

Supplementary Material of

^{13}C - ^{17}O REAPDOR NMR as a Tool for Determining
Secondary Structure in Polyamides

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Mixtures made of one part Ala-Ala-[1-¹³C]Ala and four parts Ala-[¹⁷O]Ala-Ala were dissolved in distilled water and powder samples of isotopically enriched samples of P-AAA and AP-AAA were produced by appropriate drying methods. Slow evaporation of water using a rotary evaporator produced the AP-AAA sample. The P-AAA sample was obtained by adding DMF to the water to make a 40% solution of DMF. The water was then slowly evaporated with a rotary evaporator and the precipitate was isolated from the DMF by suction filtration. The ¹⁷O-labeled peptides were made as follows. [¹⁷O]Ala was prepared from the alanine methyl ester in Na¹⁷OH/methanol solution, where Na¹⁷OH was prepared by reaction of 90% ¹⁷O-labeled water with Na metal. This [¹⁷O]Ala was 9-fluorenylmethyloxycarbonyl (Fmoc) protected using Fmoc hydroxyl-succinimide (Fmoc-OSu) in 10% NaHCO₃. Ala-[¹⁷O]Ala-Ala was then manually synthesized starting with Fmoc-Ala-Alko resin. Fmoc removal was achieved with 20% piperidine solution in dimethyl formamide. O-(7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate/diisopropylethylamine (HATU/DIEA) (3 equiv) was used for the coupling reagent. At the end of synthesis, peptide resin cleavage was performed with a solution of 2% triisopropylsilane and 12% thioanisole in trifluoroacetic acid (TFA). The product was precipitated in diethyl ether and purified by reverse-phase HPLC using a water / acetonitrile gradient and a PEGASIL ODS-II, C18 column. The ¹³C-labeled peptide was made from [1-¹³C: 99 at %]Ala by standard solid-phase synthesis procedures. Samples are prepared to parallel and anti-parallel by the recipes as reported and the structure of the prepared samples were checked by IR and ¹³C CP/MAS NMR.

The dipolar couplings D and D_e for the parallel β -sheet sample were obtained by least squares fitting of the experimental data to $\Delta S/S = 0.36 \times \Delta S/S^R(D) + 0.64 \times \Delta S/S^G(D_e)$, where $\Delta S/S^R$ and $\Delta S/S^G(D_e)$ are given in the main text. The dipolar couplings were obtained using only the data acquired with evolution times up to and including 14.4 ms. This was done because the REAPDOR dephasing curve

(equation 1) is applicable for determining dipolar couplings up to times satisfying $D\tau \approx 0.5$, which for this sample is approximately 12 ms. Since the primary interest is to determine the best dipolar coupling for the intrasheet coupling, then the fit should focus on the data where the strong intrasheet dipolar coupling is described by the rising part of the REAPDOR curve given in equation 1. Analysis of the REAPDOR experiment differs somewhat from the familiar REDOR experiment. The REDOR experiment for pairs of spin-1/2 nuclei depends only on the dipolar coupling and is described by a universal dipolar dephasing curve applicable, in principle, for all dipolar evolution times. The REAPDOR experiment is applied to quadrupolar nuclei and the corresponding dipolar dephasing depends weakly on the quadrupolar coupling constant and asymmetry parameter (see references in 3). For this reason, equation 1 was developed to describe REAPDOR dephasing without needing to know the quadrupolar coupling constant and asymmetry parameter. The consequence is that equation 1 describes the dipolar dephasing well for times $\tau \leq 0.5/D$ and only approximately for longer times. Therefore, only data with evolution times less than $0.5/D$ are used to determine the dipolar coupling.