

Experiment title: A BioSAXS Study of the Self-Assembly of Designed Arginine-Rich Hydrogelators	Experiment number: MX-1666
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Shifts: 9	Local contact(s): Adam Round <i>Received at ESRF:</i>

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Report:

We investigated the self-assembly of amphiphilic peptides mainly based on short arginine-rich sequences. Concentrated solutions were prepared with designed alternating arginine/phenylalanine octamers in aqueous medium and left to age for periods ranging from a few days up to sixteen weeks previous to experiments. Microscopy data showed the ability of these compounds to self-assemble into amyloid fibres and their propensity to form entangled polymeric networks upon time was assessed either by AFM data or by changes on the viscoelastic behaviour noticeable to the naked eye. The BioSAXS setup on BM29 was used to probe scattering profiles from these mixtures under controlled flow. In Figure 1, a typical SAXS pattern from these assays shows remarkable anisotropy on scattering distribution upon shear. By integrating the polar representation of these data over the azimuthal range, it was possible to determine the order parameter with high precision and establish a correlation between aging of peptide solutions and the formation of gel phases. Data arising from these assays were published on Ref. [1].

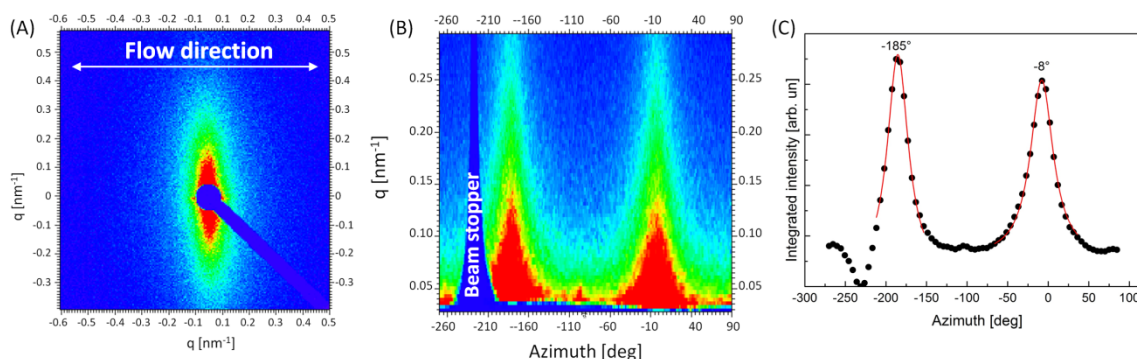


Figure 1. Anisotropic data from aged [Arg-Phe]₄ solution at 1 wt%.

We also used this beamtime to investigate the self-assembly of bolaamphiphilic peptides. Arg-Phe pairs were conjugated with a tetra-leucine segment to produce a sequence with cationic groups at both termini. SAXS data from solutions prepared with this octamer, exhibited in Figure 2, have been properly fitted according to the bilayer form factor proposed

by Pabst et al. [2], revealing the formation of nanosheets with thicknesses of about 3 nm. Cryo-TEM imaging confirmed this morphology and cytotoxicity of nanosheets was further investigated regarding human stromal corneal fibroblasts. Data from these assays are part of a paper which is currently under evaluation [3].

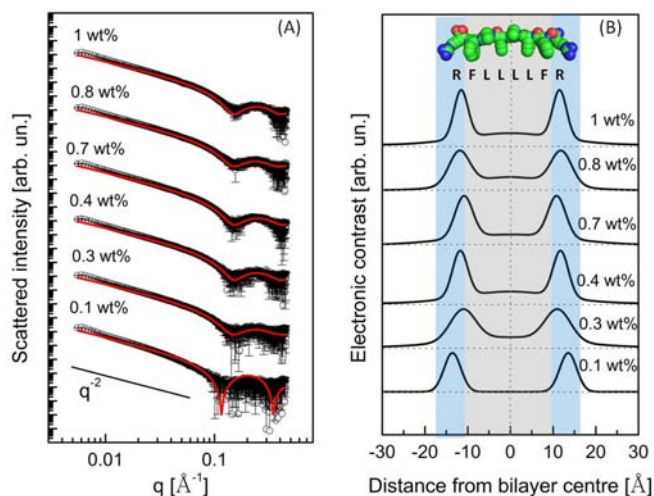


Figure 2. SAXS data from Arg-Phe-[Leu]₄-Phe-Arg solutions at concentrations indicated (A) and their corresponding electron density profiles according to the bilayer form factor proposed in Ref. [2].

In addition to arginine-rich peptides, we also took the chance to obtain structural information on self-assembled nanostructures from anionic sequences based on glutamic acid. Specifically, we probed the self-assembly pathway of nanotubes built up from the bolaamphiphile Glu-Phe-[Leu]₄-Phe-Glu. Data obtained on BM29, Figure 3, were crucial to unveil a remarkable planar-to-tubular transition, which appears accompanied by a b-to-unordered transition at secondary structure. These findings were consolidated with Cryo-TEM imaging and published in Ref. [4].

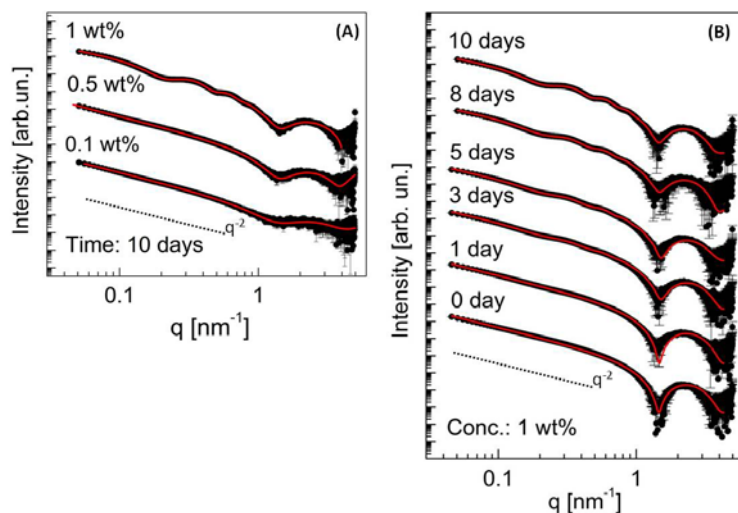


Figure 3. Scattering curves from Glu-Phe-[Leu]₄-Phe-Glu solutions at concentrations and times indicated. Data have been fitted according to bilayer or core-shell form factors (see Ref. [4]).

References

- [1] Decandio, C. C.; **Silva, E.R.**; **Hamley, I. W.**, Castelletto, V.; Liberato, M.S.; Xavier, V., Oliveira, C.L.P.; Alves, W. A. *Langmuir* (2015) 31:4513-4523;
- [2] Pabst, G., M. Rappolt, H. Amenitsch and P. Laggnier. *Phys. Rev. E* (2000) 62: 4000- 09.
- [3] **Silva, E.R.**, Walker, M. N., Reza, M.; Castelletto, V.; Ruokolainen, J., Connon, C. J., Alves, W. A., **Hamley, I. W.** *Submitted* (2015)
- [4] **Silva, E.R.**, Alves, W.A., Castelletto, V., Reza, M., Ruokolainen, J., Russain, H., **Hamley, I. W.** *Chem. Comm.* (2015) 51:11634-37.