Films obtained via drying a polymeric latex dispersion is normally colloidal crystalline where latex particles are packed into a face centered cubic (fcc) structure. Different from conventional atomic or hard sphere colloidal crystallines, the crystalline structure of these films is normally deformable due to the low glass transition temperature of the constitutive polymers in latex particles. Polymer diffusion across the interparticle boundaries can provide effective adhesive forces between particles that give more strength to the film. Because the building blocks of latex colloidal crystallites are very large with a typical size of the order of 100 nm, SANS and small-angle x-ray scattering (SAXS) are predominant techniques to study their microstructure evolution during deformation. It has been illustrated that SAXS seems to be the ideal technique for such investigation [1-4]. This is primarily due to the already existed contrast between polymeric latex particles and additives such as salt, emulsifiers and so on located in the interstices after film formation. The deformation mechanism of soft latex films with colloidal polycrystalline and fiber symmetric crystalline structure was studied by SAXS [3,4]. It was found that the crystalline lattice constants changes considerably during macroscopic deformation, resulting not only in the deformation of the crystallographic structure but also in considerable non-affine deformation at high draw ratios. The deformation behavior of the latex films changes from non-affine to affine deformation with increasing annealing temperature, which can be attributed to the diffusion of polymeric chains between adjacent latex particles resulting in an enhancement of the cohesive bonding between particles in the crystallites and at the grain boundaries.

Practically, in order to enhance the strength of latex painting coalescing aids are used because it is difficult to apply thermal annealing on large area. The aim of this work is therefore to check for the effect of solvent annealing on the micro-structural evolution during tensile deformation of a colloidal crystalline polymeric latex film.

Samples used in this study are a commercially available latex film of styrene n-butyl acrylate copolymer (Tg=20°C, particle diameter of 118 nm) [1,2]. In-situ SAXS measurements were conducted by mounting a portable stretcher at beamline BW4 at a sample to detector distance of 13920 mm. Figure 1 shows typical small angle scattering patterns taken during stretching runs. Clearly, the system transforms from an isotropic colloidal crystalline structure to a deformed state elongated along the stretching direction (ellipsoidal shaped scattering patterns) after deformation. By taking the diffraction positions along and perpendicular to the stretching direction, we obtained deformation ratio of colloidal crystalline lattice at different conditions and collected those data in Figure 2. Unlike in the case of thermal annealing where a gradual improvement of affinity of microscopic deformation with respect to the macroscopic one has been seen [3,4], solvent annealing produces a much more pronounced effect. The system became affine in deformation mechanism already for samples only underwent few minutes of solvent annealing. This behavior indicates that the presence of organic solvent in the latex film promotes interdiffusion of polymeric chains between adjacent particles to a larger extent than using thermal annealing.
Figure 1: Selected SAXS patterns of uniaxially drawn latex films annealed for 20 min in solvent. The macroscopic draw ratio is indicated on each pattern. The tensile direction is horizontal.

Figure 4: Crystallographic draw and compression ratios of the colloid crystallites along ($\lambda_{c,h}$) and perpendicular ($1/\lambda_{c,v}$) to the stretching direction as a function of the macroscopic draw ration ($\lambda_{m,h}$) for samples before annealing and after annealed in solvent for different durations. The dash line indicates the behavior expected for affine deformation. The respective values are calculated from the shifts in the q-positions of the Bragg peaks.

References