Surface and bulk structure of poly-(lactic acid) films studied by vibrational sum frequency generation spectroscopy

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Introduction

- Biodegradable and biocompatible polymers
- Devices polymers for drug delivery and implants

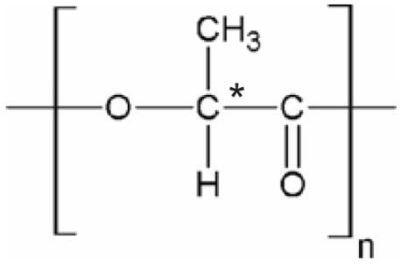
→ Poly-(lactic acid) (PLA)

Applications of PLA :

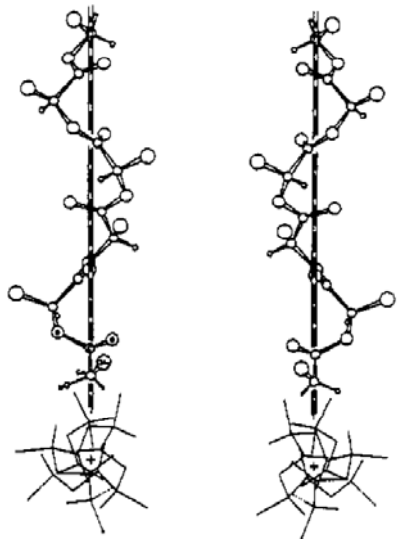
- Bone fixation devices
- Blood vessel repair
- Medicine delivery systems

The structural formula of Poly-(lactic acid) (PLA)

structural formula

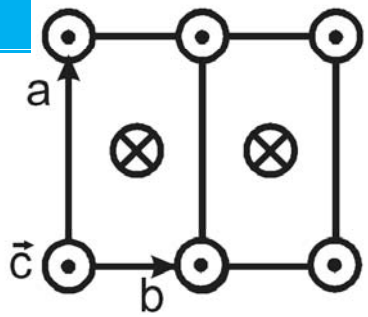


The central carbon atom constitutes a chiral center.



Poly（L-lactide)　Poly (D-lactide)

Unit cell



- The crosses (dots) indicate a helix directed into (out of) the plane of the paper.

- The axes of the unit cell are denoted by a, b, and c, where c is along the helical axis.

- Cell dimensions are a = 1.06, b = 0.61, and c = 2.88 nm (parallel to the c axis)

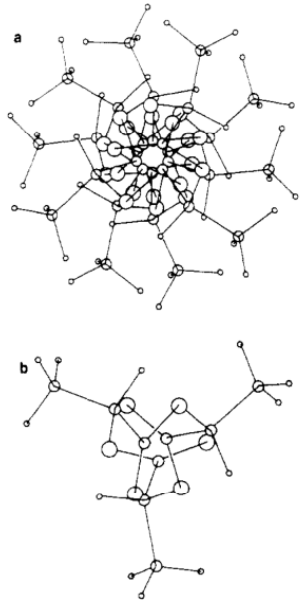


Figure 5. Projections perpendicular to the helical axis of a −10/3 helical conformation (a) and a −3/1 helical conformation (b).

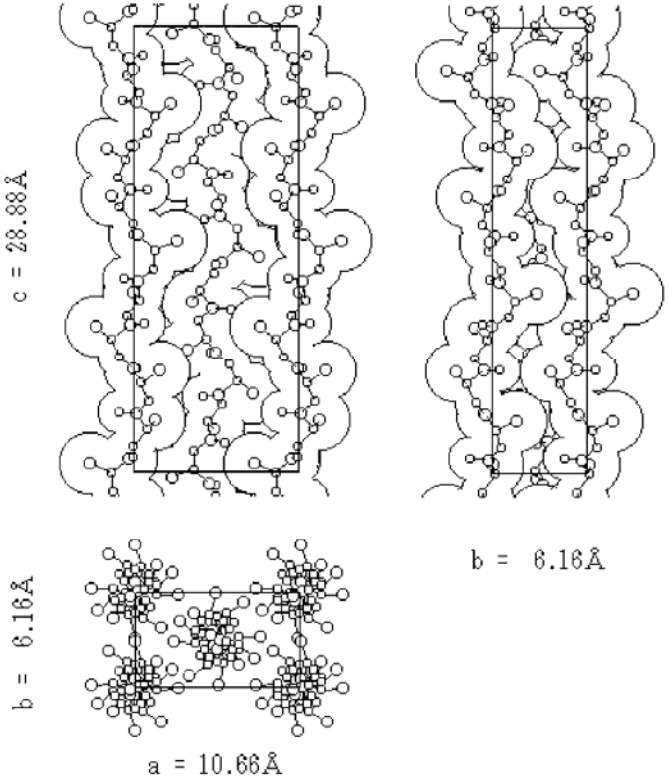


Figure 5. Crystal structure of the α-form of PLLA. Upper left: *ac* projection; upper right: *bc* projection, lower: *ab* projection. In the *ac* and *bc* projections, chains are enveloped with van der Waals radii of the constituent atoms.

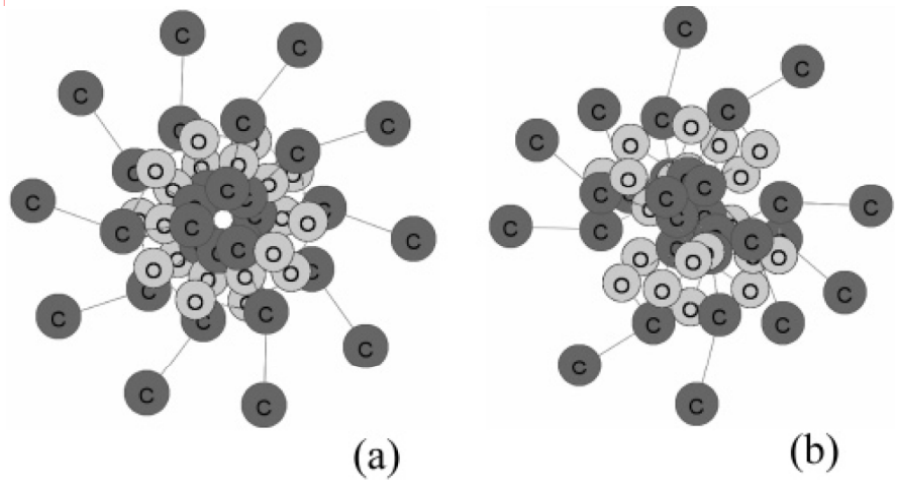


Figure 1. Two proposed forms of the α-crystals: (a) Aleman/Puiggali/ Lotz coordinates; (b) Sasaki/Asakura coordinates. Hydrogens are abbreviated to aid clarity.

Preparation of Samples

Three different kinds of polymers :

- poly(L-lactic acid) (PLLA)
- poly(D-lactic acid) (PDLA)
- Racemic poly(DL-lactic acid) (PDLLA)

Spin coated condition: polymer powder + chloroform :2.5 wt% solution

↓

on glass substrates at 3000 rpm for 1 min

↓

films of thicknesses : ~0.8 μm (measured by ellipsometry)

Films :

- Enantiomeric amorphous films : - melting the spin coated films at 190 ^{o}C
  - quenching in liquid nitrogen.
- Crystalline films: the spin coated films annealed at ~80 ^{o}C for 10 min.
- PDLLA and PLLA/PDLA films : only spin coated films

Sum-frequency generation- second-order nonlinear optical process

The SF Intensity : $$I_{\mathrm{SFG}}(\omega) \propto \left| E_{\mathrm{IR}}(\omega) \sum_n \int_{-\infty}^{\infty} \chi^{(2)}(\omega') E_{\mathrm{VIS}}(\omega' - \omega) \mathrm{d}\omega' \right|^2$$

$$\chi^{(2)}(\omega) = \chi^{(2)}_{\mathrm{NR}} + \sum_n \chi^{(2)}_n(\omega)$$

$$= A_{\mathrm{NR}} \mathrm{e}^{\mathrm{i}\Delta\phi} + \sum_n \frac{A_n}{(\omega - \omega_{0n}) + \mathrm{i}\Gamma_{\mathrm{n}}},$$

E_{IR} : the envelope of the IR spectrum
E_{VIS} the envelope of the visible spectrum
A_n : the amplitude
ω : the IR frequency
ω_{0n} : the peak centers
Γ_n : the damping constants of the vibrational mode n.
$\Delta\phi$: the relative phase difference between the resonant and the non-resonant fields

Setup

Laser system : 1 kHz broadband high power Ti:Sapphire laser

The IR pulses : centered around 3000 cm^{-1} with a FWHM of 150 cm^{-1}, a pulse duration of 175 fs.

The visible pulses : centered at 800 nm and shaped to a FWHM of 5 cm^{-1} .
Pulse energies : 10(IR) and 3 (vis) μJ near the sample
Focus diameter : 0.75 mm.

The VSFG experiments were performed in a reflection geometry, with incoming angles of 60 ^{o} (IR) and 40 ^{o}C(vis) with respect to the surface normal.

Result

Transmission IR spectra in the C-H strecting region

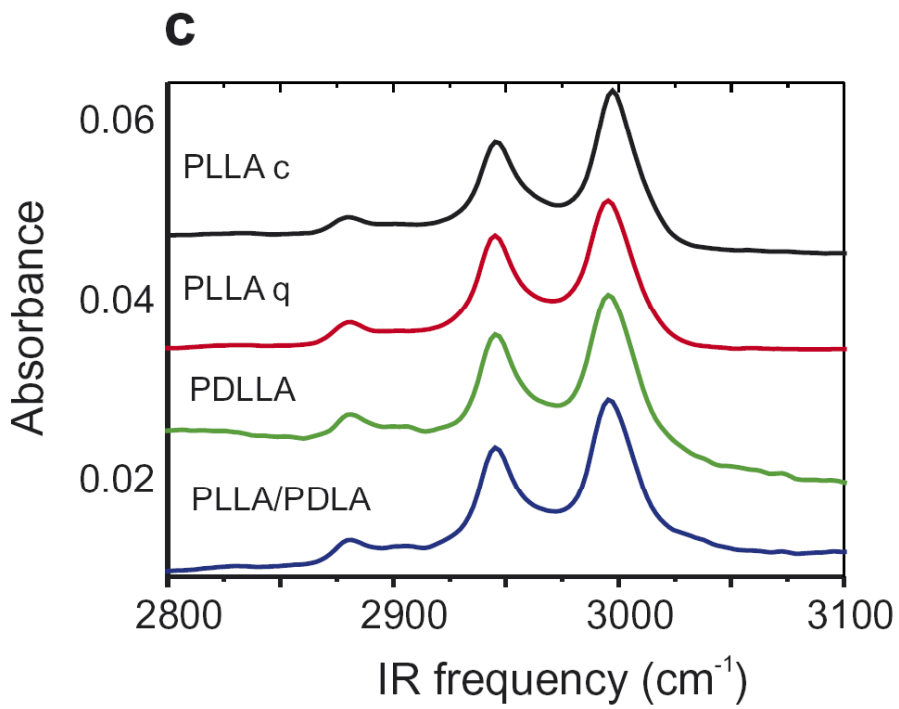


Fig. Transmission IR spectra from top to bottom of a crystalized PLLA film, a quenched (amorphous) PLLA film, a PDLLA film and a PDLA/PLLA film.

- the four IR spectra resemble each other closely, despite different configurations and properties of the different films.

- the difference in crystallinity is apparent,
  this does not show from the spectra

- PLA : poly(L-lactic acid) (PLLA)
  poly(D-lactic acid (PDLA)

- PDLLA : The stereo-complexed polymer with randomly inserted D and L monomer units in a single chain is an amorphous polymer

- PDLA/PLLA : The stereo-complexed polymer built from a 1:1 solution of PLLA and PDLA chains

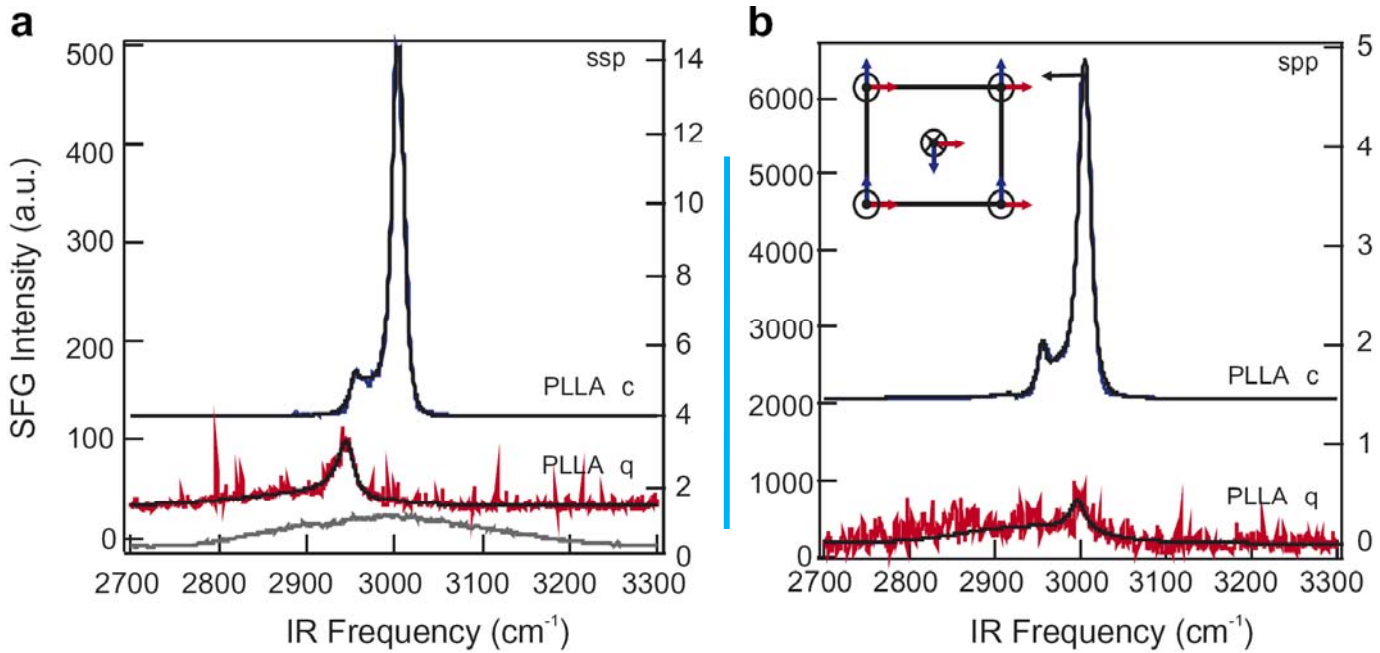


Fig. 2. VSFG spectra of (a) the surface (ssp), the bulk (b, spp), of an amorphous and a crystalline PLLA film. In (a) the (scaled) non-resonant spectrum with ppp polarization combination of a gold surface is also displayed. The left axis reflects the intensity of the crystalline film, while the right axis reflects the intensity of the quenched film. Data in all spectra are comparable in intensity. The spectra are offset for clarity. The inset in (b) illustrates how an anti-parallel arrangement may lead to amplification of a subset of normal modes along one of the crystalline axes.

quenched film :
a symmetric methyl stretch at 2947 cm^{-1}
($\Delta\phi = 0$; $A_{2947} = 1.18 \pm 0.06$; $\Gamma = 12.0 \pm 0.8$ cm^{-1}),
the anti-symmetric methyl stretch mode at 2997cm^{-1}
($A_{2997} = 0.18 \pm 0.04$; $\Gamma = 13.0 \pm 2.6$ cm^{-1})

crystalline film:
2954 cm^{-1}($\Delta\phi$=100; $A_{2954} = 8.9 \pm 0.5$; $\Gamma = 7.0 \pm 0.4$$cm^{-1}$),
2997 cm^{-1}($A_{2997} = 16.6 \pm 0.3$; $\Gamma = 15.0 \pm 0.3$$cm^{-1}$),
2965 cm^{-1}($A_{2965} = 14.4 \pm 2.8$; $\Gamma = 13.0 \pm 3.9$$cm^{-1}$),
3007 cm^{-1} ($A_{3007} = 22.5 \pm 4.5$; $\Gamma = 8.7 \pm 0.4$$cm^{-1}$).

quenched film : one peak of the antisymmetric methyl stretch mode at 2997 cm^{-1}
($\Delta\phi = 0$; $A_{2997} = 1.3 \pm 0.16$; $\Gamma = 11.0 \pm 2.2$ cm^{-1})

crystalline PLLA film :
2954 cm^{-1}($\Delta\phi = 100$; $A_{2955} = 32.6 \pm 1.3$; $\Gamma = 6.4 \pm 0.3$ cm^{-1}),
2965 cm^{-1}($A_{2965} = 46.2 \pm 10.1$; $\Gamma = 14.0 \pm 3.5$ cm^{-1}),
2997 cm^{-1}($A_{2997} = 36.1 \pm 1.6$; $\Gamma = 13.0 \pm 0.26$ cm^{-1}),
3007 cm^{-1}($A_{3007} = 75.6 \pm 1.7$; $\Gamma = 9.0 \pm 0.5$ cm^{-1})

In crystalline structure of PLLA

- PLLA form : The α- crystalline structure

- PLLA chain forms : left-handed helix with C_{10} symmetry

→ chirality in the whole chain

- Unit cell chain form : chains are packed in a pseudo-orthorombic

anti-parallel arrangement with a unit cell containing two helices

- PLLA crystal : - $P2_12_12_1$ space group

- D_2 symmetry group

→

- non-centrosymmetric

- six tensor elements

$\chi^{(2)}_{xyz} = \chi^{(2)}_{yxz}$ (B_1 symmetry)

$\chi^{(2)}_{xzy} = \chi^{(2)}_{zxy}$ (B_2 symmetry)

$\chi^{(2)}_{yzx} = \chi^{(2)}_{zyx}$ (B_3 symmetry)

←

Probe with the polarization combinations
(spp, psp, pps)

Table 2. Group Symmetry Species Assignment to PLA α-Crystal Vibrations, from Polarized Infrared Spectra on Oriented Films and 2D Spherulites

C_{10}, A polarzd	C_{10}, E_1 depolarzd	D_2, A polarzd	D_2, B_1 depolarzd	D_2, B_2 depolarzd	D_2, B_3 depolarzd
				3006	3015
2997	2996	2997		2999	2997
				2965	
2945	2946	2947		2947	2947
		2882			2883
1776		1775	1777		1769
1757	1763	1764		1763	1759
				1750	1750
1457	1456		1457		1456
				1447	1443
1385	1386			1387	1387
				1382	
			1371		
	1359			1360	1360
1369	1305			1303	1306
			1293		1294
1294	1266			1223	1214
1267	1216			1212	1207
1185		1181		1201	
1182					1141
	1135			1136	1135
1129		1128		1108	
	1094		1090		1094
1090				1054	
	1047	1042			
1044	923		958		
958					
872	872	874	872		
	757				
		736	736		
737		711	712		
712					
	691				
		412			
		401			
		439			
		299			
		205			
		166			
		158			

For the D_2 crystal of PLLA,

- B_1 modes : no infrared in the C-H stretch region

- either B_2 or B_3 modes : exist 2947 and 2997 cm^{-1}
(they have components along both the *a* and *b* axes)

- B_2 modes: only exist 3007 cm^{-1}
(with a changing dipole moment in the *b* direction)

In amplitude,

the strongest ssp spectrum ≈14×the weak sps spectrum(not showen)

- b axis is preferentially oriented parallel to the surface normal

- c axis are preferentially oriented in the surface plane.

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In the amorphous film of PLLA

the observed spp signal can

either indicate a small amount of crystallinity or

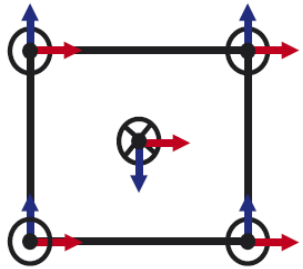
indicate the allowed chiral elements for isotropic bulk material.

if present in the amorphous film → Support the magnitude of the chiral elements

The presence of two anti-parallel chiral chains within one unit cell leads to a **double effect** in the SFG spectra.

-First, the anti-parallel arrangement of two chiral chains enhances the nonlinear optical signal.

- This cancels the polarization in two directions.
-The direction along the rotation axis is not inverted however, so that large intensities can be measured in that direction.



-Second, two chains in one unit cell impose additional site symmetry which causes the modes to split into two modes.

the effect of chirality

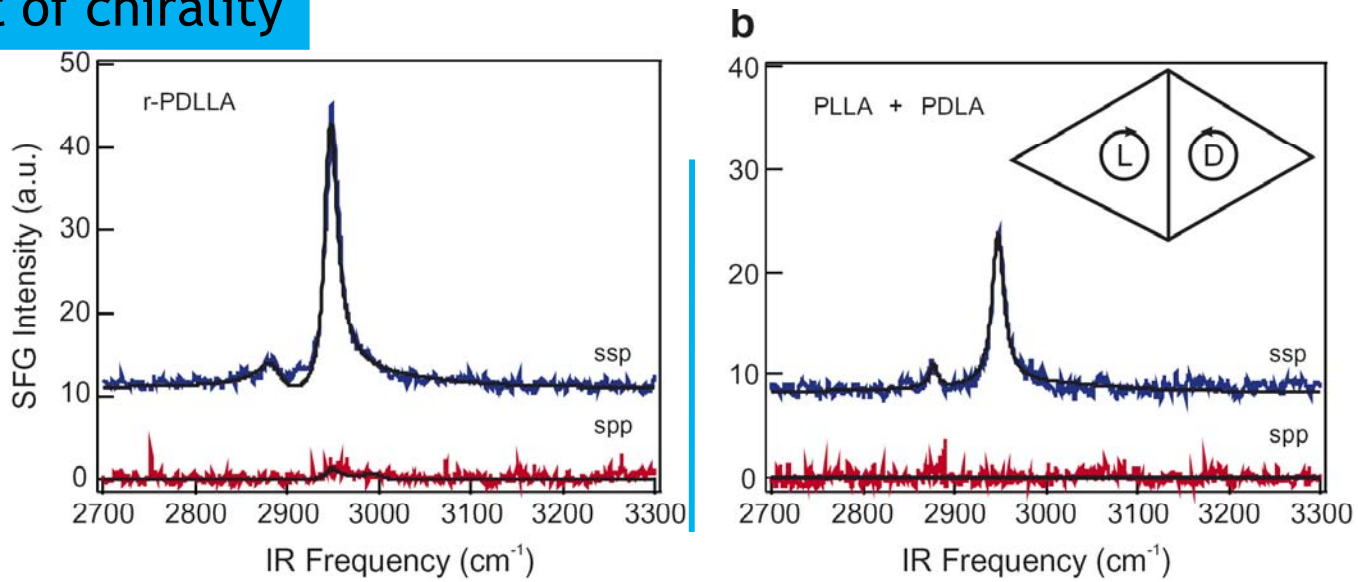


Fig. 3. VSFG spectra of PDLLA films (a) and films composed of PLLA and PDLA (b) taken with ssp and spp polarization. The IR profile is shown in Fig. 2. The black lines are fits to the spectra. The inset in (b) shows an illustration of the crystalline form of the PLLA:PDLA stereo-complex with two chains in a triclinic unit cell.

The PDLLA ssp spectrum modes:
2888 cm^{-1}($\Delta\phi$ = 0; A_{2888}=4.0±0.2; Γ=15.0±0.9 cm^{-1});
2947 cm^{-1} (A_{2947} = 5.6 ± 0.2; Γ = 8.5 ± 0.6 cm^{-1}),

The PDLLA spp spectrum shows a very weak signal.

A film is racemically composed, the spp signal most likely finds its origin in a tiny amount of 'ordered' monomers that may be formed in the polymerization process.

stereo-complex contain peaks :
2888 cm^{-1}($\Delta\phi$= 0; A_{2888}=0.7±0.07;Γ=5.0±0.9 cm^{-1}) ,
2947 cm^{-1}(A_{2947} = 2.5 ± 0.1; C = 7.9 ± 0.5 cm^{-1})

A crystalline structure the D and L chains organize into a parallel fashion, with a 3_1 helical substructure

The difference between the PDLLA and the PLLA:PDLA films :

the peak widths(indicate the high degree of crystallinity)

Time-domain SFG studies can generate more insight into these matters [34].

For the spp spectrum we observe no signal for the same film.

Conclusion

1. For the four different types of films,
   we find that the methyl groups are sensitive markers for the chain-chain ordering

2. The crystalized PLLA films display a strong signal, with almost identical spectral features in the ssp and spp spectra
   → both structures are comparable
   → the interface does not play a large role in determining the structure

3. The very weak SFG signals on the films composed of stereo-regular amounts of monomers (PDLLA) in single chains, and stereo-regular amounts of polymer chains (PDLA/PLLA)

→Shows the large signal observed for the PLLA is induced by the crystalline structure