Structure determination of the collagen and silk-type environments in the blue mussel *Mytilus edulis* byssal threads

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Mussels attach themselves to substrates on the seashore via extra-corporeal threads called byssus. These are complex biopolymers essentially made of proteins with unique mechanical properties. Byssal threads are composed of three distinct regions: an initial corrugated and elastic proximal part followed by a smooth and stiff distal part and finally the plaque that attaches the animal to the substrate. The core of the fibre is composed of three pepsin resistant proteins, PreCol-P, PreCol-D and PreCol-NG. Each of these proteins is composed of a collagen centre flanked by elastin-like (PreCol-P), silk-like (PreCol-D) or plant cell wall-like (PCW) (PreCol-NG) regions [1].

In order to correlate the molecular structure of the constituents of this fibre to its macroscopic mechanical properties, the molecular structure of byssal threads of the blue mussel *Mytilus edulis* was studied by high-resolution solid-state NMR. Measurements were carried out at high field (21.1 T) in order to resolve resonances in the different proteins constituting the fibre. $^{13}$C-$^{13}$C dipolar correlation spectra were recorded and the two-dimensional spectra provided sufficient resolution to assign the various spin systems to the corresponding amino acids (Figure 1). This unique material proves to be well ordered at a molecular level despite its composition heterogeneity as evidenced by the very narrow measured $^{13}$C linewidths below 1.5 ppm. The spectra are dominated by residues in collagen environments as determined from the chemical shift analysis. Chemical shift predictions were carried out using the software *Shift X* and the torsion angles of the collagen regions thus determined [2]. The most abundant glycine and alanine residues can be resolved in up to three different environments. Intense alanine peaks were detected with chemical shifts consistent with an anti-parallel β-sheet structure which are assigned to silk-like regions. This result was further confirmed by the short $T_1$ $^{13}$C relaxation time measured for the corresponding alanine $C_β$ resonance. Our results, thus, determine the structure of collagen and silk-type domains in byssal threads and provide a detailed assignment of minor residues in collagen helices.