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

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Poly-(lactic acid)(PLA) is a biodegradable and biocompatible polymer used in various biomedical applications as in absorbable sutures, drug delivery, and implants.[1] Thus characterization of surface and bulk structures has been an issue of primary interest from both scientific and technological points of view. We investigated the surface and bulk properties of poly-(L-lactic acid) (PLLA) films having different degrees of crystallization. The crystallinity of the film varied by changing annealing times was assessed by the size and abundance of spherulites measured with polarization microscope, and the surface and bulk structures of various PLLA films were examined by vibrational sum-frequency generation (SFG) and Raman spectroscopy.

The PLLA films were spin-coated on glass substrates at 3000 rpm for 30 seconds. The amorphous films were produced by melting the spin-coated films at 196°C followed by quenching in liquid nitrogen. To generate crystalline films, the quenched films were annealed at 129°C for different times. SFG is a second-order nonlinear optical process, and has been utilized to selectively probe surfaces and interfaces. To realize SFG spectroscopy, we used a system based on a mode-locked picosecond Nd:YAG laser (25 ps, 10 Hz). The two input beams, one at 0.532 μm and the other tunable in the infrared between 3.6 and 3.2 μm (2800 ~ 3100 cm^{-1}, generated by optical parametric processes) were overlapped at the sample surface, and sum-frequency output in the reflection direction was detected for analysis. Two polarization combination were used our experiment; SSP (S for SFG signal, S for visible beam, and P for infrared beam, respectively) and SPP. In isotropic, chiral media, the polarization combinations of SSP and SPP are expected to exhibit mainly surface and bulk properties, respectively.[2],[3]

Figure 1 shows polarization microscope images of the PLLA films. These images show varying degrees of filling by the spherulites, regarded as a progression of crystallization. Several minutes of annealing was found enough to crystallize the entire film. In contrast with Raman spectra (not shown) which hardly changed for different samples, the SFG spectra show significantly difference in the region of CH_x vibration. Figure 2 is SFG spectra taken at (a) SSP, and (b) SPP polarization combinations for different annealing times. SPP spectra, in particular, showed a big difference in intensity and spectral shape as crystallization progressed, which correlates well the corresponding

polarization microscopy images in Fig. 1. On the other hand, SSP spectra of PLLA films did not change as much for the films at different crystallization stages. We propose that the large SFG signal observed for the PLLA films are induced by the crystallization, which enhances selectively the part of the second-order nonlinearity arising from the chirality of the medium.

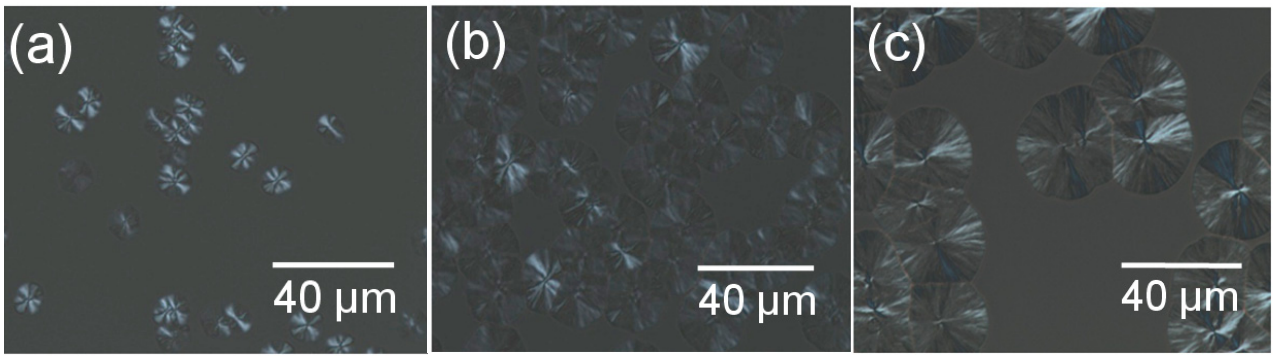

Fig. 1. Polarization micrscope images of PLLA films made with different annealing times; (a) 1 minutes, (b) 2 minutes, and (c) 3 minutes.

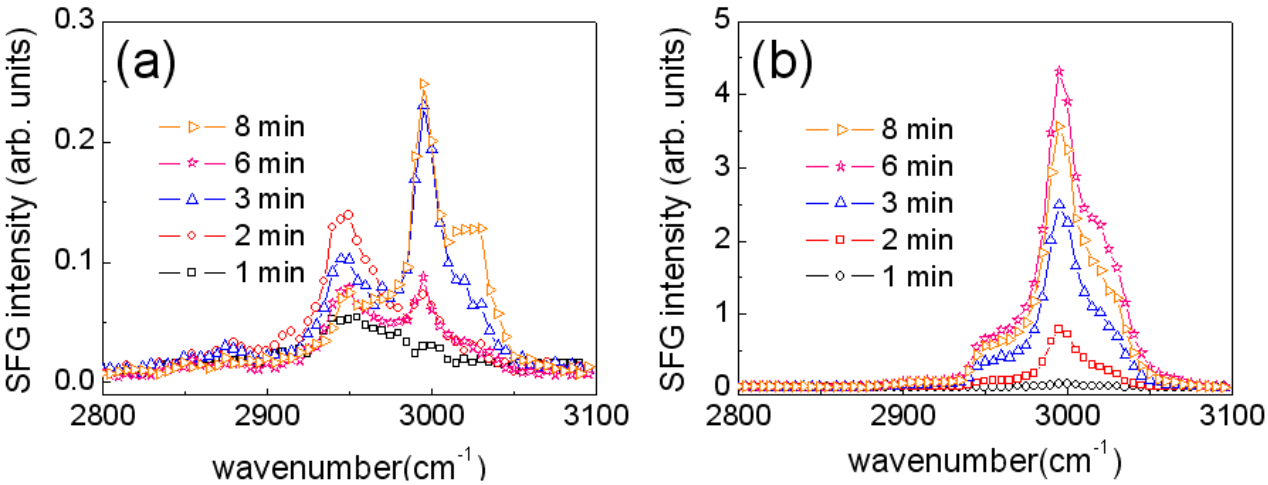

Fig. 2. SFG spectra of PLLA films taken at (a) SSP, and (b) SPP polarization combinations.

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