A $^{15}\text{N}$-$^{1}\text{H}$ Dipolar CSA Solid-State NMR Study of Polymorphous Polyglycine ($\text{CO-CD}_{2}^{15}\text{NH}$)$_{n}$

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Abstract. The solid-state $^{1}\text{H}$ MAS (magic-angle spinning), $^{3}\text{H}$ static, $^{15}\text{N}$ CP (cross polarization)-MAS and $^{15}\text{N}$-$^{1}\text{H}$ dipolar CSA (chemical shielding anisotropy) NMR (nuclear magnetic resonance) spectra of two different modifications of C$_{\alpha}$-deuterated $^{15}\text{N}$-polyglycine, namely PG I and PG II ($\text{CO-CD}_{2}^{15}\text{NH}$)$_{n}$, are measured. The data from these spectra are compared to previous NMR, infrared, Raman and inelastic neutron scattering work. The deuteration of C$_{\alpha}$ eliminates the largest intramolecular $^{1}\text{H}$-$^{1}\text{H}$ dipolar coupling. The effect of the remaining (N)H-(N)H interaction ($\sim$ 5 kHz) is not negligible compared to the $^{15}\text{N}$-$^{1}\text{H}$ coupling (about 10 kHz). Its effect on the dipolar CSA spectra, described as a two-spin system, is analyzed analytically and numerically and it is shown that those parts of the powder spectrum, which correspond to orientations with a strong dipolar $^{15}\text{N}$-$^{1}\text{H}$ interaction, can be described as an effective two-spin system, permitting the measurement of the strength of the $^{15}\text{N}$-$^{1}\text{H}$ dipolar interaction and the orientation of the dipolar vector with respect to the $^{15}\text{N}$ CSA frame. While in the PG II system the $^{15}\text{N}$ CSA tensor is collinear with the amide plane, in the PG I system the CSA tensor is tilted ca. 16° with respect to the ($\delta_{11},\delta_{22}$) CSA plane.

1 Introduction

Poly-$\alpha$-aminoacids are model systems for the studies of hydrogen bonding in polypeptides and proteins. This is a key factor for the stabilization of secondary and tertiary structures. Polyglycine ($\text{CO-CH}_{2}^{15}\text{NH}$)$_{n}$ is the homopolypeptide of the simplest amino acid. There is no side chain and thus no asymmetric C$_{\alpha}$. This polymer is unique for the evaluation of the conformational thermodynamics and the analysis of the spectral features of the backbone [1–4]. In the solid state, polyglycine exhibits structural polymorphism and may adopt two different secondary structures, namely a β-sheet (polyglycine I, PG I) and a 3$_{1}$-helix (polyglycine II, PG II) (Fig. 1). These conformations are related to the biologically important structures of collagen, silk fibroin and aperiodic glycine-rich proteins [5–8], as well as nylon materials [9].