Crystals Made of Close-Packed Polymeric Spheres: A Neutron Scattering Study on Latex Films

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The dense packing of polymeric spheres in latex films has been investigated by means of small-angle neutron scattering. The films were prepared by evaporation of the water out of a dispersion consisting of monodisperse charged particles (diameter 130 nm). Analysis of the Bragg peaks found in the scattering data reveals that the particles are arranged in a face-centered-cubic lattice structure with well defined crystalline domains. Furthermore, it is found that the system still owns memory about its initial structure upon prolonged annealing at temperatures far above its glass temperature. An interesting suppression of some Bragg peaks due to the influence of the particle scattering form factor is observed.

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Latices are colloidal dispersions consisting of compact spherical polymer particles in a fluid phase. The size of the spheres is typically of the order of several hundreds of nanometers. Usually, the polymeric spheres carry surface charges—as is also the case in the system studied in this Letter—in order to prevent the particles from coagulation. These dispersions represent interesting model systems which offer the possibility to investigate experimentally many-body effects more conveniently than in the case of gases or liquids consisting of single atoms or low-molecular-weight molecules. The advantage stems from the fact that both the typical time scale as well as the respective length scale lie in a window which is easily accessible by experiment [1-6]. Until now most investigations were concerned with colloidal crystals as found in *liquid* dispersions. These systems can be realized with a volume ratio of spheres down to 10^{-3} because of the repelling Coulomb forces acting among the charged spheres. The samples which were prepared for the experiments discussed in this Letter consist of close-packed particles. These latex films are prepared from the dispersion by complete evaporation of the liquid water phase. Some experiments concerning the structure of systems made of close-packed spheres have been performed [7-9]. But, the system as well as the method proposed here yield new insights into the structure of latex films and allow for the investigation of new aspects as will be discussed below. Besides being interesting for fundamental reasons our investigations are of some potential value with respect to the application of industrially produced latices in paints for buildings and cars, in surface refining of paper, etc.

During the process of film formation three subsequent processes can be discerned: increasing concentration of the polymeric material during evaporation of the fluid ending in a dense packing of the particles [10,11], deformation of the particles into polyhedra and beginning coalescence because of surface and capillary forces [12,13], and further coalescence caused by the interdiffusion of polymeric chains emanating from adjacent particles [14,15]. But, despite the many efforts which have been made in order to examine these processes, still there are many open questions: For example, which specific structure has evolved after completion of the film formation process and to what perfection? To which degree do the particles keep their identity once the film has been made? What happens to the structure of the dry film when the film is exposed to water again?

In order to obtain answers to these questions we performed small-angle neutron scattering (SANS) experiments on latex films. The contrast which is necessary in the SANS experiments, in order to render information about the structure, is provided by the difference between the scattering length of the polymers in the latex spheres on the one hand and the scattering lengths of salt, emulsifier, and interstitial microvoids on the other hand. Presently, little is known about the actual fractions of the nonpolymeric components. But, making use of Babinet's theorem, it suffices in a first-order approach to regard the film as a two-phase system with the polymeric particles being the component which gives rise to the observed scattering phenomena. Different amounts of D_2O have been brought into the samples in order to increase the scattered intensity and to study the influence of water on the film structure. This dispersion from which the films were made is a commercially available styrene/*n*-butyl-acrylate copolymer latex with about 50% by weight of each monomer and a polymer content of about 50% by weight dispersed in water. The particle size distribution is quite narrow with an average diameter of 130 nm. Films were prepared by simply evaporating the water at different temperatures. The glass transition temperature of the films is in the room-temperature range. Equilibrated latex films with a defined D_2O content between 0% and 50% have been prepared. In the following we restrict ourselves to a discussion of experiments on samples with a low D_2O content. The SANS experiments were performed at the D11 instrument of the high flux reactor at the Institut Laue Langevin (ILL) in Grenoble. The wavelength λ of the neutrons was 1 nm with a wavelength distribution of $\Delta\lambda/\lambda = 0.09$. The data were sampled and manipulated in the standard way in order to obtain the scattering curves $I(q)$. $I(q)$ denotes the intensity of neutrons scattered by an angle Θ with respect to the beam sent onto the sample. q is defined by $q = 4\pi \sin(\Theta/2)/\lambda$. The samples exhibited diffraction of the powderlike (Debye-Scherrer) type. The data are not given on an absolute scale since it was not possible to determine the effective thickness of the samples, because of the presence of unavoidable air bubbles.

Some representative scattering curves taken on films which were prepared by evaporation of water at room temperature and at 70 °C, respectively, are shown in Fig. 1. In addition, $I(q)$ of a film prepared at room temperature and subsequently annealed at 180 °C for 20 min is depicted in Fig. 1. As can be seen from the data set *A* in Fig. 1, dry films already yield structure peaks which are caused by crystalline ordering of the spheres as will be discussed below. The scattering is due to the aggregation of nonpolymeric material, which is not miscible with the polymeric matrix, into the interstices between the spheres. Another contribution might arise from the existence of interstitial microvoids. It is interesting to note that tempering of a dry film at 180 °C for 20 min does not lead to a homogeneous distribution of the nonpolymeric material in the polymeric matrix: The respective scattering data *C* in Fig. 1 look similar to the data *A* which were obtained on a nonannealed film. Thus, even after prolonged tempering at elevated temperatures far above the glass temperature of the polymeric material the film still owns a memory of its original structure.

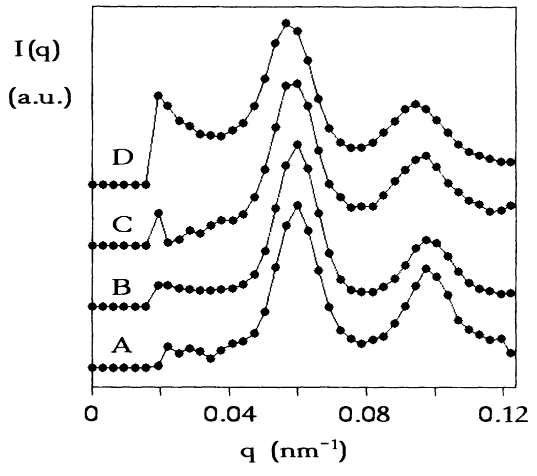

FIG. 1. Scattering vector dependence of the neutron intensity scattered by latex films which were prepared from the dispersion by the evaporation of water at room temperature (*A*,*B*,*C*) and at 70 °C (*D*), respectively. Sample *C* has been annealed at 180 °C for 20 min. The D_2O content was 0% (*A*,*C*) and 5% (*B*,*D*). The intensity values of the data *A*, *C*, and *D* have been multiplied by 15, 9, and 1.7, respectively. The first six points on the left side of each data set correspond to zero intensity (beamstop) in all cases. The solid lines are a guide for the eye.

When small amounts of D_2O ($<10\%$ by weight) are absorbed by films which were prepared at room temperature no qualitative change of the scattering curves is observed; see Fig. 1, data *B*. But it is found that the scattered intensity increases strongly in these cases. This leads us to the conclusion that the D_2O diffuses into the interstices to the (water soluble) nonpolymeric material and/or interstitial microvoids. Scattering data taken from measurements on films prepared at 70 °C exhibit maxima in $I(q)$ at about the same q values as the $I(q)$ curves obtained from films prepared at room temperature. Thus, the type of underlying structure which is responsible for the occurrence of the peaks does not change. One observes a broadening of the peaks when the water has been evaporated at a higher rate (at 70 °C). This effect can be easily understood since the large evaporation rate leads to a faster packing process which in turn results in a less well-defined crystalline structure, i.e., smaller domains and more lattice faults than in the case of film formation at room temperature. This effect gives rise to the observed broadening of the peaks. In addition to the two pronounced Bragg peaks one finds in the samples which were prepared at elevated temperatures an increasing scattering intensity towards very small values of q when exposing the films to D_2; see data *D* in Fig. 1. This contribution to the scattering curve hints at the existence of aggregates of D_2O (inducing cracks) of a size exceeding the length scale of about 100 nm. In the case of films annealed at 180 °C the addition of a few percent of D_2O leads to the disappearance of the peaks shown in Fig. 1, data *C*, because of a strong scattering phenomenon with rising intensity towards small q values. Probably, the spheres have been glued together due to coalescence. Homogeneous polymer domains have been created with inclusions of nonpolymeric material in the former interstices. This material can no longer be swollen by D_2O. The strong scattering at low q is caused by D_2O in grain boundaries and the like where the coalescence has taken place less completely. A closer inspection of the data given in Fig. 1 reveals additional information about the systems as will be discussed elsewhere [16].

The knowledge of the scattering behavior of a system *a priori* does not allow for an unequivocal structure model. But, because of the many facts which are known about the physics of dispersions and latex films we can safely assume that the maxima found in the scattering data indeed can be identified as being Bragg peaks stemming from the scattering of a "powder" of crystalline domains as is the case in Debye-Scherrer experiments in conventional crystallography. An interesting effect which does not occur when interpreting powder diagrams obtained with common crystals is the fact that in the present case some Bragg peaks are suppressed due to the scattering contribution from the voluminous close-packed particles by which the films are built: The scattering intensity can be written as $I(q) \sim S(q)P(q)$, where $S(q)$ is the scattering contribution due to the structure made up by the particles (lattice scattering) and $P(q)$ is the form factor of the individual particles. $P(q)$ of an atom is only slowly decaying in the q range of interest when discussing $S(q)$. The situation is very different in the present case where $P(q)$ is given by [17]

$$P(q) = 9\{[\sin(qr) - qr\cos(qr)]/(qr)^3\}^2 , \qquad (1)$$

with r being the particle radius. In Fig. 2 we show $P(q)$ and $S(q)$ as calculated for the case of homogeneous spheres with radius r which are close packed in a face-centered-cubic (fcc) structure. r is chosen to be the radius of the particles under investigation, namely, 65 nm.

When calculating $I(q) \sim S(q)P(q)$ in order to obtain the theoretical scattering curves of an ideal fcc lattice made of close-packed spheres one learns from Fig. 2 that some $S(q)$ peaks are strongly suppressed by the $P(q)$ term. Of the five fcc peaks expected in the chosen q range only two are left when taking into account $P(q)$.

The sharp peaks discussed so far on a theoretical basis are smeared in an experiment because of several reasons: apparatus effects (finite wavelength distribution, collimation effects) and deviations of the real system from ideality (finite domain size, lattice defects, polydispersity, nonsphericity of the particles). Taking into account all these points in a rather crude approach by folding the delta peaks with a single Gaussian smearing function according to relation (2) we arrive at the curve shown in Fig. 3 which is depicted together with measured data taken at a film which was prepared at room temperature:

$$S(q) \sim \sum_{\{q_i\}_{\text{fcc}}} P(q_i)\exp[-(q-q_i)^2/(2\sigma^2)] . \qquad (2)$$

$\{q_i\}_{\text{fcc}}$ denotes the set of reciprocal-lattice vectors of the fcc lattice with a lattice constant of 184 nm $= r\sqrt{8}$. Using the known value of the diameter of the spheres ($d = 130$ nm) and the respective lattice constant of 184 nm, the only relevant fit parameter—besides shifting and scaling in the ordinate direction—is σ, describing the widths of both Gaussians; see (2). The coincidence between the fitted curve and the measured data is better than could be expected, especially with regard to the peak intensities, when noting that—in the present approach—we did not take into account the following points: multiplicities of the reflecting planes, preferred deposition of latex spheres in (111) planes along the plane of the film [13], q dependence of the scattered intensity due to instrumental effects [18], and deformation of the latex spheres. These points will be discussed elsewhere [16].

Taking into account collimation effects and the wavelength distribution of the D11 instrument [18,19] we come to the conclusion that in the case of films prepared at room temperature the deconvoluted data should exhibit sharp Bragg peaks indicating that the crystalline order is well defined with a significant domain size. In addition, electron microscopic investigations reveal crystalline domains exceeding the length scale of some dozen particles. Work is in progress in order to put these approaches on a quantitative basis. A detailed analysis of the influence of the D_2O content on the film structure as well as an explicit discussion of the problem of fitting a theoretical model which contains all smearing effects to the data will be given elsewhere [16]. A similar analysis to the one leading to Figs. 2 and 3 was performed for body-centered-cubic and hexagonal-close-packed lattice structures. The respective predicted scattering behaviors

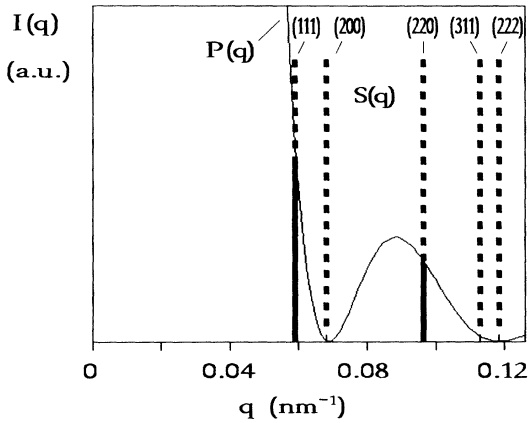

FIG. 2. Thin line: q dependence of the particle form factor $P(q)$ of a homogeneous sphere with radius 65 nm. Bold lines (dashed and solid parts): positions of the Bragg peaks $S(q)$ as expected in the case of an ideal face-centered-cubic lattice made from close-packed spheres of radius 65 nm. The dashed parts indicate the degree of suppression of these peaks when calculating the total scattered intensity $I(q) \sim P(q)S(q)$; only two peaks are left (solid bold lines).

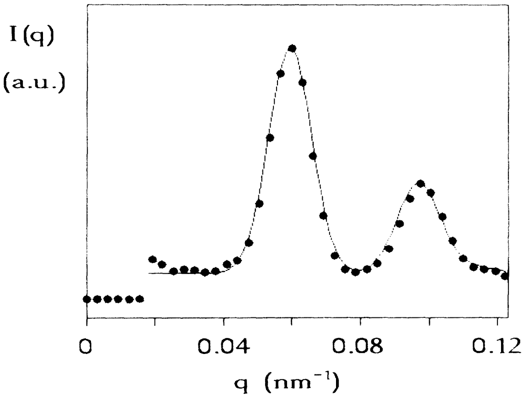

FIG. 3. Solid line: convolution of the $P(q)S(q)$ contribution of the ideal system in Fig. 2 with a single Gaussian smearing function. Points: data measured on a film prepared at room temperature with a D_2O content of 2%.

differ strongly from the $I(q)$ curves which were found in our experiments. We conclude that indeed a fcc structure is realized.

In summary, we have shown that it is easily possible to prepare colloidal crystals consisting of close-packed particles by choosing the appropriate system. The polymeric spheres pack in a face-centered-cubic lattice structure with a lattice constant of 184 nm. Good coincidence between the scattering data and a theoretical description of the system is found with only one relevant fitting parameter. Because of the distinct scattering curves and the pronounced dependence of these curves on certain experimental parameters we think that many interesting aspects can be studied on the present and similar systems, including the following: first, the examination of the influence of packing rate as well as controlled polydispersity on the film structure and, second, the change in film structure upon annealing at different temperatures and subsequently exposing the film again to water thus studying to which degree the spheres have been glued together by coalescence processes.

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