

# Solid-state $^{13}\text{C}$ NMR analyses of the structures of crystallized and quenched poly(lactide)s: Effects of crystallinity, water absorption, hydrolytic degradation, and tacticity

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## ABSTRACT

The effects of crystallinity, water absorption, hydrolytic degradation, and tacticity on the solid structure and chain mobility of poly(lactide)s were investigated by solid-state  $^{13}\text{C}$  NMR spectroscopy. The following results were obtained from the line shapes of the carbonyl and methine carbons in  $^{13}\text{C}$  NMR spectra and their spin-lattice relaxation behavior. The crystallized poly(L-lactide) (PLLA) specimens in the dried, hydrated, and hydrolyzed states had two components, rigid and mobile components which can be, respectively, assigned to the crystalline and non-crystalline components. Upon water absorption, the chain mobility in the non-crystalline component of PLLA-C remained unvaried, reflecting a very small effect of the incorporated water molecules at room temperature. In contrast, the elevated chain mobility in the crystalline component and unclear splitting of carbonyl carbon strongly suggest that the water molecules are incorporated in the crystalline lattice. Upon removal of the non-crystalline components by hydrolytic degradation of crystallized PLLA, the chain mobility was slightly elevated in both crystalline and non-crystalline components by the lowered crystalline thickness and shortened non-crystalline chains. The non-crystalline specimens, PLLA (PLLA-Q) and poly(DL-lactide) (PDLLA), could be analyzed to contain two components, rigid and soft components, with the similar conformation but different restricted states of chains which cause high and low chain mobility. The insignificant difference in the spectral shapes and  $T_{1\rho}$  values between PLLA-Q and PDLLA strongly suggests that the effects of difference in the chain regularity and interaction on the spectral shapes and  $T_{1\rho}$  values are very low.

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## 1. Introduction

Poly(L-lactide) [i.e. poly(L-lactic acid) (PLLA)] has been attracting much attention because it is biodegradable, compostable, producible from renewable resources, and nontoxic to the environment and the human body [1–14]. PLLA has also high mechanical performance comparable to that of polyethylene, polypropylene, and polystyrene. Due to these reasons, PLLA is used for biomedical, pharmaceutical, industrial, and commodity applications. PLLA is hydrolytically degraded in the presence of water and gives low-molecular-weight water-soluble lactic acid oligomers and monomers. Such degradation products can be further metabolized in the human body or assimilated in microbes, and finally yield carbon dioxide and water. The raw material of PLLA is mainly starch from plants, which is photosynthesized from carbon dioxide and water.

Therefore, carbon dioxide will not be increased by the disposal of PLLA. This concept is called “carbon neutral”.

Numerous studies have been performed on the highly ordered structures and their formation, physical properties, and hydrolytic and thermal degradation behavior of PLLA-based materials, using a wide variety of methods and procedures [1–14]. Among various methods, solid-state  $^{13}\text{C}$  NMR spectroscopy is powerful for monitoring the ordered and disordered structures, the molecular mobilities and fractions of the components. Kister et al. reported spectral shape differences between quenched and crystallized PLLA specimens [15]: Each  $^{13}\text{C}$  resonance line of the quenched and crystallized PLLA is a broad singlet and a sharp multiplet, respectively. On the other hand, we have investigated the structure of the stereocomplex formed between PLLA and poly(D-lactide) [i.e. poly(D-lactic acid) (PDLA)] and found that the stereocomplex is composed of five components; i.e., ordered rigid and disordered soft crystalline components forming the stereocomplex (racemic) crystallites, the respective crystalline components composed of PLLA and PDLA, and the non-crystalline component [16]. Thakur

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et al. investigated PLLA and poly(lactide) [i.e., poly(lactic acid) (PLA)] having different *l*-lactide/*D*-lactide ratios and found that the nanometer- and micrometer-range orders in PLLA appear to affect the  $^{13}\text{C}$  NMR spectra [17]. However, the effects of crystallinity, water absorption, hydrolytic degradation, and tacticity of different PLAs on the solid structure and chain mobility have not been reported so far. To elucidate these effects, in this paper, we prepared the melt-crystallized and quenched PLLA films, quenched poly(*D*L-lactide) [i.e., poly(*D*L-lactic acid) (PDLLA)] films, and the melt-crystallized PLLA films subjected to further water-swelling or hydrolytic degradation, and characterized the structure and chain mobility by high-resolution solid-state  $^{13}\text{C}$  NMR spectroscopy.

## 2. Experimental

### 2.1. Materials

PLLA ( $M_n = 6.0 \times 10^5 \text{ g mol}^{-1}$ ,  $M_w/M_n = 2.0$ ) and PDLLA ( $M_n = 2.8 \times 10^5 \text{ g mol}^{-1}$ ,  $M_w/M_n = 2.0$ ) were purchased from Polysciences, Inc. (Warrington, PA, USA) and purified by precipitation using dichloromethane for PLLA or acetone for PDLLA as solvent and methanol as precipitant. The PLLA and PDLLA films having a thickness of 200  $\mu\text{m}$  were prepared by a solution-casting method using dichloromethane as solvent. The crystallized and quenched PLLA films were prepared by the following procedure [18,19]. Each PLLA film was placed between two Teflon sheets, sealed in a glass tube under reduced pressure, and melted at 200°C for 5 min. Then, one was directly quenched into iced water, which is abbreviated as the PLLA-Q film. Another was crystallized at 140°C for 10 h and quenched into iced water. The latter is abbreviated as the PLLA-C film. The PDLLA film was thermally treated by the same procedure as for the PLLA-Q film.

### 2.2. Water absorption and hydrolytic degradation

The water-absorbed PLLA-C, abbreviated as PLLA-C(W), was prepared by immersion of PLLA-C in distilled water (HPLC grade, Nacalai Tesque, Kyoto, Japan) at 25°C for 48 or 120 h. The period of immersion was determined based on the reported experimental result that the water absorption at 25°C saturated at 48 h [20]. For preparing PLLA crystalline residues (i.e., extended-chain crystallites), hydrolytic degradation of the PLLA-C films was performed in 0.15 M phosphate-buffered solution (PBS) at pH 7.4 at 97°C for 70 h. These degradation conditions were selected for the maximum removal of the chains in the non-crystalline region on the basis of the previous investigations [21,22]. After the hydrolytic degradation, PLLA crystalline residues [abbreviated as PLLA-R ( $M_n = 7.2 \times 10^3 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.3$ , recovery of 30–60%)] were rinsed sufficiently with distilled water at room temperature, followed by drying under reduced pressure for 7 days. The distilled water used here was of HPLC grade (Nacalai Tesque Inc., Kyoto, Japan).

### 2.3. Measurements

$M_n$  and  $M_w$  of the polymers were evaluated in chloroform at 40°C by a Tosoh GPC system with a RI-8020 refractive index monitor equipped with two TSK GMH<sub>XL</sub> gel columns using polystyrene standards. The glass transition temperature ( $T_g$ ), cold crystallization temperature ( $T_{cc}$ ), melting temperature ( $T_m$ ), cold crystallization enthalpy ( $\Delta H_{cc}$ ), and melting enthalpy ( $\Delta H_m$ ) of each specimen were determined with a Shimadzu DSC-50 differential scanning calorimeter (Table 1). The ca. 3 mg specimens were heated at a rate of 10°C min $^{-1}$  under a nitrogen gas flow at a rate of 50 mL min $^{-1}$ .  $T_g$ ,  $T_{cc}$ ,  $T_m$ ,  $\Delta H_{cc}$ , and  $\Delta H_m$  were calibrated using tin, indium and benzo-phenone as standards. The degrees of crystallinity ( $x_c$ ) of specimens were evaluated according to the following equation [21]:

**Table 1**

Thermal properties of PLA specimens.

Sample code	$T_g$ (°C)	$T_{cc}$ (°C)	$T_m$ (°C)	$\Delta H_{cc}$ (J g $^{-1}$ )	$\Delta H_m$ (J g $^{-1}$ )	$x_c$ (%)
PLLA-C	58.5	— <sup>b</sup>	185.2	0	60.7	45
PLLA-C(W) <sup>a</sup>	51.6	— <sup>b</sup>	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>
PLLA-Q	58.1	112.6	178.0	−37.4	37.2	0
PDLLA	52.3	— <sup>b</sup>	— <sup>b</sup>	0	0	0
PLLA-R	— <sup>b</sup>	— <sup>b</sup>	180.2	0	88.6	66

<sup>a</sup> Immersed in distilled water for 120 h and measured up to 100°C in the wet state.

<sup>b</sup> Not detected.

<sup>c</sup> Not measured.

$$x_c = (\Delta H_{cc} + \Delta H_m)/135 \quad (1)$$

where 135 J g $^{-1}$  is  $\Delta H_m$  of the PLLA crystals having an infinite size [23]. By definition,  $\Delta H_{cc}$  and  $\Delta H_m$  are negative and positive, respectively.

CP/MAS  $^{13}\text{C}$  NMR measurements were performed at room temperature on a Chemagnetics CMX-200 spectrometer operating at a static magnetic field of 4.7 T.  $^1\text{H}$  and  $^{13}\text{C}$  radio frequency field strengths ( $\gamma B_1/2\pi$ ) were 62.5 kHz for both CP and dipolar decoupling processes according to the previously reported procedure [24]. The CP contact time was 0.8 ms and the recycle time after the acquisition of a free induction decay (FID) was 7 s. Each sample was packed into a 7 mm cylinder-type MAS rotor with an O-ring seal [25–27]. The MAS rate was about 3.5 kHz. Totally, 400–600 FIDs were accumulated using 4 k data points in the frequency range of 10 kHz. The CPT1 pulse sequence [28] was used for  $^{13}\text{C}$  spin-lattice relaxation time ( $T_{1C}$ ) measurements.

$^{13}\text{C}$  NMR and DSC measurements of PLLA-C, PLLA-Q, and PDLLA, and PLLA-R were performed in a dry state. Only for PLLA-C, such measurements were also carried out in a wet state. The wet PLLA-C films for  $^{13}\text{C}$  NMR and DSC measurements were prepared by immersion in water for 48 and 120 h, respectively [20], which are abbreviated as PLLA-C(W).

## 3. Results

### 3.1. CP/MAS $^{13}\text{C}$ NMR spectra

Fig. 1 shows the CP/MAS  $^{13}\text{C}$  NMR spectra of PLLA-C, PLLA-C(W), PLLA-R, PLLA-Q, and PDLLA. The resonance lines of carbonyl, methine, and methyl carbons of the quenched PLLA-Q and PDLLA films are rather broad singlets, whereas those of the crystallized PLLA-C, PLLA-C(W), and PLLA-R films are sharp multiplets. The comparison between the formers and the latters suggests that the sharp multiplets should be attributed to crystalline components. The resonance lines of the methine and methyl carbons of water-absorbed PLLA-C, i.e., PLLA-C(W), are similar to those of the dried PLLA-C, although the splitting of each peak of carbonyl carbon of PLLA-C(W) was unclear compared to that of PLLA-C. In contrast, the splitting of each peak of PLLA-R is much clearer than the cases of PLLA-C and PLLA-C(W) probably because the broad non-crystalline component was appreciably removed by the hydrolysis. The well-split peaks of PLLA-R should be caused by the highly ordered helical structure in the  $\alpha$ -form crystalline lattice, which remained after hydrolytic degradation and removal of disordered chains in the isotropic non-crystalline component. On the other hand, the line shape of PLLA-Q is found to be very similar to that of PDLLA, in good agreement with the result reported by Kister et al. [15].

### 3.2. $^{13}\text{C}$ spin-lattice relaxation

$T_{1C}$  decay curves obtained by the CPT1 method were analyzed for the respective samples by using the non-linear least squares

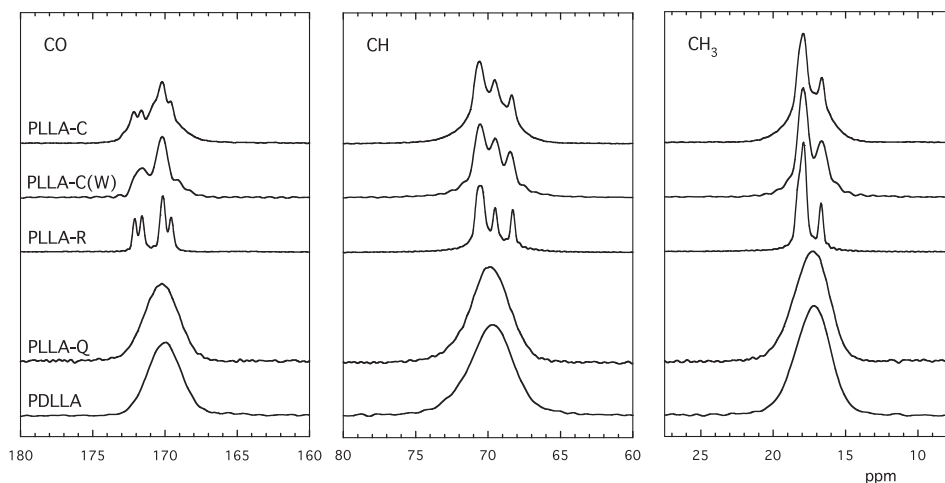


Fig. 1. CP/MAS  $^{13}\text{C}$  NMR spectra of PLLA-C, PLLA-C(W), PLLA-R, PLLA-Q, and PDLLA.

method. The typical results of the  $T_{1\rho}$  analyses of the carbonyl and methine carbons are shown for PLLA-C in Fig. 2. In agreement with the presence of the crystalline and non-crystalline components detected by DSC, each decay curve can be expressed as a sum of two

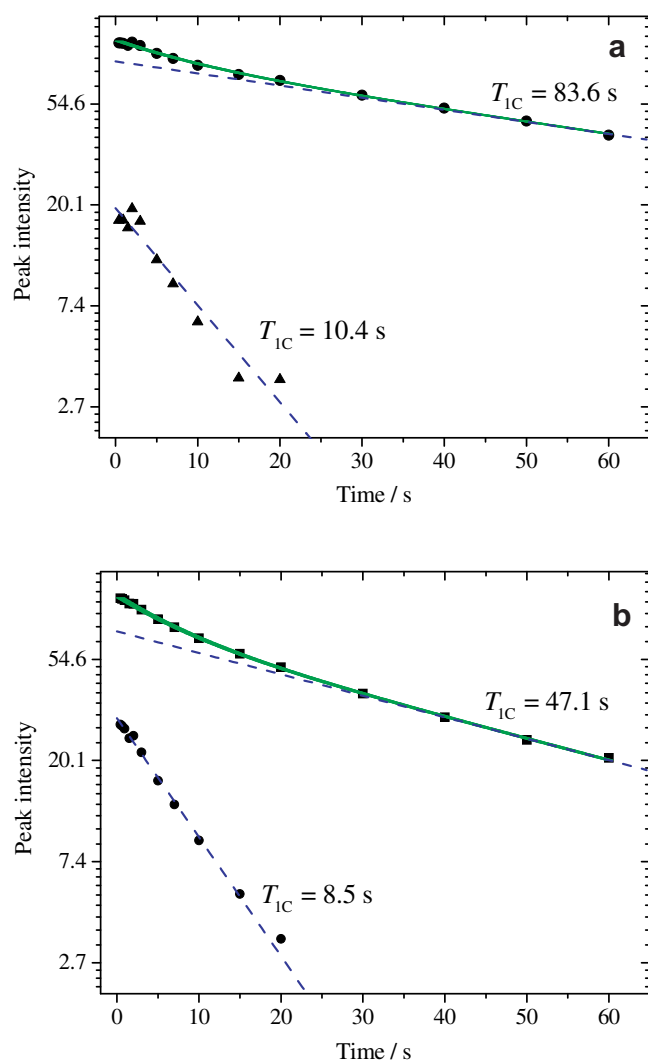


Fig. 2.  $^{13}\text{C}$  spin-lattice relaxation decays of different resonance lines of PLLA-C. (a) carbonyl and (b) methine carbons.

exponentials having different  $T_{1\rho}$  values. Similar two component analyses were also successfully carried out for the respective carbons for PLLA-C(W) and PLLA-R and the  $T_{1\rho}$  values thus obtained for these crystallized samples are summarized in Table 2. As can be expected, the components having larger and smaller  $T_{1\rho}$  values should be assigned to the crystalline and non-crystalline components, respectively. Upon water absorption of PLLA-C, the  $T_{1\rho}$  values of the non-crystalline component are found to remain unchanged although those of the crystalline component seem to appreciably decrease. Upon hydrolytic degradation and subsequent removal of the non-crystalline component in PLLA-C, the  $T_{1\rho}$  values of the non-crystalline component significantly decrease while those of the crystalline component are not appreciably decreased.

By using such differences in  $T_{1\rho}$ s, the spectra of the crystalline and non-crystalline components can be separately obtained by the procedure previously reported [16,29]. The spectra of the crystalline components were recorded by setting the decay time  $\tau$  in the CPT1 pulse sequence to values 5 times larger than the  $T_{1\rho}$  values of the non-crystalline components. Under this condition, the non-crystalline components disappear because of their small  $T_{1\rho}$ s. In contrast, the spectra of the non-crystalline components could be obtained by subtracting the spectra of the crystalline components from the spectra almost without  $T_{1\rho}$  decays that were obtained by setting  $\tau = 0.1$  s in the CPT1 pulse sequence. The CP/MAS  $^{13}\text{C}$  NMR spectra of the crystalline and non-crystalline components thus obtained for PLLA-C, PLLA-C(W), and PLLA-R are shown in Figs. 3 and 4, respectively.

The  $T_{1\rho}$  analyses of the carbonyl and methane carbons for PLLA-Q and PDLLA were also carried out, the results for PLLA-Q being shown as an example in Fig. 5. The  $T_{1\rho}$  decays of non-crystalline polymers are not always single exponential decays probably because their structure and molecular motions are so complex that the simple  $T_{1\rho}$  relaxation theory cannot be strictly applied to them. Nevertheless, the respective decays were simply analyzed by

Table 2

$T_{1\rho}$  values of carbonyl and methine carbons of different PLA samples.

Specimen	$T_{1\rho}/\text{s}$			
	Carbonyl carbon		Methine carbon	
PLLA-C	83.6 [0.81]	10.4 [0.19]	47.1 [0.70]	8.5 [0.30]
PLLA-C(W)	71.3 [0.77]	11.4 [0.23]	40.0 [0.63]	7.4 [0.37]
PLLA-R	77.1 [0.85]	6.3 [0.15]	46.8 [0.76]	5.0 [0.24]
PLLA-Q	54.6 [0.74]	4.4 [0.26]	34.6 [0.66]	6.6 [0.34]
PDLLA	54.0 [0.88]	8.3 [0.12]	36.0 [0.65]	6.7 [0.35]

The values in parentheses are fractions determined by the  $T_{1\rho}$  analyses using peak intensities.

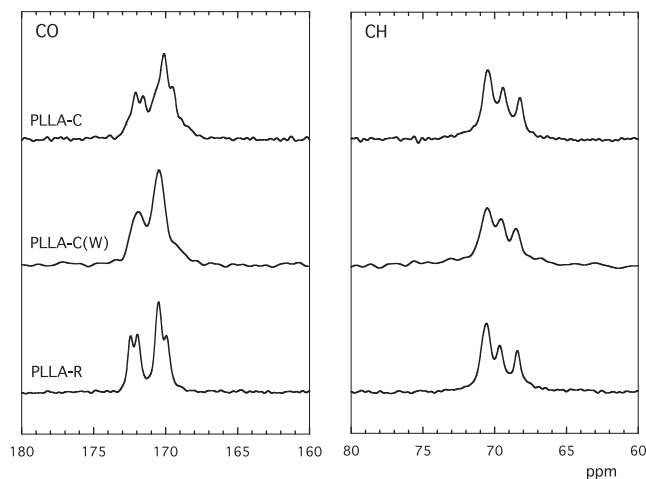


Fig. 3. CP/MAS  $^{13}\text{C}$  NMR spectra of the crystalline components of PLLA-C, PLLA-C(W), and PLLA-R.

assuming the presence of two components as shown in Fig. 5 and  $T_{1C}$  values thus obtained for PLLA-Q and PDLLA are also summarized in Table 2. Moreover, the CP/MAS  $^{13}\text{C}$  NMR spectra of the components with larger and smaller  $T_{1C}$  values were obtained for PLLA-Q and PDLLA by the same procedure utilized to obtain the spectra of the crystalline and non-crystalline components in the crystallized PLLA samples, as shown in Fig. 6.

Interestingly, there are no significant differences in the line shapes, which are expressed as Gaussian curves, and in chemical shifts between the two components for both PLLA-Q and PDLLA, indicating that the structures may be not so different in the two components if they actually exist. In addition, PLLA-Q and PDLLA also show no significant differences in the chemical shift, spectral shape, and  $T_{1C}$  value of each component, except for the relatively short  $T_{1C}$  value of the carbonyl carbon for PLLA-Q.

#### 4. Discussion

The components with larger and smaller  $T_{1C}$  values of PLLA-C, PLLA-C(W), and PLLA-R are assigned to the crystalline and non-crystalline components, respectively. In PLLA-C, the  $\alpha'$ -form crystallites are formed instead of  $\alpha'$ -form (disordered  $\alpha'$ -form) crystallites because this specimen was crystallized at  $140^\circ\text{C}$  that was

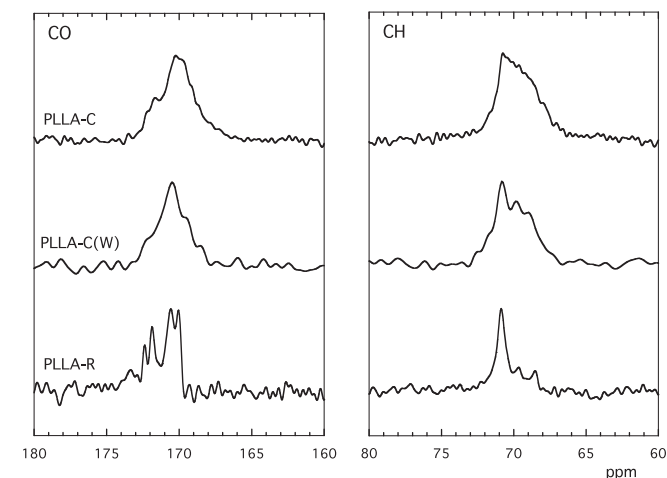


Fig. 4. CP/MAS  $^{13}\text{C}$  NMR spectra of the non-crystalline components of PLLA-C, PLLA-C(W), and PLLA-R.

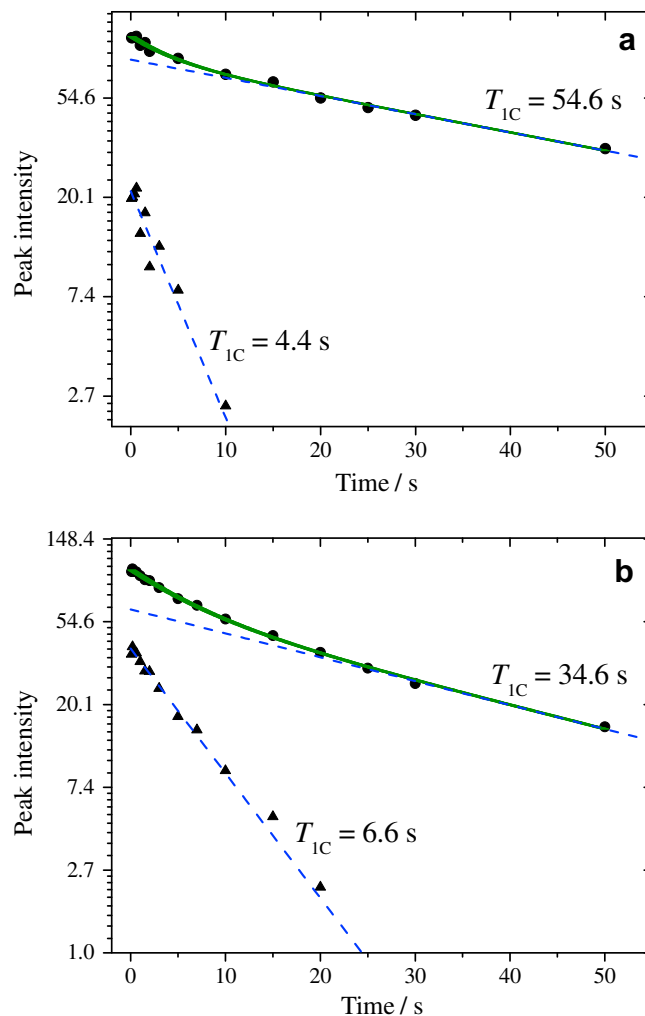
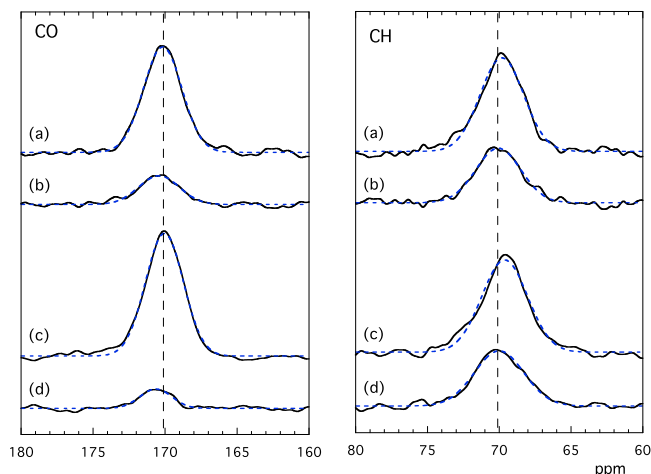


Fig. 5.  $^{13}\text{C}$  spin-lattice relaxation decays of different resonance lines of PLLA-Q. (a) carbonyl and (b) methine carbons.

higher than the transition temperature of  $\alpha'$ -form to  $\alpha$ -form [30–32]. No further thermal treatment was carried out for PLLA-C (W) and PLLA-R specimens. Therefore, the multiplets of PLLA-C, PLLA-C(W), and PLLA-R seen in Fig. 4 should be mainly attributed to the  $10_3$  helical chains having different packing sites in the  $\alpha$ -form crystallites. However, the interfacial component between the crystalline and isotropic non-crystalline components could not be detected by the  $T_{1C}$  analyses in the present study, contrary to the cases by the  $^{13}\text{C}$  spin–spin relaxation analyses for the crystallized polyethylene samples [33,34].

After the immersion of PLLA-C in water in a short period of 48 or 120 h, no significant hydrolytic degradation and additional crystallization should take place [18,19]. Therefore, although  $T_g$  of PLLA is decreased by  $7^\circ\text{C}$  by water immersion (Table 1), the unchanged  $T_{1C}$  values of the non-crystalline components as seen for PLLA-C(W) in Table 2 mean that much higher molecular mobilities ( $\sim 10^8 \text{ s}^{-1}$ ) associated with  $T_{1C}$  values remained unchanged for the non-crystalline components even in the presence of water as a plasticizer. However, the findings that the  $T_{1C}$  decrease of the crystalline component upon water absorption and the unclear splitting of the carbonyl carbon of PLLA-C(W) compared to PLLA-C strongly suggest that the water molecules diffuse into the crystalline lattice and the incorporated water molecules somewhat disturb the helical structure of PLLA. After hydrolytic degradation, the  $T_{1C}$  values of the non-crystalline components of PLLA-R are appreciably decreased





**Fig. 6.** CP/MAS  $^{13}\text{C}$  NMR spectra of the components with large (a,c) and small (b,d)  $T_{1\rho}$  values of PLLA-Q (a,b), and PLLDLA (c,d). Respective components simulated with the Gaussian functions are shown with broken lines.

(Table 2). The decreases in  $T_{1\rho}$  values for the crystalline and non-crystalline components can be ascribed to the decreased thickness of crystallites and shortened non-crystalline chains that are connected to the crystalline chains at their one ends, respectively. The presence of non-crystalline chains in PLLA-R could not be traced by X-ray diffractometry [31,32], but could be monitored by CP/MAS  $^{13}\text{C}$  NMR spectroscopy. The CP/MAS  $^{13}\text{C}$  NMR spectrum of the non-crystalline component in PLLA-R was obtained by subtracting the spectrum of the crystalline component from the almost total spectrum. The respective resonance lines of the non-crystalline component in PLLA-R are composed of multiple peaks and their chemical shifts are different from those of the crystalline component as seen in Figs. 3 and 4. Considering the fact the removal of the isotropic non-crystalline component by hydrolytic degradation, the residual non-crystalline component in PLLA-R should be attributed to the interfacial non-crystalline component existing between the crystalline and isotropic non-crystalline regions in PLLA-C before hydrolytic degradation. Since this component shows the sharp multiplets similar to those of the crystalline component, the respective chains should adopt the  $10_3$  helical structure although it may be considerably disordered and their molecular motions may be much enhanced as suggested by short  $T_{1\rho}$  values. Below  $T_g$ , it is still difficult to discriminate between the interfacial and isotropic non-crystalline components in crystallized PLLA samples by using solid-state  $^{13}\text{C}$  NMR techniques. However, the analysis of the hydrolytically degraded product clearly indicates the presence and the structure of the interfacial component in the crystallized PLLA sample.

It is well known that the  $T_{1\rho}$  decays of non-crystalline polymers are not always expressed by single exponentials but frequently by the Korrausch-Williams-Watts (KWW) equation:

$$M(t) = M(0)\exp(-t/T_{1\rho})^\beta \quad 0 < \beta \leq 1 \quad (2)$$

As already stated, we analyzed the spin-lattice relaxation decays of PLLA-Q and PLLDLA by assuming the existence of two components having large and small  $T_{1\rho}$  values and these analyses seem successful. However, the CP/MAS  $^{13}\text{C}$  NMR spectra of the two components in these samples are found to have very similar line shapes which can be expressed by Gaussian curves (Fig. 6). This finding suggests that the two components may be not significantly different in structure and the discrimination of the two components may be due to the insufficient time average of the two components in the time scale of  $T_{1\rho}$  measurements. Nevertheless,

there may exist mobile and much less mobile components that temporarily fluctuate at random in the respective quenched samples.

It should be also noted that the line shapes of PLLA-Q and PLLDLA are greatly different from those for the non-crystalline components in PLLA-C, PLLA-C(W), and PLLA-R and this suggests that the chains in PLLA-Q and PLLDLA may adopt a random coil. If the non-crystalline chains in PLLA-Q would be composed of one component, the phase separation into the crystalline and non-crystalline components occurs through cold crystallization by suitable annealing above  $T_g$ . If the non-crystalline chains in PLLA-Q would consist of two components as a result of temporary fluctuation or so-called memory effect, the conformation of component with low chain mobility may be altered to form crystalline regions above  $T_g$  [35] and the chains with high mobility remain as non-crystalline. In this case, the chain mobilities of the components with larger and smaller  $T_{1\rho}$  values in PLLA-Q become lower upon crystallization (Table 2). The lowered  $T_{1\rho}$  values of the component with lower chain mobility are due to the formation of the rigid crystallites, whereas the decreases in  $T_{1\rho}$  values of the component with higher chain mobility may be induced by the formation of rigid helical structure in the interfacial regions and of the restrained structure in the isotropic non-crystalline region upon crystallization.

## 5. Conclusions

The resonance lines of carbonyl, methine, and methyl carbons of the quenched PLLA-Q and PLLDLA films are rather broad singlets, whereas those of the crystallized PLLA-C, PLLA-C(W), and PLLA-R films are sharp multiplets. The crystallized specimens, PLLA-C, PLLA-C(W), and PLLA-R have two components, rigid and soft components (i.e., crystalline and non-crystalline components, respectively), as can be expected. Upon water absorption, the chain mobility in the non-crystalline component of PLLA-C remained unvaried, reflecting a very small effect of incorporated water molecules at room temperature. In contrast, the elevated chain mobility in the crystalline component and unclear splitting of the carbonyl carbon strongly suggest that the water molecules are incorporated in the crystalline lattice, resulting in the somewhat disordered helical structure. Upon hydrolytic degradation, the chain mobility was slightly increased in both crystalline regions and non-crystalline regions by the lowered crystalline thickness and shortened non-crystalline chains, respectively. Similar to the crystallized specimens, the non-crystalline specimens, PLLA-Q and PLLDLA could be analyzed to contain two components, rigid and soft components, with the similar conformation but different restricted states of chains which cause high and low chain mobility. The insignificant difference in the spectral shapes and  $T_{1\rho}$  values between PLLA-Q and PLLDLA strongly suggest that the effects of difference in the chain regularity and interaction on the spectral shapes and  $T_{1\rho}$  values are very low.

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