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Synthesis of Poly(lactic acid) with Branched and Network Structures Containing Thermally Degradable Junctions

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ABSTRACT: Polyperoxide, as a new kind of thermally degradable polymer, is synthesized by the radical alternating copolymerization of a 1,3-diene monomer with oxygen. The introduction of polyperoxide units into any other polymer is useful for the fragmentation of polymers and a change in the physical properties of polymeric materials. In the present study, we demonstrate the synthesis and fragmentation of poly(L-lactic acid) (PLLA) modified with thermally degradable branching and cross-linking points, which consist of a repeating polyperoxide structure as the degradable junctions. We prepared several PLLA with a dienyl group at the α- and/or ω-chain ends by the anionic and metal-catalyzed polymerizations of L-lactide. Radical alternating copolymerization of the mono- and difunctional PLLA with oxygen was carried out to obtain branched polymers and gels. These branched and cross-linked PLLA materials readily degraded upon heating to yield linear PLLA chains.

Introduction

Polymeric materials are often required to be readily decomposed and to drastically change their physical properties after use for a given purpose during a given time. The synthesis of recyclable and degradable polymers is very important for polymer science and technology supporting a green sustainable society.[1−3] Especially, the synthesis of degradable polymers having a highly cross-linked three-dimensional network structure is one of the recent challenging topics.[4−12] Recently, we have developed a new type of degradable polymer by radical alternating copolymerization with diene monomers and molecular oxygen as the starting monomers via a conventional polymerization process.[13−19] The obtained polyperoxides (**PP**) have unique features as follows: easy preparation by conventional methods,[13,14] rapid degradation by various stimuli including heating, radiation, redox, and enzyme,[15] radical chain degradation to yield controlled low-molecular-weight products,[15,16] the facile synthesis of degradable **PP** gels,[17] the introduction of functional groups into the side chain,[18,19] and so on. In the present study, we demonstrate a new synthetic method for degradable branched or network polymers using the introduction of a **PP** structure as the thermally degradable junction into polymers. This is useful for the fragmentation of polymers or a change in the physical properties of polymeric materials. We synthesized poly(L-lactic acid) (PLLA) with a dienyl group at the α- and ω-chain ends by the ring-opening polymerization of L-lactide. The controlled polymerizations of lactide have been intensively investigated[20−26] as well as a broad range of the application of PLLA as biodegradable and carbon-neutral polymer materials.[27−33] In our strategy, the radical alternating copolymerization of an end-functional PLLA with oxygen is carried out to obtain branched and gel PLLAs containing degradable **PP** units as the branched and cross-linking points (Figure 1). We investigated the thermal degradation properties of branched and cross-linked PLLAs. The crystallinity of PLLA depending on the polymer branching structures was also examined.

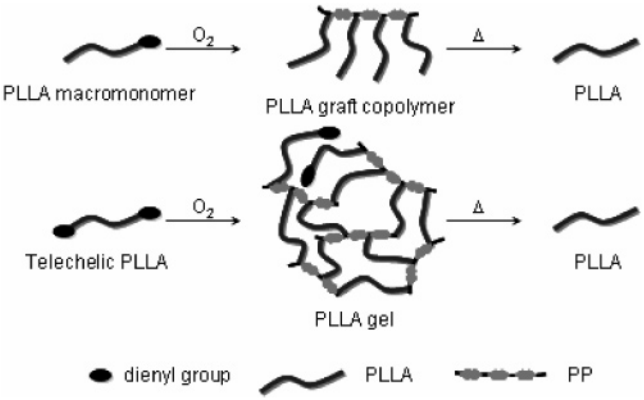

Figure 1. Concept of the synthesis and degradation of branched and cross-linked PLLAs.

Experimental Section

General Procedures. The number- and weight-average molecular weights (M_n and M_w) were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) as an eluent using a Tosoh CCPD RE-8020 system and calibration with standard polystyrenes. The calibration with standard poly(methyl methacrylate)s and poly(ethylene oxide)s gave similar molecular weight values because the molecular weight of PLLA synthesized in this work is not high ($M_n = (3-13) \times 10^3$). The NMR spectra were recorded on a JEOL JMN A-400 spectrometer. Thermogravimetric and differential thermal analysis (TG and DTA) were carried out using a SEIKO TG/DTA 6200 in a nitrogen stream at a heating rate of 10 °C/min. The wide-angle X-ray diffraction profile was recorded on a RIGAKU X-ray diffractometer RINT-Ultima 2100 with Cu Kα radiation ($\lambda = 1.5418$ Å). Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was carried out using a Shimadzu AXIMA-CFR Plus instrument equipped with a N_2 laser (337 nm) operated at a pulse rate of 10 Hz. The ions were accelerated with pulsed ion extraction at a voltage of 20 kV and detected using a microchannel plate detector. The analyzer was operated in a linear mode. A polymer sample was dissolved in THF (1.0 mg/mL) in the presence of dithranol as the matrix material, cast, and dried for providing laser desorption/ionization. Theoretical calculations by a density functional theory (DFT) method were carried out at the (RO)B3LYP/6-311G*//(U)B3LYP/6-311G* level of theory using Spartan'04.

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Materials. L-(−)-Lactide (LLA, Wako Pure Chemical Ind., Ltd., Osaka) and DL-lactide (DLLA, Tokyo Kasei Kogyo Co., Ltd., Tokyo) were recrystallized from ethyl acetate. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) (Wako Pure Chemical Ind., Ltd., Osaka) was recrystallized from methanol. Sorbyl alcohol [(*E*,*E*)-2,4-hexadien-1-ol] (Tokyo Kasei Kogyo Co., Ltd., Tokyo) was distilled under reduced pressure (bp 55 °C/0.5 mmHg). *n*-Butyllithium (nBuLi, 1.6 mol/L in *n*-hexane, Kanto Chemical Co., Ltd., Tokyo) and tin(II) bis(2-ethylhexanoate) (SnOct$_2$) (Wako Pure Chemical Ind., Ltd., Osaka) were used as received.

Synthesis of 1−3. Polymerization of LLA was carried out with lithium alkoxides derived from sorbyl alcohol or ethanol with nBuLi in a Schlenk flask under an argon atmosphere. To obtain a PLLA macromonomer with α-dienyl group (**1**), BuLi in *n*-hexane (1.6 mol/L, 0.64 mL) was added to 1.2 equiv of sorbyl alcohol in dry THF (2 mL) with a syringe at −78 °C and stirred for 30 min. To the solution maintained at 20 °C, LLA in THF (1.25 mol/L, 8 mL) was added with a syringe and stirred for 1 h. The polymerization was terminated by the addition of a small amount of acetic acid. The reaction mixture was poured into a large amount of diethyl ether and *n*-hexane (60/40 by volume) to precipitate the resulting PLLA, which was filtered, washed with cold diethyl ether, and then dried in vacuo. The isolated PLLA was reprecipitated using a mixture of chloroform/diethyl ether and *n*-hexane as the solvent and precipitant, respectively, and dried in vacuo overnight at room temperature. The polymer yield was gravimetrically determined. Yield was 62.6%. M_n and M_w/M_n values were determined to be 3.5×10^3 and 1.4, respectively, by GPC calibrated with standard polystyrenes.

For the synthesis of a PLLA macromonomer with an ω-dienyl group (**2**), a dry ethanol and nBuLi were used as the initiator. After stirring a mixture of ethanol (1.2 mmol) and nBuLi (1.0 mmol) in THF at −78 °C for 30 min, LLA in THF (1.25 mol/L, 8 mL) was added at 20 °C. After the polymerization, excess sorbic acid chloride (3 equiv) was added with a syringe at −78 °C, and the mixture further stirred for 1 h. The precipitation and the purification of polymer were carried out by a method similar to that for the synthesis of **1**. Yield 52.5%. $M_n = 3.3 \times 10^3$ and $M_w/M_n = 1.3$ by GPC.

3 as the telechelic polymer, i.e., a PLLA with dienyl groups at the α- and ω-chain ends, was synthesized by a similar method. The polymerization of LLA was initiated with a mixture of sorbyl alcohol and nBuLi in THF at −78 °C and then terminated with 3 equiv of sorbic acid chloride. Yield 79.2%. $M_n = 3.5 \times 10^3$ and $M_w/M_n = 1.5$ by GPC.

The structure of the obtained PLLA was confirmed by ^{1}H and ^{13}C NMR spectroscopies. The spectral data for **1**, **2**, and **3** are shown as follows.

1: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.25 (dd, J = 15.2 and 10.4 Hz, $\mathrm{C}H\mathrm{{=}CHCH_2}$), 6.05 (dd, J = 15.2 and 10.4 Hz, $\mathrm{CH_3CH{=}C}H$), 5.77 (dq, J = 15.2 and 6.8 Hz, $\mathrm{CH_3C}H\mathrm{{=}CH}$), 5.58 (dt, J = 15.2 and 6.8 Hz, $\mathrm{CH{=}C}H\mathrm{CH_2}$), 5.16 (q, J = 6.8 Hz, $\mathrm{C}H\mathrm{CH_3}$ of PLLA), 4.62 (d, J = 6.0 Hz, $\mathrm{CH{=}CHC}H_2$), 4.36 (q, J = 7.2 Hz, terminal-$\mathrm{C}H\mathrm{CH_3}$), 1.77 (d, J = 6.8 Hz, $\mathrm{C}H_3\mathrm{CH{=}CH}$), 1.58 (d, J = 7.2 Hz, $\mathrm{CHC}H_3$ of PLLA). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.61 (C=O), 68.97 ($C\mathrm{HCH_3}$), 16.68 ($\mathrm{CH}C\mathrm{H_3}$).

2: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.22 (m, $\mathrm{COCH{=}C}H$), 6.18 (m, $\mathrm{CH_3C}H\mathrm{{=}C}H\mathrm{CH{=}CH}$), 5.83 (d, J = 15.2 Hz, $\mathrm{COC}H\mathrm{{=}CH}$), 5.16 (q, J = 6.8 Hz, $\mathrm{C}H\mathrm{CH_3}$ of PLLA), 4.19 (q, J = 6.4 Hz, $\mathrm{CH_3C}H_2\mathrm{O}$), 1.85 (d, J = 4.8 Hz, $\mathrm{C}H_3\mathrm{CH{=}CH}$), 1.58 (d, J = 6.8 Hz, $\mathrm{CHC}H_3$ of PLLA), 1.27 (t, J = 6.8 Hz, $\mathrm{C}H_3\mathrm{CH_2O}$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.76 (C=O), 69.13 ($C\mathrm{HCH_3}$), 16.77 ($\mathrm{CH}C\mathrm{H_3}$).

3: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 (m, $\mathrm{COCH{=}C}H$), 6.17−6.28 (m, $\mathrm{C}H\mathrm{{=}CHCH_2O}$, $\mathrm{COCH{=}CHC}H\mathrm{{=}C}H$), 6.04 (dd, J = 15.2 and 12.0 Hz, $\mathrm{C}H\mathrm{CH{=}CHCH_2O}$), 5.74−5.85 (m, $\mathrm{CH{=}C}H\mathrm{CH_2O}$, $\mathrm{COC}H\mathrm{{=}CH}$), 5.58 (dt, J = 15.2 and 7.6 Hz, $\mathrm{C}H\mathrm{{=}CHCH{=}CHCH_2}$), 5.16 (q, J = 6.8 Hz, $\mathrm{C}H\mathrm{CH_3}$ of PLLA), 4.62 (t, J = 6.0 Hz, $\mathrm{CH{=}CHC}H_2$), 4.36 (q, J = 6.8 Hz, terminal-$\mathrm{C}H\mathrm{CH_3}$), 1.86 (d, J = 5.2 Hz, $\mathrm{C}H_3\mathrm{CH{=}CHCH{=}CHCO}$), 1.77 (d, J = 6.8 Hz, $\mathrm{C}H_3\mathrm{CH{=}CHCH{=}CHCH_2}$), 1.58 (d, J = 6.8 Hz, $\mathrm{CHC}H_3$ of PLLA). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.72 (C=O), 69.10 ($C\mathrm{HCH_3}$), 16.74 ($\mathrm{CH}C\mathrm{H_3}$).

Synthesis of 4. *Bis(2,4-hexadienyl) 5-hydroxyisophthalate (HHI).* Isophthalic acid was protected with a *tert*-butyldimethylsilyl group according to the method reported in the literature.[34] The protected isophthalic acid (2 mmol) was reacted with sorbyl alcohol using dicyclohexylcarbodiimide (6 mmol) in the presence of 4-(dimethylamino)pyridine (0.6 mmol) as the catalyst in THF at 0 °C for 1 h and then at room temperature for 6 h. The bis(2,4-hexadienyl) ester with the protected 4-hydroxyl group was isolated in 80% yield by column chromatography with aluminum oxide using chloroform as an eluent. Deprotection with tetrabutylammonium fluoride (1 mol/L in THF, 3 mL) was carried out in THF at 0 °C for 1 h,[34] followed by extraction with recrystallization from acetone and hexane (1/1 by volume) for providing HHI in 62% yield. The spectral data are as follows.

HHI: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.25 (s, aromatic H, 1H), 7.76 (s, aromatic H, 2H), 6.34 (dd, J = 15.2 and 10.8 Hz, $\mathrm{C}H\mathrm{{=}CHCH_2O}$, 2H), 6.09 (dd, J = 15.2 and 10.4 Hz, $\mathrm{CH_3CH{=}C}H$, 2H), 5.70−5.83 (m, $\mathrm{C}H\mathrm{{=}CHCH{=}C}H$, 4H), 4.83 (d, J = 6.4 Hz, $\mathrm{CH{=}CHC}H_2\mathrm{O}$, 4H), 1.78 (d, J = 6.4 Hz, $\mathrm{C}H_3\mathrm{CH{=}CH}$, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.13 (C=O), 156.52, 132.84, 123.85, and 121.51 (aromatic C), 136.13 ($C\mathrm{H{=}CHCH_2O}$), 132.39 ($\mathrm{CH{=}}C\mathrm{HCH_2O}$), 131.03 ($\mathrm{CH_3CH{=}}C\mathrm{H}$), 123.97 ($\mathrm{CH_3}C\mathrm{H{=}CH}$), 66.67 ($\mathrm{CH{=}CH}C\mathrm{H_2O}$), 18.86 ($C\mathrm{H_3CH{=}CH}$).

Polymerization of LLA with HHI. The bulk polymerization of LLA (10 mmol) was carried out with HHI (1 mmol) as the initiator and SnOct$_2$ (0.33 mmol) as the catalyst in a degassed sealed tube at 120 °C for 6 h. The product was dissolved in chloroform and precipitated into a large amount of diethyl ether. The isolated polymer was reprecipitated with chloroform/diethyl ether and dried in vacuo overnight at room temperature. Yield 75.5%, $M_n = 5.5 \times 10^3$, and $M_w/M_n = 1.3$. The structure of the polymers was confirmed by ^{1}H and ^{13}C NMR spectroscopies.

4: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.59 (s, aromatic H, 1H), 7.76 (s, aromatic H, 2H), 6.34 (dd, J = 14.8 and 10.4 Hz, $\mathrm{C}H\mathrm{{=}CHCH_2O}$, 2H), 6.09 (dd, J = 15.2 and 10.4 Hz, $\mathrm{CH_3CH{=}C}H$, 2H), 5.70−5.83 (m, $\mathrm{C}H\mathrm{{=}CHCH{=}C}H$, 4H),6.17−6.28 (m, $\mathrm{C}H\mathrm{{=}CHCH_2O}$, $\mathrm{COCH{=}CHC}H\mathrm{{=}C}H$, 4H), 6.04 (dd, J = 15.2 and 12.0 Hz, $\mathrm{C}H\mathrm{CH{=}CHCH_2O}$, 2H), 5.74−5.85 (m, $\mathrm{CH{=}C}H\mathrm{CH_2O}$, $\mathrm{COC}H\mathrm{{=}CH}$, 4H), 5.58 (dt, J = 15.2 and 7.6 Hz, $\mathrm{C}H\mathrm{{=}CHCH{=}CHCH_2}$, 2H), 5.16 (q, J = 6.8 Hz, $\mathrm{C}H\mathrm{CH_3}$ of PLLA), 4.85 (d, J = 6.8 Hz, $\mathrm{CH{=}CHC}H_2$, 4H), 4.36 (q, J = 6.8 Hz, terminal-$\mathrm{C}H\mathrm{CH_3}$), 1.78 (d, J = 6.4 Hz, $\mathrm{C}H_3\mathrm{CH{=}CHCH{=}CHCO}$, 6H), 1.59 (d, J = 7.2 Hz, $\mathrm{CHC}H_3$ of PLLA). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.90 (C=O), 69.30 ($C\mathrm{HCH_3}$), 17.03 ($\mathrm{CH}C\mathrm{H_3}$).

Copolymerization of 1−4 with Oxygen. PLLA **1**−**4** (typically 1 g), AMVN as the radical initiator (PLLA/initiator = 50/1 by weight), and 1,2-dichloroethane (PLLA/solvent = 1/2 by weight) were charged into an unsealed Pyrex tube. The copolymerization was carried out with bubbling O$_2$ at 30 °C. After the polymerization, the reaction mixture was poured into a large amount of diethyl ether to precipitate the polymers, which were filtered, washed, and then dried in vacuo overnight at room temperature. The conversion of a dienyl group at the polymer chain end into **PP** was calculated from the results of GPC measurements using UV (254 nm) and refractive index (RI) detectors.

Results and Discussion

Synthesis of PLLA Macromonomers 1 and 2. The α- and ω-functional macromonomers were prepared by the anionic polymerization of LLA with sorbyl alcohol and sorbic acid chloride as the initiator and terminator, respectively (Schemes 1 and 2).

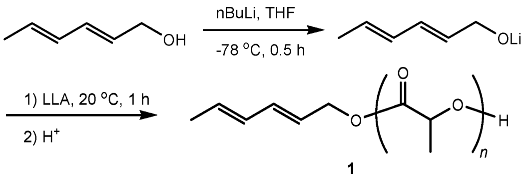
Table 1 shows the results for the synthesis of **1**. The macromonomer **1** was obtained in a 38−94% yield during the polymerization of LLA for 1 h at 20 °C. The M_n value of **1** was $(2.5-6.3) \times 10^3$, and the M_w/M_n value was 1.2−1.7. The M_n value decreased with a decrease in the monomer concentra-

Table 1. Anionic Polymerization of LLA for the Synthesis of Macromonomer 1[a]

run	[LLA]/[nBuLi] (mol/mol)	[SA]/[nBuLi] (mol/mol)	yield (%)	$M_n \times 10^{-3}$ (GPC)[b]	M_w/M_n (GPC)[b]	$M_n \times 10^{-3}$ (NMR)[c]	chain-end functionality α-dienyl
1	50	1.2	94.4	6.3	1.7	5.8 (6.9)[d]	0.90
2	25	1.2	85.6	5.0	1.7	3.7 (3.2)[d]	0.85
3	10	1.2	62.6	3.5	1.3	2.7	0.90
4	5	1.2	37.8	2.5	1.2	1.7	0.86

[a] SA: sorbyl alcohol. Polymerization conditions: [LLA] = 1.25 mol/L in THF at 20 °C for 1 h. [b] Calibrated with standard polystyrenes. [c] Based on the ratio of peak intensity for methine protons in a PLLA inner chain (peak *g* in Figure 2) and that of a methine proton in the ω-chain end (peak *i*). [d] Calculated by $M_n = 144 \times \text{conv} \times [\text{LLA}]/[\text{nBuLi}] + 98(\alpha\text{-chain end}) + 1(\omega\text{-chain end})$.

Scheme 1



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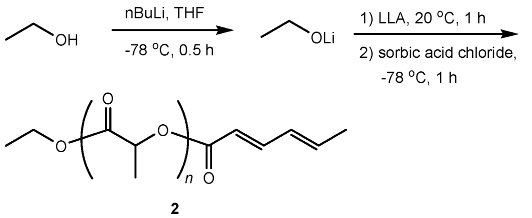


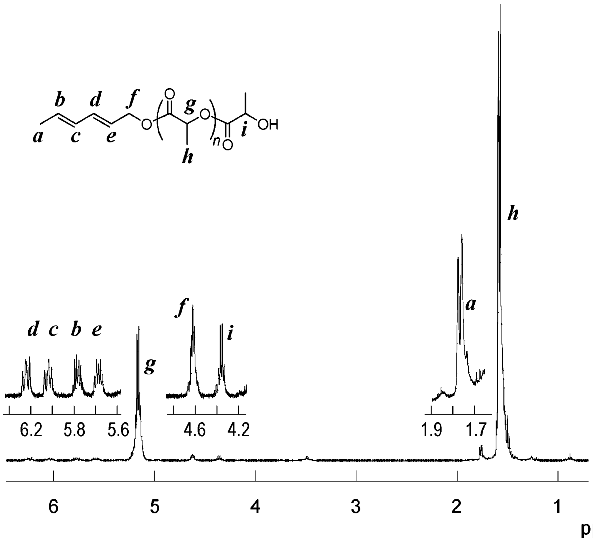


Figure 2. ^{1}H NMR spectrum of **1** obtained by anionic polymerization of LLA initiated with sorbyl alcohol and nBuLi and then terminated with acetic acid (run 3 in Table 1). $M_n = 3.5 \times 10^3$ and $M_w/M_n = 1.3$. The functionality of the α-dienyl group is 0.90.

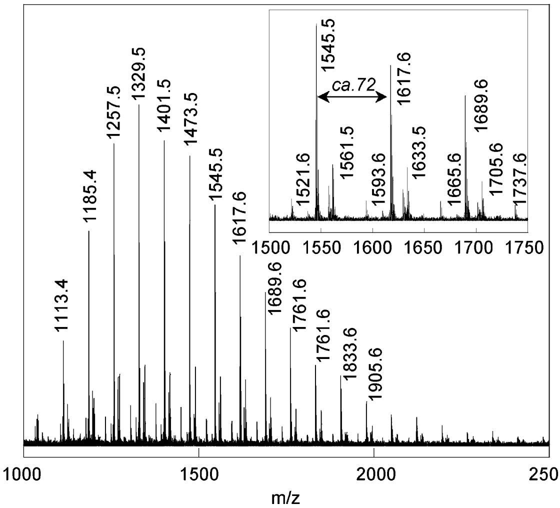


Figure 3. MALDI-TOF-MS of PLLA obtained by the anionic polymerization of LLA with sorbyl alcohol and nBuLi (run 4 in Table 1). The polymerization was terminated with acetic acid. $M_n = 2.5 \times 10^3$ and $M_w/M_n = 1.2$. The functionality of the α-dienyl group is 0.86. The inset shows the expanded spectrum.

tion, that is, an increase in the ratio of the sorbyl alcohol used as the initiator to the monomer. The decrease in the yield and M_w/M_n values at lower [LLA]/[nBuLi] ratios (runs 3 and 4) is possibly due to the loss of an oligomer during the precipitation procedure to isolate PLLA.

In the ^{1}H NMR spectrum of **1** (Figure 2), characteristic peaks due to both chain end groups were observed. Peaks *a*−*f* are assigned as the dienyl group introduced into the α-chain end of PLLA. The ω-chain end with a terminal hydroxyl group is confirmed by the methine hydrogen of the terminal repeating LLA group (peak *i*). The molar ratio of the α-chain end group was 0.85−0.90 relative to the ω-chain end group. A hydroxyl group is always introduced into the ω-chain end of PLLA by a chain transfer or a termination procedure during polymerization under the conditions used in the present study. On the other hand, the fraction of a dienyl group introduced at the α-chain end was less than unity. This fact suggests the occurrence of some undesired reaction during the polymerization. The most possible reaction is the abstraction of an α-methine proton of LLA and the subsequent reinitiation from the resulting LLA monomeric anion.[20] Such a chain transfer to a lactide monomer would reduce the α-chain end functionality of PLLA. Therefore, we examined the NMR spectrum of PLLA, but no direct evidence for a chain transfer to the monomer was obtained.

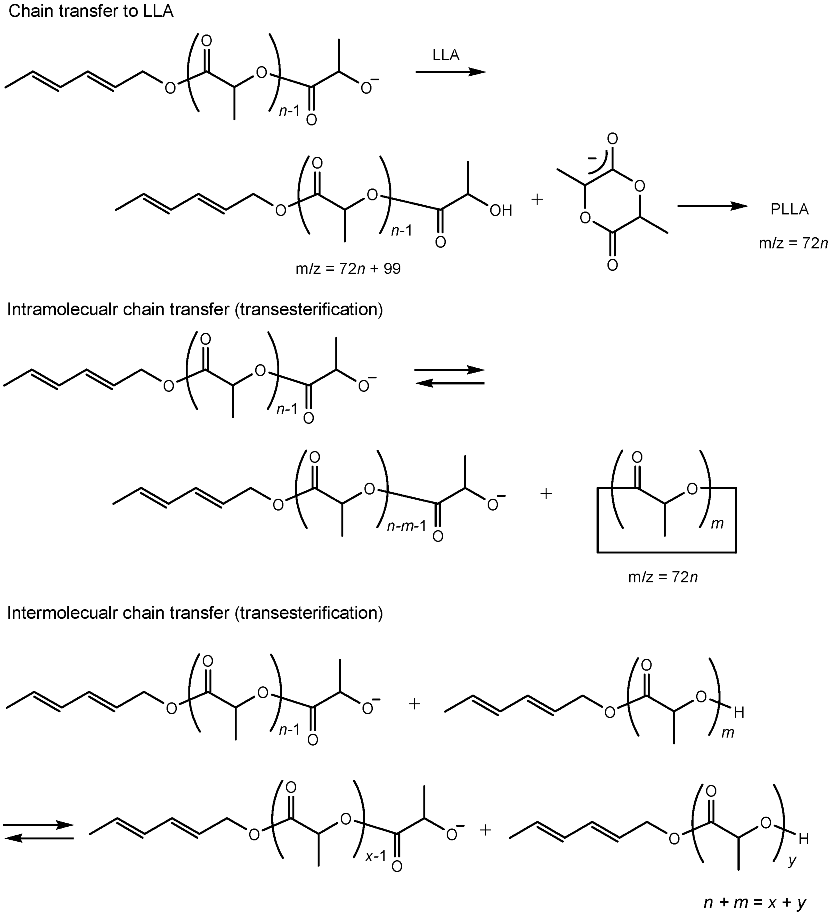
Next, we examined the terminal groups of PLLA by MALDI-TOF-MS. The obtained mass spectrum is shown in Figure 3. Several series of peaks which have a repeating period corresponding to one repeating unit of LLA (72.06 g/mol) were detected. A series of major peaks with the *m*/*z* values of 1113.4, 1185.4, 1257.5, ..., 1905.6 as seen in Figure 3 are assigned to PLLA including a dienyl group as the α-chain end doped with a Li^+ ion; $m/z = 72.06n$ (inner-chain) + 98.04 (α-chain end) + 1.01 (ω-chain end) + 6.94 (Li^+). Another series including peaks at 1561.5, 1633.5, and 1705.6 (the inset in Figure 3) correspond to PLLA with a similar chain-end structure, doped with a Na^+ ion (22.99 g/mol) instead of a Li^+ ion. In addition, other minor peaks were also observed at *m*/*z* of 1593.6, 1665.6, and 1737.6. These peaks are assigned to Li^+-doped PLLA with a lactidyl unit in the α-chain end (Scheme 3), which is produced by a chain transfer of the anion of polymer chain end to the monomer (lactide). However, the same *m*/*z* values are also expected from cyclic PLLA, which can be produced by the intramolecular chain transfer of the propagating anion as the active species. The intramolecular chain transfer has no effect on the intensity ratio of signals due to the α- and ω-chain end in the NMR spectrum.

Table 2. Anionic Polymerization of LLA for the Synthesis of Macromonomer 2[a]

						chain-end functionality		
run	[LLA]/[nBuLi] (mol/mol)	yield (%)	$M_n \times 10^{-3}$ (GPC)[b]	M_w/M_n (GPC)[b]	$M_n \times 10^{-3}$ (NMR)[c]	α-ethoxy	ω-dienyl	ω-OH
5	50	∼100[d]	6.0	1.7	5.4 (7.3)[e]	0.93	0.31	0.69
6	25	94.2	5.0	1.7	3.7 (3.5)[e]	0.86	0.60	0.40
7	10	52.5	3.3	1.3	2.5	0.86	0.74	0.26
8	5	36.1	2.8	1.2	2.0	0.89	0.68	0.32

[a] Polymerization conditions: [LLA] = 1.25 mol/L, in THF at 20 °C for 1 h. Polymerization was terminated with sorbic acid chloride at −78 °C for 1 h; [ethanol]/[nBuLi] = 1.2, [sorbic acid chloride]/[nBuLi] = 3. [b] Calibrated with standard polystyrenes. [c] Based on the ratio of peak intensity for methine protons in a PLLA inner chain (peak *f* in Figure 4) and the sum of those for a methine proton (peak *j*) and a dienyl proton (peak *e*) in the ω-chain end. [d] The solution was apparently solidified during polymerization. [e] $M_n = 144 \times \text{conv} \times [\text{LLA}]/[\text{nBuLi}] + 45(\alpha\text{-chain end}) + 95(\omega\text{-chain end})$.

Scheme 3



Interestingly, the mass spectrum shown in Figure 3 consists of several series of 72.06 g/mol of molecular weight for one lactic acid repeating unit [$-C(=O)CH(CH_3)O-$], but not 144.12 g/mol for the lactidyl units (dimer). This differs from the expectation based on the fact that lactide was used as the starting monomer during the polymerization. When intermolecular chain transfer frequently occurs during the polymerization, the PLLA chains have a repeating structure based on 72.06 mass unit (Scheme 3). Similar results have been reported for other anionic and metal-catalyzed polymerizations in the literature.[24,25]

Table 2 summarizes the results for the synthesis of ω-functionalized macromonomer **2**. When the ratio of the monomer to the initiator is high ([LLA]/[nBuLi] = 50), the polymerization mixture solidified during polymerization. After polymerization for 1 h, sorbic acid chloride was partly reacted with the propagating chain end, resulting in a low efficiency for the introduction of a dienyl group. During the polymerization at lower ratios of monomer to initiator, the ω-dienyl group was introduced with an efficiency of 0.60−0.74. The ^{1}H NMR spectrum of the isolated **2** is shown in Figure 4. A methine proton assigned to the terminal LLA unit having a neighboring hydroxyl group was detected at 4.36 ppm in addition to the expected signals due to the ω-dienyl group as peaks *a*−*e*. The reaction of the living chain end with sorbic acid chloride was carried out under various conditions; for example, at room temperature and for a long reaction time, the introduction efficiency was not improved. The protonation of a propagating chain end is assumed to occur due to intermolecular and intramolecular chain transfer reactions during the polymerization but not in the termination process.

Copolymerization of 1 and 2 with Oxygen. The radical alternating copolymerization of **1** and **2** with oxygen was carried out to obtain graft copolymers consisting of a **PP** main chain and a PLLA side chain (**PP-1** and **PP-2**). The repeating structures of **PP-1** and **PP-2** are expected to be different from each other, as shown in Scheme 4, because the regioselectivity of the propagation during the alternating copolymerization of diene monomers with oxygen importantly depends on the

Table 3. Copolymerization of Macromonomers 1 and 2 with Oxygen in 1,2-Dichloroethane at 30 °C[a]

run	monomer	time (h)	conversion (%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
9	**1**[b]	6	41	4.4	7.9	1.8
10	**1**[b]	12	48	5.0	9.0	1.8
11	**1**[b]	36	75	7.3	13.1	1.8
12[c]				4.1[c]	6.2[c]	1.5[c]
13	**2**[d]	6	40	3.9	5.9	1.5
14	**2**[d]	12	71	4.0	5.6	1.4
15	**2**[d]	36	95	4.1	6.2	1.5
16[e]				3.4[e]	4.1[e]	1.2[e]
17	**HA**	6	31	3.1	5.3	1.7
18	**HA**[f]	6	14	2.3	4.4	1.9
19	**MS**	6	44	3.3	5.6	1.7
20	**MS**[f]	6	24	1.1	1.7	1.5

[a] Macromonomer/AMVN/solvent = 50/1/100 by weight was used. During copolymerization, each 5 mg of AMVN was further added stepwise at 6 h intervals. The conversion was estimated by GPC using dual (RI and UV) detectors. M_n, M_w, and M_w/M_n are shown as the values for the mixture of a macromonomer and a graft polymer without peak separation for runs 1−18. [b] Macromonomer **1** obtained by run 3 in Table 1. $M_n = 3.5 \times 10^3$, $M_w = 4.9 \times 10^3$, $M_w/M_n = 1.4$. The functionality of the α-dienyl group is 0.90. [c] After thermal degradation of **PP-1** (run 11) at 110 °C for 5 h. [d] Macromonomer **2** obtained by run 7 in Table 2. $M_n = 3.3 \times 10^3$, $M_w = 4.4 \times 10^3$, $M_w/M_n = 1.3$. The functionality of the ω-dienyl group is 0.74. [e] After thermal degradation of **PP-2** (run 15) at 110 °C for 5 h. [f] Monomer/AMVN/solvent = 5/1/200 by weight.

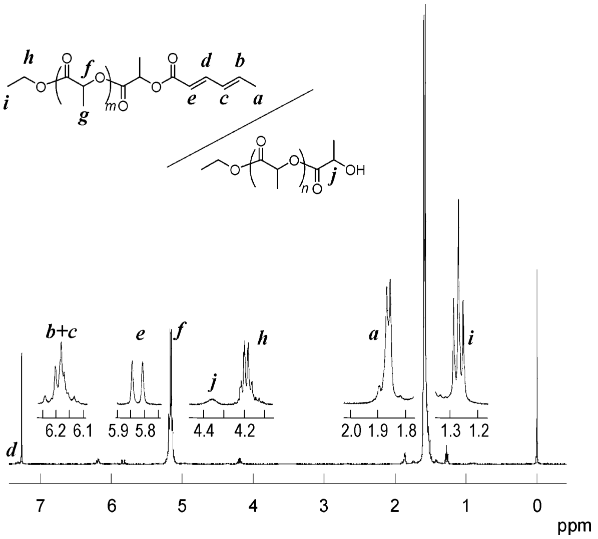


Figure 4. ^{1}H NMR spectrum of **2** obtained by anionic polymerization of LLA initiated with ethanol and nBuLi and terminated with sorbic acid chloride (run 7 in Table 2). $M_n = 3.3 \times 10^3$ and $M_w/M_n = 1.3$. The functionality of the ω-dienyl group is 0.74.

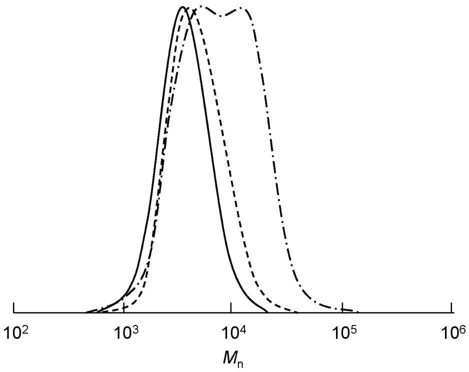
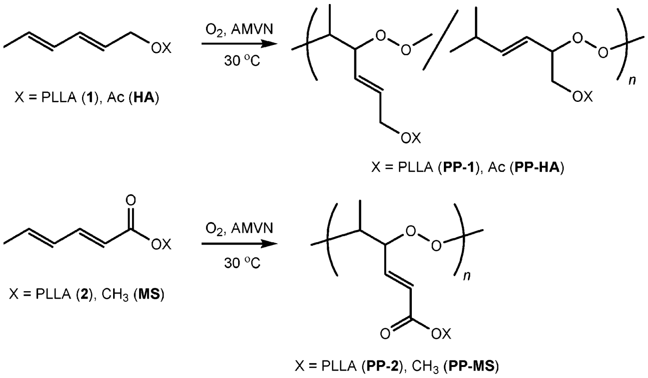


Figure 5. GPC elution curves of **1** ($M_n = 3.5 \times 10^3$, $M_w/M_n = 1.4$) (solid line), **PP-1** ($M_n = 7.3 \times 10^3$, $M_w/M_n = 1.8$) (dashed and dotted line), and the degradation product of **PP-1** (dotted line) after heating at 110 °C for 5 h ($M_n = 4.1 \times 10^3$, $M_w/M_n = 1.5$).

Scheme 4



substituents of the used dienes.[14,16,19] The conversion and the molecular weights of the obtained **PP-1** and **PP-2** are shown in Table 3.

The GPC elution curves of **1** and **PP-1** are partly overlapped but are differentiated from each other (Figure 5). Because the isolation of **PP** from a mixture with the unreacted macromonomer was difficult, we used a dual detection system consisting of UV (254 nm) and RI detectors to determine the conversion of a macromonomer to a polymacromonomer. The resulting **PP-1** has no absorption around 254 nm, while **1** has strong absorption due to the hexadienyl group. It was assumed that both the polymers have the same refractive index value for the calculation. As shown in Table 3, the conversion of **1** into **PP-1** increased to 75% for the 36 h copolymerization. The M_n value of **PP-1** also increased to 7.3×10^3. As shown in the GPC elution curve in Figure 5, **PP-1** includes the fractions of **PP** with the molecular weight range of 10^4−10^5. The peak top of the higher-molecular-weight part of the elution carve is over 10^4. The macromonomer **2**, which has a sorbate-like structure, gave a slightly higher conversion (40−95%) than that for **1**. A change in the M_n value of **PP-2** was small during the polymerization when compared to the results of the polymerization of **1**. More details cannot be discussed because the M_n and M_w/M_n in Table 3 are the values for a mixture of the unreacting macromonomers and the resulting **PP** without any peak separation. In order to examine the reactivity of the macromonomers during the copolymerization with oxygen, we carried out the copolymerization of 2,4-hexadienyl acetate (**HA**) and methyl sorbate (**MS**) as the low-molecular-weight model compounds for the macromonomer **1** and **2**, respectively (Scheme 4). The results are shown in Table 3 (runs 17−20). **PP−MS** was obtained in a higher polymer yield than **PP−HA**, but their molecular weights were similar. From the elution curves of **PP** and the experimental results using **HA** and **MS** as the model compounds, the degree of the polymerization of **PP** is speculated to be ca. 5−10 at least. A further increase in the molecular weight of **PP** is difficult, as has already been shown in the previous results for the copolymerization of diene monomers with oxygen under various conditions.[13−15,19]

Table 4. DFT Calculations for Regiospecific Propagation during Diene Monomers as the Model for Macromonomers[a]

		addition of peroxy radical to diene			BDE of formed C—O bond		
monomer	X	ΔH_5 (kcal/mol)	ΔH_2 (kcal/mol)	$\Delta H_5 - \Delta H_2$ (kcal/mol)	$BDE_{5,4}$ (kcal/mol)	$BDE_{5,2}$ (kcal/mol)	regioselectivity
HA	CH_2OCOCH_3	−8.99	−7.44	1.55	18.90, 18.51	18.81, 19.00	low
MS[b]	CO_2CH_3	−9.95	−0.87	9.08	15.17, 15.02	7.35, 9.45	high

[a] **MS**: methyl sorbate; **HA**: 2,4-hexadienyl acetate. ΔH_5 and ΔH_2 are the enthalpy changes for the reactions in Scheme 5. For $BDE_{5,4}$ and $BDE_{5,2}$, energies were calculated for two diastereomers. See also Scheme 6. [b] Reference 16.

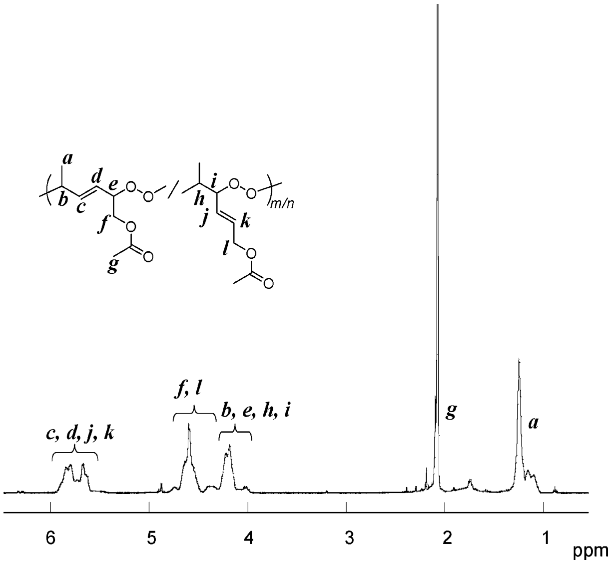


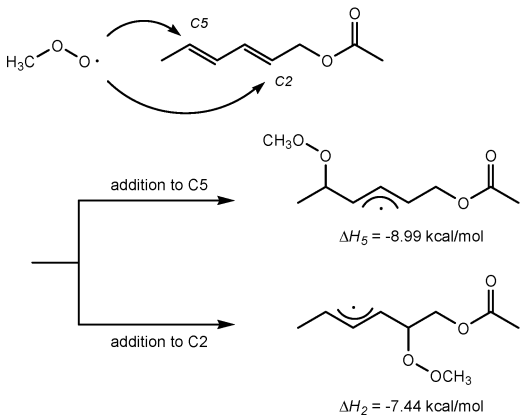
Figure 6. ^1H NMR spectrum of **PP−HA** obtained from **HA** as the model compound for **1** with oxygen.

Direct determination of the main-chain structure of **PP-1** and **PP-2** was attempted by NMR spectroscopy, but this failed because of broad peaks due to the main chain and the presence of the PLLA side chain. Therefore, we examined the structure of **PP−HA** by the ^1H NMR spectrum and theoretical calculations. Figure 6 indicates the presence of both the 5,4- and 5,2-repeating structures of **HA** units in the resulting **PP−HA,** similar to the **PP** obtained from 2,4-hexadiene previously reported.[14]

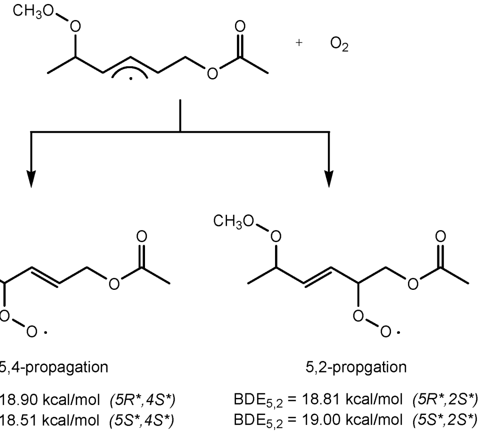
Theoretical calculations were carried out for **HA** as the model compound of **PP-1,** and the results were compared with those for **MS** as the model of **PP-2**. During the alternating radical copolymerization of sorbic esters with oxygen, propagation consists of the two successive regiospecific reactions: one is the regiospecific addition of a propagating peroxy radical to a diene monomer, and the other is the regiospecific reaction of an allyl radical with molecular oxygen.[16] In the present study, reaction enthalpy for the addition of a methyl peroxy radical to **HA** was calculated at the B3LPY level of the theory with a basis set of 6-311G*. The calculation results are summarized in Table 4.

The structure of peroxy radicals formed by the addition to **HA** at the 5- and 2-carbons is shown in Scheme 5. The enthalpy changes by the addition of a methyl peroxy radical to the C5 and C2 carbons of **HA** were $\Delta H_5 = -8.99$ kcal/mol and $\Delta H_2 = -7.44$ kcal/mol, respectively. The reaction at the C5 position is more preferred by 1.55 kcal/mol, but this difference is much smaller than the value (9.08 cal/mol) for **MS** with a conjugating substituent on the diene moiety. During the copolymerization of **HA** and oxygen, addition occurs to both the 5- and 2-positions of **HA**, while the copolymerization of **MS** provides a highly controlled regioselective structure due to an exclusive addition to the 5-carbon.

Scheme 5



Scheme 6



We subsequently investigated the regioselectivity in the second step of the alternating propagation mechanism (Scheme 6). It has been reported that the reaction of a carbon-centered radical with molecular oxygen is reversible and that the bond dissociation energy (BDE) of a carbon-to-oxygen bond for a substituted peroxy radical is closely related to the kinetic constant of β-dissociation, which is the reaction reverse to propagation.[35] Therefore, we estimated the BDE values for the reaction of an allyl radical with oxygen at the C4 and C2 positions ($BDE_{5,4}$ and $BDE_{5,2}$, respectively). The conclusion is that the difference in the BDE values of the 5,4- and 5,2-adduct radicals is small and that both propagations are possibly occur during the copolymerization of **HA**, which is much different from the highly regiospecific propagation of **MS** previously reported.

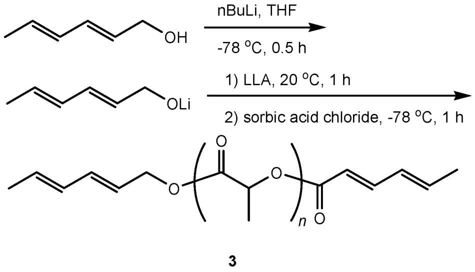
Thus, we have revealed that the 1,3-diene derivatives having no α-carbonyl substituent such as **1** and **HA** have low regioselectivity regarding the 5- and 2-addition of a peroxy radical in the first step and no selectivity regarding the 5,4- and 5,2-propagation in the second step during propagation. For the structure control of degradation products, the regiocontrol of propagation is indispensable, but an easy degradation property requires only the alternating repeating structure of oxygen and

Table 5. Anionic and Metal-Catalyzed Polymerization for the Synthesis of Difunctional PLLA 3 and 4[a]

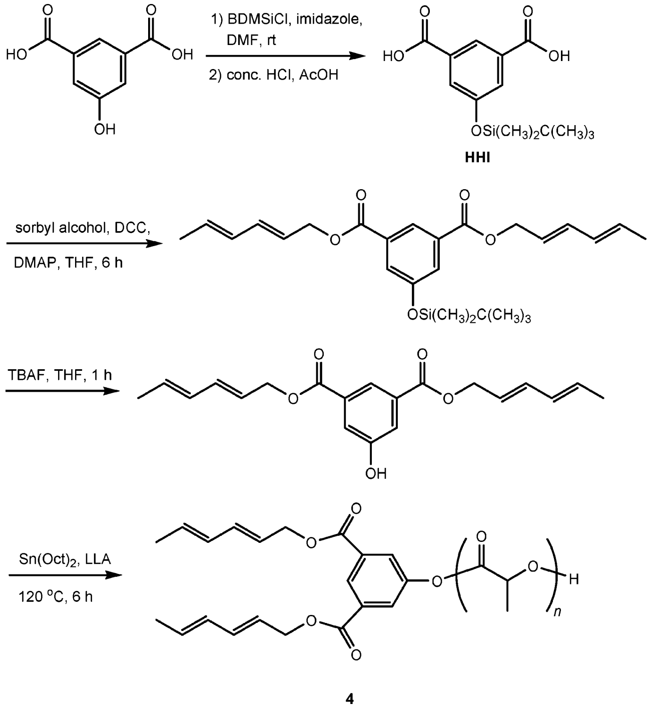
run	[LLA] (mol/L)	initiator (mol/L)	catalyst (mol/L)	temp (°C)	time (h)	yield (%)	$M_n \times 10^{-3}$ (GPC)[a]	M_w/M_n (GPC)[a]	chain end functionality α-dienyl	ω-dienyl	ω-OH
21[b]	1.25	SA (0.15)	nBuLi (0.125)	20	1	79.2	3.5	1.5	0.86	0.61	0.39
22[b]	1.25	SA (0.025)	nBuLi (0.021)	20	1	93.4	7.3	1.6			
23[c]		HHI	Sn(Oct)$_2$	120	6	75.5	5.5	1.3	1.76	0	1.0

[a] Calibrated with standard polystyrenes. [b] Polymerization was carried out in THF and terminated with sorbic acid chloride. SA: sorbyl alcohol. [c] Bulk polymerization with LLA 10 mmol, HHI 1 mmol, Sn(Oct)$_2$ 0.03 mmol.

Scheme 7



Scheme 8



a diene in the main chain. Therefore, **PP-1** and **PP−HA** can be used as degradable polymers because they still have a highly alternating structure.

Preparation of Difunctional PLLA. In the present study, we also prepared two kinds of difunctional PLLA for synthesizing branched and cross-linked **PP** with degradable junctions. The telechelic PLLA (**3**) having two dienyl groups at the both chain ends was prepared by a method similar to the synthesis of macromonomers **1** and **2** (Scheme 7). On the other hand, the α,α-difunctional PLLA was prepared by the metal-catalyzed polymerization of LLA with HHI as the initiator (Scheme 8). The metal-catalyzed polymerization[21−25] is useful for the α-funtionalized polymers. The results of these polymerizations are shown in Table 5. The difunctional PLLA with an M_n of $(3.5-7.3) \times 10^3$ and an $M_w/M_n = 1.3-1.6$ was obtained in 75−93% yield by the anionic and metal-catalyzed polymerizations. The functionality of the introduction of diene groups at the α- or ω-chain end per PLLA chain was 1.47−1.76.

The copolymerizations of **3** as the telechelic polymer and **4** as the α,α-difuntional polymer with oxygen were carried out in 1,2-dichloroethane for 12 h. In the case of **3**, the polymerization mixture was poured into a large amount of chloroform and separated into an insoluble polymer (gel) (**PP-3G**) and a soluble part (**PP-3S**). The soluble part includes the branched polymer and the unreacted **3,** and the M_n of **PP-3S** was higher than that of the original **3**. The ratio of the gel fraction as the insoluble part was 39.3 wt %. The copolymerization of **4** was carried out under the identical conditions, but no gelation was observed. The M_n and M_w/M_n values greatly increased from 5.5×10^3 to 1.3×10^4 and 1.3 to 4.0, respectively, after the copolymerization. This indicates the formation of a highly branched structure. The two reacting diene groups of **4** are located close to each other and tend to intramolecularly react during the copolymerization with oxygen. This results in the formation of a cyclic structure but does not undergo intermolecular cross-linking. Consequently, the produced **PP-4** may have a starlike polymer shape.

Thermal Degradation. After the toluene solution of **PP-1** was heated at 110 °C for 5 h, the polymer was recovered by reprecipitation and analyzed by GPC (run 12 in Table 3). The obtained GPC elution curve is already shown in Figure 3. The M_n value (4.1×10^3) observed after the thermal degradation was similar to that of the original macromonomer **1** ($M_n = 3.5 \times 10^3$). When the terminal structure of the polymer after thermal degradation was examined by ^{1}H NMR spectroscopy, an aldehyde group was detected. Previously, we have reported the radical chain degradation of PP obtained from various diene monomers resulting in the formation of low-molecular-weight aldehyde products.[14,15] The NMR results observed in this study agree well with the expected one, but its content was not determined. For **PP-2** and **PP-4**, similar results were obtained (run 16 in Table 3 and run 27 in Table 6, respectively). These results strongly indicate that a peroxy linkage as the branching point in **PP-1**, **PP-2**, and **PP-4** readily degrades and that the side-chain PLLA segments are recovered without decomposition.

The TG/DTA measurement of the dried **PP-3G** was carried out to confirm the presence of a peroxy group. In the TG curve, no weight loss was observed below 300 °C, at which temperature decomposition of PLLA starts. In the DTA curve, both an endothermic peak due to the melting of PLLA and an exothermic peak ($T_{max} = 138$ °C) due to the degradation of peroxy linkages were observed. In fact, when **PP-3G** swollen with toluene was heated in a sealed tube at 110 °C for 3 h, the cross-linking points of **PP-3G** degraded, and all the remaining PLLA was soluble in toluene after cooling to room temperature (Figure 7). This supports that the network structure of **PP-3G** includes thermally degradable junctions.

Wide-angle X-ray diffraction measurements were carried out to evaluate the crystallinity of the linear and the branched PLLA produced in the present study. We confirmed that **PP-3S** has a low crystallinity (22%) due to its highly branched structure,[36] while the linear PLLA such as **3** has a high crystallinity (41%),

Table 6. Copolymerization of 3 or 4 with Oxygen in 1,2-Dichloroethane at 30 °C[a]

run	PLLA	time (h)	conv[b] (%)	gel fraction (%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
24	**3**[c]	12	57.7	39.3	7.3[d]	13.1[d]	1.8[d]
25[e]				0	5.2	5.6	1.4
26	**4**[f]	12	71.0	0	13.0	52.0	4.0
27[g]				0	6.3	8.8	1.4

[a] PLLA/AMVN/solvent = 50/1/100 by weight. During polymerization, each 5 mg of AMVN was further added stepwise at 6 h intervals. [b] Estimated by GPC using RI and UV detectors. [c] Obtained by run 21 in Table 5. $M_n = 3.5 \times 10^3$, $M_w = 4.9 \times 10^3$, $M_w/M_n = 1.5$. [d] For soluble part (**PP-3S**). [e] After thermal degradation of gel fraction (**PP-3G**, run 24) at 110 °C for 5 h. [f] Obtained by run 23 in Table 5. $M_n = 5.5 \times 10^3$, $M_w = 4.4 \times 10^3$, $M_w/M_n = 1.3$. [g] After thermal degradation of **PP-4** (run 26) at 110 °C for 5 h.

Table 7. Crystallinity and Film Formation of PLLA with a Different Chain Structure

polymer	structure	$M_n \times 10^{-3}$	crystallinity[a] (%)	transparent film
macromonomer **1**	linear	3.5		no
PP-1	comblike	7.3		no
macromonomer **3**	linear	3.5	41	no
macromonomer **3**	linear	7.3		no
macromonomer DL-**3**[b]	linear	4.1	c	yes
PP-3S[d]	highly branched	7.3	22	yes
PP-3S after degradation[e]	linear[e]	5.2[e]	38[e]	no[e]
PP-3G[f]	gel			no
macromonomer **4**	linear	5.5	44	no
PP-4	starlike	13.0	34	no
PP-4 after degradation[e]	linear[e]	6.3[e]	43[e]	no[e]

[a] Estimated by wide-angle X-ray diffractions. [b] DL-Lactides (racemic isomers) were used for the polymerization in the synthesis of PDLLA. [c] Amorphous. [d] $CHCl_3$-soluble part of the products from copolymerization of macromonomer **3** (run 24 in Table 6) with oxygen at 30 °C for 12 h. [e] After heating at 90 °C for 5 h. [f] Insoluble part.

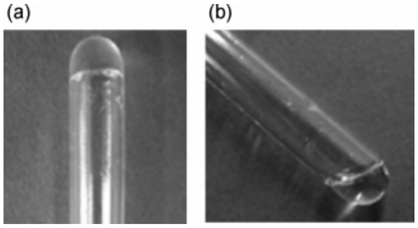


Figure 7. (a) **PP-3G** gel swollen with toluene and (b) a solution obtained after heating of the gel at 100 °C for 3 h.

as shown in Table 7. **PP-3S** provides a transparent film by casting of a chloroform solution as well as the PDLLA, which was obtained from anionic polymerization of DL-lactide. In contrast, the linear PLLA including **PP-3S** after thermal degradation and the precursor **3** gave no transparent film due to their high crystallinity. The crystallinity of **PP-3S** increased to 38% after thermal degradation at 90 °C for 5 h, similar to the value for the original macromonomer **3**. The crystallinity of **4** slightly decreased due to the formation of a branched structure during the copolymerization with oxygen from 44 to 34% because **PP-4** as the α,α-difuntional polymer consists of a starlike branching structure.

In conclusion, we synthesized macromonomers and a telechelic PLLA with a dienyl group at the α- and/or ω-chain ends by the ring-opening anionic and metal-catalyzed polymerizations of lactide. The subsequent radical copolymerization of the obtained PLLA with oxygen gave PLLA graft polymers and gels containing peroxy repeating units as the branched and cross-linking points. The branched and cross-linked PLLA readily degraded upon heating to yield linear soluble PLLA. In addition to the thermal degradation, if it is desired, the degradation of a peroxy linkage can be accomplished by other stimuli such as UV irradiation, pH change, enzyme addition, and so on.[15] PLLA is one of the most important and attractive polymers in recent years. In the present study, we have demonstrated that the branched and cross-linking structures of PLLA using polyperoxide repeating structures as the thermally degradable junctions are valuable for the control of polymer properties. A similar approach using degradable peroxy junctions will be applied to controlling the physical properties not only of PLLA but also of other conventional polymers.

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