimethylene carbonate increases,  $L_G$  decreases, but  $L_T$  do not change remarkably. Fig. 4 shows  $^{13}\text{C}$  NMR spectra of copolymers with various block compositions.

For polymers 11–13,  $I_{GGG}$  assigned as  $x$  is much higher than  $I_{TGG}$  ( $x'$ ),  $I_{GGT}$  ( $x''$ ),  $I_{TGT}$  ( $x'''$ ), whereas  $I_{GGG}$  and  $I_{TGT}$  are nearly equal for polymer 14. The polymerization was performed at a temperature, where transesterification could be occurred. Thus, it seems that transesterification is more pronounced in the copolymers with the higher content of trimethylene carbonate. As shown in Fig. 4(a), the polymer 14 with the 3:7 feed ratio of [GG]/[T] showed the high intensity of the TGT signal ( $x'''$ ) at 173.1 ppm resulted in the shorter  $L_G$ . Also, the TGT resonance clearly appeared for polymer 13 with the 5:5 feed ratio of [GG]/[T]. On the other hand, as the composition of [GG]/[T] increased to 6:4 or 8:2, the peak intensity of the TGT sequence ascribed to transesterification was negligible.

The results showed that the reactivity of the each monomer, the the comonomer composition, and the transesterification in the polymerization process are the key factors to determine the final microstructure of the copolymer chains, thereby making it possible to predict the average sequence length of each block.

### 3.3. Relationship between microstructure and thermal properties of the copolymers

The influence of microstructure on thermal properties of the copolymers was examined by DSC analysis. In Fig. 5,

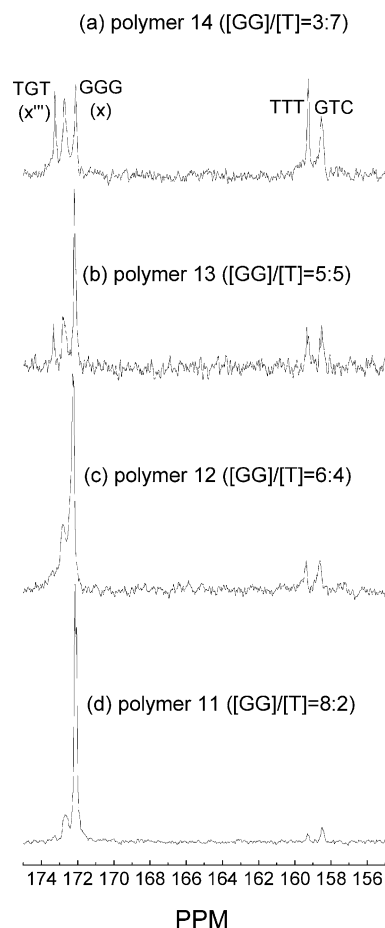


Fig. 4. Carbonyl signals in the  $^{13}\text{C}$  NMR spectra of copolymers with various comonomer compositions. (a) Polymer 14, (b) polymer 13, (c) polymer 12, and (d) polymer 11.

DSC thermograms of copolymers of various compositions are shown. The melting endotherms corresponding to the crystalline polyglycolide phase was observed for the copolymers of various compositions. On the other hand, the melting endotherm by poly(1,3-trimethylene carbonate)

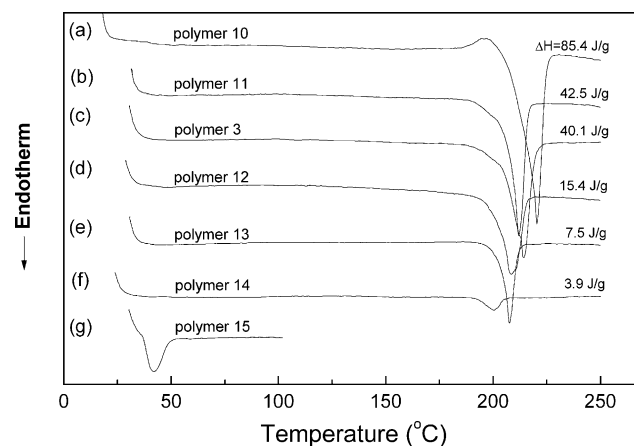


Fig. 5. DSC thermograms of polymers. (a) Polymer 10, (b) polymer 11, (c) polymer 3, (d) polymer 12, (e) polymer 13, (f) polymer 14, and (g) polymer 15.

was not observed for all compositions. However, glass transition behavior of the copolymers was dependent on the copolymer compositions, and  $T_g$  decreased with increasing the composition of trimethylene carbonate. The thermogram of polymer 1 ([GG]:[T]=10:0) showed the melting endotherm normally observed with the high molecular weight polyglycolide [26]. As the feed amount of 1,3-trimethylene carbonate increased, the heat of fusion ( $\Delta H$ ) decreased, since the degree of crystallization decreased with increasing the 1,3-trimethylene carbonate fraction in the copolymers. This is well reflected in the decrease of  $L_G$ . It is interesting to note that even the copolymer (polymer 14) with the relatively short  $L_G$  showed the crystalline melting only at around 200 °C, although  $L_G$  and  $L_T$  of polymer 14 was almost the same. This indicates that  $L_G$  of 2.8 is enough to construct the crystalline polyglycolide domain, whereas polymer 4 and polymer 5 with  $L_G$  of 2.0 and 1.5, respectively, are not enough to form the crystalline polyglycolide structure. This also strongly supports that the glycolide microsequence affects significantly the crystalline phase of the copolymers, thereby determining the melting properties of the copolymers. This observation was consistent with the results reported for the copolymers of glycolide and  $\epsilon$ -caprolactone [17]. The unique point of this study is to analyze the microstructure of the copolymer of two different polymeric species, the polyester and the polycarbonate. The copolymer cited in Ref. [17] was based on only polyester structures, polyglycolide and poly( $\epsilon$ -caprolactone). The copolymer of glycolide and 1,3-trimethylene carbonate showed similarity in terms of the microstructural effect on the melting properties as in the case of the copolymer of polyglycolide and poly( $\epsilon$ -caprolactone). However, for the copolymer of the polyester and the polycarbonate, this work is the first report on relationship between the microstructure and thermal properties. The data in this work suggest that the molecular weight of the copolymer as well as the average block length of the glycolide unit in the copolymer is the main factor to determine the crystalline melting behavior, such as melting temperature and  $\Delta H$  of the copolymers.

#### 3.4. Relationship between microstructure and polymer degradation

The copolymer of glycolide and trimethylene carbonate was allowed to degrade in a phosphate buffered saline at 37 °C (pH 7.4). Degradation behavior was monitored by the change of the inherent viscosity of the copolymers. Our preliminary study showed that the copolymer composition as well as the microstructure significantly affected the degradation properties of the copolymer. The effect of the composition on degradation rate was examined for polymer 3 and polymer 14 with 7:3 and 3:7 [GG]/[T] ratios. The time for the decrease of inherent viscosity to 50% of the initial value was about 4 weeks for polymer 3 and 8 weeks for polymer 14, respectively. It was previously reported that the

degradation rate of polyglycolide is higher than that of poly(1,3-trimethylene carbonate) [27]. Thus, this supports that the degradation rate of the copolymer become faster with increasing the glycolide content. To examine the effect of chain microstructure on degradation behavior, the viscosity change of polymer 1 and 3 with different  $L_G$  but with the the same composition was estimated. Interesting, the polymer 1 with a more blocky chain microstructure degraded much slowly than polymer 3. Inherent viscosity of polymer 1 decreased to reach the 50% level of the initial value after about 6 weeks. This indicated that the higher the irregularity in sequence results in the faster degradation rate of the copolymer. Further study is required to elucidate the detailed relationship between the degradation properties of the copolymers and the average block length and the microstructure. The full characterization regarding microstructural effect on degradation of the copolymers will be performed using  $^1\text{H}$  NMR, DSC, and ESI-MS, and published elsewhere as a second part of this work.

#### 4. Conclusions

The linear copolymers of glycolide and 1,3-trimethylene carbonate were synthesized, and their microstructures were analyzed using  $^{13}\text{C}$  NMR spectroscopy. The data in this study showed that many factors such as the transesterification process, and the comonomer reactivity and composition were the key factors in determining the final microstructure of synthesized glycolide/1,3-trimethylene carbonate copolymer. Thermal analysis showed a close relationship between crystallinity of the copolymer and the average sequence block length. The microstructural analysis using NMR spectroscopy can be usefully applied to predict thermal and mechanical properties, biodegradability, and processability of a diverse class of aliphatic copolymers.

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