Anionic Ring-Opening Copolymerization of L-Lactide with a Five-Membered Cyclic Carbonate Having a Glucopyranoside Structure

By Osamu HABA,* Nanako FURUICHI, and Yosuke AKASHIKA

The anionic ring-opening copolymerization of L-lactide (LL) with a five-membered cyclic carbonate having the glucopyranoside structure, methyl 4,6-*O*-benzilidene-2,3-*O*-carbonyl-*α*-D-glucopyranoside (MBCG), was carried out using potassium *tert*-butoxide (*t*-BuOK) as the initiator and tetrahydrofuran (THF) as the solvent at 30 °C for 12 h. The mole fractions of LL in the copolymer (f_{LL}) of all copolymers were nearly equal to the corresponding mole fraction of LL in the feed (F_{LL}). Deprotection of the copolymer was performed using trifluoroacetic acid in dichloromethane. ^{1}H NMR spectra of the resulting product indicated that deprotection was completely achieved due to the absence of the aromatic proton signals.
KEY WORDS: Copolymerization / Ring-Opening Polymerization / Biodegradable / Sugar / Glucose /

Poly(L-lactic acid) (PLLA), which is generally prepared by the ring-opening polymerization of L-lactide (LL), has been used in a wide range of applications, such as biomedical materials, beased on its biodegradable, biocompatible, low-toxic, and renewable properties. In order to improve its physical properties or bio-functionalities, the copolymers of L-lactide with other monomeric units, such as ethers,[1–5] esters,[6–9] amides,[4,10] carbonates,[11–15] etc., have been prepared.

We have reported the ring-opening polymerization of a five-membered cyclic carbonate, methyl 4,6-*O*-benzylidene-2,3-*O*-carbonyl-*α*,D-glucopyranoside (MBCG), which was prepared from methyl *α*-D-glucopyranoside.[16] It is well known that such five-membered cyclic carbonates are not suitable as the monomers in the ring-opening polymerization because a considerable amount of carbon dioxide eliminates during the polymerization that produces the polyether product.[17–20] However, we have found that the anionic ring-opening polymerization of MBCG smoothly proceeds without the elimination of carbon dioxide to give the polycarbonate containing no polyether repeating units. Thus, MBCG is a rare five-membered cyclic carbonate having the ring-opening polymerization capability, and therefore, it is interesting to investigate its copolymerization behavior with other cyclic monomers.

In this study, we carried out the anionic ring-opening copolymerization of LL with MBCG. The resulting product was converted to hydroxyl-bearing copolymers by removing the benzylidene protecting groups (Scheme 1). That should be expected to add some functionalities to PLLA, such as hydrophilicity and reactivity.

EXPERIMENTAL

Measurements

The infrared (IR) spectra were recorded using a HORIBA FT-210 spectrometer. The ^{1}H and ^{13}C NMR spectra were
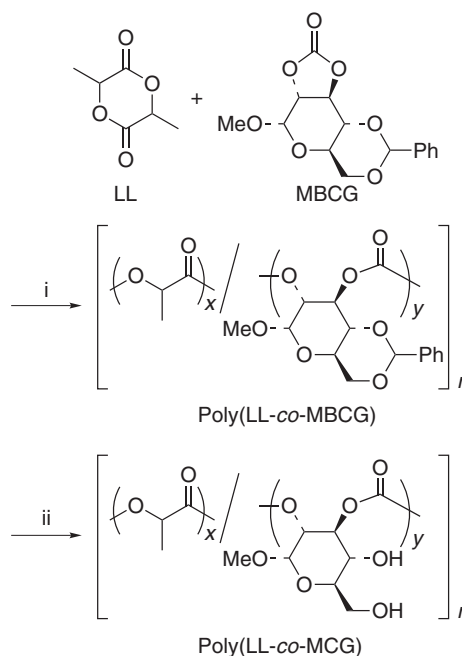
Scheme 1. Copolymerization of LL with MBCG and acid-catalyzed deprotection. Conditions: i) *t*-BuOK, THF, 30 °C, ii) CF$_3$COOH, H$_2$O, CH$_2$Cl$_2$, 25 °C.

measured in CDCl$_3$ by a JEOL JNM-ECX 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer at room temperature. The chemical shift values were in ppm downfield from tetramethylsilane (0.0 ppm) and CDCl$_3$ (77.0 ppm) used as the internal standards for the ^{1}H and ^{13}C measurements, respectively. The number-average (M_n) and weight-average (M_w) molecular weights were estimated by size-exclusion chromatography (SEC) using a Tosoh DP-8020 pump, a Viscotek TDA MODEL-300 refractive index (RI) detector and polystyrene gel columns (Tosoh TSK gels G2500H, G3000H, G4000H and GMH) in DMF containing 1 wt % LiBr

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using a calibration curve of polystyrene standards. The thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC) results were recorded by a Seiko SSC/5200 (DSC 220) instrument at the heating/cooling rate of 10 °C/min under a nitrogen atmosphere.

Materials

Tetrahydrofuran (THF, Kanto Chemicals) was refluxed over sodium-benzophenone ketyl and distilled just before use. Potassium *tert*-butoxide (*t*-BuOK) was purchased as a 1.0 M solution in THF (Aldrich) and used as received. Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (1)[21] and methyl 2,3-*O*-carbonyl-4,6-*O*-benzylidene-α-D-glucopyranoside (MBCG)[22] were prepared according to the literature. A commercial L-lactide (LL) (Kanto Chemicals) was recrystalized from ethyl acetate and sublimed *in vacuo* just before use. Trifluoroacetic acid (Kanto Chemicals), methyl chloroformate (Wako Chemicals), acetyl chloride (Kanto Chemicals), and all other chemicals were commercially available and used as received.

Copolymerization of L-Lactide with MBCG

A typical procedure was as follows: In a test tube equipped with a 3-way stopcock and filled with nitrogen, LL (0.19 g, 1.3 mmol) and MBCG (0.41 g, 1.3 mmol) were dissolved in THF (0.8 mL, 3.0 mol·L^{-1}). The solution was heated to 30 °C, then an initiator, *t*-BuOK (1.0 M solution in THF, 0.10 mL, 0.10 mmol) was added *via* a syringe. The solution was stirred at this temperature for 12 h. Acetic acid (12 μL) was added to quench the reaction, and the solution was poured into ice-cold methanol (50 mL). The white precipitate was collected by filtration, reprecipitated from CHCl$_3$-methanol and dried *in vacuo* at room temperature. Yield 0.49 g (83%). $M_n =$ 5,100 (SEC). The LL content in the obtained copolymer was estimated using the ^{1}H NMR spectrum by comparing the peak area ratios of the methyl proton around 1.2 ppm and the aromatic proton around 7 ppm.

Deprotection from the Copolymer

A typical procedure was as follows: In a 10 mL flask, the copolymer (0.21 g, $f_{LL} = 0.48$) was dissolved in dichloromethane (2.0 mL). To this solution was added a 90% aqueous trifluoroacetic acid solution (0.11 mL). After the solution was stirred for 1 h at room temperature, the resulting polymeric product was poured into diethyl ether (50 mL). The precipitated polymer was separated by filtration and dried *in vacuo* at room temperature to a constant weight. Yield 0.17 g (99%). $M_n =$ 8,700 (SEC).

Model Compounds

Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside (2a) and Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside (2b). To a solution of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (5.6 g, 20 mmol) and triethylamine (2.2 g, 22 mmol) in THF (20 mL), acetyl chloride (2.3 g, 23 nnol) was dropwise added at 0 °C. The mixture was then stirred overnight at room temperature. The resulting yellow solution was poured into ice-

water and the precipitate was collected by filtration. The crude material was purified by column chromatography on silica gel (24 g) with ethyl acetate/*n*-hexane (1/2, v/v). Compounds **2a** and **2b** were obtained as fractions at $R_f = 0.23$ and 0.04, respectively.

2a: Yield, 2.3 g (7.1 mmol, 35%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) = 7.50–7.49 (m, 2H, Ar), 7.39–7.38 (m, 3H, Ar), 5.56 (s, 1H, PhCH), 4.96 (d, $^3J_{1-2} = 4.1$, 1H, H-1), 4.79 (dd, $^3J_{2-1} = 3.7$, $^3J_{2-3} = 9.9$, 1H, H-2), 4.30 (dd, $^3J_{6eq-5} = 4.6$, $^2J_{6eq-6ax} = 10.1$, 1H, H-6eq), 4.19 (t, $^3J_{3-2} = ^3J_{3-4} = 9.6$, 1H, H-3), 3.86 (dt, $^3J_{5-4} = ^3J_{5-6ax} = 4.6$, $^3J_{5-6eq} = 9.4$, 1H-H-5), 3.77 (t, $^3J_{6ax-5} = ^2J_{6ax-6eq} = 10.1$, 1H, H-6ax), 3.57 (t, $^3J_{4-3} = ^3J_{4-5} = 9.16$, 1H, H-4), 3.41 (s, 3H, OCH$_3$), 2.47 (s, 1H, C(3)-OH), 2.17 (s, 3H, -CH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) = 170.8 (CH$_3$C=O), 136.9, 129.3, 128.3, 126.2 (Ar), 102.0 (PhCH), 97.4 (C-1), 81.3 (C-4), 73.5 (C-2), 68.8 (C-6), 68.5 (C-3), 61.9 (C-5), 55.3 (OCH$_3$), 20.9 (-CH$_3$).

2b: Yield 0.64 g (2.0 mmol, 10%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) = 7.45–7.44 (m, 2H, Ar), 7.36–7.35 (m, 3H, Ar), 5.49 (s, 1H, PhCH), 5.32 (dd, $^3J_{2-1} = 3.7$, $^3J_{2-3} = 9.9$, 1H, H-2), 4.80 (d, $^3J_{1-2} = 4.1$, 1H, H-1), 4.30 (dd, $^3J_{6eq-5} = 4.6$, $^2J_{6eq-6ax} = 10.1$, 1H, H-6eq), 3.86 (dt, $^3J_{5-4} = ^3J_{5-6ax} = 5.0$, $^3J_{5-6eq} = 9.6$, 1H-H-5), 3.74 (t, $^3J_{6ax-5} = ^2J_{6ax-6eq} = 10.1$, 1H, H-6ax), 3.66 (t, $^3J_{3-2} = ^3J_{3-4} = 3.6$, 1H, H-3), 3.55 (t, $^3J_{4-3} = ^3J_{4-5} = 10.1$, 1H, H-4), 3.46 (s, 3H, OCH$_3$), 2.25 (s, 1H, C(2)-OH), 2.12 (s, 3H, -CH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) = 171.1 (CH$_3$C=O), 137.0, 129.1, 128.2, 126.1 (Ar), 101.5 (PhCH), 100.0 (C-1), 78.6 (C-4), 72.2 (C-2), 71.8 (C-3), 68.9 (C-6), 62.7 (C-5), 55.5 (OCH$_3$), 21.0 (-CH$_3$).

Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-methoxycarbonyl-α-D-glucopyranoside (3a). To a solution of **2a** (1.5 g, 4.6 mmol) and pyridine (0.36 mL, 5.4 mmol) in THF (4.5 mL), methyl chloroformate (0.41 mL, 5.4 mmol) was dropwise added at 0 °C. The mixture was then stirred overnight at room temperature. The resulting yellow solution was poured into crushed ice (50 g) containing concentrated hydrochloric acid (1 mL), extracted with CHCl$_3$ and washed with water. The organic layer was dried over MgSO$_4$, and concentrated under reduced pressure. The resulting brown oil was purified by column chromatography on silica gel with ethyl acetate/*n*-hexane (1/2, v/v) to give **3a** as a colorless viscous oil (0.46 g, 1.2 mmol, 26%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (pm) = 7.45–7.44 (m, 2H, Ar), 7.36–7.34 (m, 3H, Ar), 5.50 (s, 1H, PhCH), 5.38 (t, $^3J_{3-2} = ^3J_{3-4} = 10.0$, 1H, H-3), 4.98 (d, $^3J_{1-2} = 3.6$, 1H, H-1), 4.90 (dd, $^3J_{2-1} = ^3J_{2-3} = 4.1$, 1H, H-2), 4.29 (dt, $^3J_{5-4} = ^3J_{5-6ax} = 5.0$, $^3J_{5-6eq} = 10.2$, 1H-H-5), 3.91 (dd, $^3J_{6eq-5} = 4.5$, $^2J_{6eq-6ax} = 9.7$, 1H, H-6eq), 3.74 (t, $^3J_{6ax-5} = ^2J_{6ax-6eq} = 10.4$, 1H, H-6ax), 3.74 (s, 3H, COOCH$_3$), 3.69 (t, $^3J_{4-3} = ^3J_{4-5} = 9.5$, 1H, H-4), 3.41 (s, 3H, OCH$_3$), 2.10 (s, 3H, -CH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) = 170.4 (CH$_3$C=O), 155.0 (EtOC=O), 140.0, 129.2, 128.3, 126.3 (Ar), 101.7 (PhCH), 97.6 (C-1), 79.2 (C-4), 73.3 (C-3), 71.7 (C-2), 68.9 (C-5), 62.3 (C-6), 55.5 (OCH$_3$), 55.2 (OCOOCH$_3$), 20.9 (-CH$_3$).

Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-methoxycarbonyl-α-D-glucopyranoside (3b). This compound was prepared from

2b (0.27 g, 0.83 mmol) by a procedure similar to that for **3a**. Yield 0.067 g (0.17 mmol, 21%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.43–7.42 (m, 2H, Ar), 7.34–7.33 (m, 3H, Ar), 5.60 (t, $^3J_{2-1} = {}^3J_{2-3} = 10.1$, 1H, H-2), 5.49 (s, 1H, PhCH), 5.01 (d, $^3J_{1-2} = 3.7$, 1H, H-1), 4.76 (t, $^3J_{3-2} = {}^3J_{3-4} = 3.7$, 1H, H-3), 4.30 (dd, $^3J_{6eq-5} = 4.6$, $^2J_{6eq-6ax} = 10.1$, 1H, H-6eq), 3.93 (dt, $^3J_{5-4} = {}^3J_{5-6ax} = 5.0$, $^3J_{5-6eq} = 9.9$, 1H-H-5), 3.79 (s, 3H, COOCH$_3$), 3.76 (t, $^3J_{6ax-5} = {}^2J_{6ax-6eq} = 10.5$, 1H, H-6ax), 3.63 (t, $^3J_{4-3} = {}^3J_{4-5} = 9.6$, 1H, H-4), 3.41 (s, 3H, OCH$_3$), 2.05 (s, 3H, -CH$_3$). ^{13}C-NMR (CDCl$_3$, 100 MHz) δ (ppm) = 169.7 (CH$_3$C=O), 155.2 (EtOC=O), 137.0, 129.2, 128.3, 126.2 (Ar), 101.6 (PhCH), 97.5 (C-1), 79.3 (C-4), 74.9 (C-2), 68.9 (C-3, C-6), 63.4 (C-5), 55.5 (OCH$_3$), 55.3 (OCOOCH$_3$), 20.9 (-CH$_3$).

RESULTS AND DISCUSSION

Anionic Copolymerization of LL and MBCG

We have reported that the cyclic carbonate MBCG could be polymerized without any decarbonylation by anionic initiators, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and potassium *tert*-butoxide (*t*-BuOK).[16] The alkoxide initiators also have been reported to be effective for the anionic polymerization of LL.[23–26] We then used *t*-BuOK as an initiator for the copolymerization of LL with MBCG because it should be effective for both monomers. All the copolymerizations were carried out in THF at 30 °C for 12 h, which was determined by the each reported homopolymerization condition at 60 °C for 12 h for MBCG and at 0 °C for 6 h for LL. These results are listed in Table I. The homopolymerization of MBCG in THF had been heterogeneous,[16] but all the copolymerization proceeded homogeneously probably due to the enhanced solubility caused by introduction of the comonomeric LL units. The resulting methanol-insoluble products were obtained as white powders in good yields and were soluble in CHCl$_3$, THF and DMF. The mole fractions of LL in the products (f_{LL}), which were estimated from the ^{1}H NMR spectra, tend to be slightly greater than those in the feeds (F_{LL}). SEC traces of all the products were unimodal. When the F_{LL} was 0.1, the

number-average molecular weight (M_n) of the polymer was 5300. The molecular weight was constant around 5000 until F_{LL} was 0.50, then increased with the increasing F_{LL}, and reached 10900 when the ratio was 0.9.

Structure of the Copolymer

The ring-opening copolymerization, especially initiated by ionic initiators, frequently tends to produce a block copolymer or a mixture of homopolymers depending on the reactivity of the used monomers.[27,28] In order to confirm the presence of copolymeric MBCG–LL linkage in the polymerization product, we prepared two model compounds, **3a** and **3b**, and compared them to the copolymerization product based on their ^{13}C NMR spectra. The model compounds are methyl 4,6-*O*-benzylidene-α-D-glucopyranoside having an ester group at the 2-*O*- or 3-*O*-position and a carbonate group at another position. We assumed that the ester and the carbonate groups in **3** should represent the MBCG–LL and MBCG–MBCG linkages, respectively. Scheme 2 shows the synthetic route for **3**. The preparation of **3** was started by methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**1**), which was converted into mono-*O*-acetylated compounds **2** with acetyl chloride in the presence of pyridine. The 2-*O*-acetyl and 3-*O*-acetyl products (**2a** and **2b**, respectively) could be easily separated by column chromatography on silica gel. The acetylated position was determined by the ^{1}H-^{1}H and ^{13}C-^{1}H COSY spectra. The pure **2a** and **2b** were independently reacted with methyl chloroformate in the presence of pyridine to produce **3a** and **3b**, respectively.

Figure 1 shows the ^{13}C NMR spectra of the copolymerization product (run 6) as well as the homopolymers, PLLA and poly(MBCG). Although all the peaks due to both homopolymers could be observed, some peaks, which were not found in

Table I. Anionic ring-opening copolymerization of LL with MBCG[a]

run	F_{LL}[b]	Yield[c] %	f_{LL}[d]	M_n[e] × 10^{-3} g mol^{-1}	M_w/M_n[e]
1	0.0	83	0	4.4	2.9
2	0.10	92	0.16	5.3	2.6
3	0.20	87	0.25	4.9	2.3
4	0.30	82	0.35	4.8	2.8
5	0.40	74	0.38	4.6	2.8
6	0.50	83	0.48	5.1	2.4
7	0.60	78	0.60	6.0	2.8
8	0.70	81	0.68	9.8	2.0
9	0.80	83	0.79	10.8	2.1
10	0.90	90	0.89	10.9	2.6
11	1.0	70	1.0	10.7	1.9

a) Initiator, *t*-BuOK; temp., 30 °C; time, 12 h; [LL + MBCG]$_0$ = 3.0 mol L^{-1}; [*t*-BuOK]$_0$ = 0.12 mol L^{-1}. b) Mole fraction of LL in feed. c) Methanol-insoluble part. d) Mole fraction of LL in copolymer. e) Estimated by SEC eluted with DMF using polystyrene standard.
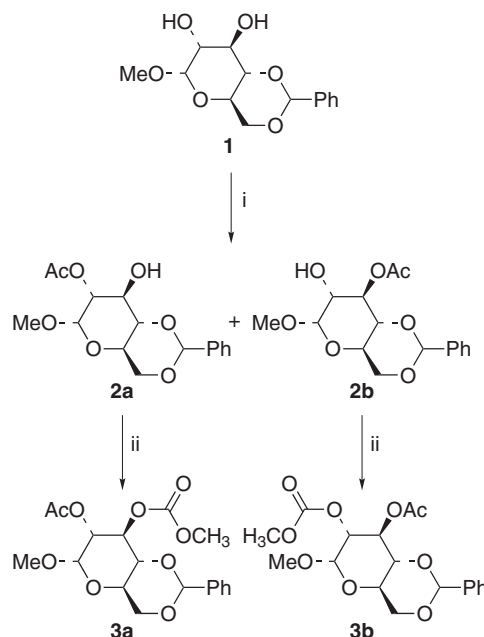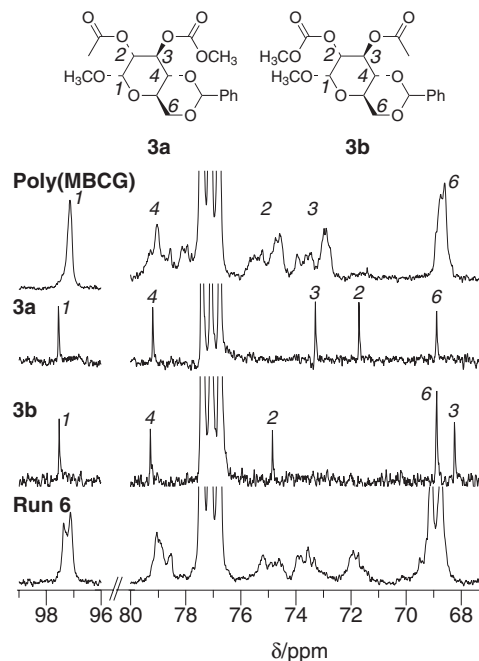

Scheme 2. Synthesis of model compounds **3a** and **3b**. Conditions: i) AcCl, Et$_3$N, THF, rt, ii) MeOCOCl, pyridine, THF, rt.
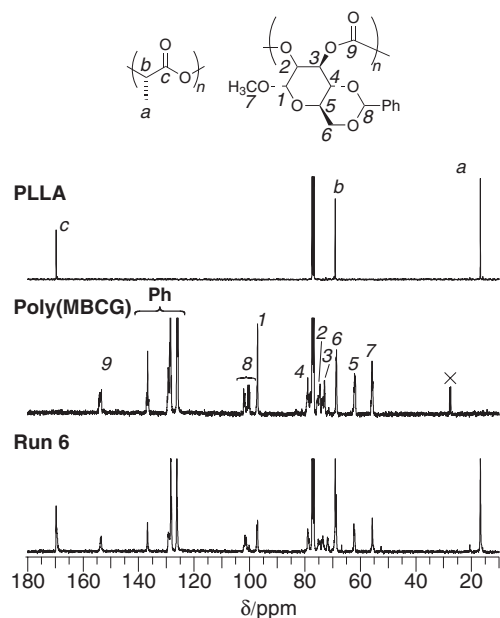
Figure 1. 100 MHz ^{13}C NMR spectra of PLLA, poly(MBCG) and poly(LL-co-MBCG) (Run 6) measured in CDCl$_3$ at 25 °C.

Figure 2. Expanded 100 MHz ^{13}C NMR spectra of poly(MBCG), model compounds **3a** and **3b**, and poly(LL-co-MBCG) measured in CDCl$_3$ at 25 °C.

homopolymers, appeared, for example, at 72 ppm. We assumed that these peaks are due to the MBCG-LL linkage. Figure 2 shows the expanded ^{13}C NMR spectrum of the copolymerization product and the model compounds, **3a** and **3b**. The ^{13}C NMR spectra of the model compounds indicate that the ester groups tend to shift the peaks of the attached carbon atoms to higher magnetic fields than the carbonate groups. The peak at 72 ppm in the copolymer, which was not observed in the homopolymer, agreed with the peaks due to C-2 of **3a**. Unfortunately, the C-3 peak of **3b** appeared at 68 ppm was not observed in the spectrum of the polymer. This peak might overlap with the C-6 of MBCG and the methyne carbon of LL, and the presence of an ester linkage at the 3-position could not be confirmed. In addition, the C-1 peak of the copolymerization product split into 97.5 ppm and 97.1 ppm, which correspond to that of **3** and poly(MBCG) that appeared at 97.5 and 97.1 ppm, respectively. Thus the copolymerization products contain LL-MBCG linkages, and therefore the copolymerization should proceed randomly.

Finally, the copolymerization was carried out for the shorter time, in order to estimate the monomer reactivity ratio. The results are listed in Table II. The copolymerization was too fast. When F_{LL} was 0.51, the copolymer yield reached to 90% for 10 s. Shorter polymerization time such as 1–3 s gave lower yield (below 20%) of the polymer. The copolymerization close to each homopolymerization (such as $F_{LL} = 0.12$ or 0.89) was too fast to suppress the copolymer yield. Using the copolymer composition at the lower polymerization yield (below 20%), the copolymer composition curve was made as shown in Figure 3. The monomer reactivity ratio was estimated to be $r_{LL} = 1.15$ and $r_{MBCG} = 1.47$ by Fineman-Ross method. These reactivity ratios clearly support the random copolymerization between LL and MBCG.

Table II. Anionic ring-opening copolymerization of LL with MBCG in short time

F_{LL} [b]	Time s	Yield[c] %	f_{LL} [d]	M_n [e] × 10^{-3} g mol^{-1}	M_w/M_n [e]
0.12	2.0	63	—[f]	—[f]	—[f]
0.20	2.0	40	0.16	6.5	1.6
0.31	1.0	13	0.26	6.6	1.6
0.41	2.0	11	0.35	8.3	1.7
0.51	10.0	90	—[f]	—[f]	—[f]
0.60	3.0	20	0.61	10.7	1.6
0.70	2.0	5	0.69	9.7	1.5
0.78	0.5	trace	—[f]	—[f]	—[f]
0.89	2.0	61	0.87	12.1	2.4

a) Initiator, t-BuOK; temp., 30 °C; [LL + MBCG]$_0$ = 3.0 mol L^{-1}; [t-BuOK]$_0$ = 0.12 mol L^{-1}. b) Mole fraction of LL in feed. c) Methanol-insoluble part. d) Mole fraction of LL in copolymer. e) Estimated by SEC eluted with DMF using polystyrene standard. f) Not determined.

Deprotection from the Copolymer

The acetals from benzaldehyde are known as a protective group for diols, and can easily be removed under acidic or hydrogenation conditions.[29] Hydroxyl groups produced by removing the benzylidene acetal of the MBCG units might give the copolymers some functionality, such as hydrophilicity, reactivity, and biofunctionality as a sugar. Thus we then examined the deprotection from the copolymers. The reaction was carried out using 90% aqueous trifluoroacetic acid in dichloromethane at 20 °C for 1 h. The reaction mixture was poured into diethyl ether and the precipitation was collected. Table III lists the results of the deprotection. The diethyl ether insoluble products were quantitatively obtained from all the
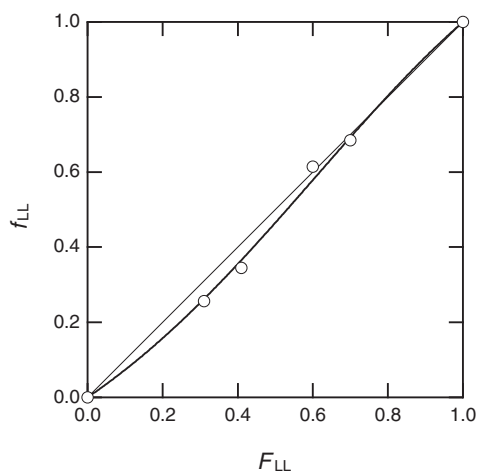
Figure 3. Plots of the mole fraction of LL in copolymer (f_{LL}) versus mole fraction of LL in feed (F_{LL}) for the copolymerization of LL with MBCG at 30 °C with t-BuOK in THF. The solid line indicates the values calculated with r_{LL} = 1.33 and r_{MBCG} = 1.62.
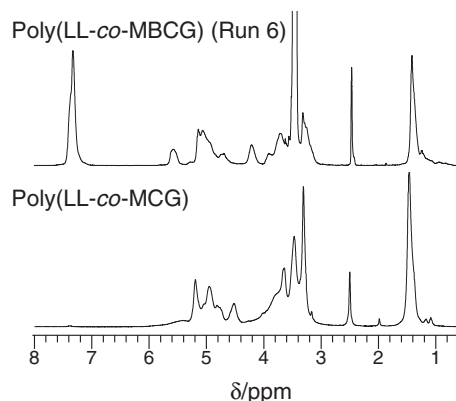
Table III. Deprotection of the copolymers

f_{LL} [a]	Yield [b] %	M_n [c] × 10^{-3} g mol^{-1}	M_w / M_n [c]
0.16	>99	6.1	2.8
0.25	>99	8.0	1.7
0.35	>99	9.1	1.8
0.38	93	6.3	2.1
0.48	>99	8.7	1.6
0.60	>99	12.2	1.7
0.68	>99	15.8	1.4
0.79	63	14.6	1.8
0.89	79	12.1	1.6

a) Mole fraction of L-Lactide in copolymer. b) Diethyl ether-insoluble part.
c) Estimated by SEC eluted with DMF using polystyrene as standard.

copolymers without any significant decrease in the molecular weight. The complete deprotection was confirmed by the ^{1}H NMR (Figure 4) and the IR (Figure 5) spectra. A broad peak due to the phenyl groups around 7 ppm observed in the ^{1}H NMR spectrum before the deprotection completely disappeared after the deprotection. In the IR spectrum, a peak due to the carbonyl groups at 1750 cm^{-1} remained, and the peak due to the hydroxyl groups appeared at 3400 cm^{-1}. These results clearly indicated that the deprotection completely proceeded to produce the copolymer having hydroxyl groups, while the polyester-carbonate main chain was not affected under the acidic conditions.

Thermal Properties

The thermal properties of the polymers were evaluated by TGA and DSC. The temperatures for a 5% weight loss (T_{d5}) and the glass transition temperature (T_g) of the copolymers before and after the deprotection are listed in Table IV. The T_{d5}, which was 315 °C for poly(MBCG), decreased with an increase in the LL content and reached 222 °C at f_{LL} of 0.89,

Figure 4. 400 MHz ^{1}H NMR spectra of poly(LL-co-MBCG) and poly(LL-co-MCG) measured in CDCl$_3$ at 25 °C.
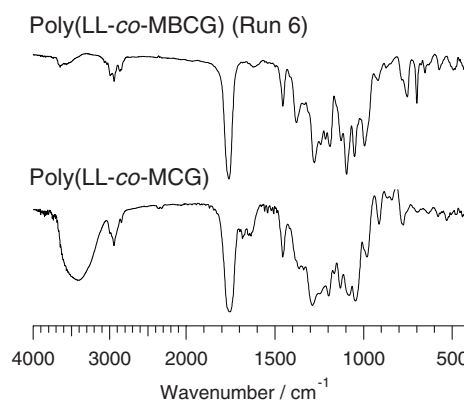

Figure 5. IR spectra of poly(LL-co-MBCG) and poly(LL-co-MCG) measured in KBr.

Table IV. Thermal properties of the copolymers

f_{LL}	before deprotection		after deprotection	
	T_{d5} [a]	T_g [b]	T_{d5} [a]	T_g [b]
0.0	315	215	250	170
0.16	270	161	245	185
0.35	264	152	243	140
0.48	246	117	230	107
0.68	237	94	234	64
0.89	222	60	245	n.d. [c]

a) 5% Weight loss temperature measured by TGA. ΔT = 10 °C/min.
b) Glass transition temperature recorded by DSC on the second heating scan. ΔT = 10 °C/min. c) Not determined.

whereas the T_{d5}'s after the deprotection were almost constant around 240 °C. In the DSC traces, all the copolymers showed only one T_g between those of poly(MBCG) (215 °C) and PLLA (50–60 °C). Figure 6 shows the DSC traces of 1:1 (w/w) mixture of the corresponding homopolymers and the copolymer obtained in run 6. The mixture shows two T_g's corresponding to the T_g's of the homopolymers, while the copolymer shows one T_g at 117 °C. This might support the results that the copolymerization successfully produced the random co-
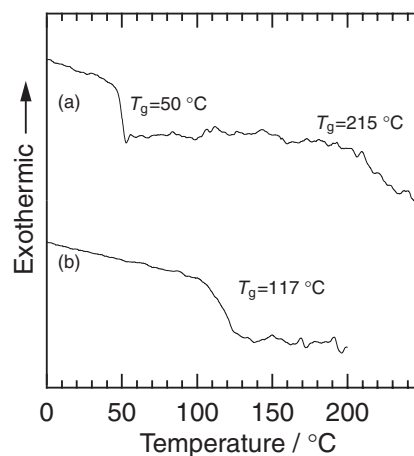
Figure 6. DSC traces of (a) 1:1 (w/w) mixture of PLLA and poly(MBCG), and (b) the copolymer having f_{LL} of 0.48 (run 6).

Table V. Solubilities of the copolymers before and after the deprotection to some solvents

Polymer	Solvent					
	H_2O	DMF	MeOH	THF	$CHCl_3$	MePh
before deprotection						
$f_{LL} = 0.0$	−	++	−	++	++	+
0.35	−	++	−	++	++	+
0.68	−	++	−	++	++	+
1.0	−	++	−	++	++	+
after deprotection						
$f_{LL} = 0.0$	−	++	+	+	+	+
0.35	−	++	+	+	+	+
0.68	−	++	+	++	+	+

a) Concentration, 10 mg/mL; temp., r.t. Signatures; ++: soluble, +: partially soluble or swelling, −: insoluble.

polymers as mentioned above. It is well known that PLLA is a crystalline polymer and melts at 160–170 °C, but we could not find the melting point of the copolymers in the DSC traces below 180 °C even for the copolymer with the f_{LL} of 0.89 even after a thermal treatment at 90 °C for 2 h. It is known that PLLA takes a left-handed 10_7 helical conformation in its crystalline state.[30] The bulky and rigid comonomeric MBCG units might prevent the helix formation of the PLA units.

Solubility of the Copolymers

The solubilities of the copolymers in some solvents were examined to determine any difference in the copolymers before and after the deprotection. Table IV shows the results. Before the deprotection, the copolymers were soluble in $CHCl_3$, THF, and DMF, and insoluble in water and methanol. This tendency was not affected by the difference in the f_{LL}. After the deprotection, the copolymers became swollen in the nonpolar solvents such as THF and $CHCl_3$. The hydroxyl-bearing copolymers were still insoluble in water, but swelled in methanol. Thus, the copolymer became slightly hydrophilic due to the deprotection.

SUMMARY

We carried out the anionic copolymerizations of LL with MBCG with t-BuOK as an initiator in THF at 30 °C. By comparing the structures of the copolymerization products with the model compounds **3**, the copolymerizations successfully proceeded and the products possessed some MBCG-LL linkages. The copolymers were treated with trifluoroacetic acid to produce hydroxyl-bearing copolymers. During the deprotection, no significant degradation of the main chain was observed. All the copolymers did not show a melting point, and thus were amorphous. The deprotected copolymer did not dissolve in water, but was partially soluble in methanol. Thus, the hydrophilicities of the copolymer were improved by the deprotection.

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