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Short communication

Synthesis of high-molecular-weight poly(L-lactic acid) through the direct condensation polymerization of L-lactic acid in bulk state

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Abstract

A strategy was attempted to produce high-molecular-weight poly(L-lactic acid) (PLLA) through the direct condensation polymerization of L-lactic acid in bulk state. Polymerizations were carried out with titanium(IV) butoxide (TNBT) as a catalyst employing different duration of decompression, esterification and polycondensation. The molecular weights were characterized by using the gel permeation chromatography (GPC). The stereosequences were analyzed from the ^{13}C NMR spectra on the basis of the triad fractions.

Keywords: High molecular weight; Poly(L-lactic acid); Direct condensation polymerization; Stereosequence

1. Introduction

Direct condensation polymerization of L-lactic acid in bulk state has been known to produce poly(L-lactic acid) (PLLA) with molecular weight of order of only ~10^4 g/mol due to the unfavorable reaction equilibrium constant [1]. As the low-molecular-weight PLLA thus produced is too brittle to be used as a useful material, increase of the molecular weight of PLLA is imperatively demanded. High-molecular-weight PLLA is produced commercially by the ring opening polymerization of L-lactide, which in turn is made by decomposition of the low-molecular-weight PLLA. Solution polymerization of L-lactic acid also yields high-molecular-weight PLLA by using a large volume of solvent compatible with PLLA [2,3]. Solvents with high boiling point are used for the removal of the dissociated water by means of the so-called azeotropic distillation technique [1]. Multiple reactors and complex facilities are needed for these processes and thus raise the production cost of PLLA. Moreover flammability and toxicity of the solvents make the solution process less attractive.

In comparison with the well-established method for the catalytic ring-opening polymerization of L-lactide [4–6], the direct dehydropolycondensation of L-lactic acid has received much less attention. Yamaguchi et al. [7] studied the direct polycondensation of L-lactic acid with various Brönsted and Lewis acid catalysts, in which the recycled solvent was passed through a tube packed with molecular sieve to keep the concentration of water in the solvent less than 3 ppm. Moon et al. [8] examined the melt/solid polycondensation of L-lactic acid catalyzed by tin chloride dihydrate/*p*-toluene sulfonic acid binary system. Otera et al. [9] observed that

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Table 1
Characteristics of the poly(L-lactic acid)

Sample	Time of the esterification at 760 Torr (h)	Duration of the decompression from 760 to 1 Torr (h)	Time of the polymerization at 1 Torr (h)	M_w (10^3 g/mol)	PDI
PLLA1	3	7	40	130	3.30
PLLA2	3	3	40	30	4.51
PLLA3	7	3	40	120	3.49
PLLA4	3	3	50	30	5.51
PLLA5	3	3	20	15	1.80

distannoxanes could be effective catalysts for the direct dehydropolycondensation of L-lactic acid to PLLA. Appropriately substituted distannoxane catalysts are themselves hydrophobic in nature because of the bulky alkyl groups around the tin atoms and, therefore, can act as water-tolerant catalysts.

We observed, contrary to the common expectation, that the molecular weight of PLLA became as high as 130,000 g/mol from the direct condensation polymerization of L-lactic acid in bulk state even in the absence of any additional reaction promoters, if the decompression step and/or the esterification step was well controlled. The configuration of the PLLA thus produced was determined by using ^{13}C NMR.

2. Experimental

L-Lactic acid was added to a three neck reactor (500 ml) that was connected to a vacuum system via a liquid nitrogen trap. To remove water the reactor was immersed in an oil bath at 100 °C under nitrogen atmosphere for 1 h. The reactor was heated in an oil bath to 180 °C under mechanical stirring (300 rpm), and then was added titanium(IV) butoxide (TNBT, 0.08 ml) under nitrogen atmosphere. After the esterification reaction, the reactor was evacuated by reducing the pressure to 500 Torr step by step, and then the pressure was further reduced to 1 Torr gradually. The reaction was continued at 1 Torr and 180 °C for another 40 h. The resulting polymer was dissolved in chloroform, and microfiltered through a 0.45 μm pore membrane filter. The polymer was precipitated by pouring the polymer solution into an excess of methanol, filtered, and dried in a vacuum oven at 60 °C to a constant weight.

Molecular weights were measured by gel permeation chromatography (GPC, Waters 410 detector) using with polystyrene as the standard. Proton-decoupled ^{13}C NMR spectra were recorded on a Varian UnityINOVA 400-MHz NMR spectrometer. $CDCl_3$ served as a solvent and tetramethylsilane served as an internal standard for all ^{13}C NMR measurements. The relative peak areas were proportional to the number of carbon atoms.

3. Results and discussion

The duration of the esterification reaction and the rate of the pressure reduction from atmospheric pressure to 1 Torr were varied to produce five different PLLAs as shown in Table 1.

The GPC profiles of PLLA1 and PLLA2 samples are compared in Fig. 1. A bimodal GPC profile was observed for both of the PLLAs. For the PLLA1, the first and second peaks correspond to $M_w \sim 130{,}000$ and to $M_w \sim 900$, respectively. In case of the PLLA2, the first and second peaks correspond to $M_w \sim 30{,}000$ and ~ 400, respectively.

It is worth noting here that the duration of the decompression of the reaction pressure to 1 Torr is important to produce high-molecular-weight PLLA. If the polymerization reactor was decompressed extremely slowly step by step for 7 h, the molecular weight of PLLA reached as high as ~130,000. To the best of our knowledge, the present study reports, for the first time, that high-molecular-weight PLLA was produced from the direct bulk condensation polymerization of L-lactic acid in the absence of any additional reaction promoters.

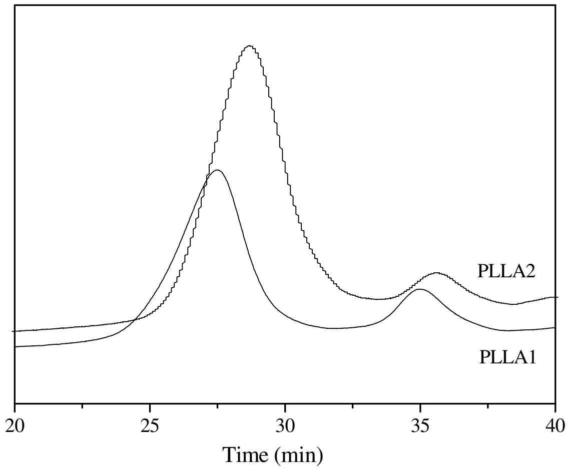

Fig. 1. GPC profiles of PLLA1 and PLLA2.

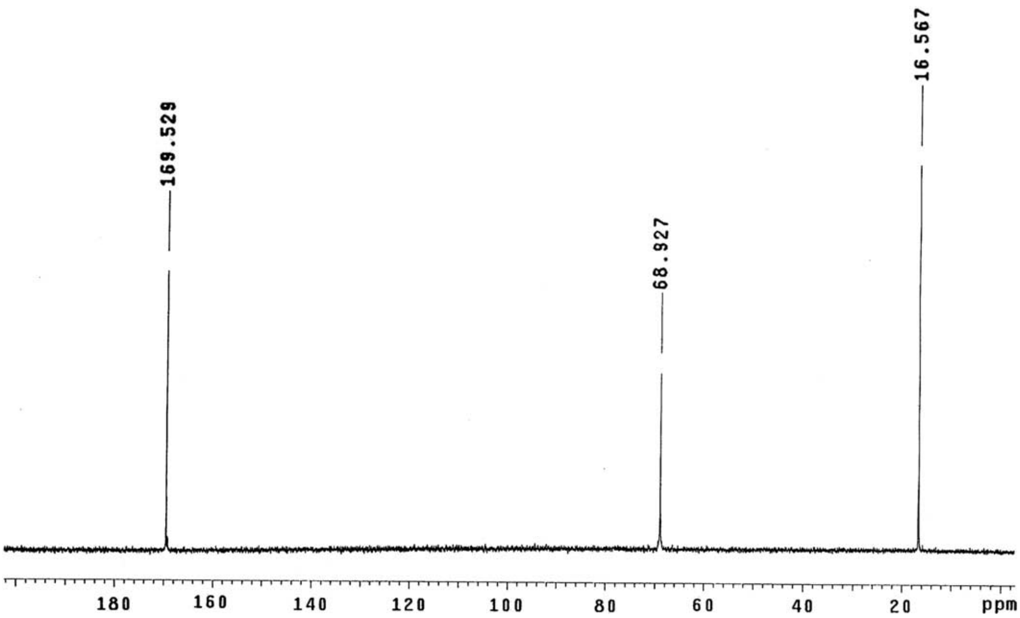

Fig. 2. ^{13}C NMR spectra of PLLA1.

Increase of the time for the esterification reaction from 3 to 7 h also raised the molecular weight of PLLA from 30,000 to 120,000.

At 100 MHz, all the PLLAs gave similar ^{13}C NMR spectra composed of three lines, located at $\delta = 16.6$, 68.9 and 169.5 ppm as shown in Fig. 2. These three lines correspond to the methyl, methine and carbonyl carbon atoms, respectively. The attempts to detect the fine structure coming from the stereosensitivity in the methyl and methine peaks were failed.

The expansion and line narrowing of the C=O region by the resolution enhancement technique led to the patterns composed of several lines whose respective intensities depended on the nature and enantiomeric composition of the PLLAs.

The extent of racemization of PLLAs was examined with ^{13}C NMR as shown in Fig. 3. The spectra for PLLA1 and PLLA2 exhibited five characteristic signals at 169.15, 169.19, 169.29, 169.37 and 169.52 ppm. According to the theoretical stereosequence distributions, the signal at 169.52 ppm was assigned to the isotactic (i, mm) sequence of the carbonyl carbon atom of successive L-lactic acid units. The peaks in the region between 169.29 and 169.37 ppm were tentatively assigned to the heterotactic (h, rm) sequence, and the peak at 169.15 ppm was assigned to the syndiotactic (s, rr) sequence.

^{13}C NMR spectra of PLLA composed of L- and D-lactic acid units were analyzed and the fine structures in the carbonyl atoms were discussed by Chabot and Vert [10]. Considering different components, the authors divided the carbonyl spectrum into three regions. The unique peak at the downfield was attributed to the isotactic triad. On the basis of such analysis, the extent of D-lactic acid units in PLLA1 and PLLA2 was estimated to be 12.9 mol% and 16.4 mol%, respectively.

The racemization reactions are most likely due to the dynamic equilibrium of ester interchange reactions occurring between the polymer chains [11]. During the ester interchange reaction, there are two ways in which the ester linkages between successive lactic acid units can cleave and reform. One is acyl–oxygen cleavage, which does not involve the chiral carbon in question. The other is alkyl–oxygen cleavage, in which the covalent bond between oxygen and the chiral carbon breaks and subsequently reforms; this results in an inversion of the configuration.

The change from the L-form to the D,L-form in the presence of the TNBT catalyst due to the racemization has been analyzed with DSC and XRD [12]. The strong proton acid promotes the breaking of the ester bond through the typical carbonyl–oxygen bond cleavage.

The results of the present study indicate that the probability of alkyl–oxygen cleavage increased, and resulted in the formation of the inverted configuration, as the reaction temperature rose. Nevertheless, the polymerization temperature as high as 180 °C was absolutely demanded to produce high-molecular-weight PLLA, because a large amount of very low molecular weight oligomeric species was formed (data not shown) from the direct condensation polymerization of L-lactic acid at lower polymerization temperatures.

In the case of the dehydropolycondensation reaction catalyzed by TNBT, the D-lactic acid units seemed to be

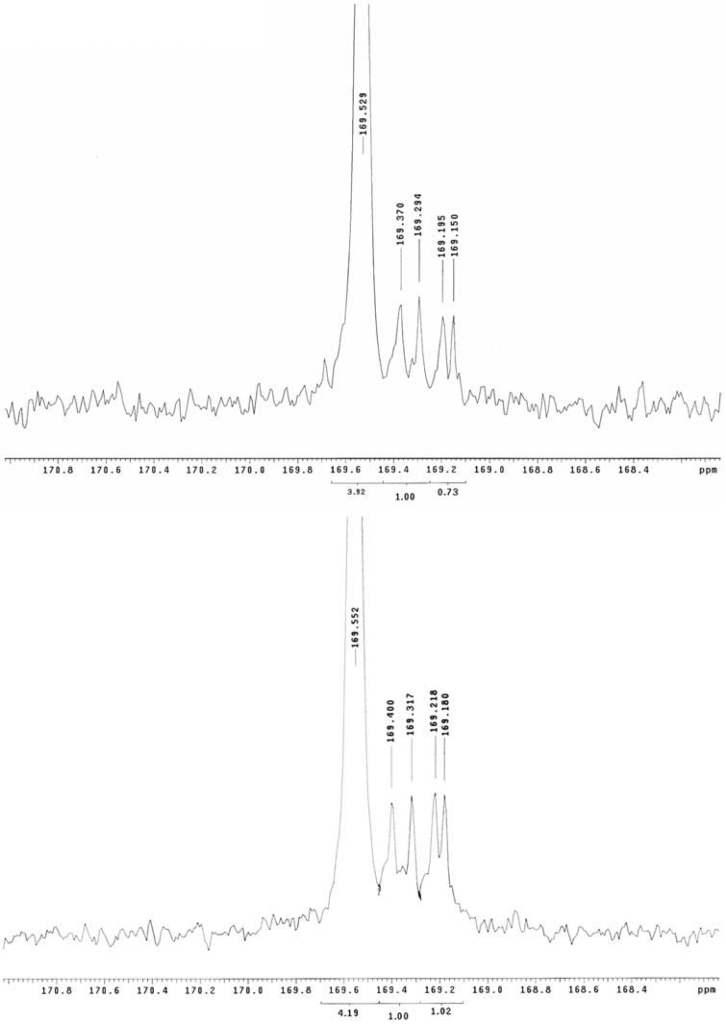

Fig. 3. ^{13}C NMR spectra of the carbonyl groups of PLLA1 and PLLA2.

incorporated into the backbone in a purely random manner. The splitting pattern of the signals was identical to those reported earlier in the literature [10].

4. Conclusion

PLLA was synthesized by the direct bulk condensation polymerization using titanium(IV) butoxide as a catalyst at different polymerization time. The duration of the decompression of the reaction pressure to 1 Torr is important to produce high-molecular-weight PLLA. When the polymerization reactor was decompressed extremely slowly step by step for 7 h, the molecular weight of PLLA reached as high as ~130,000. Increase of the time for the esterification reaction from 3 to 7 h also raised the molecular weight of PLLA from 30,000 to 120,000. ^{13}C NMR spectra of PLLA were analyzed to determine the configuration of the PLLA. The extent of D-lactic acid units in PLLA1 and PLLA2 was estimated to be 12.9 mol% and 16.4 mol%, respectively.

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