

# Solid State NMR Analysis of Poly(L-lactide) Random Copolymer with Poly( $\epsilon$ -caprolactone) and Its Reactive Extrusion Process

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Received 30 August 2010; accepted 12 April 2011

DOI 10.1002/app.34674

Published online 22 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A random copolymer based on poly(L-lactide) (PLA) with poly( $\epsilon$ -caprolactone) (PCL) was prepared and characterized by mechanical testing and solid state NMR, compared with a polymer blend. For a monofilament sample consisting of PLA/PCL random copolymer, there were negative correlations between the CL content and the mechanical properties: tensile strength, tensile elastic modulus, flexural rigidity, and flexural hysteresis decreased with increasing CL content. In contrast, the mechanical properties of the polymer blend were only slightly changed by

addition of the CL unit. For the random copolymer, the addition of a small amount of CL reduced relaxation times,  $T_{1C}$  and  $T_{1\rho H}$ , gradually. The  $T_{1C}$  and  $T_{1\rho H}$  values correlated closely with the tensile elastic modulus and the tensile strength, respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1865–1873, 2012

**Key words:** random copolymer; polymer blend; fiber; mechanical properties; solid state NMR; relaxation time analysis

## INTRODUCTION

In recent years, solid state NMR has been applied to a variety of areas, enabled by advances in electronic devices and measurement technologies.<sup>1</sup> The use of solid state NMR as a characterization method is expected to expand to a wide range of polymer science because it does not require any destructive sample treatments.<sup>2</sup> Especially, in the field of textiles, research using solid state NMR has become increasingly extensive in recent years, since the mechanical and thermal properties of textile fibers are significantly affected by high-order structure and morphology of their material.<sup>3,4</sup> It is also well known that the mechanical properties of a fiber depend on the motion of its polymer molecules. For study of molecular motion with solid state NMR, relaxation time analysis is the most popular method, since the relaxation time, which reflects the molecular motions, dynamically changes with molecular com-

position and production process. The molecular motions in diverse shapes of materials can be revealed by various relaxation time analyses. The polymer containing multiple components could be analyzed using <sup>13</sup>C spin-lattice relaxation time in the laboratory frame ( $T_{1C}$ ): previous published work suggested that internal and interfacial crystalline regions can be assigned by the  $T_{1C}$  analysis of a biodegradable polymer, and went on to discuss the relationship between  $T_{1C}$  and molecular mobility.<sup>5</sup> For the polymer blend, both crystalline and amorphous phases could be distinguished by <sup>1</sup>H spin-lattice relaxation time ( $T_{1H}$ : in the laboratory frame;  $T_{1\rho H}$ : in the rotation frame) analysis, which also elucidated the mobility difference between the phases.<sup>6</sup> Furthermore, using the cross polarization time and  $T_{1\rho H}$ , the relationship between morphology and mechanical properties was revealed for poly(ethylene terephthalate) with natural rubber.<sup>7</sup>

On the other hand, solid state NMR studies on poly(L-lactide) (PLA) in “fiber form” are very limited; to our knowledge, only the draw direction of PLA films has been investigated by solid state <sup>13</sup>C NMR to date.<sup>8</sup> In regard to “materials” based on PLA, however, solid state <sup>13</sup>C NMR analyses and relaxation time measurements are also effective for structural and molecular motion analyses, since PLA has multiple components, including the crystalline and

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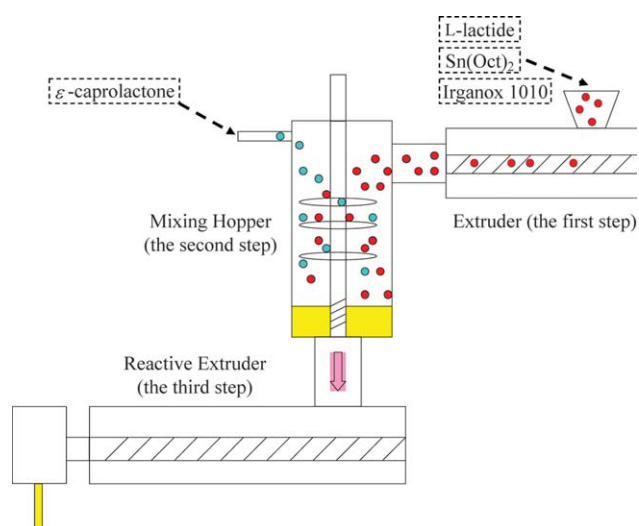
amorphous phases.<sup>9,10</sup> Several reports have been published on the relaxation time analysis of PLA materials, including stereocomplex material, polymer blends, and a copolymer. An investigation of the phase structure by relaxation time analysis was carried out for PLA stereocomplex: the presence of four components was established by peak deconvolution and  $T_{1\rho}C$  analysis.<sup>11</sup> The relationship of the molecular motion and the  $T_{1\rho}C$  value was studied for the PLA polymer blend, concluding that changing of the semicrystalline phase to amorphous caused a reduction of  $T_{1\rho}C$  and an activation of the molecular motion.<sup>12</sup> The relaxation time reflected inclusion of PLA/poly( $\epsilon$ -caprolactone) (PCL) diblock copolymer into  $\alpha$ -cyclodextrin (CD):  $T_{1\rho}C$  showed dramatic changes in the mobility in the CD channel, while  $T_{1\rho}H$  showed phase separation of the bulk polymer.<sup>13</sup>

Although solid state NMR plays important roles in analyzing the detailed structure and the molecular motion as mentioned above, it offers great potential in the application to real industrial analytical needs, including variability caused by production processes. We have previously reported the analysis of PLA in melt spinning and melt drawing processes and its biodegradability in various conditions.<sup>14</sup> We also assembled a reactive extrusion molding machine, which can produce the monofilament directly from monomers. For new application of solid state NMR to the real industrial fields, we examined correlation between changes of mechanical properties due to manufacturing process and structural information at the molecular level. In this article, we described copolymerization of L-lactide (LA) and  $\epsilon$ -caprolactone (CL) is induced to manufacture a monofilament fiber of random copolymer using the reactive extrusion molding machine. The production process furnished monofilaments of various CL content, of which the molecular weights and amounts of recovered monomers varied with the variability of process conditions. We have carried out mechanical testing and solid state NMR measurement on the monofilament in terms of the variability of the CL content, the monomer content, and the molecular weight. Correlation of the CL content, the mechanical properties, the  $^{13}C$  MAS NMR spectra, and the magnetic relaxation time are examined and discussed in this article.

## EXPERIMENTAL

### Materials

Industrial grade LA (L content: 88%, Musashino Chemical Laboratory) was used without further purification. High grade CL was purchased from Tokyo Chemical Industry. Tin (II) 2-ethylhexanoate [ $Sn(Oct)_2$ ,



**Figure 1** Diagram of the reactive extrusion molding machine [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Wako Pure Chemical Industries] was used as a catalyst and Irganox 1010 (Ciba Japan Co.) was used as an antioxidant for the polymer obtained. A polymer blend sample of PLA with PCL was made by the solution cast method from  $CHCl_3$  solution using pelletized poly(L-lactic acid) PLA (Mitsui Chemicals) and PCL (Daicel Chemicals Industries). A PLA-PCL block polymer was made by the successive polymerization of LA and PCL, which was prepared by the polymerization of CL in the presence of a small amount of ethanol; details on the method may be found elsewhere.<sup>15</sup> The molecular weights of the PLA-PCL block polymers were in the range from 5000 to 10,000. All solvents for the polymerization and casting were used without purification of anhydrous grade reagents.

### Typical copolymerization procedure of L-lactide and $\epsilon$ -caprolactone with the reactive extrusion equipment

A melt copolymerization of LA and CL was performed by the reactive extrusion machine as shown in Figure 1. A mixture of industrial grade LA (240 g), 0.3 wt % of  $Sn(Oct)_2$ , and 0.3 wt % of Irganox 1010 was placed in a 500 mL beaker and gently mixed. The mixture was put into the feeder of a single screw extruder, stirred at 5 rpm and 30°C, and extruded into a mixing hopper. With heating at 120°C under a nitrogen atmosphere, the mixture was stirred by a shuttlecock-type screw at 5 rpm for 30 min. Then, 60 g of CL was added into the mixing hopper by a 50 mL plastic injector and the resultant mixture was stirred by the shuttlecock-type screw at 5 rpm and 120°C for 60 min under the nitrogen, followed by further stirring for 60 min under vacuum.

Through a gear pump equipped under the mixing hopper, the melting mixture was introduced into the single screw extruder part of the reactive extrusion machine, from which the melting mixture was extruded with the screw running at 5 rpm and heating at 140°C. Finally, the melted copolymer was extruded through a spinning die into water at ambient temperature to provide monofilament fibers.

### Characterization and mechanical testing of PLA polymer alloys

Gel permeation chromatography (GPC) measurement was conducted at 40°C with a Toso GPC-H8020 instrument equipped with a Toso TSKgel GMH<sub>HR</sub>-M column and a differential refractometer detector. Chloroform was used as the eluent at a flow rate of 1.0 mL/min, and the molecular weight were calibrated with polystyrene standards.

Differential scanning calorimetry (DSC) data were recorded on a Rigaku-Denki TAS-100 to obtain glass transition ( $T_g$ ) values. Samples of PLA and the copolymer (5 mg) were heated at a rate of 10 K/min over a temperature range of 0–250°C.

Tensile mechanical properties were measured using a Tensilon system (RTC-1250, Orientec Co.) at 20°C and relative humidity 65%, where the cross head speed was set at 200 mm/min and the length of specimens was 200 mm. All the tensile properties given in this article represent average values of 10 trials according to the JIS L 1013 testing methods for man-made filament yarns. Flexural rigidity and hysteresis were presented as average values of three trials obtained by measurements using a Kato Tech Co. KSB-FB fabric tester. In the mechanical testing, the random copolymer was measured as the monofilament, while the polymer blend was measured in the form of a dog-bone shaped test piece.

### NMR measurements

The  $^1\text{H}$  spectra and  $^{13}\text{C}$  in the solution were measured on a Varian INOVA-300 spectrometer operated at 300 MHz and 75.42 MHz with  $\text{CDCl}_3$  as the solvent, respectively. The solid state  $^{13}\text{C}$  NMR spectra were measured on Varian INOVA-300 spectrometer operated at 75.42 MHz for the  $^{13}\text{C}$  nuclei and 13 ms of acquisition period with 63 kHz of  $^1\text{H}$  decoupling radio frequency as a continuous wave. Fiber samples were cut and placed in  $\text{ZrO}_2$  rotors of 7 mm in diameter and spun at the magic angle at 4 kHz. The CP/MAS (cross polarization and magic-angle spinning) NMR spectra were measured using the regular CP/MAS sequence at 2 ms contact time with 4.2  $\mu\text{s}$  of the  $\pi/2$  pulse for the  $^1\text{H}$  nuclei. The contact time was optimized by the measurements of several selected samples with variable contact times (100–

8000  $\mu\text{s}$ ). The single  $^{13}\text{C}$  pulse method was measured with 4.8  $\mu\text{s}$  of the  $\pi/2$  pulse for the  $^{13}\text{C}$  nuclei and was labeled as the DD/MAS (dipolar decoupling and magic-angle spinning) NMR. The recycled time between the  $\pi/2$  pulses was 5 s both in CP/MAS and DD/MAS.

The  $^1\text{H}$  spin-lattice relaxation time in the laboratory frame ( $T_1H$ ) was indirectly measured via detection of  $^{13}\text{C}$  resonance enhanced by cross-polarization applied after a  $\pi$  pulse to  $^1\text{H}$  nuclei with the inversion recovery method. The  $^1\text{H}$  spin-lattice relaxation time in the rotation frame ( $T_{1\rho}H$ ) was indirectly measured via detection of  $^{13}\text{C}$  resonance enhanced by cross-polarization applied after a  $\pi/2$ - $\tau$ -spin lock pulse (63 kHz of radio frequency) with variable spin lock times in a range of 100–8000  $\mu\text{s}$ . The  $^{13}\text{C}$  spin-lattice relaxation time in the laboratory frame ( $T_1C$ ) was measured with the conventional Torchia pulse sequence.<sup>16</sup> The relaxation time analyses were performed with the same contact time and acquisition period as the spectrum acquisition at a range of 21–25°C with enough cooling air flow to prevent temperature rise.

## RESULTS AND DISCUSSION

### Preparation and characterization of PLA polymer alloys

Figure 1 gives an outline of the reactive extrusion molding machine used in the experiment. The machine consists of three main parts: a single screw extruder (the first step), a mixing hopper (the second step), and single screw reactive extruder (the third step). Although generally a solid sample was put into the feeder of the first single screw extruder and liquid samples were put into the vent hole of the second mixing hopper, a mixture of solid and liquid samples could be put into the feeder of the single screw extruder. The melt polymerization of LA with CL proceeded without ethanol as a catalytic promoter to provide a clear glassy monofilament from the spinning die.

The CL content and the amount of monomer recovered in the monofilaments were determined by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  solution: the CL contents according to the ratio between magnitudes at 4.01–4.27 ppm and 5.00–5.29 ppm peaks, the LA monomer according to 5.00–5.09 ppm peaks, and the CL monomer according 4.20–4.27 ppm peaks.<sup>17</sup> Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR in solution indicated that the monofilament consisted of random copolymer.<sup>18</sup> The composition and molecular weight of the monofilament consisting of PLA/PCL copolymers are summarized in Table I. Although the amount of unreacted LA monomer included in most of the fibers was below 10 mol %, considerable amounts (10–44 mol %) of

**TABLE I**  
Preparations of the Monofilament Consisting of PLA/PCL Copolymer

Entry	CL content <sup>a</sup> (mol %)	LA monomer in the fiber (mol %)	CL monomer in the fiber (mol %)	CL content in the polymer chain <sup>b</sup> (mol %)	LA/CL ratio in the polymer chain <sup>b</sup>	$M_n$ ( $10^4$ g mol <sup>-1</sup> )	$M_w/M_n$	$T_g$ (°C)
1	0.0	4.62	—	—	—	4.24	1.88	50.1
2	6.2	7.57	44.3	3.8	25.3	3.64	2.03	33.0
3	8.3	4.88	29.0	7.5	12.3	4.00	1.75	— <sup>c</sup>
4	12.6	5.79	23.4	10.2	8.80	1.53	2.94	— <sup>c</sup>
5	13.5	13.1	28.7	11.4	7.77	3.64	1.85	— <sup>c</sup>
6	17.0	4.95	8.94	16.2	5.17	1.60	2.59	— <sup>c</sup>
7	20.3	11.3	20.3	18.6	4.38	3.29	1.83	— <sup>c</sup>
8	20.8	6.88	24.9	18.5	4.41	1.64	2.90	— <sup>c</sup>
9	24.1	20.7	34.6	20.8	3.81	3.15	2.00	16.9

<sup>a</sup> Determined from the monofilament by <sup>1</sup>H NMR in solution.

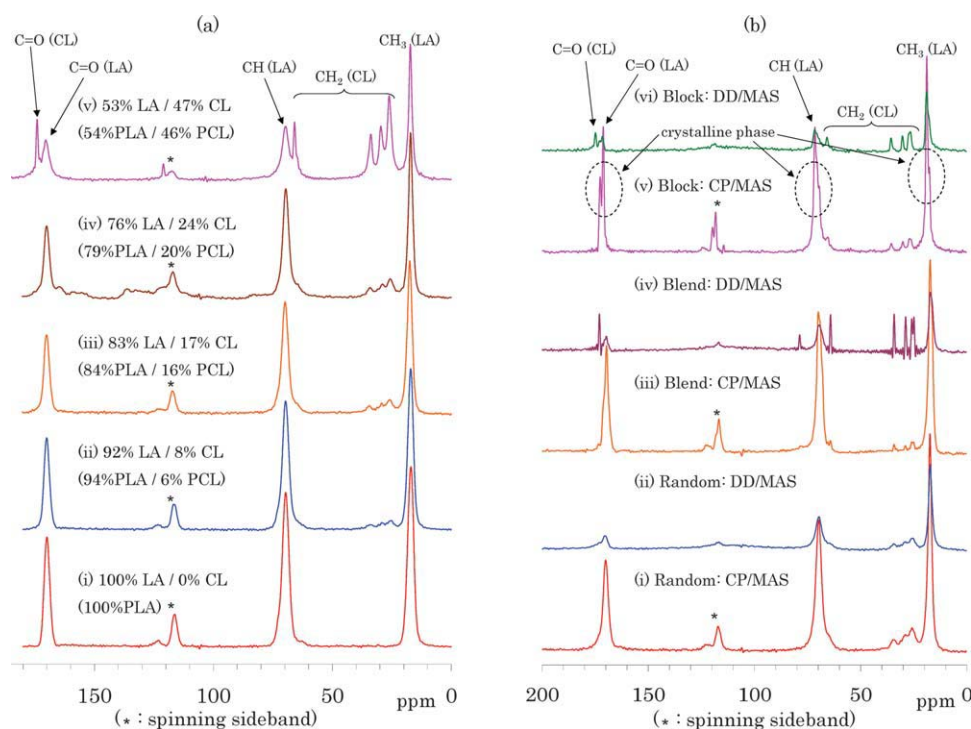
<sup>b</sup> Determined from the polymer content except the remaining monomers by <sup>1</sup>H NMR in solution.

<sup>c</sup> Data could not be collected.

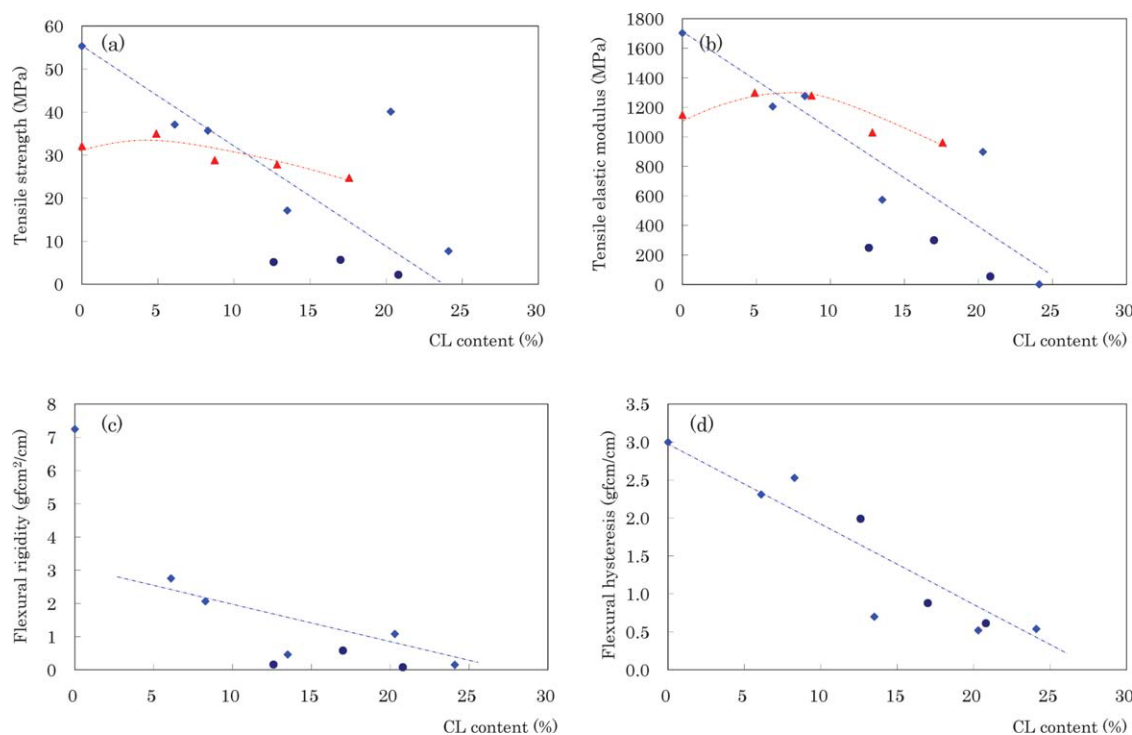
remaining CL monomer existed in the fibers. Thus, the CL content in the polymer chain was slightly lower than the values within all CL units. Molecular weights could be improved to  $M_n = 70,000$  about the PLA homopolymer and  $M_n = 50,000$  about the PLA/PCL copolymer, respectively. In using the LA monomer with a little moisture (entries 4, 6, and 8 in Table I), the molecular weight fell to about 15,000. It is considered that the decrease in molecular weight was caused by increase in the number of the starting points for ring opening polymerization and hydrolysis of the polymer chain in the presence of moisture.

Below 25 mol % CL content, however, the reactive extrusion molding machine produced enough monofilaments for the mechanical testing, even including the considerable amount of remaining CL monomer.

For the random copolymer monofilaments having PCL contents in the range of 0–20% and a massive sample containing 46% PCL, <sup>13</sup>C CP/MAS NMR was measured and the results are shown in Figure 2(a). The existence of monomer and the molecular weight of the polymer slightly affected the CP/MAS NMR spectra in our tests; peak intensities of CL, however, were somewhat lower compared with the



**Figure 2** <sup>13</sup>C CP/MAS spectra: (a) PLA/PCL random copolymers in various CL contents (left); (b) PLA polymer alloys containing 20 wt % CL (right) [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).].

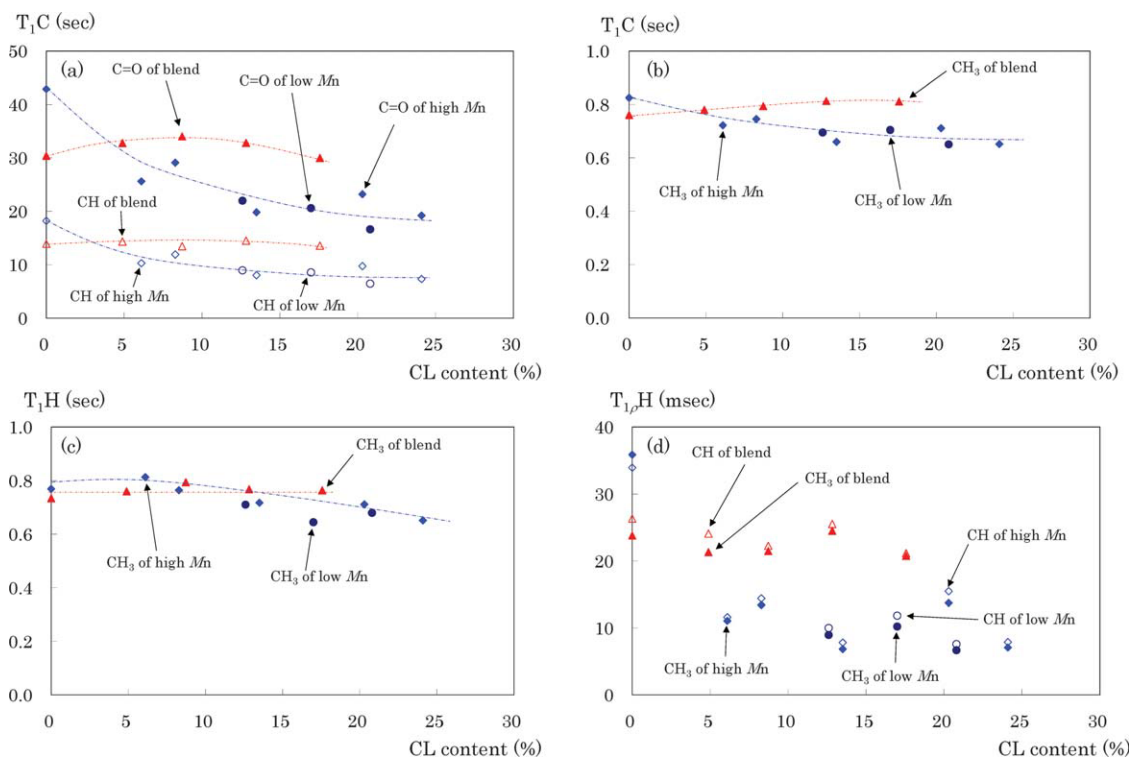


**Figure 3** Mechanical properties of the random copolymer (blue-filled diamond: High  $M_n$  polymer, dark blue-filled circle: C=O of low  $M_n$  polymer) and the polymer blend ([red filled triangle]): (a) tensile strength (left upper); (b) tensile elastic modulus (right upper); (c) flexural rigidity (left bottom); (d) flexural hysteresis (right bottom) [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).].

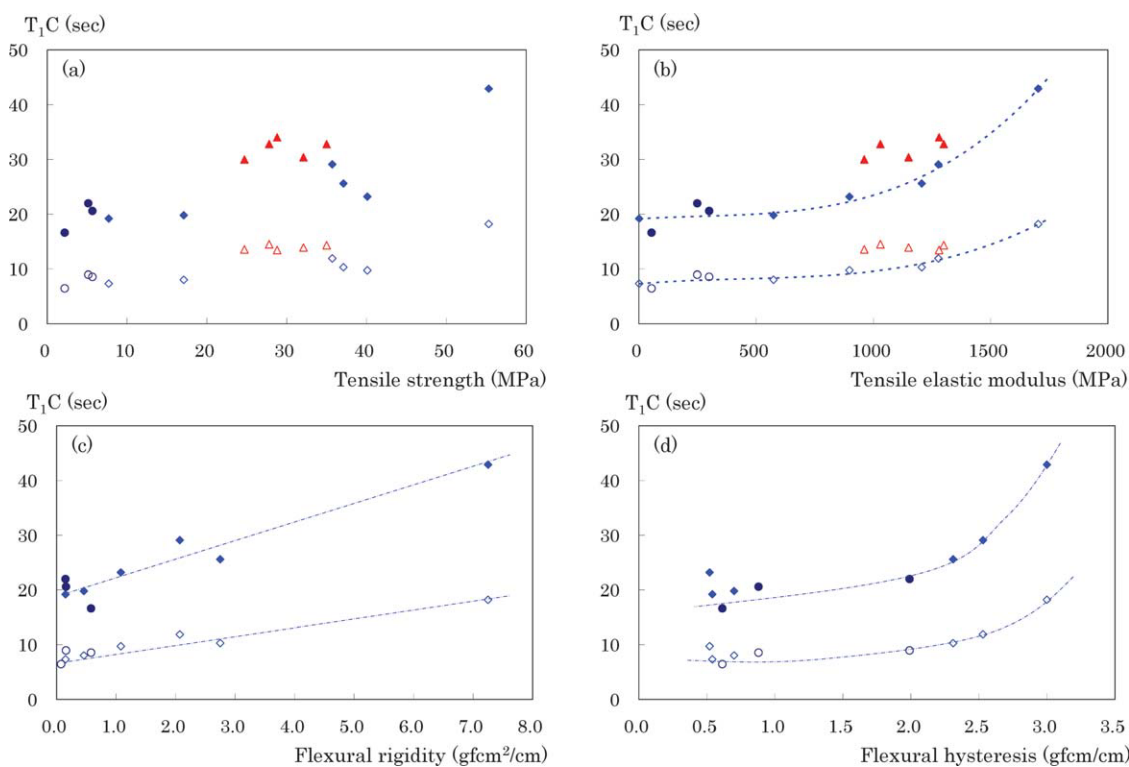
measurement results in solution in Table I. This reduction of the CL peak intensity was more pronounced both for the block copolymer prepared on a laboratory scale and for the polymer blend with the solution cast method. Figure 2(b) shows a comparison between  $^{13}\text{C}$  CP/MAS and DD/MAS NMR spectra of three polymer alloys containing 20 mol % CL; the random copolymer, the block copolymer, and the polymer blend. In the CP/MAS NMR spectra, referring to the assignment of the previous report,<sup>19</sup> the crystalline phase appeared only in the LA peaks of the block copolymer [Fig. 2(b; v)], while only amorphous phase appeared in the LA peaks of the random copolymer [Fig. 2(a)]. In both the block copolymer [Fig. 2(b; vi)] and the polymer blend [Fig. 2(b; iv)] in DD/MAS NMR spectra, intensities of CL peaks were larger than those of the random copolymer monofilament. This weakened CL peak in the CP/MAS indicates a low efficiency of  $^1\text{H}$ - $^{13}\text{C}$  cross polarization. Although the recycled time of the  $^{13}\text{C}$  single pulse was also set at 5 s in the DD/MAS, the  $^{13}\text{C}$  nuclei having long spin-lattice relaxation times were observed with strong enough peak intensity in the polymer blend. According to the above results, it is considered that the CL unit of the random copolymer is structurally constrained with the interaction of polymer chains, while the PCL unit has the freedom of movement in the polymer blend.

### Mechanical properties of PLA polymer alloys

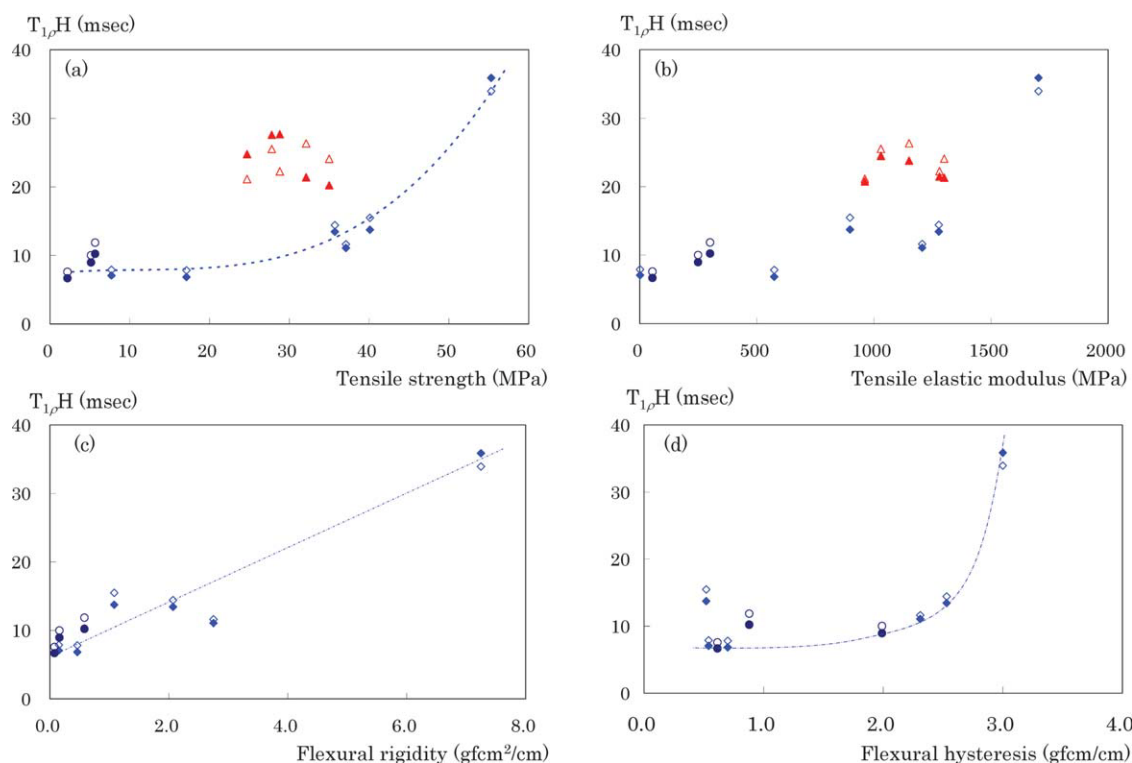
The mechanical properties of the random copolymer monofilaments produced in this study are summarized in Figure 3. In the Figures 3–6, clear trends are represented by the broken lines and slight tendencies are highlighted by the dash-dotted lines. The tensile strength and the tensile elastic modulus were reduced by addition of the CL unit: the addition of only 6.2 mol % CL reduced them to about two-thirds of those for the extruded PLA homopolymer. The flexural hysteresis also tended to decrease and furthermore, decrease of the flexural rigidity by addition of the CL unit was more rapid, to about one-third with addition of 6.2 mol % CL. These correlations between the CL content and mechanical properties had considerable variability: low molecular weight polymers (entries 4, 6, and 8: dots in the Fig. 3) showed much lower tensile strength, while the polymer including the 20.3% CL content (entry 7) had relatively high tensile strength and tensile elastic modulus. The measurements indicated that while changing the molecular weight caused variability of the mechanical properties, these properties were unaffected by changes in the LA and CL monomer contents based on the comparisons between Table I and Figure 3. In the case of 24.1 mol % CL random copolymer (entry 9), because its  $T_g$  was lower than



**Figure 4** Spin-lattice relaxation times of the random copolymer ([blue-filled diamond], [blue open diamond]: High  $M_n$  polymer; [dark blue-filled circle], [blue open circle]: Low  $M_n$  polymer) and the polymer blend ([red filled triangle], [red open triangle]): (a)  $T_{1C}$  of C=O and CH (left upper); (b)  $T_{1C}$  of CH<sub>3</sub> (right upper); (c)  $T_{1H}$  of CH<sub>3</sub> (left bottom); (d)  $T_{1\rho H}$  of CH and CH<sub>3</sub> (right bottom) [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).].



**Figure 5** Relationships to the  $T_{1C}$  values of the random copolymer ([blue-filled diamond]: C=O of High  $M_n$  polymer, [blue open diamond]: CH of High  $M_n$  polymer, [dark blue-filled circle]: C=O of low  $M_n$  polymer [blue open circle]: CH of low  $M_n$  polymer,) and the polymer blend ([red filled triangle]: C=O, [red open triangle]: CH): (a) tensile strength (left upper); (b) tensile elastic modulus (right upper); (c) flexural rigidity (left bottom); (d) flexural hysteresis (right bottom) [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).].



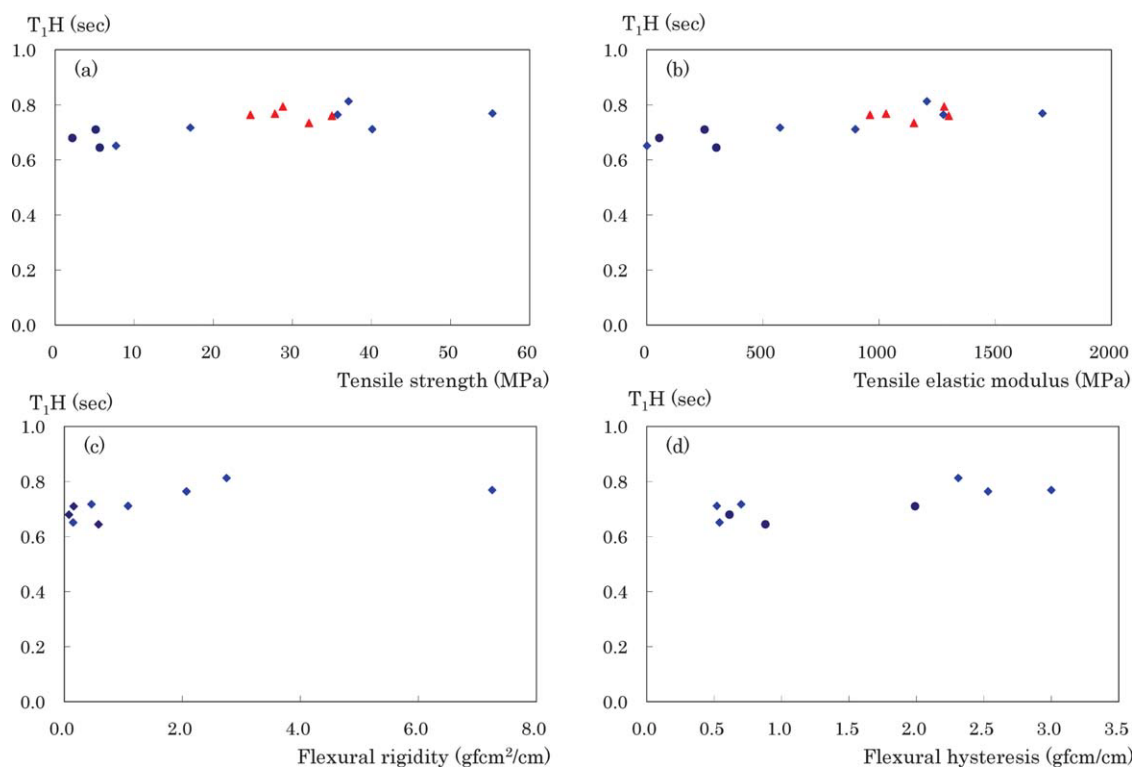
**Figure 6** Relationships to the  $T_{1\rho}H$  values of the random copolymer ([blue open diamond]: CH of High  $M_n$  polymer, [blue-filled diamond]:  $\text{CH}_3$  of High  $M_n$  polymer, [blue open circle]: CH of low  $M_n$  polymer, [dark blue-filled circle]:  $\text{CH}_3$  of low  $M_n$  polymer) and the polymer blend ([red open triangle]: CH, [red filled triangle]:  $\text{CH}_3$ ): (a) tensile strength (left upper); (b) tensile elastic modulus (right upper); (c) flexural rigidity (left bottom); (d) flexural hysteresis (right bottom) [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).].

the temperature of mechanical testing, its tensile elastic modulus was markedly lowered. The tensile strength and the tensile elastic modulus of the polymer blends are shown as triangles in Figure 3; flexural properties could not be measured because of sample hardness. Judging from Figures 3(a,b), the addition of the CL in the polymer blend seemed to have a small effect on the mechanical properties. With increasing CL content, both tensile strength and tensile elastic modulus decreased gradually after once increasing.

#### Relaxation time analysis of PLA polymer alloys

To investigate the effects of the CL content, the residual monomer, and the molecular weight on the molecular mobility concerning the mechanical properties, various spin-lattice relaxation times were measured. As shown in Figure 4(a), the  $T_1C$  values of the random copolymers exhibited similar tendencies about  $^{13}\text{C}$  nuclei between the  $\text{C}=\text{O}$  and CH groups. The addition of a small amount of CL reduced the  $T_1C$  value significantly, and then, with increasing CL content, the  $T_1C$  value gradually decreased. On the other hand, the  $T_1C$  of the  $\text{CH}_3$  group did not display significant decrease by addition of a small amount of CL, but gradually

decreased depending on the amount of CL [Fig. 4(b)]. The molecular weight and the monomer contents scarcely affected the  $T_1C$  values of the random copolymers. There was also no obvious decline in  $T_1C$  values for the polymer blend, designated by triangles in the Figure. In a preliminary study, the  $T_1H$  values were almost the same as the values determined by both CH peak and  $\text{CH}_3$  peak intensities. Therefore, we are focusing on the  $T_1H$  values determined by the  $\text{CH}_3$  peaks. Figure 4(c) shows the  $T_1H$  values of the random copolymers and the polymer blends. The decreasing tendency of the  $T_1H$  value resembled the  $T_1C$  value of the  $\text{CH}_3$  group [Fig. 4(b)]; there was a smaller range of variations about the  $T_1H$  values than  $T_1C$  values of the  $\text{C}=\text{O}$  and CH groups with increasing the CL content. The  $T_1H$  values of the random copolymer decreased gradually, while those of polymer blends scarcely decreased. Figure 4(d) shows the  $T_{1\rho}H$  values of both the random copolymers and the polymer blend. The  $T_{1\rho}H$  values seem to have some oscillations, which may be the result of reaching the accuracy limits of the spectrometer. One can argue, however, that with increasing the CL content, the  $T_{1\rho}H$  values of the polymer blend showed a small change, while those of the random copolymers significantly decreased, showing larger alternation values than the  $T_1C$  s of



**Figure 7** Relationships to the  $T_{1H}$  values of the random copolymer ([blue-filled diamond]:  $\text{CH}_3$  of High  $M_n$  polymer, [dark blue-filled circle]:  $\text{CH}_3$  of low  $M_n$  polymer) and the polymer blend ([red filled triangle]:  $\text{CH}_3$ ): (a) tensile strength (left upper); (b) tensile elastic modulus (right upper); (c) flexural rigidity (left bottom); (d) flexural hysteresis (right bottom) [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).].

CH and C=O. The molecular weight effect on the  $T_{1\rho}H$  was unclear because of the data scatter. In addition to the above, we also measured the  $^{13}\text{C}$  spin-lattice relaxation time in the rotation frame ( $T_{1\rho}C$ ). However, because sufficiently long spin lock times could not be achieved for determination of the  $T_{1\rho}C$  value, the measurements had much variation; thus we cannot discuss the  $T_{1\rho}C$  value and its correlation to the mechanical properties.

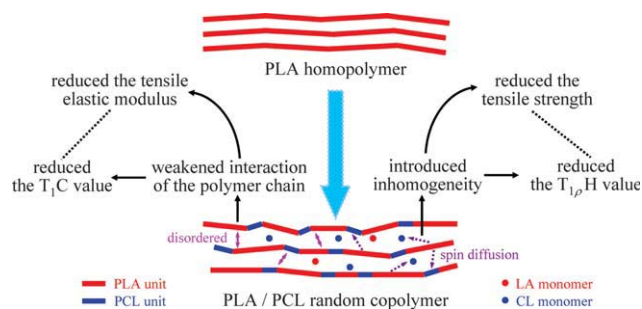
#### Relationships between the mechanical properties and the relaxation times

According to the results described above, we discover a unique correlation between the mechanical properties and the relaxation times in the random copolymer. Figure 5(a) presents plots of the  $T_{1C}$  value versus the tensile strength, and shows that the  $T_{1C}$  value increased with increasing tensile strength. The values for high molecular weight polymer exhibited a deviation from this trend in the 35–40 MPa range of the tensile strength. In contrast, the tensile elastic modulus correlated more closely with the  $T_{1C}$  value [Fig. 5(b)]. In addition, there was a weak positive correlation between the flexural rigidity and the  $T_{1C}$  value [Fig. 5(c)], while the flexural hysteresis had a nonlinear correlation with the  $T_{1C}$  value [Fig. 5(d)].

On the other hand, the relation between the  $T_{1\rho}H$  value and the tensile properties shows contrasting correlations compared with the  $T_{1C}$  value: the  $T_{1\rho}H$  value correlated more closely with the tensile strength for high molecular weight polymer [Fig. 6(a)], while there was less positive correlation between the  $T_{1\rho}H$  value and the elastic modulus [Fig. 6(b)]. The  $T_{1\rho}H$  value for the random copolymer exhibited a weak positive correlation with the flexural rigidity [Fig. 6(c)] and a nonlinear correlation with the flexural hysteresis [Fig. 6(d)], as well as the  $T_{1C}$  value. Relationships between the  $T_{1H}$  value and the mechanical properties were different from those between both the  $T_{1C}$  value and  $T_{1\rho}H$  value. As shown in Figure 7, it seems that there were weak positive correlations between the  $T_{1H}$  value and the mechanical properties; however, it was difficult to accurately discuss the molecular motion using the  $T_{1H}$  data because there were small variations about the  $T_{1H}$  values. Furthermore, as a point in common to all the spin-lattice relaxation time measurements, the relationship between the mechanical properties and the relaxation time was not influenced by the molecular weight and content of the recovered monomers (see Table I).

As described above, we observed interesting correlations between the mechanical properties and the spin-lattice time in the PLA random copolymer with





**Figure 8** Diagram of the relationship between varying the relaxation times and local region motion of the PLA/PCL random copolymer [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).].

the CL unit. Actually, many factors of the molecular motion and the morphology, affecting each other, should influence the mechanical properties. From these results, however, we can propose a hypothesis for explaining the alternation of the spin-lattice time using the molecular surroundings of the random copolymer in a local domain as shown in Figure 8. The addition of even small amounts of the CL unit disorders the orientation of the polymer chain. This weakened interaction caused an increase in the motion of the polymer chain to reduce the  $T_1C$  value. The tensile elastic modulus is predominantly affected by the motion of the backbone. The small amount of the CL unit in the polymer, and the LA and CL monomers remaining in the fibers, also introduced inhomogeneity into the polymer matrix, which causes increasing  $^1H$ - $^1H$  dipolar interaction to reduce the  $T_{1\rho}H$  value. This means that the tensile strength is more closely influenced by the inhomogeneity of the polymer matrix. On the other hand, the flexural properties are correlated with both the  $T_1C$  and  $T_{1\rho}H$  values similarly. Hence, it is considered that the flexural properties are influenced by both the motion of the polymer backbone and the inhomogeneity. To confirm our hypothesis, we are going to further study the relation of the mechanical properties and the spin-lattice targeted on the fiber produced under various conditions.

## CONCLUSIONS

Using reactive extrusion processing, a random copolymer of LA with CL was produced by melt polymerization. The random copolymer could be produced and could be spun as a monofilament fiber in the range of 0–25% PCL contents. Addition of PCL units into the monofilament consisting of the random copolymer made its tensile strength, elastic

modulus, flexural hysteresis reduce roughly in proportion to its PCL content, although the monofilaments consisting of lower molecular weight copolymer exhibited comparatively lower tensile strength and elastic modulus. Reduction of flexural rigidity with increasing the CL content of monofilament was more rapid than changes in the tensile properties. The addition of CL into the random copolymer more strongly affected the spin-lattice relaxation times. With increasing the CL contents, all of the  $T_1H$ ,  $T_{1\rho}H$ , and  $T_1C$  values of the random copolymer decreased, whereas the variations in the spin-lattice relaxation times of the polymer blend were also smaller than those of the random copolymer. The  $T_1C$  value of the random copolymer correlated more closely with the tensile elastic modulus while the relationship between the tensile strength and the  $T_1C$  value included some deviation from its trend. On the contrary, the  $T_{1\rho}H$  value of the random polymer correlated closely with the tensile strength and related to the tensile elastic modulus including scatterings. Furthermore, there were positive correlations to both the flexural rigidity and the flexural hysteresis about  $T_1C$  and  $T_{1\rho}H$ .

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