Supplementary Information: "A Small-angle X-ray Scattering Study of α-Helical Bundle-Forming Peptide-Polymer Conjugates in Solution: Chain Conformations"

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Circular Dichromism

CD measurements were performed using a Jasco J810 spectropolarimeter. Samples were dissolved in 25 mM KH_2PO_4 buffer at pH 7.4 and measured in 1 mm path length quartz cuvettes. Measurement of samples at the same concentration as those of the scattering experiments was not possible due to significant scattering at short wavelengths that reduced CD signal. Therefore, samples were measured at the highest concentration possible (300μM) while still achieving sufficient signal.

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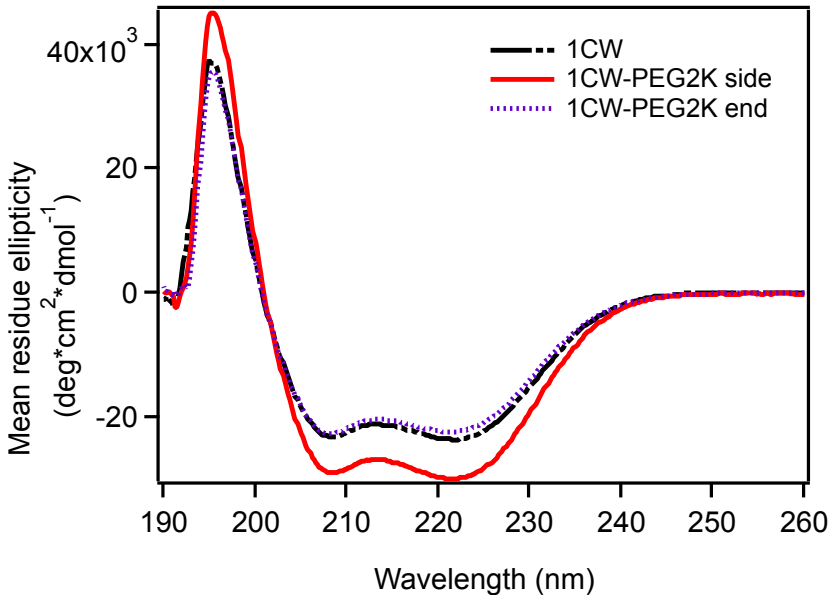

Figure 1: Circular dichroism (CD) spectroscopy data of the 1CW peptide compared to the peptide-polymer conjugates in a KH_2PO_4 buffer solution.

Figure 1 shows the circular dichromism (CD) spectra of the two conjugates and peptide alone. At pH 7.4, both the peptide and peptide-polymer conjugates a show CD spectra with clear signatures of helicity displaying negative minima at 222 and 208 nm and a positive maximum at about 195 nm.

Comparing the pure 1CW and the side-conjugate, the CD data show a weak enhancement of the helicity in the peptide-polymer conjugate. For the end-conjugated peptides a helicity similar or slightly smaller compared to the peptide is found. The increased helicity of side-conjugated peptide has been observed previously for the same system with different PEG molecular weights.[1,2] Partial disruption of the α-helix was observed for other end-conjugated peptides by Vandermeulen et al.[3]

SAXS Study of Free PEG

The SAXS data are given in the main text, here we discuss the details of the fit procedure.

The form factor for semi-flexible polymer chains was taken from the parameterization from

Pedersen and Schurtenberger.[4] In addition we included the polydispersity of the PEG molecular weight (PDI $\approx$ 1.1) although the influence on the fit results was negligible. This can be written as:[5]

$$P(Q)_{\text{chain}} = \int P(Q, M_{\text{PEG}})\, f(M_{\text{PEG}}) \mathrm{d}M_{\text{PEG}} \tag{1}$$

where for $f(M_{\text{PEG}})$ we applied a Gaussian distribution function where the width is given by: $\sigma = N_{\text{PEG}}\sqrt{PDI - 1}$. In the fits, the contour length, L, was held fixed according to the value calculated from the molecular weight and a monomer length of l_0=3.4 Å; $L = M_{PEG}/M_0 \cdot l_0$ where M_0 is the monomer molar mass. The radius of the cylindrical sub-unit assumed in the semi-flexible worm-like model was set to an (arbitrary) value of 2 Å. In the final fits, the data curves were analyzed using a simultaneous fit where only the Kuhn length length, l_K, was varied. The radius of gyration, R_g, could then be calculated according to Benoit and Doty:[6]

$$R_g^2 = \frac{L \cdot l_K}{6}\left(1 - \frac{3}{2n_b} + \frac{3}{2n_b^2} - \frac{3}{4n_b^3} \cdot (1 - \exp(-2n_b))\right) \tag{2}$$

where $n_b = L/l_K$ is the number of statistical Kuhn segments. From the fits a Kuhn length of $\approx$ 10 Å was obtained. This gives 10 $\pm$ 2, 16 $\pm$ 3 for the 1k and 2k PEG chains respectively.

For the 5k PEG chain, significant deviations between the model for worm-like chains and the experimental data were found, in particular at the intermediate Q-regime. In this case a form factor corresponding polymer chains with excluded volume statistics[7] yielded much better description of the data (dotted lines in Fig. 6 in main text) for which we obtained R_g= 34 $\pm$ 3 Å. This may be attributed to the development of excluded volume effects when the number of statistical chain segments, n_b, increases. However, from the work of Norisuye and Fujita[8] these effects are not expected to be present for chains with $n_b < 50$, which can be compared to $n_b \approx 26$ for PEG 5k. It should be noted that a model-independent fit (Guinier analysis) yielded similar results as expected since R_g is determined by the low Q data ($QR_g < 1$). The reason for this difference is not known, however since we here will restrict our discussion to the overall value of R_g, we will use the values that best describe the data.

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