

**Electronic Supplementary Information**

Microsecond and Nanosecond Polyproline II Helix Formation in Aqueous Nanodrops

Measured by Mass Spectrometry

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## Peptide Molecules in each Nanodrop

The initial size of electrospray ionization (ESI) droplets depends on the ESI-emitter tip size.<sup>1</sup> Heptane droplets with initial diameters as large as ~45% of the ESI emitter tip size were reported for a 0.45 mm outer diameter tip,<sup>2</sup> but typically ESI droplets have initial diameters of <10% of the emitter tip outer diameter.<sup>3,4</sup> The folding time constants of the PPII helix structures were obtained using emitters with ~305 and ~244 nm outer diameter tips. If the initial nanodrop size is 45% of the emitter tip diameter, then with the 10  $\mu$ M peptide solutions used here, there would be on average ~8 and ~4 peptide molecules in each of the initial ESI nanodrops at these respective diameters. However, if the initial nanodrop size is only 10% of the emitter tip diameter, then only about one in 11 and about one in 22 nanodrops would contain a peptide molecule for the ~305 and ~244 nm outer diameter tips, respectively. The same time constant measured with both tip sizes indicates that there is no interaction between peptide molecules, consistent with the vast majority of nanodrop containing either one or no peptide molecules. Thus, the unimolecular folding time constants measured here should not be affected by other peptides in the nanodrops, and hence should not be affected by changes in the concentration resulting from solvent evaporation that occurs during the nanospray process.

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