































Same as in the case of PLLA the chemical shifts of  $^{13}\text{C}$  NMR spectrum of PDDLA show smaller values in solvated model (Table 11.). The  $^1\text{H}$  NMR shifts due to CH resonance are bigger in all four structures (Table 12.).

**Table 11.**  $^{13}\text{C}$  NMR Chemical shifts ( $\delta$ , in ppm) of CO, CH and  $\text{CH}_3$  of PDDLA in vacuum (v) and water (w), respectively

PDDLA	$\alpha$		$\pi$		$10_3$		$\beta$		Exp.
	v	w	v	w	v	w	v	w	
$\delta$ (CO)	177	174	177	174	178	176	175	172	169
$\delta$ (CH)	73	68	73	69	73	67	71	67	69
$\delta$ ( $\text{CH}_3$ )	18	13	18	13	18	13	19	14	16

**Table 12'**  $^1\text{H}$  NMR Chemical shifts ( $\delta$ , in ppm) of CH and  $\text{CH}_3$  of PDDLA in vacuum (v) and water (w), respectively

PDDLA	$\alpha$		$\pi$		$10_3$		$\beta$		Exp.
	v	w	v	w	v	w	v	w	
$\delta$ (CH)	5.0	5.1	5.1	5.1	5.1	5.1	5.4	5.5	5.2
$\delta$ ( $\text{CH}_3$ )	1.7	1.7	1.6	1.6	1.7	1.6	1.5	1.6	1.5

The NMR spectra of PLA can give information about the stereochemistry of the composition. The CO chemical shifts are larger in the  $\alpha$ ,  $\pi$  and  $\beta$  forms of PLLA, while the  $\text{CH}_3$  shifts are larger in the case of the three helical structures of PLLA. The chemical shifts of  $^1\text{H}$  NMR spectra of PLLA show larger values in all cases except the CH shifts of  $\beta$ -sheet.

## CONCLUSIONS

Geometry optimization performed on polylactic acid at different levels of DFT methods suggest that the most stable of the four structures is the  $\pi$  helix and the least stable is the  $\beta$  sheet.

The calculated chemical shifts of both  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR are slightly larger than the experimental one. The solvation reduces the value of the NMR chemical shifts.

The secondary structure of poly(lactic acid) cannot be conclusively clarified from the calculated IR and NMR spectra, suggesting either a need for using more appropriate computational methods or the occurrence of previously unconsidered elements of secondary structure, or the total lack thereof.

## EXPERIMENTAL SECTION

**Materials.** Aqueous solutions of L-(+)-lactic acid from Sigma-Aldrich (80%), DL-lactic acid from Fluka (90%) were used. PLLA and PDLLA were synthesized by direct dehydropolycondensation. Lactic acid, toluene and 0.1% tin(II) 2-ethylhexanoate catalyst were mixed into a reaction vessel equipped with a Dean-Stark-type condenser, and heated to the refluxing temperature of the solvent. The reaction time was 20 h. The final product was dissolved in chloroform and precipitated in diethyl ether for purification. The polymer was then filtered out from diethyl ether and dried under vacuum.

**Measurements.** NMR spectra were recorded with a Bruker Avance 300 spectrometer at the following frequencies:  $^1\text{H}$ , 300.13 MHz;  $^{13}\text{C}$ , 75.47 MHz (reference TMS) with DMSO- $d_6$  as the solvent. IR spectra were recorded with a Vector 22 Bruker spectrometer by direct introduction method and a Jasco FT/IR Specord 600 spectrometer in KBr pills. The molecular weights were determined by MALDI-TOF MS (Matrix Assisted Laser Desorption Ionization) analysis with a Bruker BIFLEX III<sup>TM</sup> spectrometer.

**Molecular simulation.** A vibrational analysis and NMR simulation has been carried out to analyze the secondary structure of poly(lactic acid) resulted from esterification of ten lactic acid units, hereafter referred to as LA<sub>10</sub>. These models were built in the Hyperchem [28] software package using built-in options of the Editor module for creating helical structures as well as sheet. Spectroscopic parameters were predicted for helical ( $\alpha$ ,  $\pi$ , 103) and  $\beta$ -sheet structures, in an attempt to aid our on-going efforts in the synthesis and characterization of poly(lactic acid) variants.

The methods tested here include density functional (M062X/6-31G\*, M062X/6-31G\*\*, solvated M062X/6-31G\*\*) applied with standard convergence criteria as defined in Gaussian 09 [29]. Spectral parameters were invoked using the commands Freq and NMR. In terms of the importance of solvation, this is estimated by comparing values computed in water (as a limit of very polar medium) and vacuum (as a limit of completely non-polar medium). Further detail on geometry optimizations and on relative energies of the structures are given elsewhere [30].

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