ESRF	**Experiment title:** A SAXS study of the Mechanism of Shear Alignment of PEG-Peptide Conjugates	**Experiment number**: SC2985
Beamline:	**Date of experiment**: from: Feb 14 2011 to: Feb 18 2011	**Date of report**: 21/6/11
Shifts:	**Local contact(s)**: Dr Jeremie Gummel	*Received at ESRF:*

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Report:

This was a highly successful session. Due to lack of availability of PEG-peptides, we instead examined a series of related peptide amphiphiles (PAs) and amphiphilic self-assembling peptides. Most interesting was the SAXS data obtained for a peptide amphilphile C_{16}-KTTKS, related to a commercially available material called Matrixyl used in skincare applications due to its collagen-stimulating properties (the KTTKS sequence is taken from a propeptide from Human type I collagen[1]). We described the self-assembly of this PA into tapes containing bilayers in a previous publication.[2]

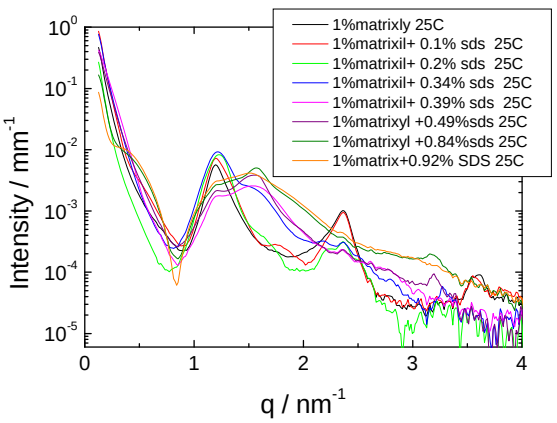
On ID02, we performed SAXS on mixtures of C_{16}-KTTKS with SDS (sodium dodecyl sulfate), the well-known anionic surfactant. We are investigating the influence of electrostatics on the self-assembly of the PA, which is also driven by hydrogen bonding and hydrophobic interactions. The samples were contained in flow-through capillaries, which permitted investigation of spontaneous flow alignment observed for some samples (*vide infra*).

SAXS profiles for 1 wt% solutions of C_{16}-KTTKS with varying concentration of SDS in the range 0 – 0.9 wt% at 25 ^{o}C are shown in Fig.1a. This data reveals a wealth of features. For C_{16}-KTTKS without added SDS the profiles show the presence of a peak at q = (1.20 ± 0.01) nm^{-1} with second and third order reflections, consistent with a layered structure with (5.24 ± 0.05) nm spacing, which corresponds to the period of C_{16}-KTTKS bilayers.[2] Upon addition of 0.1 wt% SDS, a small broad peak appears at q = 1.77 nm^{-1}. This evolves on increasing SDS concentration into a peak at q = 1.56 nm^{-1}, corresponding to a period 4.0 nm. This agrees with the spacing of stripes on the tapes observed by TEM and AFM (see eg. Fig.2).

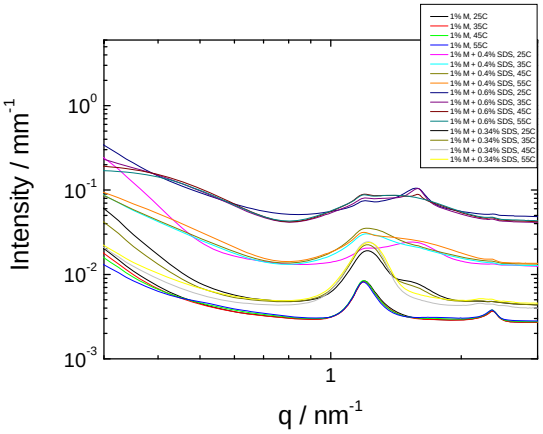
Fig.1b shows temperature-dependent SAXS data for 1 wt% C_{16}-KTTKS on its own and for 1 wt% solutions with SDS at four selected concentrations. There is no temperature dependence in the range 25 – 55 ^{o}C

studied for C_{16}-KTTKS on its own, however for the sample with 0.34 wt% SDS a transition is observed on heating from a profile that contains peaks corresponding to both 5.2 nm and 4.0 nm spacings, to one with just the 5.2

(a)



(b)



(c)

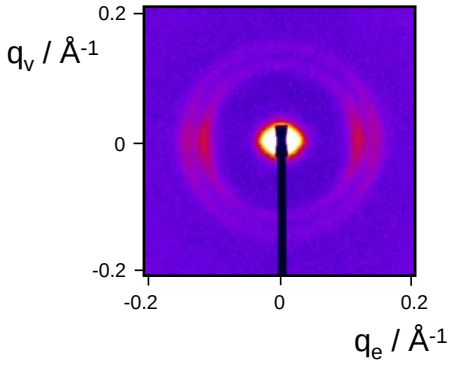


Fig.1. (a) SAXS profiles as a function of SDS concentration (at 25 ^{o}C) for 1 wt% C_{16}-KTTKS samples, (b) SAXS data for 1 wt% C_{16}-KTTKS without added SDS and with 0.4 wt% SDS as a function of temperature (selected every 10 ^{o}C) – data sets are displaced for convenience in presentation, (c) Two-dimensional SAXS pattern for a shear aligned sample of 1 wt% C_{16}-KTTKS + 0.3 wt% SDS, the pattern is rotated through 90^{o} (flow direction v vertical, e denotes vorticity direction) for comparison with fibre XRD images.

nm bilayer peak. A similar trend is observed at higher SDS concentrations, with the difference that the 4.0 nm peak at 25 ^{o}C is intense (more intense than the 5.2 nm spacing for 0.6% SDS) and does not disappear at high temperature for the 0.6 wt% SDS and 0.4% SDS samples, but rather decreases to a lower intensity than that of the 5.2 nm peak.

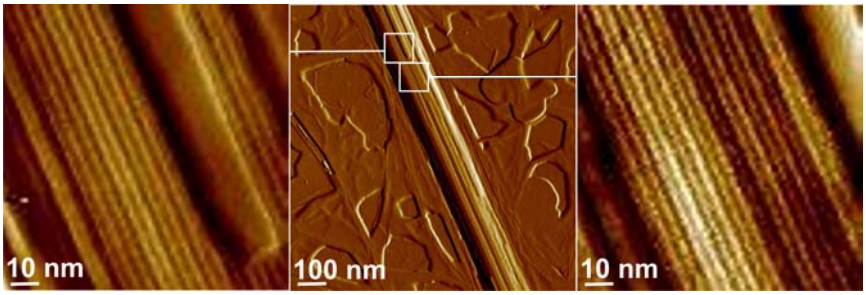


Fig.2. AFM image of striped tape (courtesy of J.Adamcik and R.Mezzenga, ETH Zürich).

SAXS was also performed on samples aligned by shear flow, to examine orientation effects. Fig.1c shows a representative image. This reveals that under flow, tapes align along the flow direction and Bragg peaks corresponding to both 5.2 nm and 4.0 nm spacings are observed perpendicular to the flow direction. This indicates that both of these periodicities are perpendicular to the tape long axis.

This is a complex system, and interpreting these subtle effects is the subject of ongoing work. This is complemented by ongoing real-space experiments using AFM and cryo-TEM to elucidate the origin of the 4 nm stripe spacing.

This work is presently being prepared for publication.[3] Several other interesting peptide systems were studied during this beamtime, and this will be written up for publication in due course.

References

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2. Castelletto, V.; Hamley , I. W.; Perez, J.; Abezgauz, L.; Danino, D. *Chem. Comm.* **2010,** 46, 9185.
3. Castelletto, V.; Hamley , I. W.; Adamcik, J.; Mezzenga, R.; Gummel, J. *in preparation* **2011.**