



	<b>Experiment title:</b> Investigation of hierarchical structure of dispersion of carbon nanotubes in a solution of flexible-chain polymers under shear flow	<b>Experiment number:</b> SC-4167
<b>Beamline:</b> ID02	<b>Date of experiment:</b> from: 28 August 2015 to: 31 August 2015	<b>Date of report:</b> 30 November 2015
<b>Shifts:</b> 9	<b>Local contact(s):</b> MOELLER Johannes	<i>Received at ESRF:</i>
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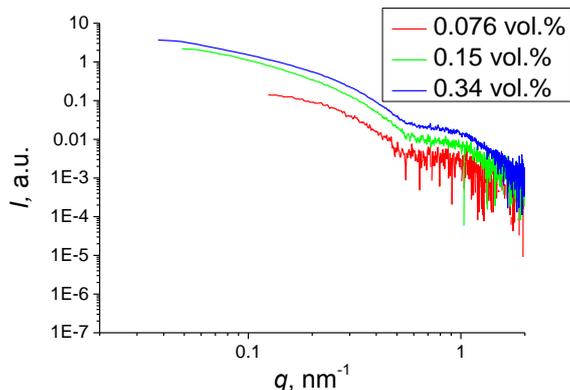
### Experiments with polyacrylonitrile (PAN) – carbon nanotubes (CNT) – DMSO systems

Shear of the pure PAN solution did not influence the solution scattering. Therefore, we used the CNT-free solution of PAN as the reference, and its scattering curve was used as background for subtraction.

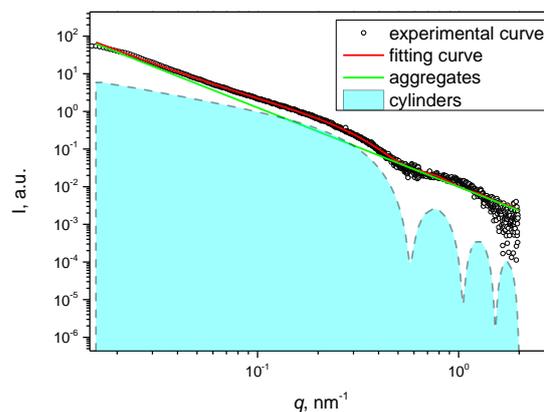
Fig. 1, *left* shows the SAXS data for the CNT-filled systems containing 11 wt% of PAN after subtraction of the scattering from the CNT-free PAN solution. The scattering data for the system containing 0.34 vol.% of CNT was fitted using a combined model of long cylinders and fractal aggregates (Fig. 2). The scattering curve can be regarded as a sum of the scattering curves of two objects: cylinders with the polydisperse length of 422–850 nm and radius of 6.7 nm and aggregates with the fractal exponent value of about 2.1. The cylinders geometry coincided with the CNT properties revealed by TEM. The fractal exponent corresponded to the case of limited probability of the particles contact (doi: 10.1080/02786820117868), coinciding with efficient wrapping of CNTs with PAN macromolecules hindering the tubes contact.

Application of shear stress on the CNT-free PAN solution and the dispersions containing 0.076 and 0.15 vol.% of the nanotubes had no effect on the scattering profile of the specimens. Rotation of the dispersion with the highest CNTs content (0.34 vol.%) resulted in the changes of the scattering at the low  $q$  range. Basic analysis of the retrieved data is given in Fig. 3.

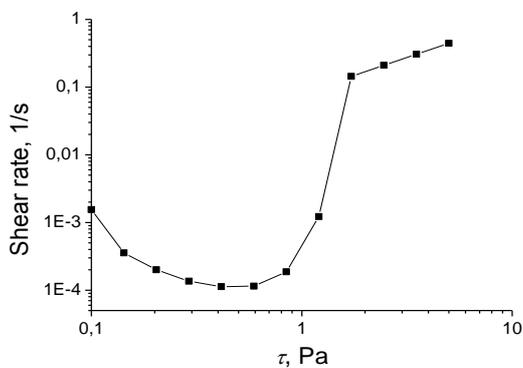
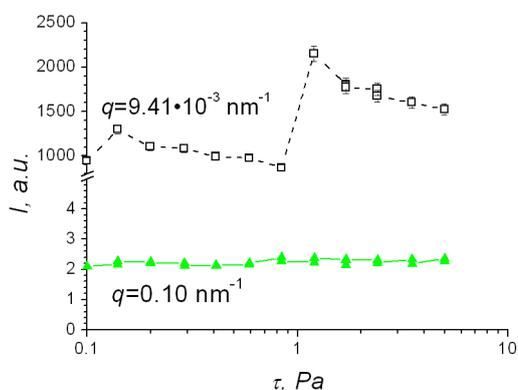
The scattering intensity at  $q = 0.1 \text{ nm}^{-1}$  was independent of the imposed stress. At  $q = 0.01 \text{ nm}^{-1}$ , at the low value of the imposed shear stress (below 1 Pa), the scattering intensity was virtually independent of the shear stress. The rheometry data recorded simultaneously (Fig. 4, *right*) revealed that the shear rate was of  $<10^{-4} \text{ s}^{-1}$  over that shear stress range. At  $\tau \approx 1 \text{ Pa}$ , the shear rate was up to  $\sim 10^{-3} \text{ s}^{-1}$  and increased further, marking the onset of well detected shear deformation of the specimen. Simultaneously, the scattering intensity grew up approximately two-fold and then steadily decreased as the shear stress went up to 6 Pa. The observed effect was attributed to the shear-induced aggregation and disaggregation of the nanotubes. This conclusion could be easily understood if we recall that dimension of scattering wave vector  $q$  is reverse proportional to size. The lower  $q$  value, the larger size is probing by the SAXS method. Importantly, the observed changes of the scattering were well outside the expected instrument inaccuracy limit (the range of  $\pm 5\%$  of the data is marked in the plot with the error bars), and was not due to the possible influence of the beam stop (the overall trend of the scattering intensity at  $q$  of  $0.02 \text{ nm}^{-1}$  was similar; however, the absolute change was smaller).



**Fig. 1.** Static SAXS curves of the CNT-PAN-DMSO dispersions (11 wt% PAN solution was used as a background). 11 wt.% of PAN, CNT content is marked in the legend.



**Fig. 2.** Fitting of the static SAXS curves for the CNT-PAN-DMSO dispersion; 11 wt.% of PAN, 0.34 vol.% of CNT. The scattering from the CNT-free PAN solution was subtracted.



**Fig. 3.** *Left)* SAXS data for the CNT-PAN-DMSO dispersion at selected  $q$  values; 11 wt.% of PAN, 0.34 vol.% of CNTs; applied shear stress of 0–5 Pa. *Right)* The flow curve of the same dispersion recorded simultaneously.

### Experiments with poly-N-vinylpyrrolidone (PVP) – carbon nanotubes (CNT) – water systems

The scattering curve shape of the CNT-free PVP solution and the dispersion containing 0.3 vol% of CNT were identical. Hence, the polymer scattering profile could be extracted from the data after subtraction of water scattering as background. The scattering of the dispersion containing 0.38 vol.% of CNT was significantly above that for the CNT-free solution of PVP, and the scattering from the CNT phase could be determined using the PVP solution scattering profile as the background.

Further processing of the scattering data is currently in progress.

### Major conclusions

- The both CNT-containing polymer solutions revealed nice scattering profiles. Above certain CNT content threshold ( $\sim 0.1$  vol.%) the scattering of the CNT is sufficient to be detected on top of the polymer/solvent system scattering.
- Fitting of the static scattering data brings important information on the CNTs organization in the dispersion.
- The effect of shear has been revealed for the highest content of the nanotubes and at the smallest wave vector; the scattering changes were assigned to reversible formation of the CNT aggregates.
- Scattering of the CNT phase after subtraction of the solvent was similar for the PVP- and PAN-containing dispersions. However, the strong scattering from DMSO (used as the solvent in the case of PAN) complicated the data processing. Evidently, study of aqueous (or probably DMF-based) dispersions can give more distinct results.