



| | | |
|--|--|---------------------------------------|
| | Experiment title: Probing in Situ the Nucleation and Growth of Polymeric Nanoparticles Stabilized by Surfactants | Experiment number: SC- 2883 |
| Beamline: ID02 | Date of experiment: from: 09.04.2010 to: 12.04.2010 | Date of report: 01.09.2010 |
| Shifts: 9 | Local contact(s): Jeremie Gummel | <i>Received at ESRF:</i> |
| Names and affiliations of applicants (* indicates experimentalists): Sergey Filippov ^{1*} , Milos Steinhart ^{1*} , Petr Stepanek ^{1*} , Jiri Panek ^{1*} , Petr Cernoch ^{1*} , Frederic Nallet ^{2*} ¹ Institute of Macromolecular Chemistry Academy of Sciences of the Czech Rep. Heyrovsky Sq.2 162 06 Praha, Czech Republic. ² <i>Université de Bordeaux, Centre de recherche Paul-Pascal, CNRS, 33600 Pessac, France</i> | | |

Report:

The aim of the experiment was to measure the kinetics of self-assembly of pH-sensitive polymeric nanoparticles stabilized by surfactants. To prepare nanoparticles we used a strategy that was based on the concept of so-called controlled phase separation. Briefly this concept could be described as follows. If we add a surfactant to the polymer solution which pH is gradually changing, pH-sensitive polymer instead of precipitation will form well-defined nanoparticles with low polydispersity.

The four types of pH-sensitive hydrophobic polymers that have been used in our research for the growth of nanoparticles were: (a) poly(N-methacryloyl-L-valine) (pNMV), (b) poly(N-methacryloyl-L-phenylalanine); (pNMPA), (c) poly(N-methacryloyl glycy-L-phenylalanyl-L-leucinyL-glycine) (pNMGPLG), and (d) poly(N-methacryloyl glycyL-L-leucine) (pNMGL). The extent of macrophase separation was controlled by the surfactants Brij 97, Brij 98 and Brij 700. The surfactants were different in the length of hydrophilic PEO chain. We have shown previously [1,2] that in a certain range of concentration and composition of the polymer/amphiphile system particles in broad range of sizes ca. 20 - 200 nm could be reproducibly prepared after a change of pH from 7 to 2. This change is reversible and the nanoparticles can be repeatedly created and dissolved by variation in pH.

The self-assembly of nanoparticles.

Figure 1a displays the intensity of scattered X-rays from the mixture of aqueous solution of Brij 98 surfactant and pNMGL ($f=c_p/c_{surf}=2.0$) solution as a function of time. Several things should be noted. At low q , “Guinier” regime is not achieved obviously due to big size of particles. Nevertheless, $I(q)$ value at the lowest experimental q grows with time, which is clearly an indication of particle growth (Figure 1a). In the middle q -range, the exponent value α is growing from -2.2 at the beginning up to -3.4 for the longer time (Figure 1b). The $q^{-2.2}$ dependence observed on early stages of self-assembly is attributed to the scattering from a loose, fractal structure. In contrast, α value of -3.4 suggests large compact objects. Thus using TR-SAXS we can monitor the self-assembly of nanoparticles when particles transform through fractal structure with loose surface into hard spheres with sharp interface.

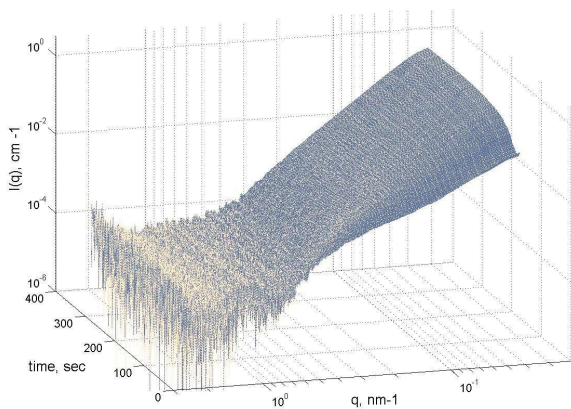


Figure 1a. The temporal evolution of the SAXS intensity for a pNMGL–Brij 98 system. $f=2.0$

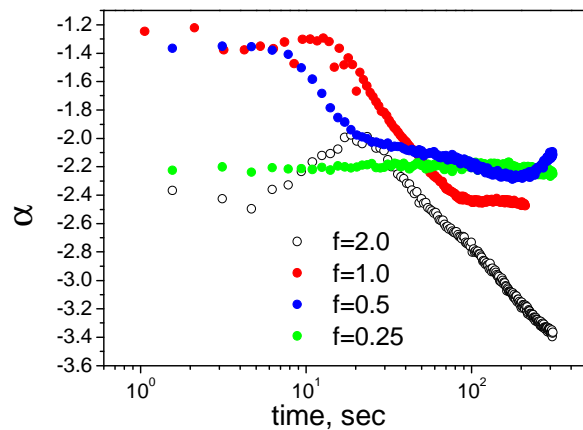


Figure 1b. The temporal evolution of the exponent value α for a pNMGL–Brij 98 system at different composition ratio f .

For the the lowest concosition ratio $f=0.25$, the behavior changes greatly. $I(q)$ value at the lowest q as well as the α exponent do not evolve with time (Figure 1b). Obviously, nanoparticles have been already formed prior to the first measurement.

From the SAXS experiments on the self-assembly of nanoparticles the following conclusions could be obtained:

1. The polymer/surfactant composition ratio f is of primary importance in nanoparticle formation, thus confirming our previous results [1,2]. Excess of a surfactant results in much faster kinetics in comparison with the solution where a polymer is in excess.
2. Our results suggest that the formation of the nanoparticles is a two stage process. In the beginning a nucleation stage occurs followed by a growth regime. The hydrophilicity of surfactants plays an important role in the formation of nanoparticles.

The breakdown of nanoparticles.

Besides the data presented herein, very interesting results also came up regarding the particles breakdown with changing of pH (Figure 2).

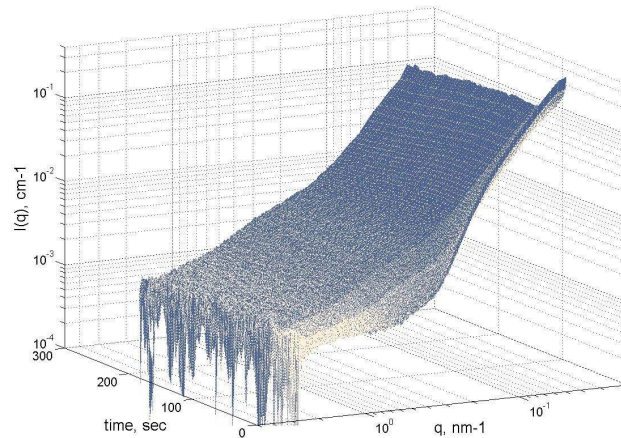


Figure 2. The temporal evolution of the SAXS intensity for a pNMGL–Brij 98 system. $f=0.25$

From the SAXS experiments the following conclusions could be deduced:

1. The nanoparticles that are formed in solutions of pH-sensitive polymers and non-ionic surfactants (Brij 97, 98) and 700 in the presence of hydrochloric acid are reversible nanoscale structures. This result is in accordance with our previous findings [1,2]
2. We didn't find any hysteresis during the nanoparticles breakdown in comparison with nanoparticles self-assembly.

This experiment has been very useful and a lot of information has been recorded. The amount of data obtained during this experiment and the quality of the information revealed from the data analysis ensure the publication of two scientific articles. We are grateful to the ESRF staff, and especially on the ID02 beam line for their help.

References:

- [1] S. Filippov, M. Hruby, C. Konak, H. Mackova, M. Spirkova, P. Stepanek, *Langmuir*, 2008, 24, pp. 9295-9301.
- [2] S. Filippov, L. Starovoytova, Č. Koňák, M. Hrubý, H. Macková, G. Karlsson, P. Štěpánek, *Langmuir*, 2010, 26, 14450–14457