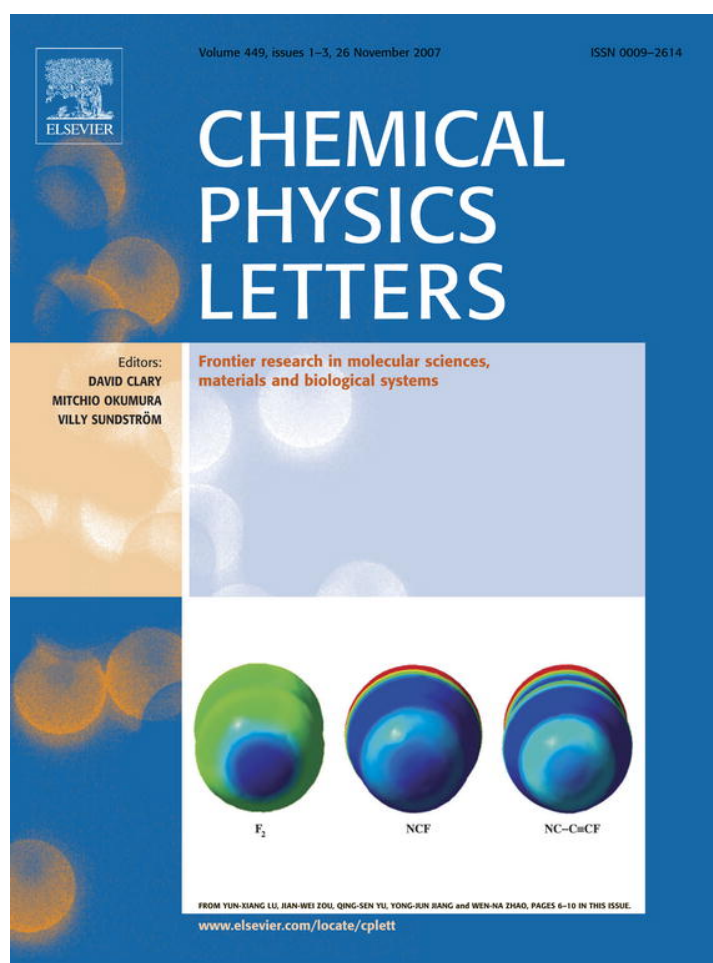


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Surface and bulk structure of poly-(lactic acid) films studied by vibrational sum frequency generation spectroscopy

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Abstract

The surface and bulk structure of various poly-(lactic acid) (PLA) films were examined by vibrational sum frequency generation (VSFG). In contrast to linear infrared spectroscopy, the VSFG spectra show significantly different characteristics in the CH stretching region. For crystalline PLLA we observed strong surface and bulk signals, which were caused by both the order and the symmetry of the space group. Amorphous PLLA and racemically composed PDLLA were found to consist of a relatively disordered bulk. Contrary to the bulk, all surfaces studied generated VSFG signal caused by the broken symmetry at the polymer/air interface.

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Biodegradable and biocompatible polymers have unique characteristics that make them suitable candidates for use in systems and devices for drug delivery and implants [1]. Poly-(lactic acid) (PLA) is an example of such a polymer. Important applications of PLA are found in bone fixation devices [2–4], in blood vessel repair [5,6], and in medicine delivery systems [4,7]. The structural formula of PLA is shown in Fig. 1a, where the central carbon atom constitutes a chiral center. Depending on the method of preparation, the enantiomeric poly(L-lactic acid), PLLA, (or PDLA) can attain various forms, including an amorphous structure and various crystalline polymorphs. The stereo-complexed polymer PDLLA with randomly inserted D and L monomer units in a single chain is an amorphous polymer that can be used to replace the stereo-regular forms, when higher temperatures and strain are required. Another form is the stereo-complex built from a 1:1 solution of PLLA and PDLA chains. This 50/50 mixture finds important applications due to its ~50 °C higher melting point (220 °C) and its superior mechanical properties when compared to the enantiomeric compounds [8,9].

The (bulk) structure of these forms of PLA has been extensively studied by linear vibrational spectroscopy (see e.g. [10–14]). Fig. 1c shows transmission infrared (IR) spectra we have acquired in the C–H stretching region of films consisting of the four above mentioned forms of PLA. As seen in Fig. 1c, the four IR spectra resemble each other closely, despite different configurations and properties of the different films. Even though the difference in crystallinity is apparent, this does not show from the spectra. The spectra contain information from both the bulk and the surface of the films, with the majority of the signal arising from the bulk due to the vast excess of polymer chains located there. However, a thorough knowledge of the surface structure of PLA is of great importance, since the surface constitutes a barrier to the surroundings and provides an adsorption site where chemical reactions can occur.

A technique very suitable for surface studies of PLA is vibrational sum frequency generation (VSFG). This is a nonlinear laser spectroscopy technique, which is inherently surface (and symmetry) sensitive under the electric dipole approximation for centrosymmetric systems (see e.g. [16–19]). The sum frequency process is a combination of an infrared (IR) and a Raman process, with a visible and an infrared photon incident on the sample, generating a third photon at the sum of their frequencies ($\omega_{\text{SFG}} = \omega_{\text{IR}} +$

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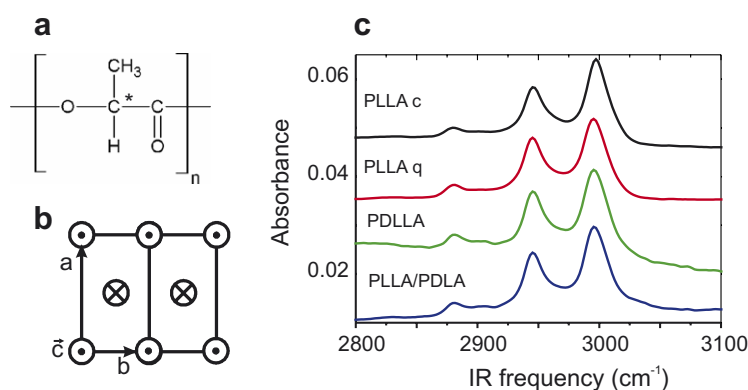


Fig. 1. (a) Structural formula of poly(lactic acid). (b) The unit cell of PLLA. The crosses (dots) indicate a helix directed into (out of) the plane of the paper. The axes of the unit cell are denoted by a , b , and c , where c is along the helical axis. Cell dimensions are $a = 1.06$, $b = 0.61$, and $c = 2.88$ nm (parallel to the c axis) [15]. (c) Transmission IR spectra from top to bottom of a crystallized PLLA film, a quenched (amorphous) PLLA film, a PDLLA film and a PDLA/PLLA film.

ω_{VIS}). The intensity of the sum frequency signal is proportional to the square of the nonlinear susceptibility tensor $\chi^{(2)}$, which contains all information regarding the orientation of molecules. $\chi^{(2)}$ can be expressed in terms of non-resonant ($\chi_{\text{NR}}^{(2)}$) and resonant ($\chi_n^{(2)}$) contributions, according to Eq. (1) [20]:

$$\begin{aligned} \chi^{(2)}(\omega) &= \chi_{\text{NR}}^{(2)} + \sum_n \chi_n^{(2)}(\omega) \\ &= A_{\text{NR}} e^{i\Delta\phi} + \sum_n \frac{A_n}{(\omega - \omega_{0n}) + i\Gamma_n} \end{aligned} \quad (1)$$

where A_n is the amplitude, ω the IR frequency, ω_{0n} the peak centers, and Γ_n the damping constants of the vibrational mode n . $\Delta\phi$ is the relative phase difference between the resonant and the non-resonant fields.

In this Letter we report a VSGF study in the C–H stretching region of amorphous and crystalline PLLA films, films composed of polymer with randomly distributed L and D monomers, and stereo-regular films of PLLA and PDLA chains. Unlike the IR spectra, completely different spectra are obtained. For these different films we determine the origin of the SFG process, which allows us to separate the bulk and the surface structure of the polymer films and to characterize them.

The PLLA films were spin coated (Laurell WS-400B-6NPP-LITE) on glass substrates (cleaned with a 3:1 solution of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (Sigma–Aldrich) in 18 M Ω cm Millipore water) at 3000 rpm for 1 min and prepared from 2.5 wt% solutions of polymer powder (Purac Biochem) dissolved in chloroform (>99 % Merck). This procedure generated films of thicknesses of ~ 0.8 μm , as measured by ellipsometry (M-2000 R from J.A. Woollam Co). Three different kinds of polymers were used in the experiments, poly(L-lactic acid), poly(D-lactic acid) and the racemic poly(DL-lactic acid). The enantiomeric amorphous films were produced by melting the spin coated films at 190 $^\circ\text{C}$ followed by quenching in liquid nitrogen. To generate the crystalline films, the spin coated films were annealed at ~ 80 $^\circ\text{C}$ for 10 min. The PDLLA and PLLA/PDLA films

were spin coated and used without further treatment. The SFG experiments were performed using a 1 kHz broadband high power Ti:Sapphire laser system [21]. The IR pulses were centered around 3000 cm^{-1} with a FWHM of 150 cm^{-1} , and a pulse duration of 175 fs. The visible pulses were centered at 800 nm and shaped to a FWHM of 5 cm^{-1} . Pulse energies near the sample were kept at 10 (IR) and 3 (vis) μJ , and the focus diameter was 0.75 mm. The VSGF experiments were performed in a reflection geometry, with incoming angles of 60 $^\circ$ (IR) and 40 $^\circ$ (vis) with respect to the surface normal. The beams were polarization selected using two wire grid BaF₂ polarizers (each polarizer had an extinction ratio of 100), a polarizer cube (extinction ratio 1:10⁵) combined with a wave plate and a Glan Thompson polarizer cube (extinction ratio 1:10⁵) for the IR, vis, and SFG, respectively. The emitted SFG was detected by a spectrograph/I-CCD camera (Andor). Plotted spectra were normalized for pulse energy and acquisition time. All IR spectra were acquired with a Bruker Vertex 70 in the transmission mode, with PLA films spin coated on ZnSe windows.

Fig. 2 displays VSGF spectra of an amorphous (quenched) and a crystalline film of PLLA. The spectra are fit using for the SFG intensity [20]:

$$I_{\text{SFG}}(\omega) \propto \left| E_{\text{IR}}(\omega) \sum_n \int_{-\infty}^{\infty} \chi^{(2)}(\omega') E_{\text{VIS}}(\omega' - \omega) d\omega' \right|^2 \quad (2)$$

where E_{IR} is the envelope of the IR spectrum as obtained from the non-resonant gold signal, E_{VIS} the envelope of the visible spectrum as measured, and $\chi^{(2)}$ is given by Eq. (1). The spectrum taken with polarization combinations s for the SFG, s for the visible and p for the IR (referred to as ssp) of the quenched film exhibits 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}), and a weak resonances of the anti-symmetric methyl stretch mode at 2997 cm^{-1} ($A_{2997} = 0.18 \pm 0.04$; $\Gamma = 13.0 \pm 2.6$ cm^{-1}) [10,13]. The low intensity (and the broad bandwidths) of the peaks reflect the disordered

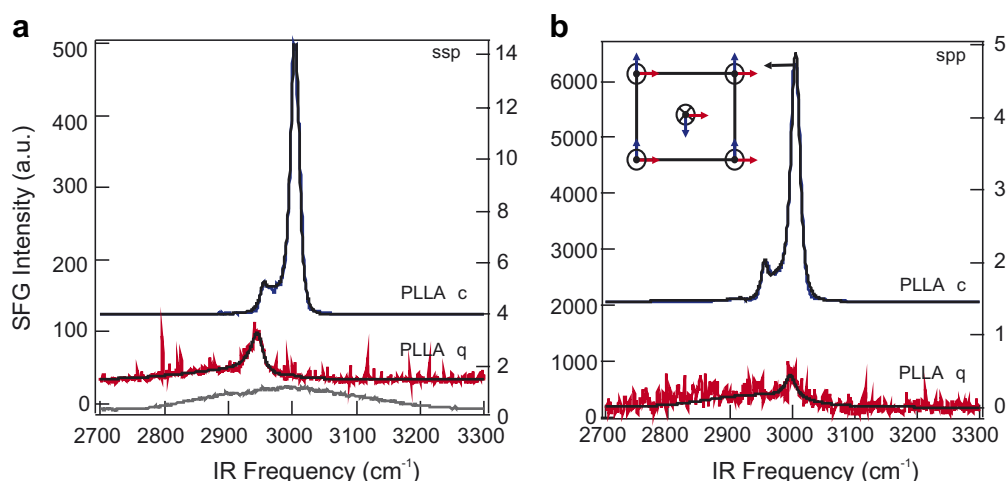


Fig. 2. VSGF spectra of (a) the surface (ssp), the bulk (b, spp), of an amorphous and a crystalline PLLA film. In (a) the (scaled) non-resonant spectrum with ppp polarization combination of a gold surface is also displayed. The left axis reflects the intensity of the crystalline film, while the right 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.

nature of the amorphous film. As the interface of the quenched film can be considered azimuthally isotropic, the origin of the ssp signal is the surface $\chi_{yz}^{(2)}$ tensor element. Consequently, we also observed signal for polarization combinations ppp and sps (but since they do not add to the present discussion they are omitted). We also observed a very weak signal, in the polarization combination spp [showing one peak of the antisymmetric methyl stretch mode at 2997 cm^{-1} ($\Delta\phi = 0$; $A_{2997} = -1.3 \pm 0.16$; $\Gamma = 11.0 \pm 2.2\text{ cm}^{-1}$)]. The origin of this signal is discussed below. The polarization combinations psp and pps showed the same information and hence they are omitted.

The ssp spectrum of the crystalline film is considerably different from the ssp spectrum of the quenched film and demonstrates the effect of annealing and formation of crystallites on the surface structure. In this spectrum we observe peaks at 2954 cm^{-1} ($\Delta\phi = 100$; $A_{2954} = 8.9 \pm 0.5$; $\Gamma = 7.0 \pm 0.4\text{ cm}^{-1}$) and 2997 cm^{-1} ($A_{2997} = -16.6 \pm 0.3$; $\Gamma = 15.0 \pm 0.3\text{ cm}^{-1}$), which correspond to the ones observed on the quenched film. Additionally, we observe modes at 2965 cm^{-1} ($A_{2965} = -14.4 \pm 2.8$; $\Gamma = 13.0 \pm 3.9\text{ cm}^{-1}$), and 3007 cm^{-1} ($A_{3007} = 22.5 \pm 4.5$; $\Gamma = 8.7 \pm 0.4\text{ cm}^{-1}$). These modes have been reported in Raman studies [13] and originate from crystal field splitting. Note that we cannot reproduce the typical spectral shape if we omit the latter two peaks.

The spp spectrum of the crystalline PLLA film exhibits very strong resonances for the same vibrational modes (with fitting parameters $\Delta\phi = 100$; $A_{2955} = 32.6 \pm 1.3$; $\Gamma = 6.4 \pm 0.3\text{ cm}^{-1}$, $A_{2965} = -46.2 \pm 10.1$; $\Gamma = 14.0 \pm 3.5\text{ cm}^{-1}$, $A_{2997} = -36.1 \pm 1.6$; $\Gamma = 13.0 \pm 0.26\text{ cm}^{-1}$, $A_{3007} = 75.6 \pm 1.7$; $\Gamma = 9.0 \pm 0.5\text{ cm}^{-1}$) and apart from a scaling factor of 10 they are quite similar to the ssp spectrum. If we compare the quenched and crystalline films however, there is an enormous difference in intensity and spectral shape.

These observations probably find their origin in the structure of the α -crystalline form of PLLA. The α crystalline structure is the most common form of crystalline PLLA and forms readily upon annealing (see e.g. [22–25,10,26]). We assume that this is also the case here, since no crystallography has been done. In this crystalline structure a single PLLA chain forms a left-handed helix with C_{10} symmetry, which thus induces chirality in the whole chain. These chains are packed in a pseudo-orthorhombic anti-parallel arrangement with a unit cell containing two helices [23] as shown in Fig. 1b. The PLLA crystal thus belongs to the $P2_12_12_1$ space group and has D_2 symmetry. It is therefore non-centrosymmetric by nature. Thus, in an SFG experiment one probes not only the $\chi^{(2)}$ elements that are originating from an (isotropic) interface but also the ones that come from the crystalline parts. For the α form of crystalline PLLA these correspond to the six tensor elements in the D_2 symmetry group. Combining this with the notion that far away from resonance (as is the case here) the Raman tensor can be assumed symmetrical [27], we have the tensor elements: $\chi_{xyz}^{(2)} = \chi_{yxz}^{(2)}$ (B_1 symmetry), $\chi_{xzy}^{(2)} = \chi_{zyx}^{(2)}$ (B_2 symmetry), $\chi_{yzx}^{(2)} = \chi_{zxy}^{(2)}$ (B_3 symmetry). These elements can be probed by the polarization combinations spp, psp, and pps. For the D_2 crystal of PLLA, there are no infrared allowed B_1 modes in the C–H stretch region [13]. Thus, the modes at 2947 and 2997 cm^{-1} should belong to either B_2 or B_3 modes, and they have components along both the a and b axes. The mode at 3007 cm^{-1} only has B_2 symmetry (with a changing dipole moment in the b direction). This is the strongest mode in the polarization combination ssp and in the weak spp spectrum (not shown) the amplitude was 14 times smaller. Thus, it is likely that the b axis is preferentially oriented parallel to the surface normal and the a and c axis are preferentially oriented in the surface plane. This observation is in correspondence with X-ray analysis [26,13]. As we are dealing with

crystalline domains [9] a detailed orientational analysis is not so relevant. Since the other polarization combinations probe $\chi^{(2)}$ elements that vanish inside the bulk of crystallites, one can probe the surface or bulk alternatively by changing the polarization of the laser beams. This works as long as the film thickness is less than the coherence length (which is $>3 \mu\text{m}$ for PLLA) and the crystallites (with a size range of $\sim 1\text{--}10 \mu\text{m}$) are isotropically distributed.

For the amorphous film, the observed spp signal can thus either indicate a small amount of crystallinity or simply indicate the allowed chiral elements for isotropic bulk material. Both explanations come from weak processes (no crystallites have been found in such films [13]), but also the chiral elements are known to be extremely small [27,28]. The latter possibility could be supported by noting that helices (if present in the amorphous film), may enhance the magnitude of the chiral elements [29,30].

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 is illustrated in the inset in the right panel of Fig. 2. To obtain an anti-parallel arrangement one chain needs to be rotated. 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. This is reflected by a large increase of signal as can be seen from Fig. 2. Second, two chains in one unit cell impose additional site symmetry [31] which causes the modes to split into two modes. This so-called Davydov splitting [32] has indeed been observed in bulk PLLA with linear vibrational spectroscopy and theoretically predicted [13].

Furthermore, we would like to note that the crystallinity of 'fully' crystallized films is never 100%, but rather around 60% (as was indeed verified by a DSC measurement). Since the VSG signal that originates from the crystalline parts is much stronger than that of the amorphous parts of the film, one effectively only observes the crystalline parts of

the film. This is in contrast to linear spectroscopy, where the amorphous phase will always contribute at least $\sim 40\%$ of the signal (proportionate to the amount of bulk material).

To investigate the effect of chirality on the spectra further, we have acquired spectra of two other types of PLA, namely racemically composed PLA chains (called PDLA, with no crystallinity and overall chirality) and a stereo-regular complex consisting of equal amounts of PLLA and PDLA (which forms a crystal with parallel D and L chains). Fig. 3a displays VSG spectra of PDLA acquired under the ssp and spp polarizations. The PDLA ssp spectrum shows modes at 2888 cm^{-1} ($\Delta\phi = 0$; $A_{2888} = 4.0 \pm 0.2$; $\Gamma = 15.0 \pm 0.9 \text{ cm}^{-1}$) and 2947 cm^{-1} ($A_{2947} = 5.6 \pm 0.2$; $\Gamma = 8.5 \pm 0.6 \text{ cm}^{-1}$), which correspond to the C–H stretch mode and the symmetric methyl stretch mode. Since the sample is amorphous, this signal comes from the interface. The PDLA spp spectrum shows a very weak signal. As this 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. The polymerization is a ring catalyzed opening reaction in which D (L) monomers have a slight preference to attach to a D (L) polymer end, so that a non-random distribution of L and D monomers may be expected. According to a circular dichroism study [33], 8–10 successive enantiomeric monomers are required to form a helical structure. Also it was found that small crystalline domains with a size of $\sim 10 \text{ nm}$ can be present. Thus, we may observe here the small fraction of monomers that does just that. The similarity between the ssp spectra of PDLA and amorphous PLLA confirms the amorphous nature of the PDLA surface.

Fig. 3b shows ssp and spp spectra of stereo-regular films formed by a 1:1 mixture of PDLA and PLLA polymer chains. In such a crystalline structure the D and L chains organize into a parallel fashion, with a 3_1 helical substructure (see the inset in Fig. 3b) [8,14]. The ssp spectrum of the

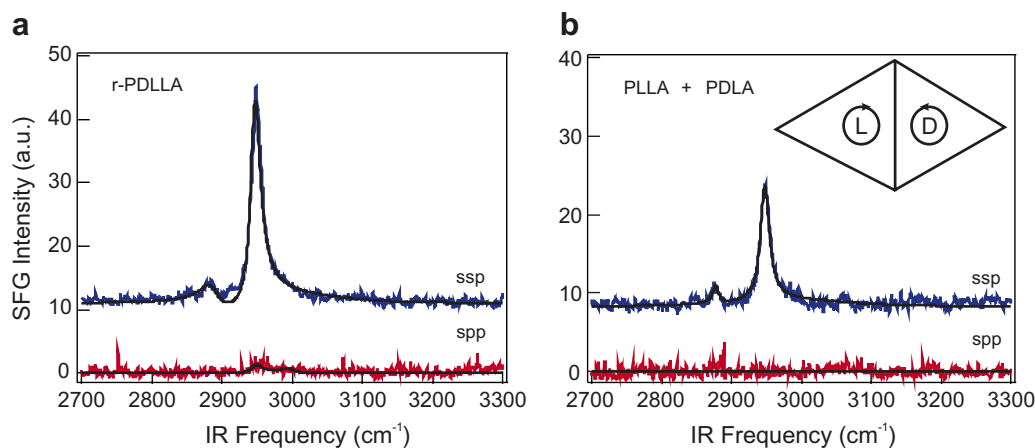


Fig. 3. VSG spectra of PDLA films (a) and films composed of PLLA and PDLA (b) taken with ssp and spp polarization. The IR profile is shown in Fig. 2. The black lines are fits to the spectra. The inset in (b) shows an illustration of the crystalline form of the PLLA:PDLA stereo-complex with two chains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

films with stereo-complex contain peaks at 2888 cm^{-1} ($\Delta\phi = 0$; $A_{2888} = 0.7 \pm 0.07$; $\Gamma = 5.0 \pm 0.9\text{ cm}^{-1}$) and 2947 cm^{-1} ($A_{2947} = 2.5 \pm 0.1$; $\Gamma = 7.9 \pm 0.5\text{ cm}^{-1}$), and correspond to the above mentioned modes. The difference between the PDLLA and the PLLA:PDLA films is the peak widths, which may 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.

This shows that the large signal observed for PLLA is indeed induced by the crystalline structure of the film. Thus, the CH_3 groups are sensitive markers of the inter-chain interactions.

Although these measurements enabled us to learn about the surface and bulk structure, as well as the difference in surface and bulk structure between the four different types of films, they do not indicate whether the chains are actually helical. For such information one needs to access the vibrational fingerprint region [21].

In conclusion, we demonstrate how VSFG studies in the CH stretching region can generate valuable information to track changes in the surface and bulk structure of amorphous PLLA and PDLLA films and crystalline PLLA and PDLA:PLLA stereo complex films. In contrast with linear vibrational spectroscopies we find that this would allow for a detailed understanding of the (surface) structure of biodegradable polymers in general, which would add significantly to the knowledge on such polymers systems that are relevant for medical and industrial applications.

For the four different types of films we find that the methyl groups are sensitive markers for the chain–chain ordering. The ssp signal of amorphous PLLA indeed reflects a disordered interface. The bulk spp signal displays a weak chiral signature. The fact that the signal to noise ratio is large enough may indicate that there are helices in the film, which are known to enhance the chiral response of the second-order nonlinear susceptibility [29,30]. The crystallized PLLA films display a strong signal, with almost identical spectral features in the ssp and spp spectra. Thus, both structures are comparable and the interface does not play a large role in determining the structure. This is likely, since the PLLA chains are known to be stiff. 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 that the large signal observed for the PLLA is induced by the crystalline structure which enhances some of the elements of the susceptibility tensor.

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