

## Supporting Information for:

# Synthesis, Stereocomplex Crystallization and Homo-Crystallization of Enantiomeric Poly(lactic acid-*co*-alanine)s with Ester and Amide Linkages

*Hideto Tsuji,<sup>a\*</sup> Shotaro Sato,<sup>b</sup> Noriaki Masaki,<sup>a</sup> Yuki Arakawa,<sup>a</sup> Akinori Kuzuya,<sup>b,c</sup>  
and Yuichi Ohya<sup>b,c\*</sup>*

<sup>a</sup> *Department of Environmental and Life Sciences, Graduate School of Engineering,  
Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan*

*E-mail: [tsuji@ens.tut.ac.jp](mailto:tsuji@ens.tut.ac.jp)*

<sup>b</sup> *Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and  
Bioengineering, Kansai University, Yamate, Suita, Osaka 564-8680, Japan*

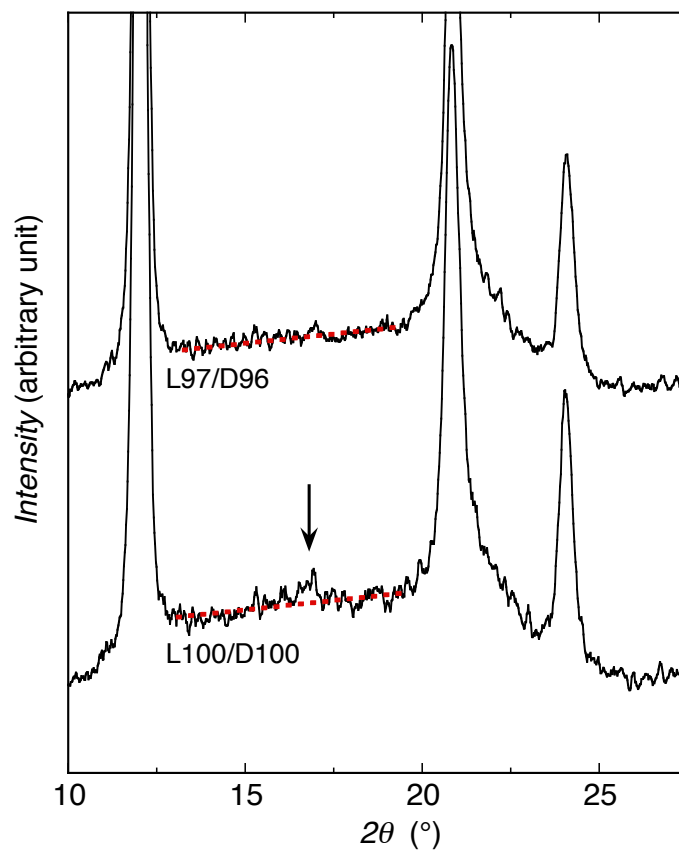
<sup>c</sup> *Collaborative Research Center of Engineering, Medicine and Pharmacology (CEMP),  
Organization for Research and Development of Innovative Science and Technology (ORDIST),  
Kansai University, Suita, Osaka 564-8680, Japan*

*E-mail: [yohya@kansai-u.ac.jp](mailto:yohya@kansai-u.ac.jp)*

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**S1. Magnified and smoothed WAXD profiles of melt-crystallized L100/D100 and L97/D96 blend sample ( $T_c = 160^\circ\text{C}$ ) (Figure S1)**



**Figure S1.** Magnified and smoothed WAXD profiles of melt-crystallized L100/D100 and L97/D96 blend sample ( $T_c = 100^\circ\text{C}$ ). The arrow indicates a main peak of homo-crystallites.

## S2. Crystallinity

**Table S1.** Crystallinity of nonblended and 50/50 blended samples.

Code	Crystallization	$X_c(\text{H})^{\text{a}}$ (%)	$X_c(\text{S})^{\text{a}}$ (%)	$X_c(\text{H+S})^{\text{a}}$ (%)
L100	Solution	60.4	0.0	60.4
L97		52.3	0.0	52.3
L94		33.7	0.0	33.7
L88		0.0	0.0	0.0
L100	Melt ( $T_c=100^\circ\text{C}$ )	65.5	0.0	65.5
L97		59.8	0.0	59.8
L94		60.6	0.0	60.6
L88		31.7	0.0	31.7
D100	Solution	61.1	0.0	61.1
D96		49.8	0.0	49.8
D94		0.0	0.0	0.0
D87		0.0	0.0	0.0
D100	Melt ( $T_c=100^\circ\text{C}$ )	71.0	0.0	71.0
D96		64.9	0.0	64.9
D94		64.9	0.0	64.9
D87		39.9	0.0	39.9
L100/D100	Solution	0.0	62.2	62.2
L97/D96		0.0	62.1	62.1
L94/D94		0.0	63.9	63.9
L88/D87		0.0	59.8	59.8
L100/D100	Melt ( $T_c=100^\circ\text{C}$ )	35.8	15.9	51.7
L97/D96		0.0	55.8	55.8
L94/D94		0.0	55.7	55.7
L88/D87		0.0	55.2	55.2
L100/D100	Melt ( $T_c=160^\circ\text{C}$ )	1.7	48.9	50.6
L97/D96		0.0	55.4	55.4
L94/D94		0.0	41.6	41.6
L88/D87		0.0	39.7	39.7

<sup>a)</sup>  $X_c(\text{H})$  and  $X_c(\text{S})$  are crystallinities of homo- and SC-crystallites, respectively.  $X_c(\text{H+S}) = X_c(\text{H}) + X_c(\text{S})$

### S3. Thermal properties

**Table S2.** Thermal properties of nonblended and 50/50 blended samples.

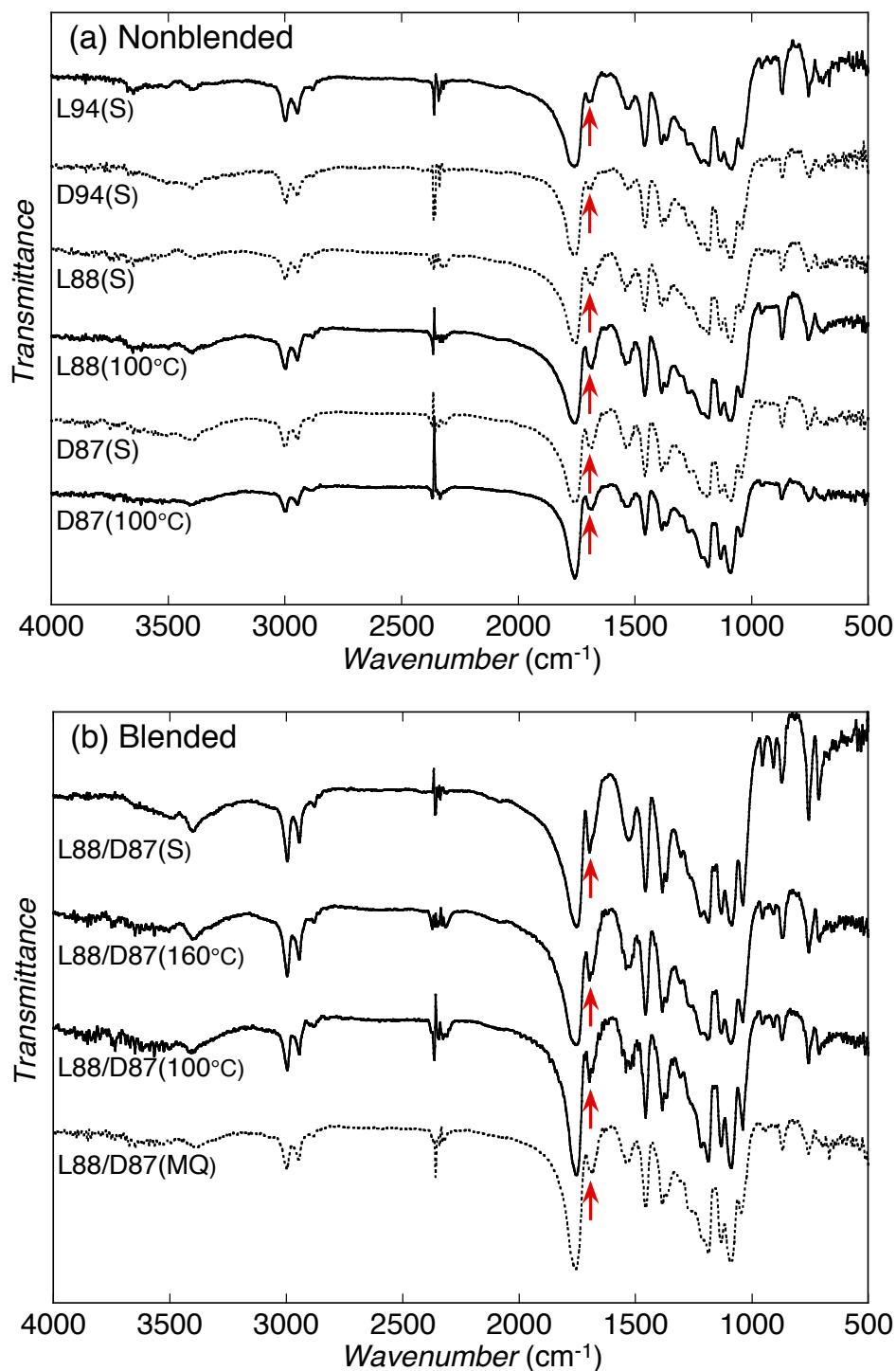
Code	Crystallization	$T_g^a$ (°C)	$T_{cc}^a$ (°C)	$T_m(H)^a$ (°C)	$T_m(S)^a$ (°C)	$\Delta H_{cc}^b$ (J g <sup>-1</sup> )	$\Delta H_m(H)^b$ (J g <sup>-1</sup> )	$\Delta H_m(S)^b$ (J g <sup>-1</sup> )	$\Delta H(tot)^b$ (J g <sup>-1</sup> )
L100	Solution	53.5		170.7		0.0	57.2	0.0	57.2
L97		51.2	94.2	164.8		-2.3	50.0	0.0	47.7
L94		50.2	105.3	155.1		-6.0	34.8	0.0	28.8
L88		57.7	114.6 <sup>c)</sup>	135.7		-1.3	1.4	0.0	0.1
L100	Melt ( $T_c=100^\circ\text{C}$ )	50.5		155.9, 169.3		0.0	54.3	0.0	54.3
L97		50.5		145.2, 162.2		0.0	41.8	0.0	41.8
L94		48.6		145.7, 153.6		0.0	39.0	0.0	39.0
L88		47.7		127.4, 134.2		0.0	21.0	0.0	21.0
D100	Solution	53.8		170.6		0.0	52.2	0.0	52.2
D96		52.6	94.1	165.6		-4.3	43.9	0.0	39.6
D94		56.3, 62.5	108.6	152.6, 156.5		-29.3	30.4	0.0	1.1
D87		56.5	115.4	134.5		-3.6	4.3	0.0	0.7
D100	Melt ( $T_c=100^\circ\text{C}$ )	50.6		156.7, 169.3		0.0	53.0	0.0	53.0
D96		50.3		146.9, 163.9		0.0	40.8	0.0	40.8
D94		49.2		149.7, 155.7		0.0	37.0	0.0	37.0
D87		50.2		128.9, 135.2, 149.4		0.0	13.8	0.0	13.8
L100/D100	Solution	56.7			240.9	0.0	0.0	43.8	43.8
L97/D96		51.5			224.8, 229.6	0.0	0.0	51.7	51.7
L94/D94		49.9			214.6	0.0	0.0	62.2	62.2
L88/D87		50.7			208.0	0.0	0.0	56.9	56.9
L100/D100	Melt ( $T_c=100^\circ\text{C}$ )	50.9	205.3	152.4	241.0	-25.3	24.5	57.0	56.2
L97/D96		39.4			215.6	0.0	0.0	42.8	42.8
L94/D94					205.0	0.0	0.0	36.8	36.8
L88/D87					191.0	0.0	0.0	16.9	16.9
L100/D100	Melt ( $T_c=160^\circ\text{C}$ )	52.1	85.3	167.2	216.5, 230.9, 241.9	-7.8	8.5	43.0	43.7
L97/D96		49.0		159.5	216.9, 221.5, 231.9	0.0	1.3	49.2	50.5
L94/D94					205.4	0.0	0.0	55.5	55.5
L88/D87		37.2	100.2	148.3	196.8	-19.2	0.3	31.6	12.7

<sup>a)</sup>  $T_g$ ,  $T_{cc}$ , and  $T_m$  are glass transition, cold crystallization, and melting temperatures, respectively.

<sup>b)</sup>  $\Delta H_{cc}$ ,  $\Delta H_m(H)$ , and  $\Delta H_m(S)$  are enthalpies of cold crystallization and melting of homo- and SC crystallites, respectively.  
 $\Delta H(tot) = \Delta H_{cc} + \Delta H_m(H) + \Delta H_m(S)$ .

<sup>c)</sup> The peak was too broad to estimate  $T_{cc}$  as peak temperature. Shown  $T_{cc}$  is the intersection temperature of two tangential lines for the higher and lower sides of the peak.

#### S4. Whole FTIR spectra of solution- and melt-crystallized L88, D87, and L88/D87 blends



**Figure S2.** FT-IR spectra of nonblended (a) and blended (b) samples. Red arrows indicate the C=O stretching peaks of amide groups in alanine units. The spectra of crystalline and amorphous samples are shown with solid and dotted lines, respectively, and (S) and (MQ) mean that the samples were prepared by solution-crystallization and melt-quenching, respectively. The melt-quenched L88/D87(MQ) was prepared by melting at 250 °C for 100 s and quenched at 0 °C for at least 5 min.