ESRF	**Experiment title:** X-ray scattering of cellulose gelation process in alkali/urea aqueous solution	**Experiment number**: SC 4112
Beamline: BM02	**Date of experiment**: from: 05/04/2015 to: 07/04/2015	**Date of report**: 02/09/2015
Shifts: 6	**Local contact(s)**: Cyrille Rochas (email: cyrille.rochas@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Yoshiharu Nishiyama* (CERMAV)

Noriyuki Isobe* (CERMAV, Laboratoire de Rhéologie et Procédés)

Report:

1. Aim of the experiments

Cellulose is often formed into film or fibre in industrial processes through dissolution and coagulation. Aqueous sodium hydroxide is an emerging candidate for next generation solvent as non-toxic and environmentally benign system. In this case, dilute sulphuric acid or its mixture with aqueous sodium sulphate solution is commonly used as coagulant in industrial plants. By using cellulose gel with high surface area from alkali/urea solvent, we observed a striking difference depending on the types of coagulant: non-aqueous coagulants give rod-like structure with hydrophobic surface, and aqueous ones give membrane-like structure with hydrophilic surface (Isobe et al., *J. Colloid. Interf. Sci.* **359**, 2011). This observation opened a way to control the property of cellulosic material without any chemical modification. For the better control of the property, it was necessary to understand the structural formation of cellulose gel with coagulant.

In the last allocated beamtime (Experiment number:02-01-843), we observed the structuration process in the Q-range of 0.01-2.0 $Å^{-1}$. The data suggested that the mode of structuration is nucleation and its growth whatever the coagulant; the nucleus is hydrophobically-stacked molecular sheet. However, the interpretation of the monotonic intensity increase toward smaller Q 0.01-0.5 $Å^{-1}$ was not clear. To understand the origin of this monotonic increase, first we need to identify which scattering feature reflects the structural information of cellulose molecule in solution.

In this beamtime, therefore, our objective was to first elucidate the small angle profiles with cellulose solution (before

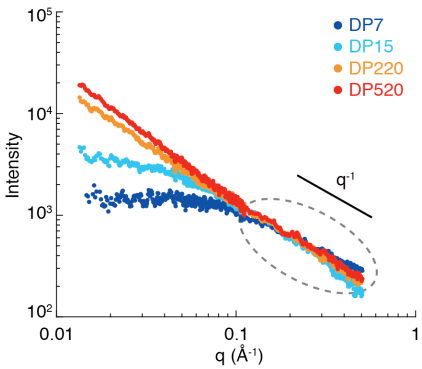

Figure 1. SAXS profiles of cellulose (0.5w/v%) dissolved in aq. 2N LiOH and 2N urea solution. DPs are 7, 15, 220, and 420.

coagulation) and then obtain systematically the time-dependent X-ray scattering data of coagulating cellulose in the Q-range of 0.01-1.0 $Å^{-1}$ Å.

2. Experiments

Solution: Cellulose samples with degree of polymerization (DP) of 7, 15, 220, and 520 were dissolved in aq. 2N LiOH/2N urea solution. Cellulose concentration was 0.5 w/v%. Data were recorded on a CCD camera at two different camera lengths (163 cm and 16 cm).

Coagulation: Cellulose samples with DP of 220 were dissolved in the solvent described above. Fifty μL of cellulose solution was filled in capillary and 350μL of coagulant (methanol) was added. A camera length of 163 cm was used. For each capillary, scattering was measured with interval of 30 minutes with typically 20 seconds exposure.

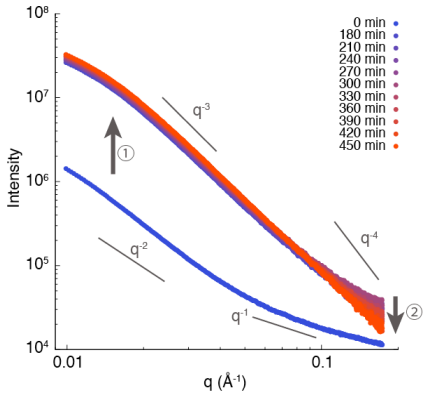

Fig. 2. Time-dependent SAXS profiles of 10w/v% cellulose solution under coagulation. Elapsed time from first contact with coagulant is shown on top right .

3. Results and discussion

Solution: SAXS profiles of solution are shown in Fig. 1. In the profiles of DP7 and 15, the Guinier region is clearly seen in the Q-range of 0.02-0.1 $Å^{-1}$ and the radii of gyration (Rg) are calculated to be 10.7 (DP7) and 20.1 Å (DP15). In addition, all curves overlap in the Q-range of 0.1-0.3 $Å^{-1}$, regardless of DP (circled area in Fig. 1). Since the power of this slope is about -1, this range contains information on cross-sectional cellulose molecule that can be approximated to a rod, the diameter of which 5~6 Å from cross-sectional Guinier plot. In the case of DP7 and 15, combined with the Rg values, the whole dimension of rod was obtained: length = 36.3 (DP7) and 69.3 Å (DP15); diameter = 5.6 and 5.6 Å. These values correspond well to an extended cellulose molecule. This result was a very first direct geometrical measurement of individual cellulose molecule in dissolved state. Therefore, the use of cellulose oligomer allows us to observe the molecular structure of dissolved cellulose, the observation of which has been hindered by unavoidable formation of aggregate in the case of higher DP.

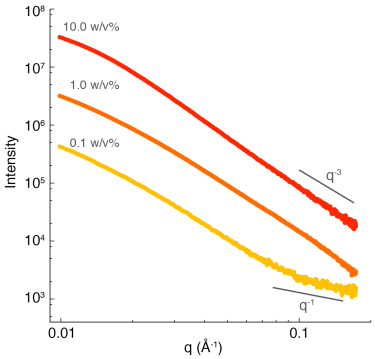

Fig. 3. SAXS profiles of coagulated cellulose, 450 mins after onset of coagulation. Cellulose concentrations are shown with the curves.

Coagulation: The time-dependent SAXS profiles of cellulose under coagulation with MeOH are shown in Fig. 2. Before the onset of coagulation, at this high concentration (10w/v%), cellulose solution (marked in blue "0 min") contained certain amount of aggregate as seen in the Q-range below 0.04 $Å^{-1}$. Since the power of slope is -2, the form of aggregate seems to be plate-like. This plate-like structure might be nucleus of coagulation. Also, there is a region with -1 slope above 0.09 $Å^{-1}$ as seen in Fig. 1. Therefore, either the aggregates have fringed micelle structure, or the solution is a binary system with molecularly dispersed part and aggregates part. With the onset of coagulation, the intensity in the small angle region is multiplied by about a factor of ten (arrow 1 in Fig. 2) and then fringes or dispersed molecules stick together (arrow 2). In Fig. 3, the SAXS profiles of coagulated cellulose with different concentrations are shown. The outlines of curves are almost identical except that there is a cross sectional region above 0.09 $Å^{-1}$ in 0.1 w/v%, suggesting that in dilute regime fringes remain after coagulation. The monotonic increase toward low Q-region is basically reflecting the dimension of gel constituent itself and not the inter-fibrillar network.

4. Perspective

In this study, we obtained whole picture of cellulose molecule in dissolved state with using cellulose oligomers for the first time. Since the structural parameters obtained are determined not only by cellulose structure but also by cellulose-solvent molecule configuration, a direct, assumption-free investigation into structural state of the dissolved cellulose will be possible.