

# Carbon-13 solid state NMR study on uniaxially oriented poly(L-lactic acid) films

Takuro Ito<sup>a</sup>, Yoshitsugu Maruhashi<sup>a</sup>, Makoto Demura<sup>b</sup>, Tetsuo Asakura<sup>b,\*</sup>

<sup>a</sup>Co. R&D Toyo Seikan Group, Yokohama, Kanagawa 240, Japan

<sup>b</sup>Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

Received 12 November 1998; received in revised form 2 March 1999; accepted 16 March 1999

---

## Abstract

The structure of uniaxially oriented poly(L-lactic acid) (PLLA) with different drawn ratios was studied in the solid state using <sup>13</sup>C NMR spectroscopy. The spectra of uniaxially oriented PLLA films were observed by changing the angle between the draw direction of the samples and the magnetic field. The observed spectra of the samples with draw ratios of 3 and 4 were well reproduced by the simulated spectra, indicating the presence of two kinds of oriented components and one unoriented component in these samples. The angles,  $\theta_{C=O}$ , between the C=O bond direction of PLLA and the oriented axis of the chain were calculated to be 132 and 128° for two oriented components, respectively, by assuming that the chemical shift tensor direction relative to the molecular symmetry axis of the carbonyl carbon nucleus of PLLA was the same as that for the carbonyl carbon of poly(ethylene terephthalate) reported previously. The angles, 132 and 128°, are in agreement with the reported angles for PLLA 3<sub>1</sub> helix model in the  $\beta$  form and PLLA 10<sub>3</sub> helix model in the  $\alpha$  form, respectively. The relatively small value of  $p$  (characterizing the distribution of the fiber axis) obtained in the simulation indicates the high orientation in the oriented domain in the PLLA film samples. The fraction of each component in the samples was also determined. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Poly(L-lactic acid); <sup>13</sup>C solid state NMR; Chemical shift anisotropy

## 1. Introduction

Poly(L-lactic acid) (PLLA) is one of the biodegradable polymers and is formed from L-lactic acid produced from natural renewable sources such as corn. This polymer decomposes rapidly and completely in a typical compost environment which makes it an ideal replacement for non-degradable polymers in numerous applications like yard-waste bag and food containers, etc. [1,2]. Thus, because of its potential applications, a large number of studies on PLLA, synthesis [3–6], morphology [7–10], thermal and mechanical properties [11–16], and degradation kinetics in both in vitro and in vivo [17–21] have been reported including the <sup>13</sup>C CP MAS NMR study [22]. Depending on the spinning and drawing conditions, two crystal structures are obtained. The pseudoorthorhombic  $\alpha$  structure ( $a = 1.06$  nm,  $b = 0.61$  nm, and  $c = 2.88$  nm) contains two chains in the unit cell and is found at relatively low drawing temperatures and/or low hot-draw ratios. On the contrary, a second  $\beta$  structure (orthorhombic unit cell with  $a = 1.03$  nm,  $b = 1.82$  nm, and  $c = 0.90$  nm) appears at

higher drawing temperatures and/or higher hot-draw ratios. The similar values of the cell dimensions are also reported by Okihara et al. [23]. The chain conformations of the  $\alpha$  and  $\beta$  structures are left-handed 10<sub>3</sub> and 3<sub>1</sub> helices, respectively. The preference for one of the two structures has been considered depending on the packing of PLLA chains strongly.

The recently developed solid state <sup>13</sup>C and <sup>15</sup>N CP NMR methods for the structural analysis of uniaxially aligned polymers including proteins are well suited for the structural analysis of polymers at atomic resolution [24,25]. In solid state NMR studies of oriented samples, orientation-dependent nuclear spin interaction tensors serve as probes with which the relative orientations of specific bond vectors can be determined. In our previous paper [26], <sup>13</sup>C solid state NMR spectra of uniaxially oriented poly(ethylene terephthalate) PET films with different draw ratios have been observed in order to determine the fraction of highly oriented and low oriented structures together with non-oriented structures in the films. In addition, the highly oriented structure is the same as that reported from X-ray diffraction analysis. However, the low oriented structure detected from such solid state NMR analysis is a unique

\* Corresponding author.

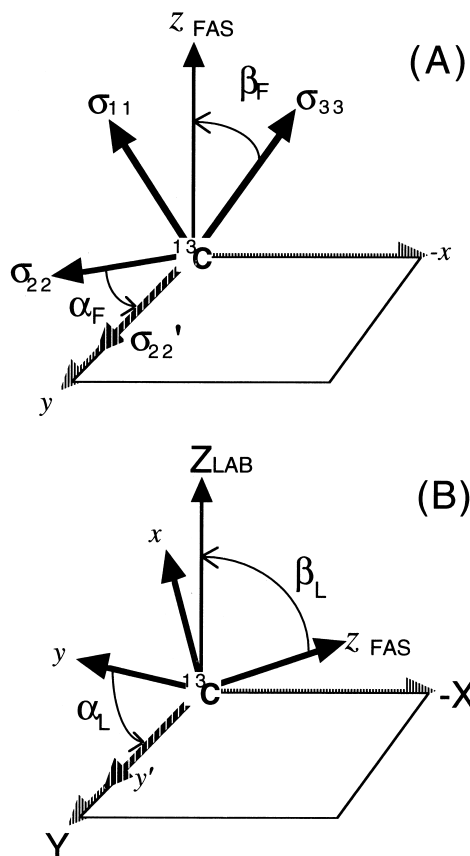


Fig. 1. Transformations from the  $^{13}\text{C}$  principal axis system (PAS) to the fiber axis system (FAS) (A) and from the FAS to the laboratory (LAB) frame of reference (B). The PAS is related to the FAS by the Euler angles,  $\alpha_F$  and  $\beta_F$ . The FAS is related to the LAB reference frame by the Euler angles,  $\alpha_L$  and  $\beta_L$ . The macroscopic fiber direction is assumed to be the same as that of the mechanically drawn direction (MD) of the PLLA film.

structure that could not be observed in the X-ray diffraction analysis. The NMR is more sensitive to the shorter range ordered structure than X-ray diffraction and can be recognized as an ordered structure with a relatively large distribution axis. In the structural analysis, the attention is focused on the carbonyl carbons with large chemical shift anisotropy. The  $^{13}\text{C}$  carbonyl carbon labeled PET samples were used to eliminate the contribution of the aromatic carbon peaks overlapped in the natural abundance  $^{13}\text{C}$  CP spectrum [27,28]. Such solid state NMR analyses have been already applied to uniaxially aligned silk fibers [29–31] and polyamide fibers [32–35]. Especially, the determination of the torsion angles of silk fibroin backbone chains was possible by the combination of  $^{13}\text{C}$  and  $^{15}\text{N}$  solid state NMR, and stable isotope labeling of the silk samples.

In the present paper,  $^{13}\text{C}$  solid state NMR spectra of uniaxially oriented PLLA films with different draw ratios are reported as a function of the angle between the mechanically drawn direction and the magnetic field in order to determine details of the structure of oriented PLLA samples including the fraction of the individual structural component.

Because of the large  $^{13}\text{C}$  chemical shift difference of

methyl, methine and carbonyl carbons in the PLLA spectra, the angular-dependent spectra could be observed for each spectrum without overlapping. However, in this paper, our attention is focused on the carbonyl carbon analysis because of the large chemical shift anisotropy. In addition, we did not discuss whether or not the PLLA chains are oriented upwards and downwards at the corresponding position in the unit cell although the coexistence of the upward and downward chains might change the PLLA spectra because of the difference in the packing effect from only upward or downward chains.

## 2. Theory

The method of the spectral analysis is essentially the same as that in the previous papers [26,29] and so is only briefly described here. The  $^{13}\text{C}$  chemical shift anisotropy (CSA) principal axis system (PAS) is the reference frame in which the  $^{13}\text{C}$  CSA tensor is diagonal with principal components  $\sigma_{11} < \sigma_{22} < \sigma_{33}$ . These tensor elements can be determined by observing the powder pattern arising from a randomly dispersed sample. The FAS (fiber axis system) is a reference frame fixed in the aligned sample, defined in such a way that such that the macroscopic fiber axis lies in the  $z$  direction (Fig. 1(A)). Here, the macroscopic fiber direction is assumed to be the same as that of the mechanically drawn direction (MD) of the films. In addition, the sample is considered to be of axial symmetry with respect to orientation.

To transform the  $^{13}\text{C}$  CSA tensor from the PAS representation to the FAS representation, the  $^{13}\text{C}$  CSA tensor is first rotated about  $\sigma_{33}$  by  $\alpha_F$  to bring  $\sigma_{22}$  into the  $xy$  plane (Fig. 1(A)) followed by a rotation about  $\sigma_{22}$  by  $\beta_F$  to bring  $\sigma_{33}$  coincident with  $z_{\text{FAS}}$ . The NMR spectra are observed in the laboratory frame of reference (LAB), in which the magnetic field ( $B_0$ ) lies in the  $Z$  direction (Fig. 1(B)). The angles,  $\alpha_L$  and  $\beta_L$ , are the Euler angles that transform the FAS into the LAB frame of reference. Only two angles are required for this transformation because the NMR experiment is sensitive only to the component of the tensor parallel to  $B_0$ . Therefore, the position of the FAS within the  $XY$  plane is arbitrary, and the Euler angle,  $\gamma_L$ , conveniently can be set to zero. The angle,  $\beta_L$ , is set in the experiment as an angle between  $z_{\text{FAS}}$  and  $Z_{\text{LAB}}$  ( $B_0$ ). On the contrary, all values of  $\alpha_L$  are equally represented in the spectrum ( $0^\circ < \alpha_L < 360^\circ$ ).

Since the samples usually have an orientational distribution around the fiber axis, a Gaussian distribution (around  $\beta_L$ ) is assumed with the distribution characterized by  $p$ , the standard deviation of the assumed Gaussian distribution, defined as follows [26]:

$$f(x) = 1/(2\pi p) \exp(-(x - \beta_L)^2/2p^2)$$

where  $f(x)$  is the probability of the oriented polymer molecules having angle  $x$  between the fiber axis and  $B_0$ .

The possible orientations obtained by the above method

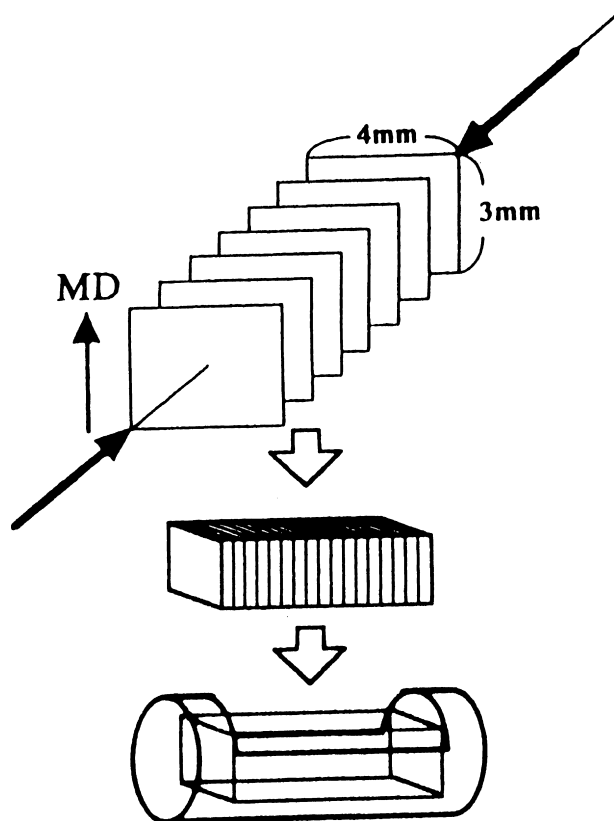


Fig. 2. Preparation of a uniaxially oriented block sample of PLLA films for  $^{13}\text{C}$  CP NMR observations as a function of  $\beta_L$ , the angle between the mechanically drawn direction MD and the magnetic field.

can be readily expressed in terms of bond angle orientations, provided the orientation of the  $^{13}\text{C}$  PAS is known relative to the bonds of interest. Here, we concentrated on the analysis of the carbonyl carbon spectrum. The angles between  $^{13}\text{C}$  PAS and molecular symmetry axis (MSA) frame of reference (the C–C bond axis, C–O and C=O bonds of PLLA molecule) for the carbonyl carbon were assumed to be the same as those for PET. Namely, the  $\sigma_{11}$  axis is approximately perpendicular to the O–C=O plane. The  $\sigma_{33}$  makes an angle of  $29^\circ$  with the C–O bond direction and  $\sigma_{22}$  is very close to the C=O bond direction in the O–C=O plane.

### 3. Experimental

#### 3.1. Materials

A commercial sample of PLLA produced from Mitsui Chemical Ltd. (Japan) was used for solid state NMR observation. The weight average molecular weight is  $M_w = 1.6 \times 10^5$  which is determined with the GPC method in chloroform at  $40^\circ\text{C}$ , using MIXED-C (300–7.5 mm) GPC column. The uniaxial films were prepared as follows. Amorphous PLLA films (2 mm thick) were first obtained by injection-molding method: melting at a temperature of  $200^\circ\text{C}$  and then quenching at  $16^\circ\text{C}$ . The uniaxial films were then

prepared with a draw rate of 10 m/min at  $70^\circ\text{C}$ , made by the one-way stretching of injection-mold sheet using Biaxial Stretching Machine (Toyo Seiki Ltd.). The films ( $4 \times 3 \text{ mm}^2$ ) with draw ratio of 2, 3, and 4 were set as shown in Fig. 2 and used for  $^{13}\text{C}$  NMR observation.

The  $[1-^{13}\text{C}]$ PLLA sample ( $M_w = 1.1 \times 10^5$ ) was prepared by the polymerization of a mixture of  $[1-^{13}\text{C}]$  L-lactic acid (98% enrichment, Shoko Tsusho Ltd., Japan) in 30 mol% and natural abundance L-lactic acid in 70 mol%. Taking into account the loss in the polymerization process, the mixture of labeled and unlabeled monomers was used. The powder of  $[1-^{13}\text{C}]$  labeled PLLA was used for the determination of the chemical shift tensors of the carbonyl carbon.

#### 3.2. $^{13}\text{C}$ NMR measurements

A JEOL EX-270 spectrometer was used for  $^{13}\text{C}$  solid state NMR observation operating at 67.8 MHz at  $25^\circ\text{C}$ . The cross-polarization (CP) technique (Hartmann–Hahn-matched conditions) with  $\text{CP}_{\text{mix}} = 2 \text{ ms}$  was used with a recycle delay of 5 s and the spin locking field strength was 1.2 mT. Phase cycling was used to minimize artifacts. A goniometer was used to adjust the sample at different angles,  $\beta_L$ , 0, 30, 60 and  $90^\circ$  between the draw direction MD and the magnetic field. Typically 15 000 FIDs were accumulated for each spectrum. The chemical shift of methyl peak of hexamethylbenzene was used as an external chemical shift reference and converted as 17.3 ppm from TMS. All the peak simulations were performed with the programs made by us [24,25] using a INDIGO II silicon graphics work station.

### 4. Results

#### 4.1. $^{13}\text{C}$ solid state NMR spectra of oriented PLLA samples

Fig. 3 shows the  $^{13}\text{C}$  CP NMR spectra of a PLLA sample (draw ratio 2) as a function of the angle,  $\beta_L$ . Because of the large  $^{13}\text{C}$  chemical shift difference among the methyl, methine and carbonyl peaks, the angular-dependence can be studied for each spectrum clearly. The three main peaks with different shapes are observed. The carbonyl peaks observed at the lowest field show large chemical shift anisotropies. The peak shapes are essentially independent of the angle between the MD direction and magnetic field which is a similar case of PET sample with draw ratio of 2 reported previously. The methyl peaks at the highest field (about 18 ppm) have shoulders at both sides and thus show chemical shift anisotropy although the degree of the anisotropy is not large. The angle dependence of the shape can be neglected. On the contrary, a small angle dependence was observed for the methine peaks; two peaks at  $\beta_L = 0^\circ$  and asymmetric peaks with a tail at the higher field with increasing  $\beta_L$ . This indicates the initial stage of the orientation of the PLLA chain is observed clearly at only the methine peak. This will be discussed later in detail.

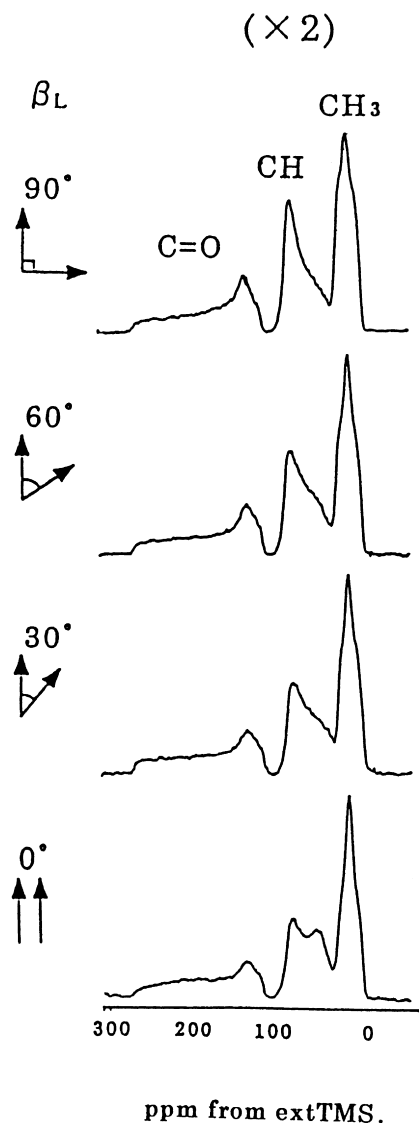


Fig. 3. The  $^{13}\text{C}$  CP NMR spectra of uniaxially draw ( $\times 2$  at  $70^\circ\text{C}$ ) PLLA film as a function of  $\beta_L$ , the angle between the draw direction and the magnetic field.

The angle-dependent spectra of PLLA samples with draw ratios of 3 and 4 are shown in Fig. 4. The line shapes of three kinds of carbons including the angle-dependent spectral patterns are similar between the samples with draw ratios of 3 and 4. The methyl peak becomes sharper than that of the sample with a draw ratio of 2 at  $\beta_L = 0^\circ$ . With increasing  $\beta_L$ , the intensities of both sides of the main methyl peak increase. At  $\beta_L = 90^\circ$ , the head of the peak tends to be flat.

The shapes of the methine peaks change dramatically with increasing  $\beta_L$ . The methine peak becomes sharp and with a shoulder at a lower field at  $\beta_L = 0^\circ$ . At  $\beta_L = 30^\circ$ , the peak becomes broader and a small peak is observed at the higher field than the main peak at  $\beta_L = 0^\circ$ . The peak becomes sharp again at  $\beta_L = 90^\circ$ , but the peak position shifts to a lower field than that at  $\beta_L = 0^\circ$ .

The carbonyl peaks also change dramatically with

increasing  $\beta_L$ . The peak looks a broad doublet at  $\beta_L = 0^\circ$  and becomes sharper at  $\beta_L = 90^\circ$ . Here, we concentrate to analyze the change in these carbonyl peaks below.

#### 4.2. $^{13}\text{C}$ solid state NMR powder pattern spectrum of $[1-^{13}\text{C}]\text{PLLA}$ sample

In the process of structural analysis for oriented polymers with angle-dependent solid state NMR, it is required to determine the chemical shift tensor values of the carbonyl peak of PLLA powder precisely. Therefore, the determination was performed with carbonyl carbon labeled PLLA powder as determined for PET sample previously. Fig. 5 shows the expanded carbonyl carbon region in the  $^{13}\text{C}$  CP NMR spectrum of  $[1-^{13}\text{C}]\text{PLLA}$  powder sample. By the simulation [29], the chemical shift tensor values were determined to be  $\sigma_{11} = 113$  ppm,  $\sigma_{22} = 134$  ppm and  $\sigma_{33} = 266$  ppm. Here, the line broadening was assumed to be 5 ppm in the simulation. Thus, the  $\sigma_{\text{iso}}$  chemical shift value of the carbonyl peak of amorphous PLLA sample was 171 ppm and coincide with the value, 170.2 ppm, reported from the  $^{13}\text{C}$  CP/MAS NMR spectrum of amorphous PLLA sample [22]. The chemical shift tensor values determined here will be used for the structural analysis of the oriented components in the PLLA samples below.

#### 4.3. Structural analyses from $^{13}\text{C}$ NMR carbonyl carbon peaks of oriented PLLA samples with draw ratios of 3 and 4

Since the spectral patterns of the carbonyl carbons including the angle-dependent patterns are similar between the samples with draw ratios of 3 and 4, only the carbonyl carbon region of the sample with draw ratio of 3 is expanded in Fig. 6. The simulated spectra (dot line) are also shown. The observed spectra can be reproduced by assuming the presence of unoriented powder component and two oriented components in the sample. The Euler angles  $\alpha_F$  and  $\beta_F$  defined in Fig. 1 were determined as 5 and  $42^\circ$ , respectively, and the distribution parameter  $p$  determined by assuming Gaussian was  $11^\circ$  for one oriented component. For another oriented component, the angles  $\alpha_F$  and  $\beta_F$  were 5 and  $35^\circ$ , respectively, with the distribution parameter  $p$  is  $9^\circ$ . By assuming that the angles between  $^{13}\text{C}$  PAS and molecular symmetry axis (MSA) frame of reference (the C–C bond axis, C–O and C=O bonds of PLLA molecule) for the carbonyl carbon are the same as those for the carbonyl carbon of PET sample, the angle,  $\theta_{\text{C=O}}$ , between the C=O bond and MD direction can be calculated. The angle,  $\theta_{\text{C=O}}$ , was  $132^\circ$  for the former oriented component which corresponds to the  $\beta$  structure and left-handed  $3_1$  helix. Similarly, the angle for the latter oriented component could be calculated as  $128^\circ$  which corresponds to the  $\alpha$  structure and left-handed  $10_3$  helix. Judging from the  $p$  value, the latter component is more highly oriented. The structural parameters obtained for these uniaxially oriented PLLA films are summarized in Table 1 together with the fraction of each component. Although the structural

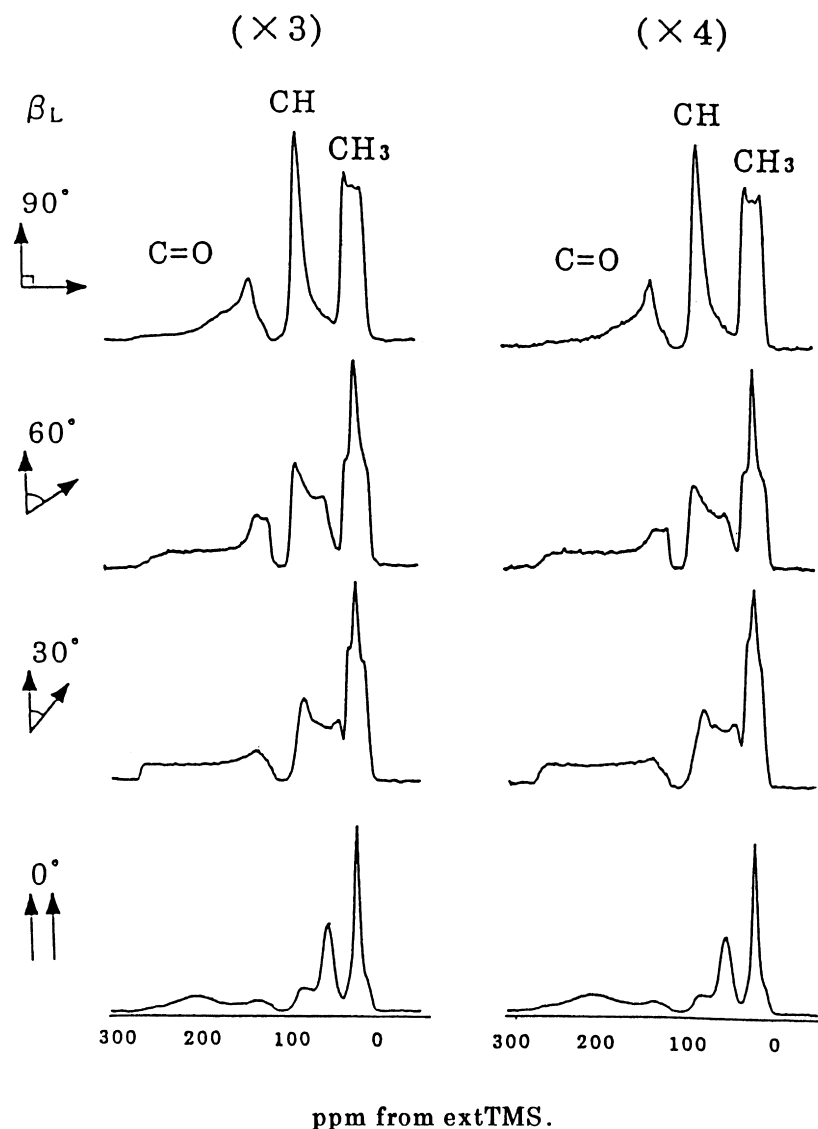


Fig. 4. The  $^{13}\text{C}$  CP NMR spectra of uniaxially draw ( $\times 3$  and  $\times 4$  at  $70^\circ\text{C}$ ) PLLA film as a function of  $\beta_L$ , the angle between the draw direction and the magnetic field.

parameters of the two oriented components are almost the same between the samples of draw ratios of 3 and 4 listed in Table 1, the fraction of each component is slightly different between two samples. That is, the fraction of the low oriented component in PLLA sample increases from 30% at draw ratio of 3 to 36% at a draw ratio of 4. Similarly, the fraction of high oriented component increases from 20% (draw ratio: 3) to 24% (draw ratio: 4). Instead of this, the fraction of the unoriented component decreases from 50% (draw ratio: 3) to 40% (draw ratio: 3).

## 5. Discussion

The large  $^{13}\text{C}$  chemical shift difference among the methyl, methine and carbonyl carbon peaks of PLLA spectra enable us to analyze all peaks from the angular-

dependent spectra for obtaining structural information although only carbonyl carbon peaks are used in this paper. Actually, the peaks of the carbonyl and methyl carbons of PLLA sample with a draw ratio of 2 shows angular-independent patterns, but the shape of the methine carbon peak is different among  $\beta_L = 0^\circ$  and other angles. This indicates the initial stage of the orientation of the PLLA chain is observed clearly at only the methine peak. Miyata et al. reported that the oriented components in the uniaxially drawn PLLA films were clearly observed between the samples with draw ratios of more than 2.5 from the DSC measurements [36]. Walls reported that the stress-induced crystallization process of PET sample occurs for uniaxially draw ratios between 2 and 3 from ATR-IR measurement [37]. Thus, even in the case of the PLLA sample with a draw ratio of 2, the initial orientation in the sample occur locally and this is

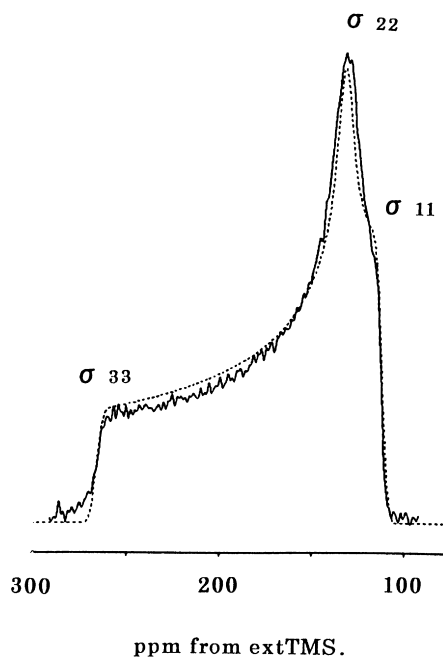


Fig. 5. The  $^{13}\text{C}$  powder pattern spectra of  $^{13}\text{C}$ -carbonyl carbon labeled PLLA powder. (The observed spectrum: solid line and the simulated spectrum: dotted line.) The  $^{13}\text{C}$  chemical shift tensors are determined as  $\sigma_{11} = 113$  ppm,  $\sigma_{22} = 134$  ppm and  $\sigma_{33} = 266$  ppm ( $\sigma_{\text{iso}} = 171$  ppm).

monitored with the methine carbon peaks with  $^{13}\text{C}$  solid state NMR.

The three different components (one disordered component and two oriented components) were observed in the spectra of the oriented PLLA samples with draw ratio of 3 and 4. The angle,  $\theta_{\text{C=O}}$ , between the C=O bond and MD direction could be calculated for the oriented components. The angle,  $\theta_{\text{C=O}}$ , was  $132^\circ$  for one oriented component which corresponds to the  $\beta$  structure and left-handed  $3_1$  helix, and  $128^\circ$  which corresponds to the  $\alpha$  structure and left-handed  $10_3$  helix for another oriented component. Hoogsteen et al. reported the presence of a mixture of  $\beta$  ( $3_1$  helix) and  $\alpha$  structures ( $10_3$  helix) in the PLLA fiber and the influence of the two crystal modifications on the ultimate fiber properties was discussed. In fibers containing a mixture of  $\alpha$  and  $\beta$  structures, the latter was considered to bear most of the load during stress–strain experiments. In addition, meridional small-angle X-ray scattering experiments by them yielded a maximum for fibers containing only a structure pointing to a lamellar folded-chain morphology. On the contrary, the  $\beta$  structure seemed to correspond to a fibrillar morphology. Differential scanning calorimetry on unconstrained fibers showed that the  $\beta$  structure melts at a lower temperature than the  $\alpha$  structure [9]. Thus, it is important to determine the relative amounts of both crystal modifications,  $\alpha$  and  $\beta$  forms, as well as the fraction of non-crystal components in oriented PLLA samples. In the spectral simulation, the high field peak of PLLA sample with a draw ratio of 3 observed at  $\beta_L = 0^\circ$  indicates the presence of the unoriented component in the

Table 1

Structural parameters (degrees) for the ordered components and fraction (%) of each component for uniaxially oriented PLLA films determined from  $^{13}\text{C}$  CP NMR (the definition of the angles,  $\alpha_F$  and  $\beta_F$ , is shown in Fig. 1(A) and  $\alpha_F$  was  $5^\circ$ )

Draw ratio at $70^\circ\text{C}$	$p^a$	$\beta_F$	$\theta^b$	Fraction (%)	Order level
×2	–	–	–	100	Disordered
	–	–	–	50	Disordered
×3	11	42	132	30	Low <sup>c</sup>
	9	35	128	20	High <sup>d</sup>
×4	–	–	–	40	Disordered
	11	42	132	36	Low <sup>c</sup>
	9	35	128	24	High <sup>d</sup>

<sup>a</sup> The orientational distribution around the fiber axis.

<sup>b</sup> The angle between the C=O bond direction and the MD direction of oriented PLLA films.

<sup>c</sup> Low ordered component.

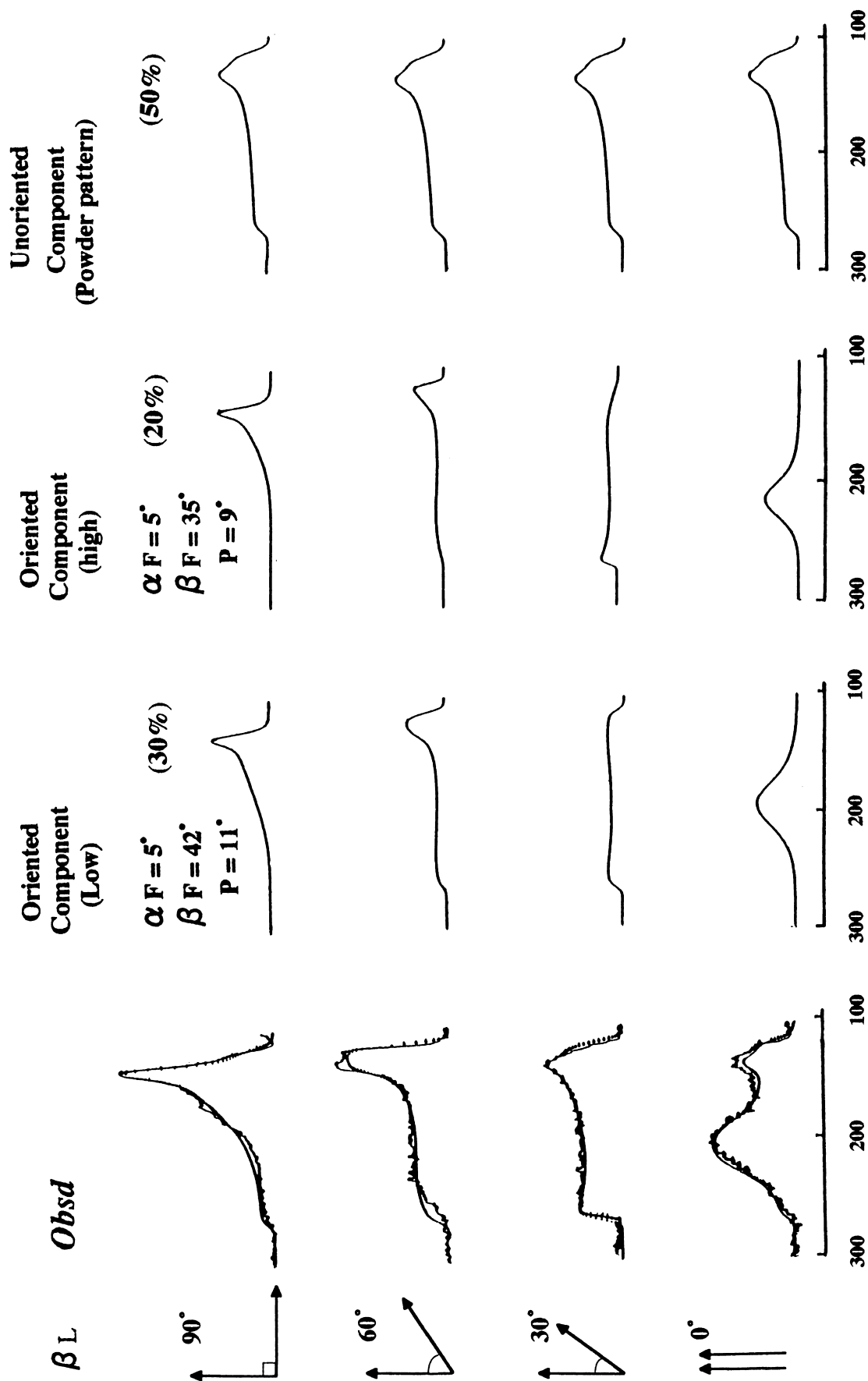
<sup>d</sup> High ordered component.

sample. Four kinds of observed spectra with different  $\beta_L$  angles should be reproduced as functions of fraction of each component,  $\alpha_F$  and  $\beta_F$  values, and  $p$  values. Thus, the structural parameters including fraction of each component can be determined with high precision. It is reasonable that the fraction of  $\alpha$  and  $\beta$  structures increases with increasing draw ratio from 3 to 4 although the degree of the increase is not much (Table 1).

Okihara et al. reported that a  $3_1$  PLLA helix ( $\beta$  structure) is more stable than the PLLA  $10_3$  helix in the  $\alpha$ -form crystal from the conformational energy calculation and therefore the  $\beta$ -form crystal in drawn films should be more stable than the  $\alpha$ -form crystal. However,  $3_1$  PLLA helix could not be packed densely in a crystal comprising helices of the same helical sense and therefore the  $\alpha$ -form is rather stable than the  $\beta$ -form in view of packing considerations. Actually, the  $\beta$ -form is easily transformed to the  $\alpha$ -form by annealing. The fraction of  $\beta$ -form is 50% larger than that of  $\alpha$ -form for oriented PLLA samples with draw ratios of 3 and 4 prepared in this experiment. This tendency is the same even if the draw ratio was changed from 3 to 4. The difference was the value of  $p$  (characterizing the distribution of the fiber axis). The value of the  $\beta$ -form is slightly larger than that of the  $\alpha$ -form although the value itself is relatively small. This is in agreement with the packing considerations by Okihara et al.

## 6. Conclusions

The  $^{13}\text{C}$  CP NMR spectra of uniaxially oriented poly(L-lactic acid) films observed as a function of the draw direction and magnetic field provide the determination of the fraction of each component, two oriented and one unoriented component. In addition, from the determination of the angles between the C=O bond axis and the draw direction for the two oriented components, the presence of the  $\beta$



ppm from ext TMS.

Fig. 6. The  $^{13}\text{C}$  CP NMR spectra of uniaxially drawn ( $\times 3$  at  $70^\circ\text{C}$ ) PLLA film observed as a function of  $\beta_L$ , the angle between the draw direction and the magnetic field. The  $^{13}\text{C}$  carbonyl carbon region was expanded. The solid and dotted lines show the observed and simulated spectra, respectively. The fractions of three components, non-oriented (50%) and the two oriented (30 and 20%) ones were determined by simulations. The structural parameters determined were  $\alpha_F = 5^\circ$ ,  $\beta_F = 42^\circ$ , and  $p = 11^\circ$  (low oriented component) and  $\alpha_F = 5^\circ$ ,  $\beta_F = 35^\circ$ , and  $p = 9^\circ$  (high oriented component), respectively.

structure (left-handed  $3_1$  helix) and the  $\alpha$  structure (left-handed  $10_3$  helix) in the sample was clarified as well as the relative amounts and the distribution of the chain axis of each structure. These structural analyses were performed with only the carbonyl carbon region in the spectra. In future, if the methyl and methine carbon regions will be analyzed with a similar manner, the results obtained here will be confirmed and a further detailed structural information of oriented PLLA films will be obtained.

### Acknowledgements

We are grateful to Mr Masanobu Ajioka, Mitsui Chemical Ltd., for preparing the isotope labeled PLLA polymer. T.A. acknowledges support from the Program for Promotion of Basic Research Activities for Innovative Biosciences and a Grant-in-Aid of the Ministry of Education, Science and Culture of Japan.

### References

- [1] Doi Y, Saito K, Sawada H, Tanaka H, Tokiwa Y, Fukuda K, Matsumura H, Yoshida Y. In: Doi Y, editor. Biodegradable plastic handbook. Biodegradable Polymer Institute Publisher, 1995.
- [2] Sinclair RG. JMS—Pure Appl Chem 1996;A33(5):585.
- [3] Kohn FE, van den Berg JWA, van Ridde G, Fejen J. J Appl Polym Sci 1984;29:4265.
- [4] Kricheldorf HR, Dunsing R. Makromol Chem 1986;187:1611.
- [5] Leenslag JW, Pennings AJ. Makromol Chem 1987;188:1809.
- [6] Jedlinksi Z, Watach W, Kurcok P, Adamus G. Makromol Chem 1991;192:2051.
- [7] Vasanthakumari R, Pennings AJ. Polymer 1983;24:175.
- [8] Kishore K, Vasanthakumari R. J Polym Sci, Polym Phys Ed 1984;22:537.
- [9] Hoogsteen W, Postema AR, Pennings J, ten Brinke G, Zugenmaier P. Macromolecules 1990;23:634.
- [10] Mazzullo S, Paganetto G, Celli A. Progr Polym Sci 1987;87:32.
- [11] Jamshidi K, Hyon SH, Ikada Y. Polymer 1988;29:2229.
- [12] Leenslag JW, Kroes MT, Pennings AJ, Vander lei B. New Polym Mater 1988;1:111.
- [13] Celli A, Scandola M. Polymer 1992;33:2699.
- [14] Engelberg I, Kohn J. Biomaterials 1991;12:292.
- [15] Leenslag JW, Pennings AJ. Polymer 1987;28:1695.
- [16] Migliaresi C, Cohn D, De Lollis A, Fambri L. J Appl Polym Sci 1991;43:83.
- [17] Migliaresi C, Fambri L, Cohn D. J Biomater Sci, Polymetr Edn 1994;5:591.
- [18] Leenslag JW, Gogolewski S, Pennings AJ. J Appl Polym Sci 1984;29:2829.
- [19] Li S, Garreau H, Vert M. J Mater Sci Mater Med 1990;1:198.
- [20] Dauner M, Muller E, Wagner B, Planck H. In: Planck H, Dauner M, Renardy M, editors. Degradation phenomena, on polymeric biomaterials. Berlin: Springer, 1992. p. 107.
- [21] Chawla AS, Chang TMS. Biomater Med Dev, Art Org 1985;13:153.
- [22] Khalid MT, Robert K, John MZ, Nancy UB, Matthew AD, Eric J. Macromolecules 1996;29:8844.
- [23] Okihara, Tsuji M, Kawaguchi A, Katayama K, Tsuji H, Suong H, Ikada Y. J Macromol Sci Phys 1991;B30(1–2):119.
- [24] Asakura T, Demura M, Nishikawa N. In: Webb GA, editor. Ann Rep NMR Spectrosc. London: Academic Press, 1997. p. 301.
- [25] Asakura T, Demura M. In: Ando I, Asakura T, editors. Solid state NMR of polymers. Amsterdam: Elsevier, 1998. p. 307.
- [26] Asakura T, Konakazawa T, Demura M, Ito T, Maruhashi Y. Polymer 1996;37:1965.
- [27] Chmelka BF, Schmidt-Rohr K, Spiess HW. Macromolecules 1993;26:2282.
- [28] Gebrielse W, Angard GH, Feyen FC, Veeman WS. Macromolecules 1994;27:5811.
- [29] Nicholson LK, Asakura T, Demura M, Cross TA. Biopolymers 1993;33:847.
- [30] Asakura T, Yamazaki Y, Seng KW, Demura M. J Mol Spectrosc 1998;446:179.
- [31] Demura M, Minami M, Asakura T, Cross TA. J Am Chem Soc 1998;120:1300.
- [32] Asakura T, Yoe J-H, Demura M, Ito T, Fujito T, Imanari M, Nicholson LK, Cross TA. Macromolecules 1993;26:6660.
- [33] Yoe J-H, Demura M, Asakura T, Fujito T, Imanari M, Nicholson LK, Cross TA. Solid State NMR 1994;3:209.
- [34] Asakura T, Yoe J-H, Ando I. Polym J 1994;26:229.
- [35] Yoe J-H, Asakura T, Shimazaki H. Makromol Chem Phys 1994;195:1423.
- [36] Miyata T, Yachida T, Masuko T. Seni Gakkaishi 1998;54:261.
- [37] Walls DJ, Coburn JC. J Polym Sci, Part B: Polym Phys 1992;30:887.