

DEFORMATION OF SOFT COLLOIDAL CRYSTALLINE STRUCTURE — THEORETICAL CONSIDERATIONS AND EXPERIMENTAL EVIDENCES BY SYNCHROTRON SMALL-ANGLE X-RAY SCATTERING ON TENSILE STRETCHED POLYMERIC LATEX FILM*

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Abstract Films obtained *via* drying a polymeric latex dispersion are normally colloidal crystalline where latex particles are packed into a face centered cubic (fcc) structure. Different from conventional atomic crystallites or hard sphere colloidal crystallites, the crystalline structure of these films is normally deformable due to the low glass transition temperature of the latex particles. Upon tensile deformation, depending on the drawing direction with respect to the normal of specific crystallographic plane, one observes different crystalline structural changes. Three typical situations where crystallographic c-axis, body diagonal or face diagonal of the fcc structure of the colloidal crystallites being parallel to the stretching direction were investigated. Tilting angle and d-spacing of several crystallographic planes as a function of draw ratio at each situation were derived. Experimental evidences for such relationships were also given by considering in-situ synchrotron small angle X-ray scattering data of a typical latex film during stretching. It turns out that the experimental results are fully in accordance with the mathematical calculations.

Keywords: Colloidal crystal; Deformation; Latex; SAXS.

INTRODUCTION

Colloidal crystals are potentially useful materials in optical filters, color films, band gap materials and so forth^[1, 2]. They have been studied by many techniques, for example, light scattering^[3], small-angle neutron scattering (SANS)^[4] and small-angle X-ray diffraction^[5]. Soft polymeric crystals derived from drying latex dispersions have also been studied widely. The drying process is usually considered to pass through three stages: increasing the particle concentration and ordering, particle deformation and polymer chain diffusion across particle boundaries^[6–8]. Latex particles assuming dodecahedral shape in the deformed state are usually packed in a face centered cubic (fcc) structure^[9–12]. For polymer particles in a latex dispersion with a typical size of the order of 100 nm, the lattice spacing of the colloid crystals is much larger than that of atomic or molecular crystals. The diffraction angle of such crystals is very small, usually smaller than 0.045° , when using $\text{CuK}\alpha$ radiation. Moreover, some nonpolymeric materials such as salt and surfactants are located in the interstices between the closely packed particles in the film, which provides enough contrast for small angle X-ray scattering (SAXS) measurement. Our previous work indicates that SAXS measurement is a powerful technique for studying the internal structure of latex films^[13–16].

One of the peculiar effects in soft polymeric latex colloidal crystalline film is that the crystalline lattice

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constants can be deformed largely upon macroscopic deformation. Although the final application of the polymeric latex films requires a thorough understanding of their structural evolution upon mechanical treatment, up to now, studies on the deformation mechanism of polymer latex films are scarce. A study of the rheological properties of silica-filled nanolatex films by means of uniaxial strain experiments was presented by Oberdisse^[17] where it was pointed out that the silica contributes differently at small and large deformation. Through a research of morphology of deformed core/shell latex films by atomic force microscopy (AFM), Lepizzera *et al.*^[18] presented evidence for two types of deformational behavior, which included matrix deformation and geometric rearrangement. Cabane *et al.*^[19] studied the deformation of cellular polymeric films with SANS technique; and pointed out that the deformation was affine when the films were stretched in the dry state, while the macroscopic stretching caused microscopic shear deformation, *i.e.*, the cells slipped past each other in wet state. In our previous work, it was reported that stretching a soft latex film resulted not only in large deformation of the crystallographic structure but also in considerable non-affine deformation at high draw ratios which was attributed to slippage between rows of particles and crystalline grain boundaries and the deformation mechanism of the latex films transformed from non-affine deformation to affine deformation with increasing annealing temperature^[13, 15].

In the present work, the crystalline structure changes during tensile deformation of crystallites with their *c*-axis, body diagonal and diagonal of face parallel to the stretching direction were studied. Changes in both crystalline lattice constants and angular distributions of the scattering vectors of specific crystallographic planes upon tensile deformation were theoretically calculated. The relationship of scattering vector and draw ratios was obtained. The thus obtained relationships were found to be in accordance with experimental results.

EXPERIMENTAL SECTION

A styrene/butadiene copolymer latex dispersion with a solid content of *ca.* 50 wt% was used^[13]. The glass-transition temperature of the sample is 5°C. The average diameter of the latex particles is 135 nm as determined by laser light scattering. The latex films were obtained by evaporating the water from the latex dispersion at room temperature for 2 weeks, yielding a transparent film of about 1.5 mm thickness.

Synchrotron SAXS measurements were performed at the beamline BW4 at HASYLAB, DESY, Hamburg, Germany. The energy of the X-ray radiation was 8.979 keV resulting in a wavelength of 0.13808 nm. The size of the primary X-ray beam at the sample position was 0.4 mm × 0.4 mm. The sample was mounted onto a tensile tester at the beam-line at a sample to detector distance of 12533 mm. At this distance, the effective scattering vector q ($q = \frac{4\pi}{\lambda_x} \sin \theta$, where 2θ is the scattering angle and λ_x the wavelength) range is 0.025–0.25 nm⁻¹. The

samples were stretched with a speed of 9 μm/s with a tensile tester at the beamline. The samples were stretched at both ends ensuring that the X-rays were scattered at a fixed position in the middle of the sample. Each SAXS pattern was collected within 40 s during a continuous stretching run. The SAXS data were calibrated for background scattering and normalized with respect to the primary beam intensity.

EXPERIMENTAL RESULTS

Before considering changes of crystalline structure upon tensile stretching, let us first look at the experimental results of a synchrotron SAXS investigation on tensile deformed latex film. Figure 1 gives the corresponding SAXS patterns both before and after tensile drawing. Obviously, the latex film possesses a polycrystalline structure as evidenced by the Debye-ring type diffraction pattern. Further investigation on the location of the diffraction peaks confirms that the film presents an fcc colloidal crystalline structure (for detailed analysis see ref. [13]–[16]). Interestingly, after the film was macroscopically stretched for 300%, the Debye-rings in the diffraction pattern became ellipsoidal shaped. Unlike in atomic or hard sphere colloidal crystalline systems, the crystalline lattice constants in the present case are deformable. The SAXS pattern of deformed sample gives clear evidence that not only the orientation but also the lattice spacing underwent variation upon stretching. It

has been concluded in our previous publications that considerable nonaffine deformation also occurred during the deformation process^[13]. In this work, we are going to clarify the relationships between the crystallographic structural parameters (such as crystalline lattice spacing and orientation) and the deformation ratio of crystallites along different directions. In the following, we thus chose crystallographic planes in crystallites under consideration which are parallel or perpendicular to the stretching direction as references to calculate the corresponding true draw ratio of the crystallites. This approach greatly reduces the complexity brought by the non-affinity of the crystallographic deformation with respect to the macroscopic one.

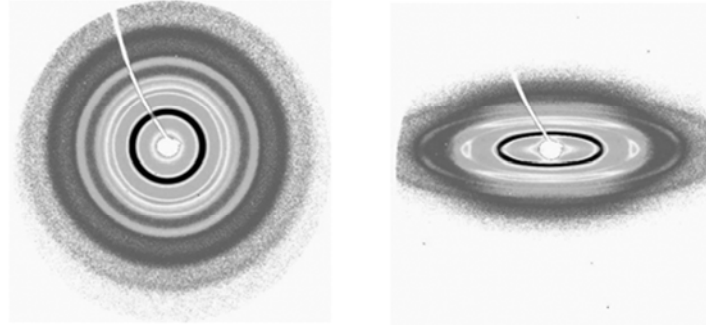


Fig. 1 SAXS patterns of latex film before (left) and after (right) being stretched to 300% Tensile direction vertical

CALCULATIONS AND COMPARISON WITH EXPERIMENTAL DATA

Constant Volume

It is crucial to check whether the volume of the crystallites retains unchanged or not during deformation. If the volume is constant, the relationship between the draw ratio and compression ratio of the crystallites is straightforward. Therefore, the possible changes in volume of the crystallites must be firstly evaluated in order to calculate draw ratio of the crystallites.

If the volume remains constant, then

$$\lambda_{//} = \left(\frac{1}{\lambda_{\perp}} \right)^2 \quad (1)$$

because

$$\lambda_{//} = \frac{q_0}{q_{//}} \quad \text{and} \quad \lambda_{\perp} = \frac{q_0}{q_{\perp}} \quad (2)$$

Then we have

$$q_{//} = \frac{q_0^3}{q_{\perp}^2} \quad (3)$$

where, λ is the draw ratio of the crystallite, q_0 scattering vector at undeformed state, subscript signs $//$ and $\perp$ denote parallel and perpendicular to the stretching direction, respectively.

The relationship between $q_{//}$ and reciprocal of the square of $q_{\perp}$ was shown in Fig. 2, which was obtained by calculating position of (111) peak in the diffraction patterns after tensile deformation. The proportionality in the plot indicates that the volume was constant during deformation. Obviously, q_0 can be obtained from the slope of the line. This yields $q_0 = 0.06298 \text{ nm}^{-1}$ which is in accordance with the value directly derived from the SAXS pattern of undeformed sample where $q_0 = 0.0621 \text{ nm}^{-1}$ is obtained.

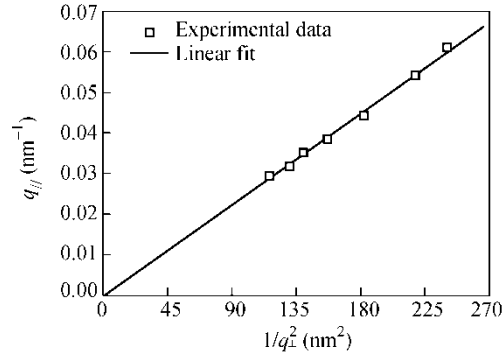


Fig. 2 The plot of $q_{\parallel}$ versus $1/q_{\perp}^2$ indicating that the volume of crystallites remains constant

Clearly, the latex film in this study has a polycrystalline structure with crystallites isotropically oriented in the sample. Mathematically, a full description of the deformed structure for each crystallite at random orientation is possible but complicated. In this work, three kinds of crystallites with different orientations, (1) c -axis parallel to stretching direction; (2) body diagonal parallel to stretching direction; (3) and diagonal of face parallel to stretching direction, were studied in detail due to the simplified geometric relations in these cases.

Crystallites with c -Axis Parallel to Stretching Direction

It is obvious that stretching an fcc structure along its c -axis results in a face-centered tetragonal (fct) structure. However, fct is not a bravias lattices. It can be divided into body-centered tetragonal (bct) unit cell that contains fewer lattice sites^[20]. Although it is known that the indices of the crystallographic planes in an fct structure must change when considering corresponding bct lattice, for clarity Miller indices of fcc/fct lattice are used in the calculation.

The value of the spacing d_{hkl} in an fcc lattice can be calculated using the equation

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (4)$$

where, a is the lattice constant of the fcc lattice, h , k and l are Miller indices. After uniaxial stretching, (see Scheme 1) the value of the plane spacing d_{hkl} in the resultant fct lattice can be calculated following the equation

$$\frac{1}{d_{hkl,\lambda}^2} = \frac{h^2}{(\frac{a}{\lambda})^2} + \frac{k^2}{(\frac{a}{\lambda})^2} + \frac{l^2}{(\lambda a)^2} \quad (5)$$

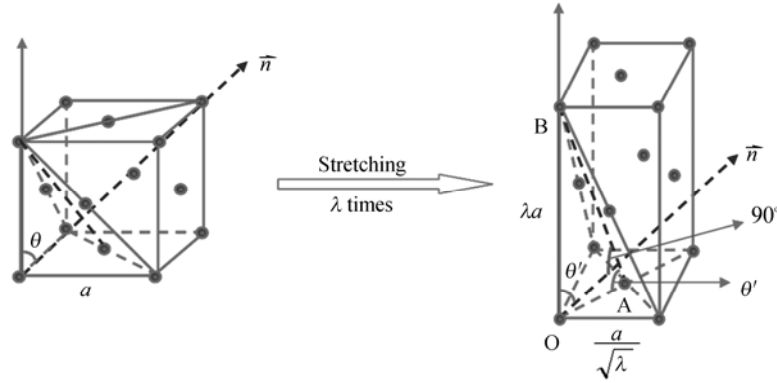
Using Bragg equation

$$d_{hkl,\lambda} = \frac{2\pi}{q_{hkl,\lambda}} \quad (6)$$

one has

$$q_{hkl,\lambda} = \frac{2\pi}{a} \sqrt{(h^2 + k^2)\lambda^3 + l^2} \quad (7)$$

Above equation denotes the relationship of q and λ during tensile deformation.



Scheme 1 Deformation of crystallite stretched along c -axis

The solid arrow indicates stretching direction, the dash arrow stands for the normal of (111) plane.

Draw ratio λ of crystallites being stretched along c -axis can be obtained by considering the change of position of q_{220} perpendicular to the stretching direction (see Eq. (2)) because the scattering vector of (220) plane is perpendicular to the stretching direction in any draw ratio for these crystallites. The q values of other planes can be derived from integrating 2-D SAXS data along respective scattering vectors using the equation^[19]

$$\tan \mathcal{G}' = \lambda^{3/2} \tan \mathcal{G} \quad (8)$$

where $\mathcal{G}$ is the azimuthal angle between q and the stretching direction before deformation; $\mathcal{G}'$ is the azimuthal angle between q and the stretching direction after deformation. It must be mentioned that it is not possible to obtain such data for single crystal from one 2D SAXS pattern. Use of such a condition in our case is due to the specific fibre symmetry after tensile deformation where diffraction peaks of crystallites under same draw ratio are all observed.

The relationships between q and λ was shown in Fig. 3 in the view of theoretical and experimental data. It was founded that they were in a good agreement with each other. It demonstrated that Eq. (7) describes the deformation behaviour of crystallites with c -axis parallel to stretching direction. Furthermore, it indicates that the deformation of those crystallites was affine with respect to the true draw ratio of the crystallites meaning that the crystallites act as an entirety during deformation.

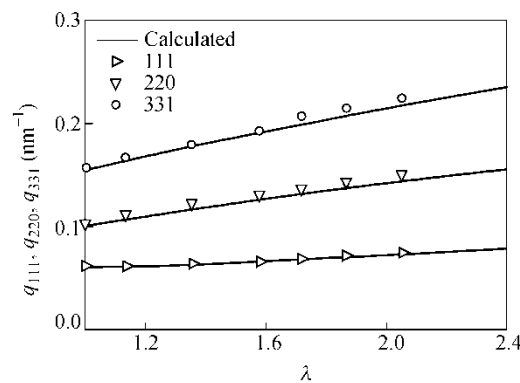


Fig. 3 Plot of q versus λ on crystallites stretched along c -axis

Solid lines are calculated values using Eq. (7); Symbols represent values obtained from experimental SAXS data.

Crystallites with Body Diagonal Parallel to Stretching Direction

In this case, the crystallites became rhombohedral lattice after stretching. The normal of (111) plane was parallel to body diagonal, *i.e.*, the stretching direction. Therefore, true draw ratios of this kind of crystallites could be

derived from Eq. (2) by considering the position of (111) peak during deformation. q values of other planes could be derived from the integrated SAXS data along scattering vectors of different directions as described by Eq. (8). We defined that $a' = a = b = c$ and $\phi = \alpha = \beta = \gamma \neq 90^\circ$ are unit cell parameters after deformation. Calculation of plane spacing of rhombohedra is straightforward when using the equation for calculating plane spacing of a triclinic lattice which is a general case for all Bravais lattices. In the equation the values of $\cos\phi$ and/or $\sin\phi$ will be used. Therefore, if the relationship of draw ratio and ϕ is founded, the relationship of draw ratio and scattering vector is established.

Scheme 2 shows the states of crystallites before and after stretching. The length of the body diagonal after stretching reads

$$L_b = 3a' \sqrt{1 - \frac{4}{3} \sin^2(\phi/2)} \quad (9)$$

therefore

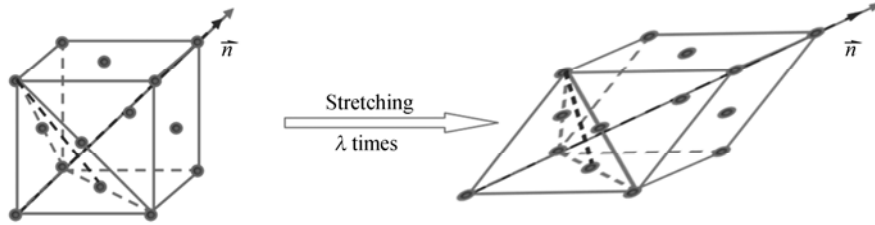
$$\lambda = \frac{L_b}{\sqrt{3}a} = \frac{a'}{a} \sqrt{3 - 4 \sin^2(\phi/2)} \quad (10)$$

where L_b stands for the length of the body diagonal after stretching. Since the volume of the crystallites remain constant, we have

$$V = a^3 = (a')^3 [2 \sin^2(\phi/2) \sqrt{3 - 4 \sin^2(\phi/2)}] \quad (11)$$

Combining Eqs. (10) and (11), we have

$$\cos\phi = \frac{\lambda^3 - 1}{\lambda^3 + 2} \quad a' = \frac{a}{\sqrt{\frac{3\lambda}{\lambda^3 + 2}}} \quad (12)$$



Scheme 2 Deformation of crystallite stretched along body diagonal

The solid arrow indicates stretching direction, the dash arrow stands for the normal of (111) plane.

Calculation of plane spacing of a rhombohedral lattice can be performed by using the equation for calculating plane spacing of a triclinic lattice which is a general case for all Bravais lattices. Therefore,

$$\frac{1}{d_{hkl,\phi}^2} = \frac{1}{1 + 2 \cos^2 \phi - 3 \cos^3 \phi} \left[\frac{(h^2 + k^2 + l^2) \sin^2 \phi}{(a')^2} + \frac{2(hk + kl + hl)(\cos^2 \phi - \cos \phi)}{(a')^2} \right] \quad (13)$$

and

$$q_{hkl,\lambda} = \frac{2\pi}{d_{hkl,\lambda}} \quad (14)$$

When Eqs. (12), (13) and (14) are combined, the relationship between q and λ is obtained, and it reads

$$q_{hkl,\lambda} = \frac{2\pi}{a} \sqrt{\frac{(h^2 + k^2 + l^2)(2\lambda^3 + 1) + 2(hk + kl + hl)(1 - \lambda^3)}{3\lambda^2}} \quad (15)$$

Comparative results between calculated and the experimentally obtained ones were collected in Fig. 4. Again, one finds a very good agreement between both. It can also be seen that the deformation of those crystallites was affine with respect to the true draw ratio.

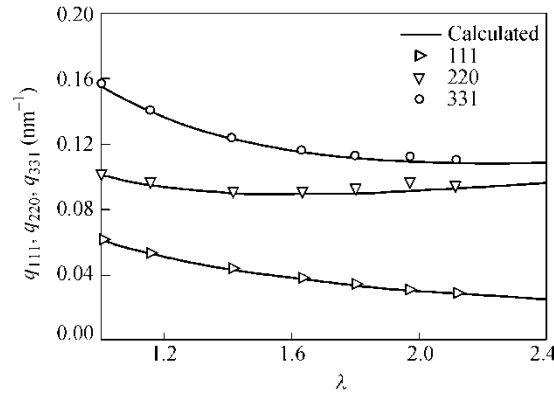


Fig. 4 Plot of q versus λ on crystallites stretched along body diagonal
Solid lines are calculated values using Eq. (15); The symbols represent values obtained from experimental SAXS data.

Crystallites with Diagonal of Face Parallel to Stretching Direction

The situation in this case is more complicated than the above two, because the unit cell parameters change to $a' = a = b$, $c' = c$ and $\alpha = \beta = 90^\circ$, $\gamma' = \gamma \neq 90^\circ$ after deformation. The processing method is similar to above considerations, *i.e.* firstly, the plane perpendicular to stretching direction was found for reference to establish true draw ratio values; secondly, the relationship between a' , c' , γ' and λ were found; Finally, the relationship between scattering vector and draw ratio can be established.

The states of crystallites before and after stretching in this case are shown in Scheme 3. After stretching the length of the diagonal of the face is

$$L_f = 2a' \cos(\gamma'/2) \quad (16)$$

Therefore

$$\lambda = \frac{L_f}{\sqrt{2}a} = \frac{\sqrt{2}a'}{a} \cos(\gamma'/2) \quad (17)$$

Since the volume of the crystallites remains unchanged, we have

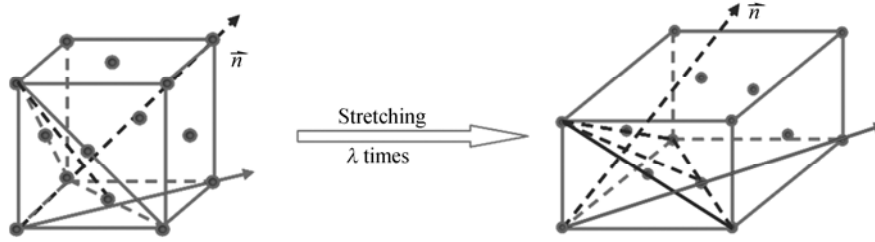
$$c' = \frac{a}{\sqrt{\lambda}} \quad (18)$$

Similar to Eq. (13) the spacing of (hkl) plane can be written as

$$\frac{1}{d_{hkl,\gamma'}^2} = \frac{1}{1 - \cos^2 \gamma'} \left[\frac{h^2}{a'^2} + \frac{k^2}{a'^2} + \frac{l^2 \cdot \sin^2 \gamma'}{c'^2} - \frac{2h \cdot k \cdot \cos \gamma'}{a'^2} \right] \quad (19)$$

When Eqs. (14), (17), (18) and (19) are combined, the relationship between q and λ is obtained

$$q_{hkl,\gamma'} = \frac{2\pi}{a} \sqrt{\frac{h^2 + k^2 + (h - k) \cdot \cos \gamma' - 2h \cdot k \cdot \cos^2 \gamma' + \lambda^3 \cdot l^2 \cdot \sin^2 \gamma'}{\lambda^2 \cdot \sin^2 \gamma'}} \quad (20)$$



Scheme 3 Deformation of crystallite stretched along diagonal of face
The solid arrow indicates stretching direction, the dash arrow stands for the normal of (111) plane.

The use of Eq. (20) is not straightforward as in the case of Eq. (15) because the $\cos\gamma'$ and $\sin\gamma'$ terms present in the equation. However, the situation becomes simple when $h = k$, where $\cos\gamma'$ and $\sin\gamma'$ are eliminated. Eq. (20) becomes

$$q_{hkl,\lambda} = \frac{2\pi}{a} \sqrt{\frac{2h^2 + \lambda^3 \cdot l^2}{\lambda^2}} \quad (21)$$

Again, a comparison between calculated and experimental values was made as was shown in Fig. 5. It demonstrated that the experimental data were in accordance to the theoretical calculations. These data shows that q_{111} values are larger than that of q_{220} when $\lambda > 1.81$ meaning that the spacing of (111) plane is smaller than that of (220) plane. This is because that the angle between the normal of planes and stretching direction changes during stretching process, which leads to the spacing of some planes decrease while others still increase.

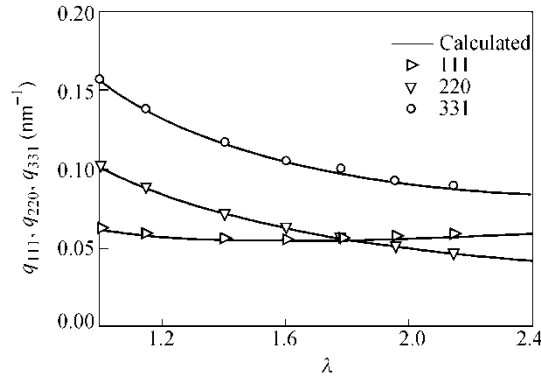


Fig. 5 Plot of q versus λ on crystallites stretched along diagonal of a face
Solid lines are calculated values using Eq. (21); The symbols represent values obtained from experimental SAXS data.

It should be mentioned here that although the macroscopic draw ratio is about 300%, the true draw ratio of the crystallites in the present case is up to about 210% because of the occurrence of the extensive non-affine deformation at large macroscopic deformation. Further experiments on other samples proved that above equations apply also to larger microscopic deformations. Such results are still under evaluation and will be published elsewhere.

CONCLUSIONS

In summary, we have considered three typical situations when a soft colloidal polycrystalline film was tensile deformed. Crystallites with orientations of c -axis, body diagonal and diagonal of a face parallel to stretching direction were studied in detail. Analytical expressions of scattering vector as a function of true draw ratio of respective crystallites for the three cases were established. Experimentally obtained synchrotron SAXS patterns

during stretching a soft polymeric colloidal crystalline latex film were used to verify the analytical expressions. It turns out that theoretical considerations fully agree with the experimental data. Furthermore, it indicates that the deformation of those crystallites was affine with respect to the true draw ratio of the crystallites meaning that the crystallites act as an entirety during deformation.

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