Appl. Magn. Reson. 17, 413–431 (1999)

A ^{15}N-^{1}H Dipolar CSA Solid-State NMR Study of Polymorphous Polyglycine (-CO-CD_2-^{15}NH-)$_n$

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Received June 4, 1999; revised July 13, 1999

Abstract. The solid-state ^{1}H MAS (magic-angle spinning), ^{2}H static, ^{15}N CP (cross polarization)-MAS and ^{15}N-^{1}H dipolar CSA (chemical shielding anisotropy) NMR (nuclear magnetic resonance) spectra of two different modifications of C_α-deuterated ^{15}N-polyglycine, namely PG I and PG II (-CO-CD_2-^{15}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_α eliminates the largest intramolecular ^{1}H-^{1}H dipolar coupling. The effect of the remaining (N)H-(N)H interaction (~5 kHz) is not negligible compared to the ^{15}N-^{1}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}N-^{1}H interaction, can be described as an effective two-spin system, permitting the measurement of the strength of the ^{15}N-^{1}H dipolar interaction and the orientation of the dipolar vector with respect to the ^{15}N CSA frame. While in the PG II system the ^{15}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-α-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 (-CO-CH_2-NH-)$_n$ is the homopolypeptide of the simplest amino acid. There is no side chain and thus no asymmetric C_α. 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].