ESRF	**Experiment title: Phase Transition and Critical Phenomena in Thermosensitive Core-Shell Latex Particles Investigated by SAXS**	**Experiment number**: **SC-530**
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Report: We have studied the volume transition in thermosensitive core-shell particles by SAXS. The latex-particles are dispersed in water and consist of a solid poly(styrene) core (diameter: 107nm) and a shell of a thermosensitive crosslinked polymer chains. The thermosensitive shell is built up from poly(N-isopropylacrylamide) chains (PNIPA) crosslinked by N,N'-methylenbisacrylamide (BIS). In addition to these systems, charged

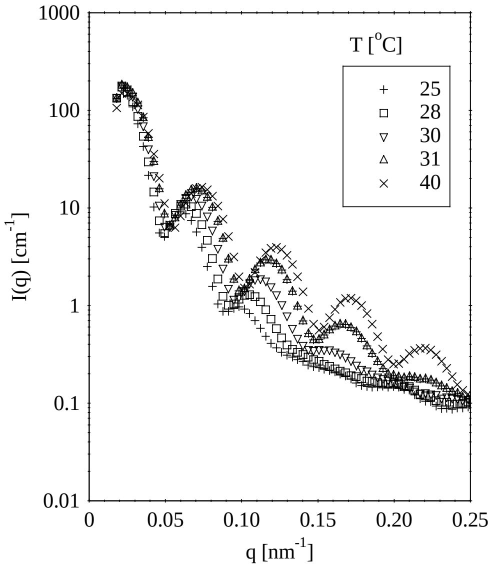

Fig. 1
SAXS-intensities of uncharged thermosensitive latex particles measured at different temperatures indicated in the graph. Core: Poly(styrene); shell: PNIPA crosslinked with 2.5Mol% BIS. For the sake of clarity only every third data point has been plotted. The data clearly indicate the volume transition: The maxima of the scattering curves are shifted to smaller q-values with decreasing temperature which indicates a swelling of the particles below the volume transition.

thermosensitive particles containing 2Mol% acrylic acid (AA) in the network were studied too in order to investigate the influence of charges onto the volume transition. Scattering curves have been measured at different temperatures. As an example fig. 1 displays the scattering curves obtained for suspensions of uncharged particles.
The treatment of the SAXS-data obtained from these particles can be done as follows [1]: There are three terms which contribute independently to the observed scattering intensity I(q) ($q=(4\pi/\lambda)\sin(\theta/2)$; θ: scattering angle; λ: wave length):

$$I(q) = I_{CS}(q) + I_{network}(q) + I_{PS}(q) \qquad (1)$$

Here $I_{CS}(q)$ is the part of I(q) due to the core-shell structure of the particles, i.e., the scattering intensity caused by a composite particles having a homogeneous core and a shell having a different electron density. $I_{PS}(q)$ denotes the scattering intensity which is caused by the density fluctuations of the solid PS-core of the particles. The polymeric network in the shell exhibits static inhomogeneities and thermal fluctuations which are taken into account by $I_{network}(q)$. [2]. It can be rendered in good approximation as

$$I_{network}(q) \approx = \frac{I_{fluct}(0)}{1+\xi^2 q^2} \qquad (2)$$

and becomes the leading term at high scattering angles. Fig. 2 demonstrates that the decomposition according to eq.(1) gives a quantitative description of the measured

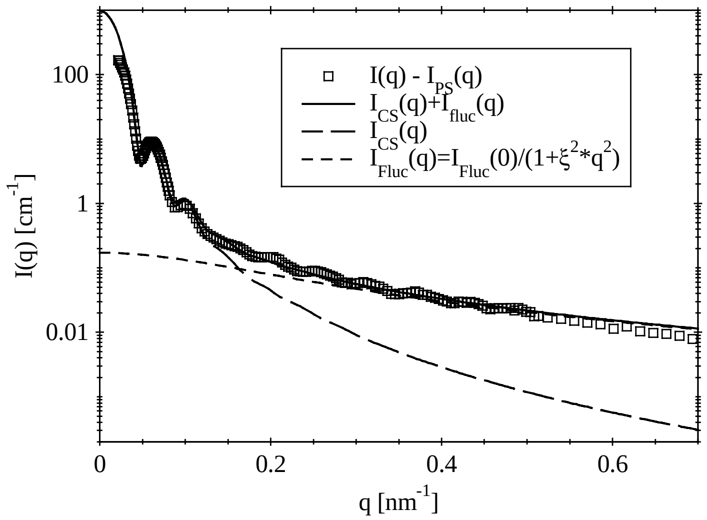

Fig. 2
Comparison of $I_{CS}(q)$ (long-dashed line) and $I_{fluct}(q)$ (short dashed line) with the scattering intensity $I(q)$-$I_{PS}(q)$ measured at 25^{o}C (squares). The solid line gives $I_{CS}(q)$+ $I_{fluct}(q)$ (cf. eq.(1) and (2)).

intensities. Due to the fixation of the chains of the network on the core particles the volume transition is strongly restricted, i.e., the transition does not lead to a fully collapsed state but only to a markedly higher volume fraction. The chains can only shrink along the direction of the surface normal but no marked contraction can result parallel to the surface.

The strong spatial constraint is also visible when considering the fit parameters $I_{fluct}(0)$ and ξ defined in eq.(2) (see fig. 3). Both quantities undergo a strong change at the volume transition but remain finite. But ξ as well as $I_{fluct}(0)$ remain finite quantities as expected for a confined system.

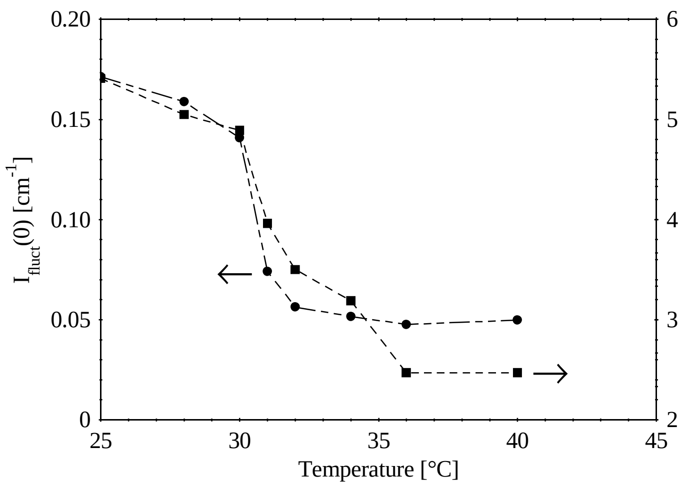

Fig. 3
$I_{fluct}(0)$ (filled circles) and the correlation length ξ (filled squares) obtained from fits of eq.(2) as function of temperature. Note that both quantities remain finite throughout the entire range of temperatures.

[1] Analysis of the Volume Transition in Thermosensitive Core-Shell Latex Particles by Synchrotron Small-Angle X-Ray Scattering, S. Seelenmeyer, I. Deike, N. Dingenouts, Ch. Norhausen, M. Ballauff, Th. Narayanan, J. Appl. Cryst., submitted