Spin-echo small-angle neutron scattering (SESANS) measurements of needle-like crystallites of gelator compounds

Pieter-Jan C J J Coumou¹, Aurelie M A Brizard², Jan H van Esch², Ignatz M de Schepper¹ and Wim G Bouwman¹

¹Delft University of Technology, Faculty of Applied Sciences, Department Radiation, Radionuclides and Reactors, Mekelweg 15, NL-2629 JB Delft, the Netherlands
²Delft University of Technology, Faculty of Applied Sciences, Department of Chemical Technology, Julianalaan 136, NL-2628 BL Delft, the Netherlands
E-mail: w.g.bouwman@tudelft.nl

Abstract. From dibenzoyl cystine, a low molecular weight gelator, we have prepared needle shaped crystals at relatively high concentrations. For the first time SESANS measurements are performed on objects with this geometry. From the measurements the average diameter can be seen directly. From a more careful analysis the width distribution is determined. The gel phase itself prepared at lower concentrations did not show any signal, in contrast to what one observes with conventional SANS. This shows the complementarity of SESANS and SANS.

1. Introduction
Spin-echo small-angle neutron scattering (SESANS) is a relatively new neutron scattering technique [1, 2, 3] to determine the scattering length density structure of materials [4] in the length range between 30 nm and 20 µm. This is derived from the polarisation as a function of the spin-echo length. Up till now the technique has mainly been applied to nearly spherical particles, as colloids [5, 6], casein micelles and aggregates [7], emulsions [8, 9] and granular materials [10, 11].

In this article we present the first measurements on clearly anisotropic particles, needle shaped crystals of gelator molecules. Hydrogels (gels of aqueous solutions) are well known, because of their applications in food, cosmetics and biomedical use. Dibenzoyl cystine (DBC) (see Fig. 1) is such a low molecular weight gelator [12]. From this material we have prepared needle shaped crystals at relatively high concentrations. From the SESANS measurements the average diameter can be seen directly. From a more careful analysis the width distribution is determined.

The gel phase itself prepared at lower concentrations did not show any signal, in contrast to what one observes with conventional SANS [13].

2. Experiment
The standard method for the preparation of a hydro-gel based on low molecular weight compounds is by completely dissolving the gelator in water. Then the compounds self-assemble into fibrils. A common way to dissolve the gelator in water is by heating the solvent. A gel is
formed when the solution cools down again. The temperature for solubility for DBC in water is above the atmospheric boiling point of water, which means that the sample has to be heated under pressure. A solvent temperature of 140°C is high enough to dissolve the gelator DBC. The gels should be prepared directly in the quartz cuvettes, since gels cannot be transferred without breaking the gel, which would affect the original micro structure. An autoclave was used to increase the boiling point of water, and thus to avoid evaporation of the solvent during sample preparation (DBC dissolution). The autoclave was put in the oven for two and a half hours at 140°C and then cooled at room temperature. The cooling process takes several hours. Seven DBC gel samples (concentrations ranging from 10 to 50 mM) were prepared with the use of the autoclave.

Optical microscopy pictures (Fig. 2) have been taken for the 25 mM DBC gel. Long needle shaped crystals can be seen. The length of the fibres is in the order of magnitude of 100 µm, the width is in the order of 1 µm. With the resolution of the microscope it was impossible to determine the width more precisely.

SESANS measures the polarisation as a function of the real-space parameter (spin-echo length) z after normalisation with the empty beam

\[ P(z) = e^{\Sigma_t (G(z) - 1)}, \]  

(1)

where \( \Sigma_t \) is the average number of times a neutron scatters when traversing the sample. \( G(z) \) is the projection of the scattering length density correlation function \( \gamma(r) \) over a distance \( r \). The projection of \( \gamma(r) \) along the neutron axis, taken to be \( x \), is

\[ G(z) = \frac{2}{\xi} \int_z^\infty \frac{\gamma(r)r}{\sqrt{r^2 - z^2}} dr, \]  

(2)

where we have the correlation length along the neutron beam axis

\[ \xi = 2 \int_0^\infty \gamma(r) dr. \]  

(3)

The correlation function \( \gamma(r, D) \) for a straight and infinitely long cylinder with a diameter \( D \) is [14]

\[ \gamma(r, D) = 1 - \frac{2F_1 \left( \frac{1}{2}, \frac{3}{2}; 3; \frac{r^2}{D^2} \right) r^3}{4D^3} - \frac{2F_1 \left( -\frac{1}{2}, \frac{3}{2}; 2; \frac{r^2}{D^2} \right) r}{D}, \]  

(4)
for $0 \leq r < D$ and

$$\gamma(r, D) = 1 - \frac{2F_1\left(\frac{1}{2}, \frac{3}{2}; 3; \frac{D^2}{r^2}\right)}{4r^2} - 2F_1\left(-\frac{1}{2}, \frac{3}{2}; 2; \frac{D^2}{r^2}\right),$$

for $D < r < \infty$.

Where $2F_1$ is the Hypergeometric function. We are unable to solve the projection $G(z)$ analytically but we have used Eq. 2 to calculate it [4]. The correlation function $\gamma(r)$ and $G(z)$ show a levelling decay saturating, not surprising, around $D$ as a function of the spin echo length.

Polydispersity can be taken into account by weighing the projected correlation function with for example the normalised log-normal distribution function $f(D)$

$$G(z) = \int_{0}^{\infty} G(z, D) f(D) dD.$$ 

We choose the log-normal distribution, since it is one of the most frequently occurring distribution functions for sizes in nature. However, we are not sensitive to the fine details of the distribution. A normal distribution would give a similar description of the measured data.

SESANS was performed at the neutron source at the Delft University of Technology. A neutron beam, polarised by a set of supermirrors, with a flux of $10^3$ neutrons/s at the sample position and a wavelength $\lambda = 0.21$ nm passed through the sample. More technical details can be found elsewhere [3]. Under ideal conditions, the set-up allows for analysis of data up to spin-echo lengths of 20 $\mu$m, although the spin-echo length is restricted to 10 $\mu$m in the present experiment. The sample cuvettes had a thickness of 10 mm.

3. Results

![Figure 3. SESANS measurements of DBC-gels prepared with increasing concentrations. The symbols represent the data, the dashed curve represents a fit with the model for the infinitely long cylinder with diameter $D$, the drawn curves represent the fits with a log-normal distribution.](#)

The SESANS measurements are shown in Fig. 3. The depolarisation increases with concentration. The curves have nearly the same shape: first a strong decay in polarisation and then a longer decaying tail. This is a clear signature of anisotropic particles. First all data were fit with the infinitely long cylinder model (the diameter $D$ and $\Sigma_t$ were the 2 fitting parameters), which gave a fair description of the data. The diameter for the lowest three
concentrations was $D = 0.50 \pm 0.07 \, \mu m$ and for the 50 mM sample $D = 1.1 \pm 0.1 \, \mu m$. A second fit was done taking a log-normal distribution for the diameter of the cylinders (having as a third fit parameter the width of the distribution). This gave a better fit for the highest concentration samples for the decaying tail. The mean diameter found remained the same as with the first fit.

The gel phase itself prepared at lower concentrations did not show any signal, in contrast to what one observes with conventional SANS [13]. The features of the gel phase are apparently too small to be observed with SESANS. This shows the complementarity of SESANS and SANS.

4. Summary

DBC molecules dissolved at high enough concentrations form needle shaped crystals. The strong preference to crystallise in one direction is not surprising, since the gelator molecules have tendency to stack preferentially in one dimension. With optical microscopy we determined the length to be $\approx 100 \, \mu m$. With SESANS on the other hand it is possible to determine the width to be $\approx 0.5 – 1 \, \mu m$. This is the first example of SESANS measurements on needle shaped particles.

Acknowledgements

We acknowledge Chris P. Duif for assistance with the SESANS measurements.

References

[1] Rekveldt M T 1996 Nucl. Instr. & Methods in Phys. Res. B 114 366–370
[2] Gähler R, Golub R, Habicht K, Keller T and Felber J 1996 Physica B 229 1–17
[3] Rekveldt M, Plomp J, Bouwman W G, Kraan W H, Grigoriev S and Blaauw M 2005 Review of Scientific Instruments 76 033901
[4] Andersson R, van Heijkamp L F, de Schepper I M and Bouwman W G 2008 Journal of Applied Crystallography 41 868–885
[5] Kruglov T, Bouwman W G, Plomp J, Rekveldt M T, Vroege G J, Petukhov A V and Thies-Weesie D M E 2003 Journal of Applied Crystallography 36 1417–1423
[6] Kruglov T, Bouwman W G, de Schepper I M and Rekveldt M T 2005 Physica B 356 218–222
[7] Tromp H and Bouwman W G 2007 Food Hydrocolloids 21 154–158
[8] Bot A, Duval F P and Bouwman W G 2007 Food Hydrocolloids 21 844–854
[9] Goddeeris C, Cuppo F, Reynaers H, Bouwman W and Van den Mooter G 2006 International journal of pharmaceutics 312 187–195
[10] Andersson R, Bouwman W G, Luding S and de Schepper I M 2008 Granular Matter 10 407–414
[11] Andersson R, Bouwman W G, Luding S and de Schepper I M 2008 Physical Review E 77 051303
[12] Menger F, Yamazaki Y, Catlin K and Nishimi T 1995 Angewandte Chemie-International edition in English 34 585–586
[13] Willemen H M, Marcelis A T M, Iter E J R, Bouwman W G, Deme B and Terech P 2004 Langmuir 20 2075–2080
[14] Gille W 2003 Powder Technology 138 124–131