



	<b>Experiment title: Formation of regular three-dimensional polymeric structures by core-shell latex particles as investigated by SAXS</b>	<b>Experiment number:</b>
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### Report:

We studied the process of film formation and the formation of three-dimensional structure by the use of core-shell particle. In a previous experiment at the ESRF (SC-594) we analyzed mainly homogenous particles. In this experiment we focused on core-shell latexsystems, and we try to characterize the ordering achieved in the first step of the film-formation (see fig.1) more quantitatively, we want to see the change in the particle shape when the sample builds a closed film and we want to find out factors of influence on the resulting order.

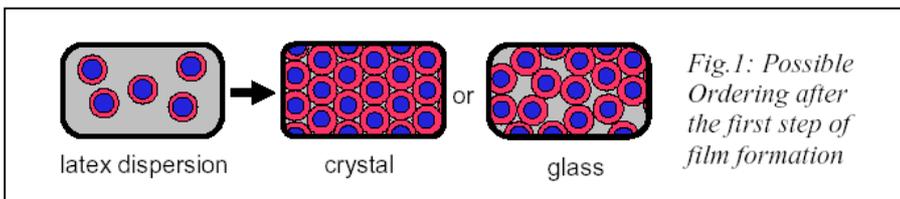


Fig.1: Possible Ordering after the first step of film formation

In the first step of film-formation there is no important difference between homogenous and core-shell like particles of the material on the surface and the interaction are identical. But finally, after a long time or after temperature exposure, even systems with a high glass-temperature will form a closed film. In this state, the only structure of films made of homogeneous latexes will be some remaining surface material. So if you want to have a structured sample in the final state, you are required to use core-shell latices. Fig.2 shows the influence of this difference for the scattering of two experimental systems.

The next step was the ordering achieved in the first step of the film formation (fig.1). Therefore we examine a high number of samples dried under different conditions. We varied the starting concentration, the drying time and temperature, and we dialyses some samples at volume concentration of about 50 vol% to remove all salt which result in a strong electrostatic interaction, e.g. a preordering of the sample in emulsion state. In all cases we receive

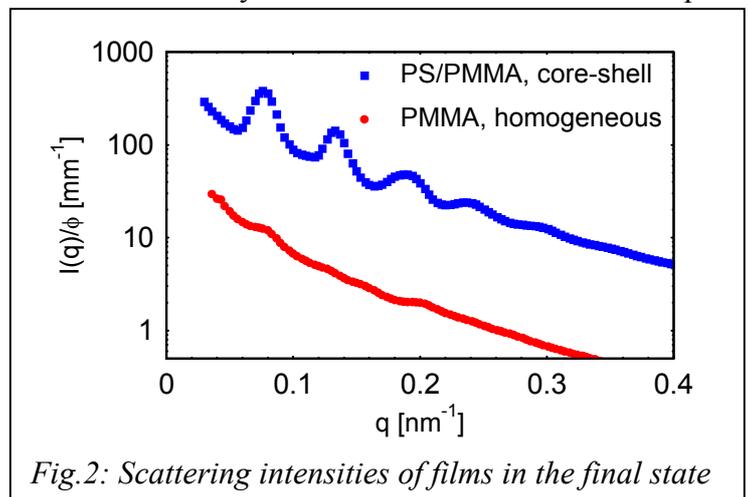
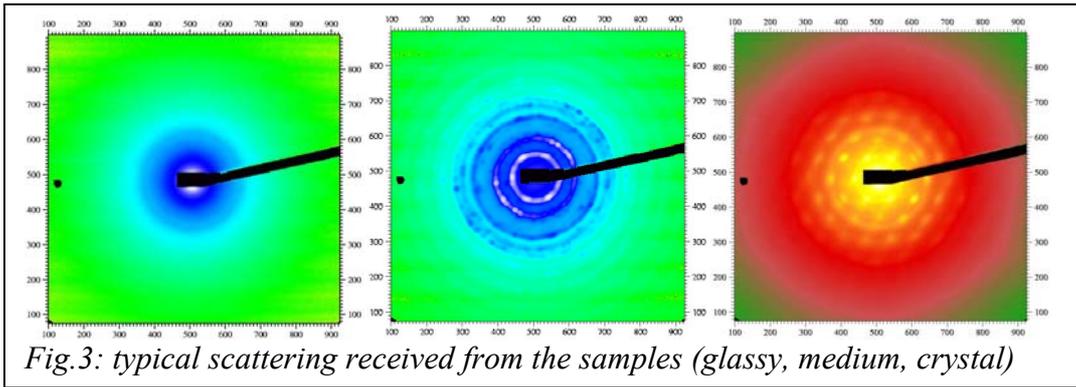


Fig.2: Scattering intensities of films in the final state

samples with local different ordering, so we measured some spots of each sample to get an impression of the average order.



Three typical states of the sample are shown in fig. 3: the glassy state (left), a crystalline state (right) and an intermediate state, a mixture of glassy regions and randomly orientated small crystals.

The dominating phase was the mixture of small crystals and some glassy regions shown in the middle of fig.3. Even the glassy regions shows a very pronounced structure factor that can be described by a polydisperse Percus-Yevick model [1]. Seldom, we find a crystal region shown at the right side of fig.3. We found no influence of the particle preparation, even the very well ordered emulsions (by dialyses) show the same degree of ordering. Therefore one can conclude that the interaction seems not to play an important role. Only the drying temperature shows a slightly influence: Temperature in the middle regime ( $\sim 60^\circ$ ) results in the best ordering we observed. A possible explanation therefore: Nearer to the glass temperature, the surface is softer and particles do not coagulate by first contact, they are able to move slightly after contact to found an optimized position in the system, but it is only a small improvement in the resulting order.

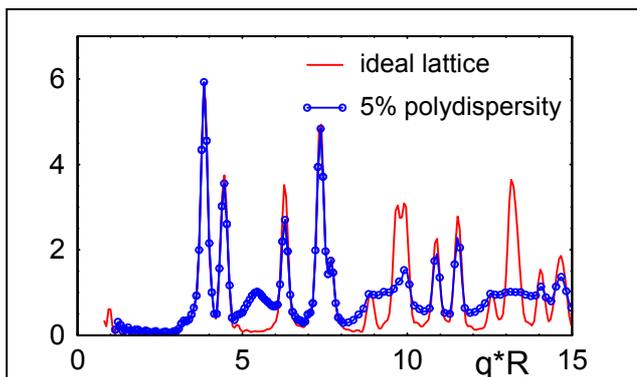


Fig.4 radial averaged structurefactor of a fcc-lattice of 2048 with polydispersity.

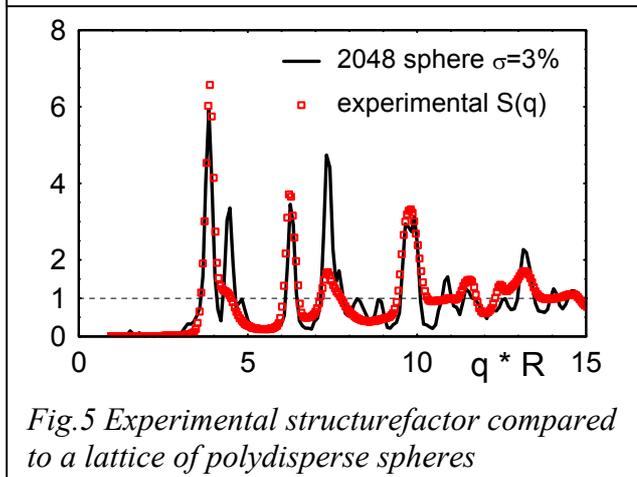


Fig.5 Experimental structurefactor compared to a lattice of polydisperse spheres

Another question is the size and degree of ordering in the crystal regions we observed. The right picture in fig. 3 shows that we do not see a high numbers of peaks and there is a remaining background between the bragg-peaks of the crystal. To explain this behaviour we perform some model calculations. A old formula from Debye allows to calculate the radial averaged scattering from an aggregate of spheres. This offers the possibility to calculate the scattering and therefore also the structure factor from a small lattice (2048 sphere) as shown in fig. 4. The second curve is the same with 5% polydispersity in the size of the particles which still remains on their ideal lattice position.

Already this small polydispersity explain the final number of bragg peaks and the background between the peaks. Fig. 5 shows the comparison between the experiment and this calculation. The deviation of the second peak could explained by the idea that we do not see an radial averaged crystal, but only a [111] and a [1-10] orientation.

In addition to this, we also examine the deforming of the particles in the final state by time-resolved scattering measurements while heating the sample at  $100^\circ\text{C}$ .

## References:

[1] Dingenouts N, Ballauff M (1998) *Macromolecules* **31**, 7423