



	Experiment title: In situ probing of PbS colloidal nanocrystals nucleation and growth using time-resolved SAXS/WAXS combined to UV-VIS spectroscopy.	Experiment number: SC4365
Beamline: ID1	Date of experiment: from: 13/12/2016 to: 15/12/2016	Date of report: <i>March 5th 2018:</i>
Shifts: 9	Local contact(s): Sylvain Prevost	
Names and affiliations of applicants (* indicates experimentalists): Benjamin Abecassis ^{1,2*} , Mickael Campos ^{3*} , Santanu Jana ^{1*} , Nicolo Castro ^{1*} , Jonathan Owen ³ 1: LPS, Université Paris Sud, Orsay. 2: Ecole Normale Supérieure de Lyon. 3: Columbia University, NY.		

Report:

Experiental Set-up:

19 mL of a 9 mL solution lead oleate in hexadecane are poured in a three-neck round bottom flask under argon. An oil bath is used to set the temperature to 110°C. The reacting fluid is pumped through a glass capillary using a peristaltic pump equipped with Vitton tubing. We wait for around 10 minutes for thermal equilibrium to be reached after the pump is set on. During the course of the reaction, the temperature inside the reacting fluid is monitored and recorded. A decrease of a few degrees is observed after the thiourea injection but the temperature quickly reaches back the set value. 1 mL of the thiourea solution in tetraglyme is sampled in a plastic syringe which is then set on a stand. The injection of this solution is controlled remotely from outside the beamline hutch with a pneumatic piston to which a TTL signal is sent. This time defines the $t=0$ s of the sequence. At this point SAXS/WAXS acquisitions are triggered. In a typical sequence, 1200 SAXS and WAXS patterns with a duration of 0.3 s are taken every second (i.e. there is a 0.7 s waiting time between two acquisition).

During all the process, we took great care to respect an air free environnement by using an argon tank and classical Schlenk line techniques.

A photograph of the set-up is shown on figure 1

Work Performed

Overall, we performed 25 kinetic sequence of which 17 ended-up exploitable. The others failed for various reasons (failure of one of the equipments, bad exposure settings etc...). We repeated several times the same sequence to ensure that the results we obtained were reapeatable. Afterwards, we varied the nature of the thiourea and looked at various reactivites at the same temperature. We then varied the Pb to S ratio since it is an imporant experimental parameter. Finally, we performed experiments on PbSe with selenoureas in order to see if the behavior we observed for PbS could be generalized to PbSe.

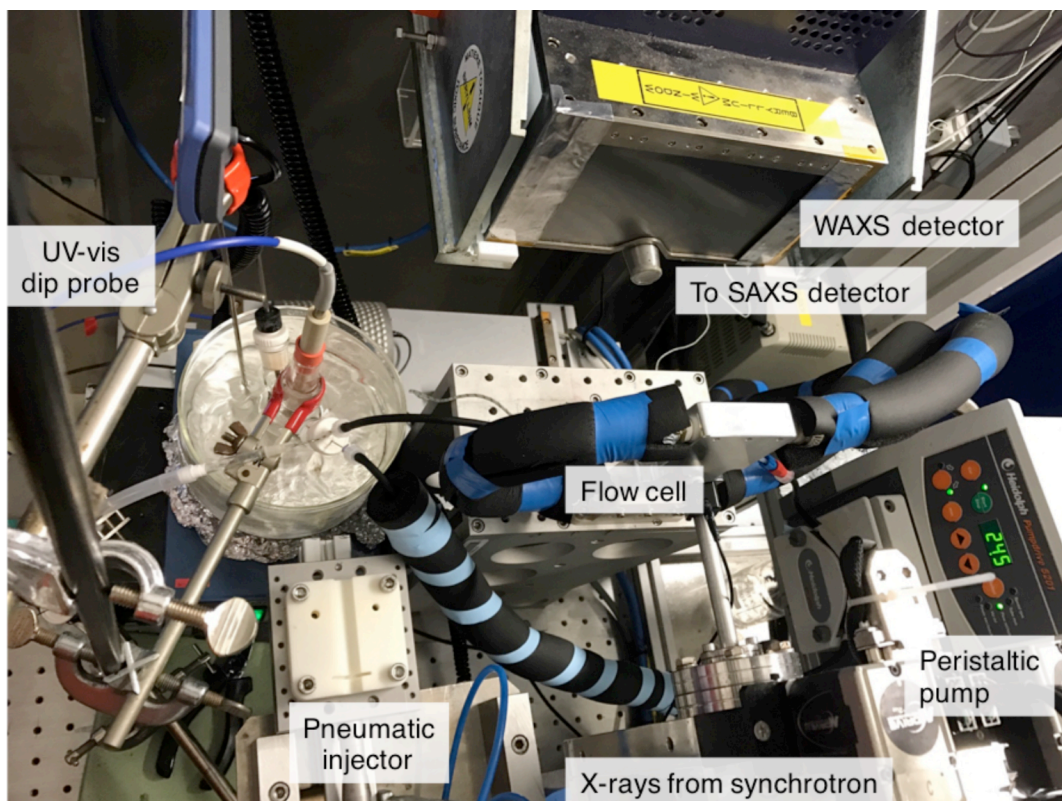
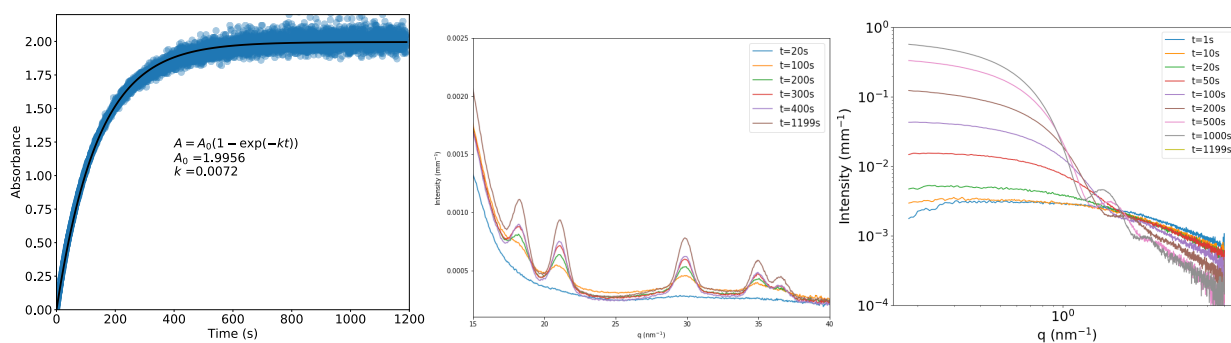


Figure 1: experimental set-up used during the experiment

Detail description of the treatment for a reference sequence.

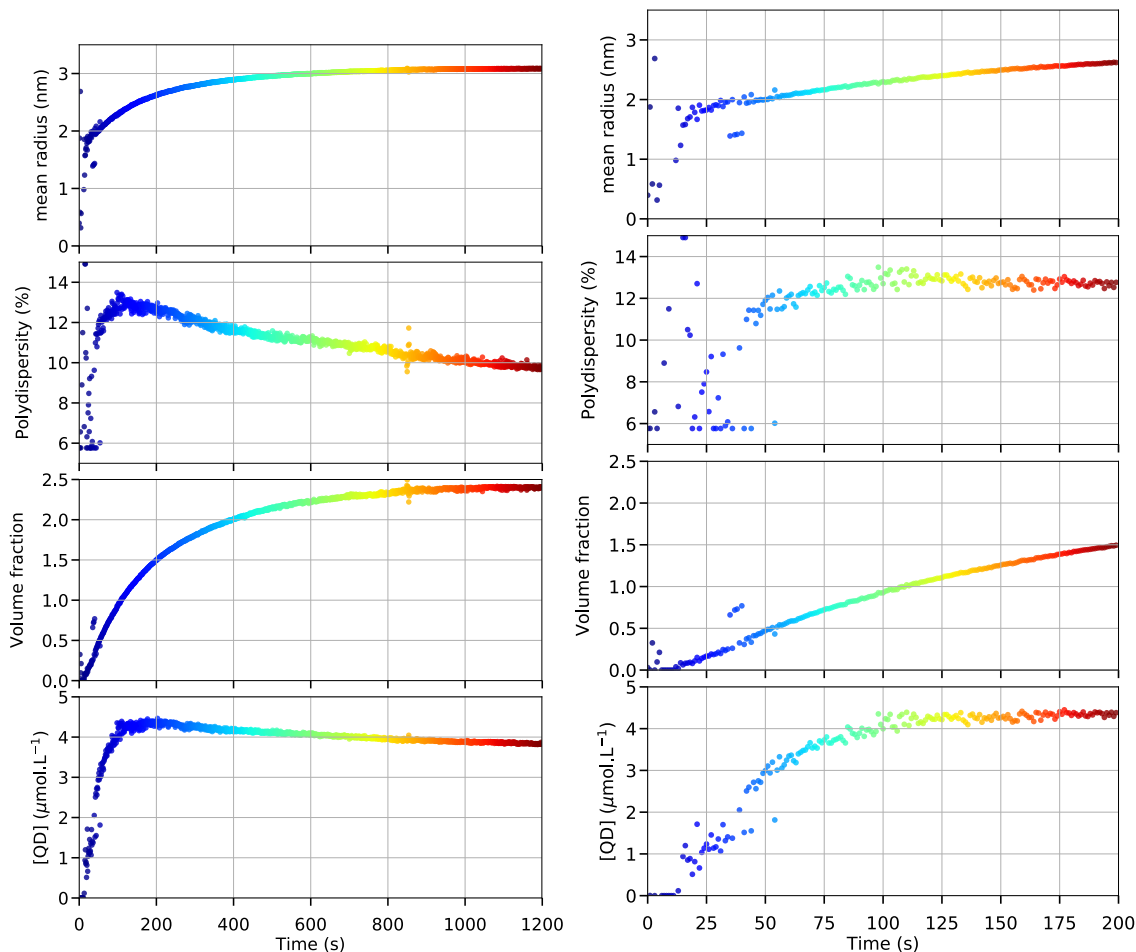
Typical SAXS and WAXS patterns along with the absorbance at 400 nm are presented on figure 2.



We observe that the kinetics is well behaved and similar to what we observed in the lab. The SAXS pattern sequence is typical of nanoparticles appearing in solution with a background of small micelle at the beginning of the reaction which gradually disappears with time. Several diffraction peaks are visible in the WAXS patterns.

The SAXS intensity is fitted with a structural model which includes a population of PbS spheres and a population of spherical micelles. We fit the first SAXS pattern of the sequence and this is considered to be the signal of the lead oleate micelles since at that time there is no nanoparticle yet. This SAXS signal is the same as the one of pure lead oleate dilute at the same concentration.

We start the fitting with the end of the sequence where the signal to noise is the highest and we pass the result of the fit of the SAXS pattern at instant t as initial guess for instant $t-1$. This reduces the spread in the fitted values during the first instants of the reaction (between 0 and 50 seconds).



Starting from $t=0$ we can see different phases.

From 0 to 13 s: nothing is visible and the number of particles is 0 while the other parameters are random (I have to suppress this range in the figure for final figure)

From 13 to 40 s: the nanoparticles start to appear but the signal is not high enough for the polydispersity to be determined with a high accuracy. Hence the Z value determined by the fit varies between 0 and 300 when we do not constrain the fit (corresponding to polydispersity varying between a few percent to 50%). This phase corresponds to the moments where the polydispersity is constant in figure 4 of report_0. There are two alternatives here. We can say that we limit the range of Z in the fits. In this case, it is constant or we can let it float but since the information is not in the data we have a noisy Z vs time curve during this phase. The noise on polydispersity is retrieved in the concentration in particles since the two are correlated and we have a noisy $[QD]$ vs time curve

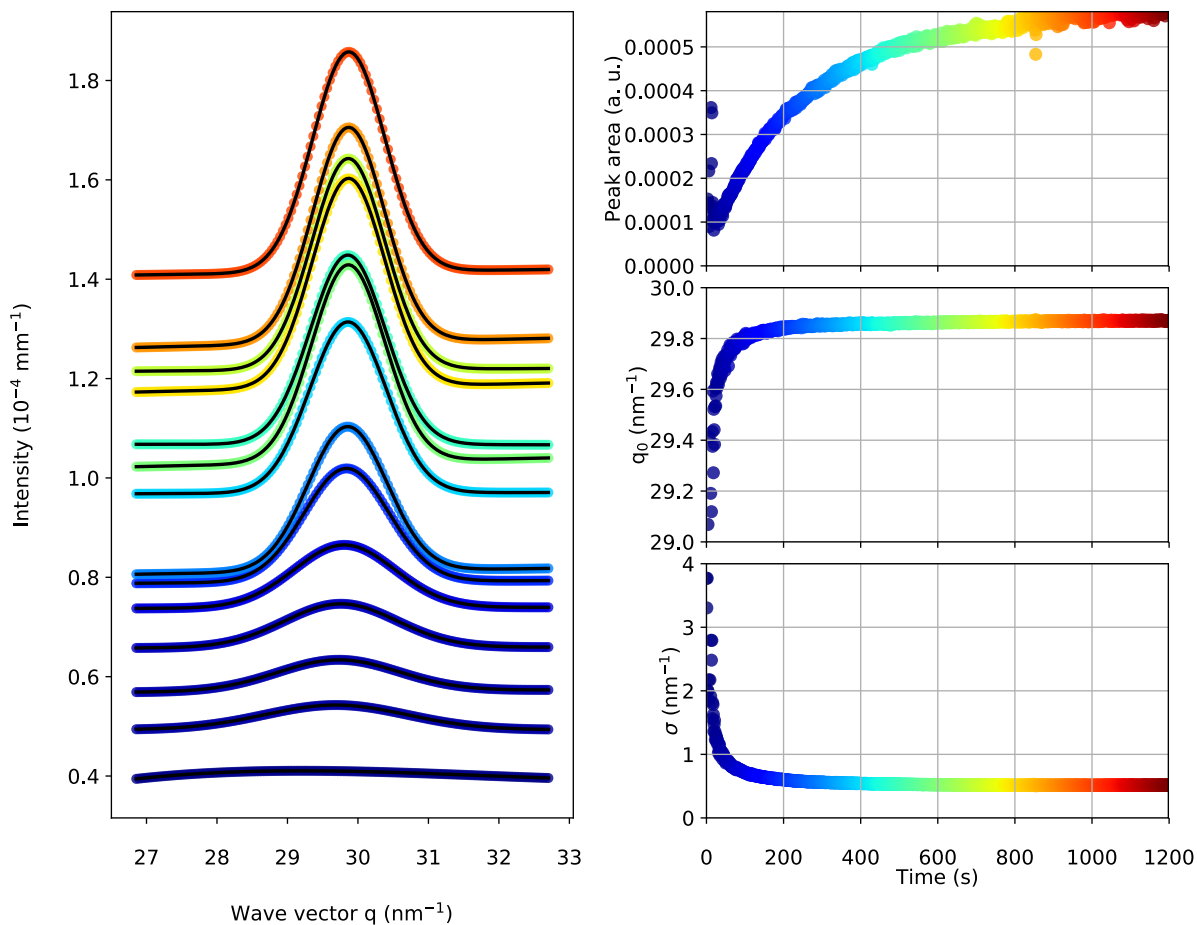
From 40 to 200 s: starting from 40 s we start to see an oscillation at high q . Hence the polydispersity can now be measured accurately. The polydispersity and $[QD]$ vs time starts to be smooth and we measure an increase in the concentration of particles from 40 to around 200s. **This prolonged nucleation phase is a surprising feature since most of the common knowledge in the field assumes a very fast nucleation phase (a few seconds at maximum) followed by diffusion controlled growth.**

From 200 s to the end: the nucleation stops and the concentration in particles decreases a bit while the polydispersity decreases also and the radius increases. At the end of the nucleation phase, half of the PbS has been consumed and the rest is used for the growth phase to reach the final radius.

All along, the number of micelles decreases which can be seen qualitatively in the fact that the intensity at high q is lower at the end of the reaction than at the beginning. This is physically sound since the micelles are consumed by the formation of the particles.

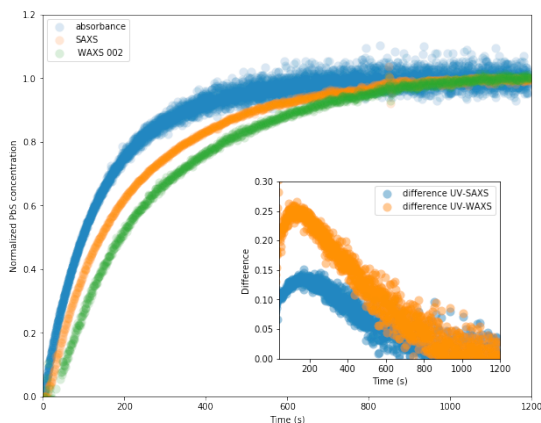
WAXS

We can observe 5 different peaks in the WAXS diagrams namely 111, 002, 022, 113 and 222 peaks at wavevectors close to 18.33, 21.17, 29.94, 35.11 and 36.67 nm⁻¹. To get quantitative information we first fit the 022 peak to a Gaussian model with a linear background. We extract from the fit: the amplitude which is proportional to the amount of crystalline material, the fwhm and the position of the maximum. The amplitude increases all along the reaction while the evolution of the peak position points towards a lattice expansion as the reaction proceeds. The FWHM decreases with time which is coherent with an increase of the particle mean size. From the Scherrer formula, we can extract a mean size from the FWHM and compare it to the mean radius found by SAXS. We find a particle size larger with SAXS than with WAXS which can be easily understood if we consider that the particles are not single crystalline and that defects are present. The fact that the ratio decreases with time can be attributed to an incomplete crystallisation of the initial particles which gain better crystallinity as the reaction proceeds.



Comparison between UV/SAXS/WAXS

We can compare the amount of PbS as monitored by UV through the absorbance, by SAXS and by WAXS. We normalize all the data to their values at the end of the reaction. We find that spectroscopy measures a higher amount of PbS than SAXS and WAXS. We can attribute this difference to PbS monomers which are in solution but not in the particles. We also see a difference between SAXS and WAXS showing that crystallization is slower than particle formation. Interestingly, the amount of PbS in monomer form (deduced by the difference between UV and SAXS) increases from $t=0$ to around 200 s and then decreases. The decay in free PbS occurs at the same time as the end of the nucleation period.



Effect of the reactivity of the thiourea.

At the same temperature and overall conditions we investigated three different thiourea which differ in their reactivity, in increasing order of reactivity:

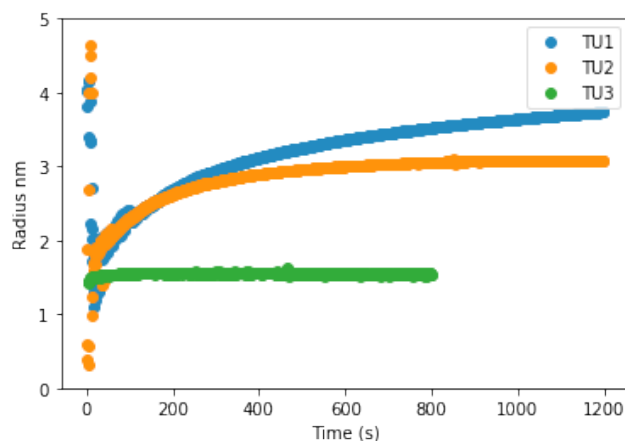
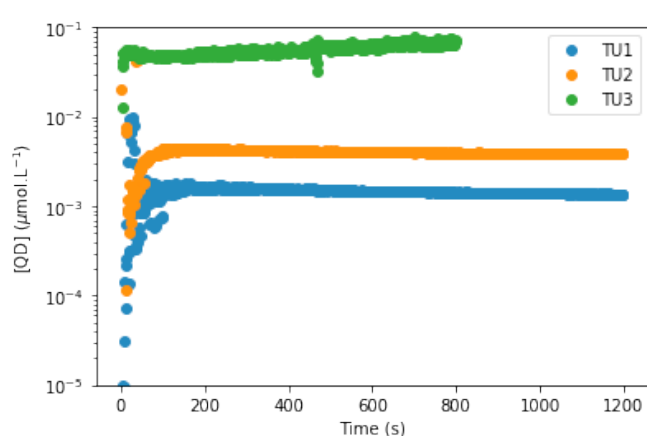
Sequence 6 : 4-MeO-Ph-DD-TU this is TU1

Sequence 8 : 4-Cl-Ph-DD-TU : TU2

Sequence 7: 3,5-2-iPr-Ph-TU: TU3

TU1 is similar to TU2 but slower. We have the same nucleation/ growth mechanism but in the end the number of particles is lower and the final radius is larger.

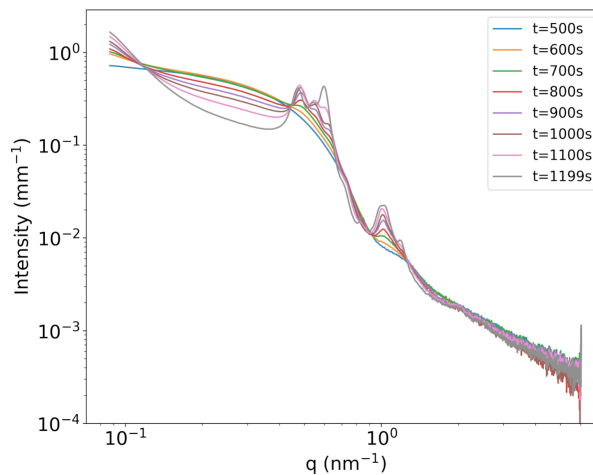
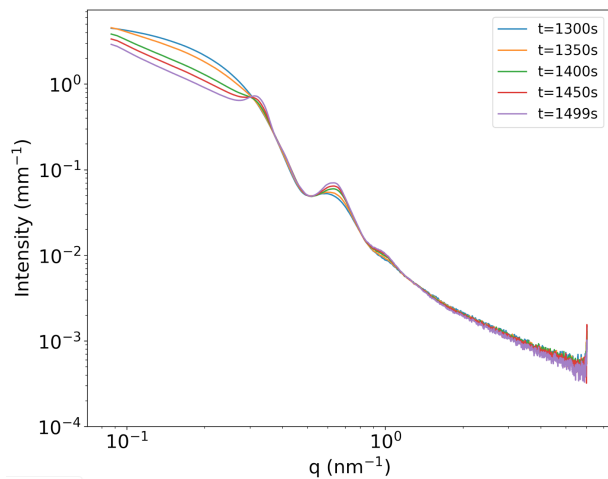
For TU3, the reaction is much faster. We can not resolve nucleation and growth and we only see one very fast nucleation period which yields a lot of small particles.



So we see that as the reactivity increases, the nucleation rate gets higher and higher and the final radius is lower and lower

PbSe kinetics

We performed 2 kinetic sequences with selenoureas instead of thiourea in order to see if the previous findings were generalizable. To our surprise we saw a very different behaviour for PbSe. In both cases we saw peaks appear in the SAXS patterns which indicates the formation of superlattices. Depending on the precursor, we either observe two peaks corresponding to a distance of 19.7 nm (for a nanoparticle radius of 8 nm before the onset of the peaks) evoking the formation of nanoparticle chains or multiple peaks showing a more complicated structure.



Other sequences and conclusion

We have made a quick examination of all the other kinetic sequences performed and are currently looking at them in a more quantitative fashion. In some cases, we noted a strong aggregation of the nanoparticles when the stoichiometry between the precursors is varied. Overall, this was a very rich and we gathered a lot of results. We are currently working with Baron Peters on theoretical issues in order to rationalize all these results. More specifically, we want to understand the long nucleation phase that we see in these experiments. Moreover, we need more beamtime to perform complementary experiments to vary the thiourea reactivity over a larger range, to investigate the effect of overall concentration and to perform other experiments on PbSe.