Stereocomplex Formation between Enantiomeric Poly(lactic acid)s. 7. Phase Structure of the Stereocomplex Crystallized from a Dilute Acetonitrile Solution As Studied by High-Resolution Solid-State ^{13}C NMR Spectroscopy

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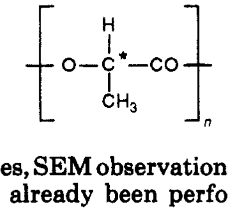
ABSTRACT: The phase structure of the stereocomplex (D1L1P) prepared from poly(D-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA) in a dilute acetonitrile solution has been examined by high-resolution solid-state ^{13}C NMR spectroscopy. Three resonance lines I–III appear at 173.3, 172.0, and 169.7 ppm respectively, for the carbonyl carbons of D1L1P. Line I is further resolved into two components with ^{13}C spin–lattice relaxation times (T_{1C}) of 128 and 17 s at 113 °C, whereas lines II and III are composed of single components with T_{1C} = 40 and 5.4 s, respectively. The components with T_{1C} = 128 and 17 s for line I can be assigned to the rigid and disordered racemic crystalline components, respectively. Line III is the contribution from the noncrystalline region, where the segments of PDLA and PLLA may be almost randomly mixed. Moreover, line II may be ascribed to the crystalline component of homopolymers incidentally produced. The total spectrum reflecting quantitatively all the components has been resolved into those four components by a line shape analysis. The degree of crystallinity estimated as a sum of mass fractions of the rigid and disordered racemic crystalline components is in agreement with that determined by differential scanning calorimetry or X-ray diffractometry. On the basis of the long period (12.0 nm) evaluated by small-angle X-ray scattering and mass fractions for the respective components, the thicknesses of the racemic crystalline and noncrystalline regions have also been determined to be 8.2 and 3.8 nm, respectively, by assuming the lamellar structure.

Introduction

Since we found that a new type of polymeric stereocomplex is formed by mixing poly(D-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA),[1] we have investigated the formation process and the structure of the stereocomplex using X-ray diffractometry,[2,3] viscometry,[4] ^{1}H NMR spectroscopy,[4] differential scanning calorimetry (DSC),[5–7] scanning electron microscopy (SEM),[7] electron diffraction (ED) analysis,[2,3,7] and polarimetry.[7] The X-ray scattering analysis revealed that in the triclinic unit cell of the crystals PDLA and PLLA chains in 3_1 helical conformation are packed side by side with the monomer residue ratio of 1:1 as a result of racemic crystallization.[2,3] When this type of racemic crystallization occurs in chloroform solution above a certain critical concentration, the viscosity of solution rises with standing time and a gel is finally formed.[4] In contrast, the stereocomplex precipitates as spherical particles of a few micrometers in diameter in an acetonitrile dilute solution.[7] The structure of poly(lactic acid) is



$$\left[-\mathrm{O}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}^*}}-\mathrm{CO}-\right]_n$$

Thermal analyses, SEM observations, ED analyses, and polarimetry have already been performed on the PLA samples racemically crystallized from the acetonitrile solution.[7] However, the phase structure for the samples, which is assumed to consist of the crystalline and noncrystalline phases, has not yet been studied. High-resolution solid-state ^{13}C NMR spectroscopy is one of the most effective methods to characterize the phase structure of crystalline polymers such as polyethylene.[10–13] Chemical shifts and magnetic relaxation parameters, which are related to the chain conformation and dynamics in the crystalline and noncrystalline phases of crystalline polymers, can be obtained by utilizing dipolar decoupling (DD), magic-angle spinning (MAS), and cross-polarization (CP) technique[14] in this spectroscopy. In this paper, we examine the phase structure of PLA racemically crystallized from acetonitrile solution by solid-state high-resolution ^{13}C NMR spectroscopy.

Experimental Section

Materials. PDLA and PLLA were synthesized and purified by the method previously reported.[15] Methyl D-lactate with an optical purity of 97% was supplied by Daicel Chemical Industries, Ltd. and hydrolyzed to D-lactic acid. L-Lactic acid with an optical purity of 98% was purchased as a 90 wt % aqueous solution from CCA Biochem bv. The oligomeric PLAs prepared by condensation polymerization of the free acids were thermally decomposed to yield the lactide monomers. Ring-opening polymerization was performed for each lactide in bulk at 140 °C for 10 h using stannous octoate (0.03 wt %) and lauryl alcohol as catalyst and initiator, respectively.[16] The resulting polymers were purified by the reprecipitation method, using methylene chloride as solvent and methanol as precipitant.

Atactic PLA, poly(DL-lactic acid) (PDLLA), was synthesized by polymerization of an equimolar mixture of D-lactide and L-lactide under almost the same conditions as for D-lactide or L-lactide. The resulting polymer was purified by the reprecipitation

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Table I
Polymerization Conditions and Molecular Characteristics of Different PLA Samples

	polymerization conditions				characteristics		
sample	SO[a] (wt %)	LA[b] (wt %)	temp (°C)	time (h)	$[\eta]$ (dL/g)	$\bar{M}_v$	$[\alpha]^{25}_D$ (deg)
D1[c]	0.03	0.5	140	10	0.89	2.5×10^4	+153
L1[d]	0.03	0.6	140	10	0.93	2.7×10^4	−154
DL1[e]	0.03	0	140	10	3.24	2.6×10^5	0

[a] Stannous octoate. [b] Lauryl alcohol. [c] Poly(D-lactic acid). [d] Poly(L-lactic acid). [e] Poly(DL-lactic acid).

method, using acetone as solvent and methanol as precipitant.

The viscosity-average molecular weights ($\bar{M}_v$) of the polymers were determined from their intrinsic viscosities $[\eta]$ in chloroform at 25 °C using the equations[17]

$$[\eta] = 5.45 \times 10^{-4} \bar{M}_v^{0.73} \quad \text{(PDLA and PLLA)} \qquad (1)$$

$$[\eta] = 2.21 \times 10^{-4} \bar{M}_v^{0.77} \quad \text{(PDLLA)} \qquad (2)$$

The specific optical rotation, $[\alpha]$, of each polymer was measured in chloroform at a concentration of 1 g/dL at 25 °C using a Perkin-Elmer Polarimeter 241 at a wavelength of 589 nm. The characteristics of the polymers used in this work are listed in Table I, together with the polymerization conditions. Here, PDLA, PLLA, and PDLLA samples are referred to as D1, L1, and DL1, respectively. $[\alpha]^{25}_D$ values were about +150° for PDLA, −150° for PLLA, and 0° for PDLLA in good accord with the reported values.[18]

A PLA stereocomplex sample, D1L1P, was obtained by the following racemic crystallization. Acetonitrile solutions (1 g/dL) of D1 and L1 were prepared separately at 80 °C and then mixed together at the same temperature. This mixture was allowed to stand in an oil bath thermostatically controlled at 80 °C for ~1 week, and resulting precipitates were separated from the solution. D1 and L1 precipitates, which are referred to as D1P and L1P, respectively, were obtained by immersing the respective 1 g/dL acetonitrile solutions in a water bath at 0 °C for 1 day and were separated from the solutions at the same temperature. After being washed intensively twice with fresh acetonitrile at the precipitation temperature, each sample was immersed in methanol at room temperature for 1 day, to remove residual acetonitrile, and dried in vacuo at 50 °C for ~1 week. D1L1P was annealed at 140 °C for 1 h or at 216 °C for 10 min in a nitrogen atmosphere, while D1P and L1P were annealed at 140 or 163 °C for 1 h. Higher annealing temperatures for the respective samples correspond to the end temperatures of lower melting endothermic peaks on DSC curves, as described later. PDLLA films (hereafter abbreviated DL1F) were obtained by the following method. A 1 g/dL acetone solution of DL1 was cast on a flat glass plate, and the solvent was allowed to evaporate at room temperature for ~1 week. The solvent molecules left in the resulting films were replaced by methanol. The films were dried in vacuo at 50 °C for another weak and annealed in a nitrogen atmosphere at 140 °C for 1 h prior to NMR measurements.

^{13}C NMR Measurements. High-resolution solid-state ^{13}C NMR measurements were carried out on a JEOL JNM-FX200 spectrometer operating under a static magnetic field (B_0) of 4.7 T. ^{1}H and ^{13}C radiofrequency field strengths $\gamma B_1/2\pi$ were 69.4 kHz for the CP process and other pulse sequences used in this work, except for the DD process, where the ^{1}H field strength was reduced to 59.5 kHz. MAS was carried out at a rate of 4.0 kHz using a cylindrical rotor made of aluminum oxide and poly(imide amide) resins. The sample temperature was calibrated using the temperature dependence[19] of relative chemical shifts of CH_2 and OH protons of ethylene glycol in a glass ampule, which was packed with KBr in a MAS rotor.[20,21] ^{13}C spin–lattice relaxation times (T_{1C}) were measured mainly by the CPT1 pulse sequence,[22] while the T_{1C}'s shorter than a few seconds were measured by the saturation–recovery pulse sequence modified for solid-state measurements.

Results and Discussion

Figure 1 shows DSC thermograms of D1P and D1L1P annealed at different temperatures, together with the result for DL1F. As reported in a previous paper,[1] the peak around 180 °C is due to melting of homopolymer crystallites, while the peak around 230 °C is due to the melting of racemic crystallites. It is, therefore, clear from Figure 1 that D1P contains the homopolymer crystallites, while D1L1P is composed of the racemic crystallites. D1P and D1L1P, both of which were annealed at 140 °C, give double melting peaks, suggesting the existence of crystals possibly with different crystal thicknesses in these samples. However, single melting peaks are observed for D1P annealed at 163 °C and D1L1P annealed at 216 °C, whose temperatures correspond to the end temperatures of the melting peaks at the lower temperature sides. In contrast, DL1F, which is completely amorphous, shows no melting peak. Melting temperatures (T_m) and enthalpies of fusion (ΔH_f) for these samples are summarized in Table II.

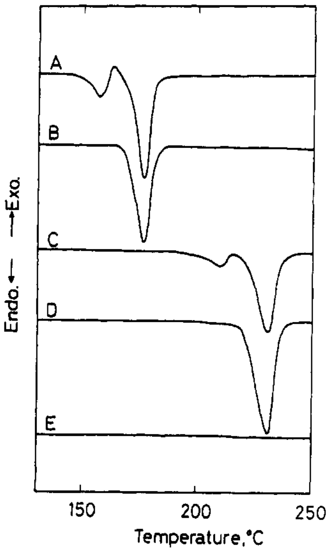

Figure 1. DSC thermograms of different PLA samples: (A) D1P annealed at 140 °C for 1 h, (B) D1P annealed at 163 °C for 1 h, (C) D1L1P annealed at 140 °C for 1 h, (D) D1L1P annealed at 216 °C for 10 min, and (E) DL1F annealed at 140 °C for 1 h.

Figure 2 shows 50-MHz CP/MAS ^{13}C NMR spectra of aliphatic and carbonyl carbons for D1P, D1L1P, and DL1F. In this figure, stick-type ^{13}C NMR spectra of these carbons are also shown for D1 in chloroform-*d* solution. Since D1 and L1 give the identical NMR spectra in both solid and solution states, only the spectra for D1 are shown in Figure 2. X-ray scattering analysis revealed that PLLA crystallizes in pseudoorthorhombic[23] or hexagonal[24] crystalline modification with 10_3-helical conformation[23] (α-form) and in β-modification with 3_1-helical conformation (β-form).[2,25] In these crystalline modifications the respective carbons should have different conformations and packing sites in the unit cells. The existence of such different carbons may result in the fine splittings of the resonance lines for D1P, although the detailed assignment for the split resonance lines has not been done in this study. On the other hand, each constituent carbon of DL1F gives a single resonance line whose chemical shift is very close to that of D1 in solution. This implies that PDLLA molecules

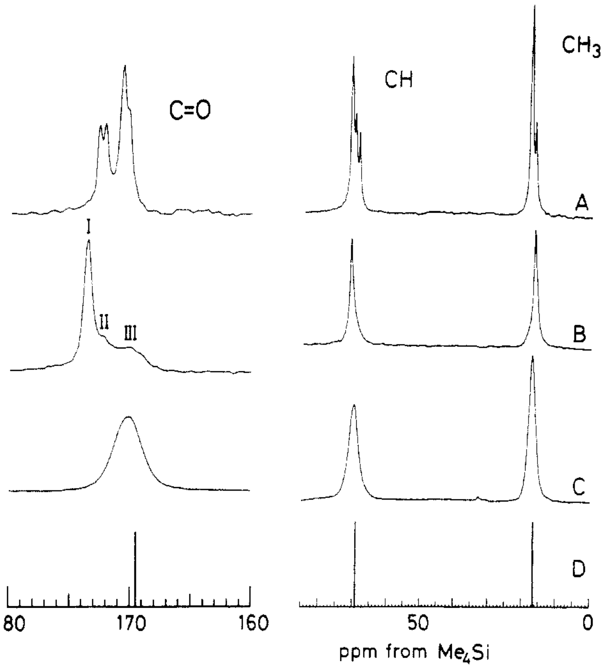

Figure 2. 50-MHz CP/MAS ^{13}C NMR spectra of different PLA samples at 40 °C: (A) D1P annealed at 163 °C, (B) D1L1P annealed at 216 °C, and (C) DL1F annealed at 140 °C. (D) ^{13}C NMR spectrum of D1 in chloroform-*d*.

Table II
Melting Temperatures T_m and Enthalpies of Fusion ΔH_f of Different PLA Samples

	annealing conditions		thermal properties	
sample	temp (°C)	time (min)	T_m (°C)	ΔH_f (J/g)
D1P[a]	140	60	157, 177	81
D1P[a]	163	60	177	79
D1L1P[b]	140	60	211, 230	98
D1L1P[b]	216	10	231	102
DL1F[c]	140	60		0

[a] Precipitated from the 1 g/dL acetonitrile solution of D1. [b] Prepared by the racemic crystallization of D1 and L1 in the 1 g/dL acetonitrile solution. [c] Films of DL1 prepared by casting the 1 g/dL acetone solution on glass.

hold a random conformation as in solution even after desolvation. In contrast, the spectrum of D1L1P is evidently dissimilar to the spectra of the D1P and DL1F. In particular, the resonance line of the carbonyl carbon of D1L1P splits into three lines, I (173.3 ppm), II (172.0 ppm), and III (169.7 ppm). Line I can be probably assigned to the racemic crystalline component, because line I is not observed for the homopolymer samples. Line III is simply assigned to the noncrystalline component consisting of segments of PDLA and PLLA, because the chemical shift of this line is very close to that for the noncrystalline DL1F or for D1 in solution. These assignments are confirmed by the results of T_{1C} measurements and a line shape analysis, as described later. Line II may be ascribed to the crystalline component of homopolymers additionally produced, because the T_{1C} value of this component is quite large, as described later. Since there is no endotherm due to the homopolymers for D1L1P, as shown in Figure 1, such homopolymer crystals must be too small in size to be detected by DSC. Further examination should be made to determine the assignment of this component.

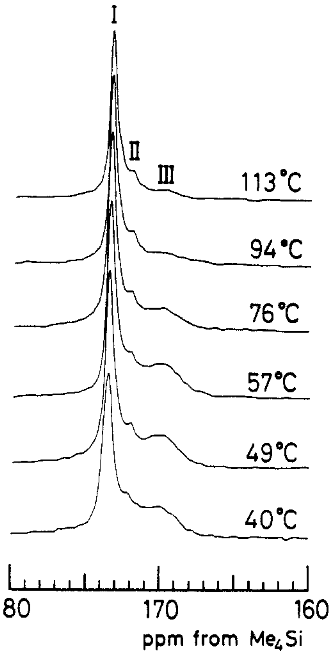

Figure 3. CP/MAS ^{13}C NMR spectra obtained at different temperatures for the carbonyl carbon of D1L1P annealed at 216 °C.

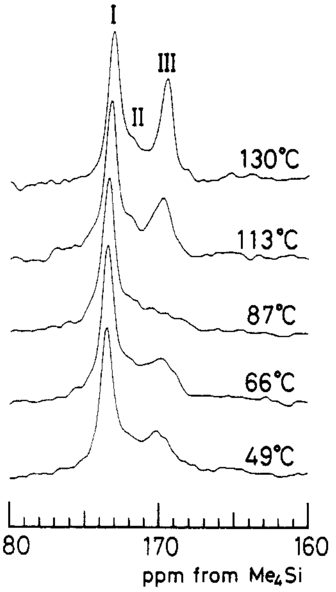

Figure 4. ^{13}C NMR spectra for the carbonyl carbon of D1L1P annealed at 216 °C, which were measured by using a 45° single pulse with a recycle time τ_1 = 15 s at different temperatures.

Figure 3 shows CP/MAS ^{13}C NMR spectra of the carbonyl carbon of D1L1P obtained at different temperatures above room temperature. Line III is decreased in intensity at temperatures above 76 °C. This may be due to the decrease in the cross-polarization efficiency or the reduction in the efficiency of the dipolar decoupling for this component by the onset of the motion with the order of 10^4–10^5 Hz in the noncrystalline region above T_g (58 °C).[26] In contrast, there seems to be no significant effect of temperature on line I, indicating that the assignment of line I as the crystalline component is plausible. Line II also seems not to change in shape and intensity over this temperature range, confirming that this line may be ascribed to the crystalline component of homopolymers.

In order to enhance the intensity of line III, dipolar decoupled MAS (DD/MAS) ^{13}C NMR spectra have been measured in a similar temperature range by using a 45° single-pulse sequence with a recycle time τ_1 of 15 s after a free induction decay (FID) (Figure 4). Line III at 170 ppm becomes broader at 49–87 °C with increasing temperature, whereas it increases in intensity and resolution above 113 °C. Since the intensity reduction of line III around 87 °C is observed regardless of the use of the CP technique, such reduction in intensity is due to the decrease

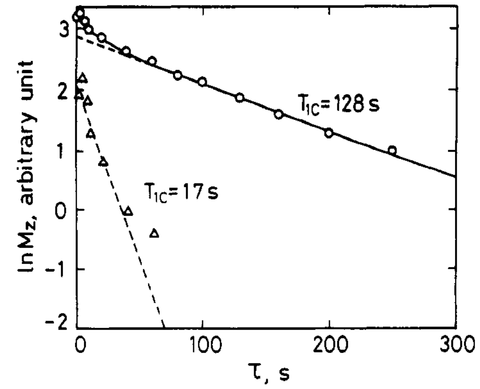

Figure 5. ^{13}C spin-lattice relaxation decay for line I of D1L1P annealed at 216 °C, which was measured at 113 °C by the CPT1 pulse sequence.

Table III
^{13}C Chemical Shifts and Spin-Lattice Relaxation Times (T_{1C}) for Resonance Lines I-III of D1L1P Annealed at 216 °C

	line		
	I	II	III
chemical shift (ppm)	173.3	172.0	169.7
T_{1C} (s)	128, 17	40	5.4

in dipolar decoupling efficiency around T_g. The narrowing of line III above 113 °C may be the glass transition process observed for the polymer by ^{13}C NMR spectroscopy. This finding supports the assignment of line III to the noncrystalline component. Comparison between the CP/MAS and DD/MAS spectra above 94 °C indicates that the decrease in peak intensity of line III above 94 °C in the CP/MAS spectra is due to reduction in the efficiency of cross polarization.

In order to investigate the phase structure of D1L1P in detail, we have performed T_{1C} measurements by the CPT1 pulse sequence and the modified saturation recovery method at 113 °C. The logarithmic peak intensity of line I obtained by the CPT1 pulse sequence is plotted as a function of the delay time τ for the spin relaxation in Figure 5. The overall decay curve (solid line) can be resolved into two exponentials (broken lines), a slower decay with T_{1C} = 128 s and a rapid decay with T_{1C} = 17 s, by the least-squares method with a computer. T_{1C} values thus obtained are listed in Table III together with the results for lines II and III. Lines II and III consist of single components with T_{1C} values of 40 and 5.4 s, respectively. The shortest T_{1C} value of line III indicates that this component is highly enhanced in molecular mobility in this sample (D1L1P). Therefore, this finding also confirms the assignment that line III is ascribed to the noncrystalline component. On the other hand, the component with T_{1C} = 128 s in line I is assignable to the racemic crystalline component, since a longer T_{1C} value suggests more restricted molecular motion under this experimental condition. The T_{1C} value of 40 s for line II suggests that this component is also significantly restricted in molecular mobility and may be therefore assignable to the crystalline component of the homopolymers.

The spectrum for the components with shorter T_{1C} values can be obtained by subtracting the spectrum (Figure 6B) of the component with T_{1C} = 128 s, which is measured by the CPT1 pulse sequence, from the total spectrum (Figure 6A) obtained by a 45° single-pulse sequence. Here, the delay time τ for the relaxation was set to 200 s in the CPT1 pulse sequence to suppress the shorter T_{1C} components, and the recycle time τ_1 was chosen to be 400 s for the single-pulse sequence to obtain the spectrum reflecting the contributions from all structural components. The carbonyl resonance line (Figure 6B) obtained by the CPT1 pulse sequence contains only the rigid racemic crystalline component. The difference spectrum (Figure 6C) thus obtained gives two resonance lines with chemical shifts of 169.7 and 173.3 ppm, which can be described by single Lorentzian functions. The downfield component, which mainly reflects the component with T_{1C} = 17 s, may be assignable to the somewhat disordered component in the racemic crystalline region, because it has almost the same chemical shift as does the rigid racemic crystalline component with T_{1C} = 128 s and the shorter T_{1C} (17 s) suggests relatively higher molecular mobility. The evidence supporting this assignment will be given below.

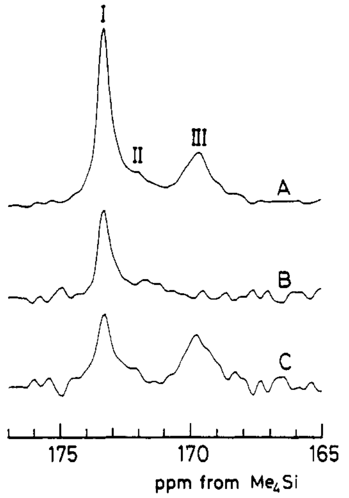

Figure 6. ^{13}C NMR spectra at 113 °C for the carbonyl carbon of D1L1P annealed at 216 °C: (A) total spectrum, (B) rigid racemic crystalline component with T_{1C} = 128 s, measured by the CPT1 pulse sequence with τ = 200 s, and (C) difference spectrum (C = A - 1.18B).

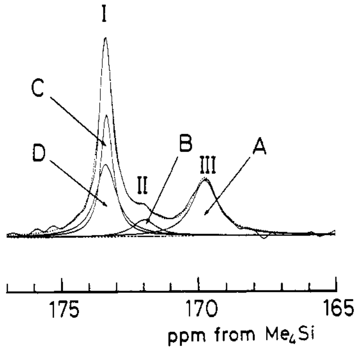

Figure 7. Component analysis of the total spectrum of D1L1P, which corresponds to Figure 6A: (A) noncrystalline component, (B) crystalline component of homopolymers, (C) rigid racemic crystalline component, (D) disordered racemic crystalline component. Integrated intensity fractions of components A-D are 0.29, 0.08, 0.31, and 0.32, respectively.

Assuming that the respective components can be described by single Lorentzian functions, the total spectrum (DD/MAS ^{13}C NMR spectrum) at 113 °C for the carbonyl carbon of D1L1P has been resolved into four components A-D by the least-squares method, as shown in Figure 7. The composite curve of the four components (broken line) is in good agreement with the observed spectrum (solid line). Components A, C, and D are the noncrystalline, rigid racemic crystalline, and disordered racemic crystalline components, respectively. Component B corresponds to line II, which may be ascribed to the crystalline component of the homopolymers. Mass fractions of components A–D are estimated to be 0.29, 0.08, 0.31, and 0.32, respectively. The degree of crystallinity as determined as a sum of the mass fractions of the components C and D is 0.63, which is almost in accord with the degree of crystallinity (x_c) of 0.72 estimated by DSC using

$$x_c = \Delta H_{f,exp}/\Delta H_f \qquad (3)$$

Here, $\Delta H_{f,exp}$ and ΔH_f are the heats of fusion experimentally obtained for a given polymer and for the corresponding polymer with $x_c = 1$, respectively; ΔH_f was assumed to be 142 J/g[27] for the case of D1L1P. Component B is neglected in this calculation, since this component was not detected by DSC, as shown in Figure 1. The degree of crystallinity roughly estimated by wide-angle X-ray scattering was approximately 0.70, which is also in agreement with the value estimated from the NMR line shape analysis mentioned above. The agreement of the degrees of crystallinity estimated by three different methods supports the assignment of the racemic crystalline component.

Small-angle X-ray scattering measurements have determined the long period of D1L1P to be 12.0 nm. For the calculation of thicknesses of the respective components, we assume a lamellar structure where the rigid and the disordered racemic crystalline components form one region and the noncrystalline component belongs to another region. The thicknesses l_j of racemic crystalline and noncrystalline regions are estimated by

$$l_j = Lv_j \qquad (4)$$

where L is the long period and v_j is the volume fraction of each component. Here, we simply assume that the volume fraction equals the mass fraction. When component B is assumed not to be included in the lamellar structure, the estimated thicknesses l_j are 8.2 and 3.8 nm for the racemic crystalline and noncrystalline regions, respectively. These values do not significantly differ from the values 7.6 and 3.5 nm obtained by assuming that component B also belongs to the lamellar structure.

Conclusions

1. The 50-MHz CP/MAS ^{13}C resonance line of carbonyl carbons for the PLA stereocomplex, which was prepared from PDLA and PLLA in a dilute acetonitrile solution, splits into three lines, I–III. Line I is further resolved into two components with T_{1C} values of 128 and 17 s, which can be assigned to the rigid and disordered racemic crystalline components, respectively. In contrast, lines II and III comprise single components with $T_{1C} = 40$ and 5.4 s assignable to the crystalline component of homopolymers and the noncrystalline component, respectively. The latter component may be composed of the random mixture of segments of PDLA and PLLA.

2. The total spectrum of the stereocomplex, which was measured by a 45° single-pulse sequence, can be resolved into four components described above by the line shape analysis, assuming that each constituent line is described in terms of a Lorentzian curve. The sum of the mass fractions of the rigid and disordered racemic crystalline components is in accordance with the degrees of crystallinity determined by DSC and X-ray diffractometry.

3. The long period of the stereocomplex is determined to be 12.0 nm by small-angle X-ray scattering. Assuming the lamellar structure, the thicknesses of the racemic crystalline and noncrystalline regions of this sample are estimated to be 8.2 and 3.8 nm, respectively.

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