Effect of Polymerization Degree on Building-up Helical Structure of Oligo(L-lactic acid)

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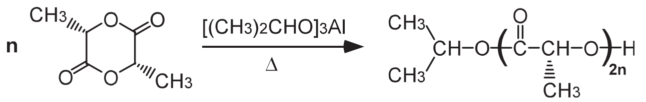
We synthesized oligo(L-lactic acid) with almost mono dispersion by using GPC fractionation technique, and could confirm from the circular-dichroic spectra that the number of repeating units of 8 to 10 was enough to build up the helical structure.

Chiral helix materials have large optical rotatory power and therefore, their application has caught much attention for optical elements and/or optical switching devices. Recently, Tajitsu et al. reported huge optical rotatory power of the chiral poly(L-lactic acid) crystals and demonstrated light modulation.[1,2] Such crystal films of poly(L-lactic acid) have no absorption in visible region, and wavelength dependency of optical and electro-optical properties was small. Therefore, such poly(L-lactic acid) crystal films were expected to apply various optical application such as polarization rotator, electro-optic modulator, and so on. However, these crystal films are difficult to process any form such as flexible and large flat area devices.

On the other hand, from the point of view of the preservation of the natural environment, highly biodegradable polymeric materials (biodegradable polymers) which can be recycled for use as a technological resource are being actively studied.[3] Because poly(lactic acid) is one of useful materials for such biodegradable application, plenty of synthetic studies have been carried out for not only thermal polymerization of the racemic monomer but also the catalytic polymerization of the chiral monomer. In the later case, the helical structure of poly(lactic acid)[4,5] was obtained by anionic polymerization using aluminium[6,7] or tin[8,9] complexes as catalyst. As such stereo-regular poly(lactic acid) is insoluble in common organic solvent, the random and/or block copolymers were also synthesized[10,11] in order to control the solubility, aggregation phase, degradation properties, and so on. However, the optical function such as optical rotatory power should densely exist for optical applications, it is anticipated that the oligomer exhibits good processability because of only low molecular weight without modification of the chemical structure.

In this study, we synthesized oligo(L-lactic acid) with narrow polydispersity using anionic polymerization technique and fractionating by gel-permeation chromatography (GPC) in order to determine the required number of repeating unit which is optimized helical structure. The anionic polymerization of oligo(L-lactic acid) followed the typical method as shown in Scheme 1.[6,7,11,12] L-lactide (LLA; purchased from Aldrich; purified by recrystallization from ethyl acetate), aluminum triisopropoxide ($\mathrm{Al(OiPr)_3}$; purchased from Tokyo Kasei; purified by distillation in vacuo) as anionic initiator were mixed in dried flask under nitrogen. The mixture was heated to 150 °C. When the reaction mixture became transparent, the temperature of mixture was lowered to 110 °C and kept for 24 h. Then, the reaction mixture was dissolved in methylene chloride, washed with 1 N HCl and water, dried over sodium sulfate. The white residue was obtained by removing solvent.



Scheme 1. Synthesis of oligo(L-lactic acid).

The polymerization degree was determined by ^{1}H NMR spectroscopy (Solvent: $\mathrm{CDCl_3}$ with 0.03% TMS) and the polydispersity by GPC (Shimadzu LC-10Vp System with Tosoh $\mathrm{G2000H_{XL}}$ chromatogel; eluent solvent was THF; calibrated by polystyrene standard), respectively. Figure 1 shows a representative ^{1}H NMR spectra of oligo(L-lactic acid) obtained from the reaction under $\mathrm{LLA/Al(O}i\mathrm{Pr)_3} = 14/1$ (mol/mol). Mainly, 4 kinds of peak were observed, the peak at 1.27 ppm (*d*), 1.59 ppm (*m*), 4.37 ppm (*q*) and 5.18 ppm (*m*) were assigned to $(\underline{\mathrm{CH_3}})_2\mathrm{CH}$–, $\underline{\mathrm{CH_3}}$–CH(O)(CO)–, $(\mathrm{CH_3})_2\underline{\mathrm{CH}}$–, and $\mathrm{CH_3}$–$\underline{\mathrm{CH}}$(O)(CO)–, respectively. As the peak around 1.6 ppm overlapped with peak of $\mathrm{H_2O}$ in solvent, the number of repeating unit (*n*) was evaluated from the area ratio of (peak d)/(peak c). Results of polymerization in various molar ratio of $\mathrm{LLA/Al(O}i\mathrm{Pr)_3}$ were summarized in Table 1, where the twice value (F) of molar ratio of $\mathrm{LLA/Al(O}i\mathrm{Pr)_3}$ were indicated as the expected repeating unit from the feed ratio. In the case of less than $\mathrm{F} = 20$, the polymerization degree n was only about half of F and polydispersion $M_\mathrm{w}/M_\mathrm{n}$ was larger than 1.2. In the case of larger than $\mathrm{F} = 28$, *n* was almost equal to F, and the polydispersion became rather narrow than $M_\mathrm{w}/M_\mathrm{n} = 1.1$. In the later case, the degree of the polymerization was controllable by feed ratio F, however, as mentioned below the melting point and optical rotatory power $[\alpha]^{25}_\mathrm{D}$ have already reached to the same value as those of high molecular weight poly(L-lactic acid). From these results, we concluded that oligo(L-lactic acid) whose number of repeating unit

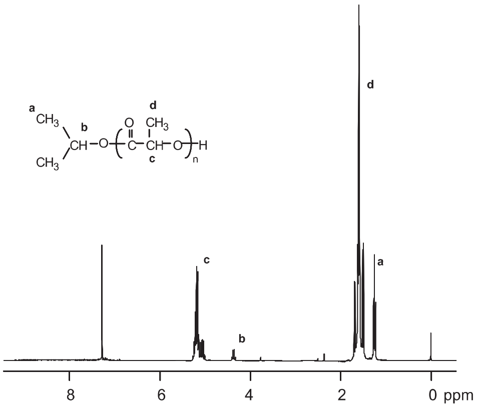


Figure 1. ^{1}H NMR spectra of poly(L-lactic acid).

Table 1. Polymerization results of poly(L-lactic acid).

$\mathrm{LLA/Al(O}i\mathrm{Pr)_3}$	Ave. n^a	$M_\mathrm{w}/M_\mathrm{n}{}^b$
5/1	5.0	1.23
10/1	8.6	1.45
14/1	33.3	1.09
18/1	35.6	1.04
20/1	37.1	1.10

[a] Determined by ^{1}H NMR.
[b] Determined by GPC (calibrated by polystyrene standard).

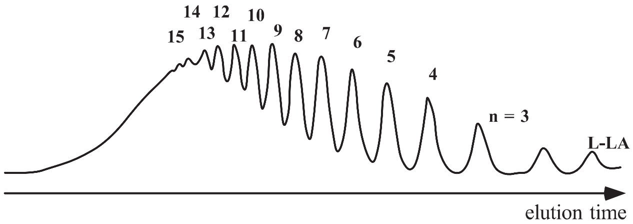


Figure 2. GPC curve of poly(L-lactic acid) (feed ratio of L-LA/Al(O*i*Pr)$_3$ = 10/1).

(n) was less than 20 with narrow dispersion could not be synthesized by the anionic polymerization according to the monomer/catalyst feed ratio. In the GPC curve of oligo(L-lactic acid) obtained from the reaction with low feed ratio, several independent peaks were observed as shown in Figure 2. Therefore, oligo(L-lactic acid) with almost monodispersion could be obtained by GPC-fractionation technique. In Figure 2, there are 15 independent peaks of oligomer in the range from $n = 3$ to 15, monomer (LLA), and one byproduct. We collected each peak fraction by GPC-fraction collector and obtained 13 fractions ($n = 3$–15; determined by ^{1}H NMR spectra) with narrow dispersity ($M_w/M_n \approx 1.001$; determined by GPC). As there were oligomers having odd number of repeating unit, ester transesterfication occurred during polymerization reaction. Moreover, oligo(L-lactic acid) having higher molecular weight obtained similar GPC-fraction procedure ($n = 16, 18, 21, 29, 42$, and 59) with narrow dispersity ($M_w/M_n \approx 1.03$). Such oligo(L-lactic acid) below $n = 13$ were liquid state at room temperature, in the range from $n = 14$–16 were sticky solid (like paraffin), and above $n = 18$ were solid state. The melting point of the oligo(L-lacrtic acid) were 80.3 °C for $n = 16$, 114.5 °C for $n = 21$ and 160.2 °C for $n = 59$, respectively. The melting point of optically pure poly(L-lactic acid) with n larger than 100 was reported to be 178 °C.[10] So, the oligomer with $n = 59$ attained to the similar nature of polymer in thermal properties. These oligo(L-lactic acid) were dissolved in acetonitrile (ca. 10^{-5}–10^{-6} M), and the circular-dichroic spectra of the solution were measured by JASCO J-820 spectropolarimeter. All oligo(L-lactic acid) have single CD peak at 210 nm (see Figure 3). The relationship between mean residual ellipticity (it means the molecular ellipticity per unit (–CO–CH(CH$_3$)–O–)) and number of repeating unit was shown in Figure 4. The mean residual ellipticity becomes the biggest in $n = 8$–10 and fixed above $n = 20$ at 80% of the maximum value. The difference of mean residual ellipticity between oligo(L-lactic acid) and L-lactic acid was supposed that oligo(L-lactic acid)s have higher-order structure. It is reported that poly(L-lactic acid) in crystal form have helical structure (10/3 pitch). Therefore, these relations suggested that helical structure of oligo(L-lactic acid) was developed according to increase of number of repeating unit below $n = 8$–10, and stabilized above $n =\approx 20$. The similar relation on the optical rotatory dispersion spectrum has been established. For example, optical rotatory power $[\alpha]$ of oligo (L-lactic acid) above $n = 10$ was -150.7 (at 700 nm) to -642.6 (at 400 nm) which is the same as those of poly(L-lactic acid).[10] These facts indicate that the number of repeating units = 8–10 is enough to build up the helical structure. Therefore, it is expected that oligo(L-lactic acid) having number of repeating unit above 8–10 have same optical properties independent of number of repeating unit. Because the phase of oligo(L-lactic acid) having number of repeating unit below 15 is liquid or sticky amorphous solid, it is possible to choose the any optical device structure.

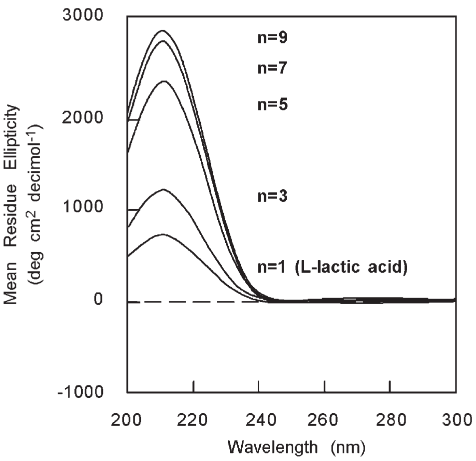


Figure 3. Circular-dichroic spectra of L-lactic acid and oligo(L-lactic acid)s in acetonitrile.

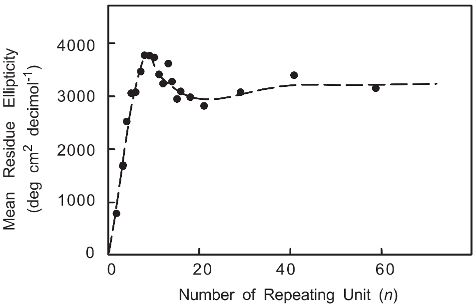


Figure 4. Relationship between number of repeating unit (n) and ellipticity per unit at 210 nm for oligo- and poly(L-lactic acid).

In summary, we synthesized oligo(L-lactic acid) with narrow polydispersity using conventional method. From the unique circular-dichroic properties about the relationship between mean residual ellipticity and number of repeating unit, we found that ellipticity of oligo(L-lactic acid) have a maximal value at $n = 8$–10 and the helical structure was completely built up at this number of repeating unit. As these oligo(L-lactic acid) have a good processability, there are advantages for large area flexible optical devices. The optical device performance, for an example such as electro-optic effect, of oligo(L-lactic acid) is examined now in progress.

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