

Heterostructures of Polymer Photonic Crystal Films

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This paper describes ways to multilayer opaline films (opaline heterostructures) composed from functional opal layers of spheres with different lattice constants. At first various monodisperse colloids—both cross-linked and un-cross-linked—were prepared from methyl methacrylate, methyl α -chloroacrylate, and methyl α -bromoacrylate. These colloids can be crystallized into large, well-oriented opaline films with the help of a “drawing apparatus” by the method of crystallization in a moving meniscus. After annealing, a second opaline film can be crystallized on top of these films and so on. Electron microscopy inspection shows a sharp borderline between the sublayers and no disorder on both sides although the lattice constants in both films can be incommensurable. Transmission and reflection measurements prove the high quality of the films. The use of a combination of thermolabile and thermostable colloids opens the possibility to prepare functional opaline heterostructures.

Introduction

Photonic crystals are attracting a lot of attention as materials for optical switches,¹ data storage,² chemical sensors,³ and lasers with low threshold.⁴ Many of these applications require a structured^{5,6} photonic crystal or heterostructure formation.⁷ This has to be combined with functionality, e.g., fluorescent dyes or thermal stability.

Preparation of well-oriented photonic structures by self-assembling of colloids is an important milestone in the race for three-dimensional photonic crystals operating in the visible. Bulk opals consist, usually, of randomly oriented crystallites that make them unfit to perform as elements of optical circuits. In contrast, thin opaline films have the advantage of their (111)-planes being nicely parallel to the substrate.^{8,9} Unfortunately, they possess a complicated height profile, if made by crystallization of a latex suspension on horizontal hydrophilic substrates.^{8,9} Samples crystallized in a narrow cell between two glass slides¹⁰ result in uniformly thick

films, but they are bounded to remain in this cell. The crystallization by capillary forces in a moving meniscus seems to be the most promising method to prepare well-oriented opal films of equal thickness.^{11–15} It is worth noting also that these opaline films can be processed further, e.g., for the preparation of heterostructures.¹⁴ As hetero-opals we understand multiple-layer opaline films composed from opal layers of spheres with different lattice constant, different dielectric function, or both. Crystallization in a moving meniscus has been previously used with silica opals.^{16,17} In this case, either the substrate was moved horizontally¹⁸ or a vertically oriented substrate was immersed in the suspension of silica spheres in alcohol.^{13,19,20} In this way also, heterostructures are accessible.¹⁴ The latter method allows a limited control over the speed of the meniscus movement. In addition, it is limited to solvents with high vapor pressure (e.g., ethanol). As these solvents swell the polymer latex, this process cannot be applied for

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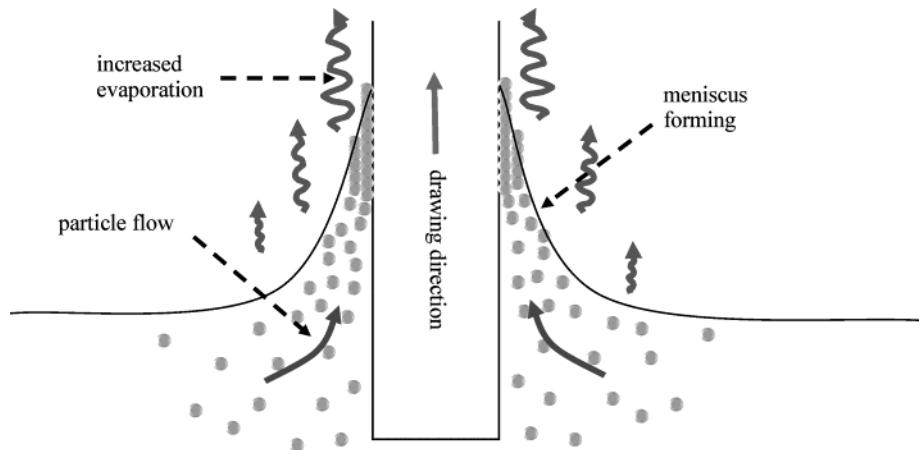


Figure 1. Schematic illustration of the crystallization in a moving meniscus.

polymer opals. Polymer opals have, however, some advantages compared with silica opals. At first, large crystallites (over 100 μm) can be obtained easily.⁸ Then they can be functionalized with fluorescent dyes.⁹ They can be patterned by E-beam writing,^{9,21} and their properties (refractive index, thermal stability, etc.) can be modified easily.⁸

Therefore, we developed an apparatus to crystallize opaline films from polymers vertically in a moving meniscus by lifting the sample out of the colloidal suspension in water (see Figure 1). Just after finishing this work, a paper that describes a very similar setup was published.²² In our case, very smooth lifting was achieved due to decreasing the speed down to 100 nm/s. This method works especially well with the polymer colloids, which do not sediment as quickly as silica spheres because their density is close to that of water. Thereby it is possible to prepare well-oriented crystal films of several square centimeter areas with uniform thicknesses. Moreover, the latter can be preset by the choice of crystallization parameters.

Formation of hetero-opals is a way to introduce artificial planar defects in opaline crystals, while staying with fast self-organization processes.¹⁴ Parameters such as lattice constant or chemical composition experience the abrupt changes along the normal to the plane of hetero-opaline film. Correspondingly, the optical properties of opal layers differ dramatically across the interface. In the context of photonic crystals, the mismatch of optical modes between different layers can be used for light localization and guiding in prospective optical devices. While hetero-opals have already been made with silica opals, polymer opals offer here the advantage to change the refractive index, to incorporate fluorescent dyes, to do E-beam writing, and so on. The use of thermolabile colloids makes it—in addition—possible to create switchable heterostructures as described in this paper. The way to change colloids chemically is to use different monomers, for example, to use monomers with heavy atoms and to do cross-linking. Monomers with heavy atoms give, for example, the possibility to differentiate between sections with a different composition, e.g., by energy-dispersive X-ray detection (EDX). Cross-linking allows it to increase the thermal stability.

In this paper, we report the synthesis of new monodisperse colloids, which might include heavy atoms, and their crystallization to homogeneous photonic crystal films using a moving meniscus. Furthermore, we show the formation and characterization of functional heterostructures with colloids of different sizes, compositions, and thermal stability.

Experimental Section

The drawing machine consists of an engine from Minimotor. It is slowed by transmissions to a few hundred nanometers per second. The engine is controlled by a voltmeter from Laboratory Power Supply.

The latices were synthesized using commercially available chemicals without further purification. Methyl α -chloroacrylate (MCA) and methyl methacrylate (MMA) were bought from Acros, and 2,3-dibromopropionic acid methyl ester was from Fluka and triethylamine from Lancaster.

Methyl α -bromoacrylate (MBA) was synthesized after Walborsky.²³ To a solution of 198 mmol of 2,3-dibromopropionic acid methyl ester in 150 mL of diethyl ether and 150 mL of hexane was added 252 mmol of triethylamine, and the resultant mixture was stirred for 4 h at room temperature. The solution was filtered, washed with water, and distilled in a vacuum (64 °C, 70 mbar) to give a colorless liquid.

The colloids were synthesized as described in ref 8 without the use of toluene. In a 250-mL flask, 140 mL of purified water was flushed with nitrogen for 1 h at 90 °C. Depending on the size of the latices, 4–15 mL of monomer and 5 mL of a 10% potassium peroxodisulfate solution were added. After 1 h, the polymerization was stopped with air. The solution was stirred in air for another 20 min, filtered, centrifuged, and redispersed several times to give monodisperse latices in water. This works well for MMA and to some extent for MCA. For less water-soluble monomers (MCA and MBA), the synthesis of core–shell colloids is necessary to achieve the required monodispersity. First, polymer latices from MMA were synthesized as described above. However, the polymerization was not terminated with air but the second monomer (MCA or MBA) was added and polymerized for ~30 min more. After this period of time, the reaction was stopped with air and worked up as written above. To increase the thermal stability some of the latices were cross-linked with ethylene glycol–bismethacrylate. Usually 5% cross-linker was added to the monomer.⁸ In core–shell colloids, only the shell was cross-linked. The sizes of the latices used are shown in Table 1. They were determined optically from the position of the stop band (see below).

The photonic crystal films were prepared using the drawing device and suspensions with concentrations between 3 and 8 wt %. For heterostructures, the first layer has to be sintered

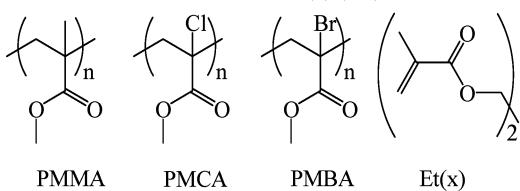
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Table 1. Suspensions and the Optical Properties of Photonic Crystal Films

colloids	polymer ^a	λ_{max} (nm)	diameter (nm)
C1	PMMA	404	182
C2	PMMA	558	251
C3	PMMA	620	280
C4	PMMA	640	288
C5	PMMA	645	290
C6	PMMA	767	344
C7	PMMA	885	398
C8	PMMA/Et(5)	506	227
C9	PMMA/Et(5)	538	242
C10	PMMA/Et(5)	570	256
C11	PMMA/Et(5)	589	264
C12	PMMA/Et(5)	608	273
C13	PMMA/Et(5)	697	313
C14	PMMA-PMCA/Et(5) (1:1)	443	198
C15	PMMA-PMCA/Et(5) (4:1)	650	292
C16	PMMA-PMCA/Et(5) (5:1)	676	303
C17	PMMA-PMCA/Et(5) (8:1)	777	349
C18	PMMA-PMBA/Et(5) (4:1)	643	286
C19	PMMA-PMBA/Et(5) (9:1)	781	349



^a PMMA, poly(methyl methacrylate); PMCA, poly(methyl α -chloroacrylate); PMBA, poly(methyl α -bromoacrylate); first polymer is in the core. /Et(5) means 5% ethylene glycol-bismethacrylate in the polymer; (x:y), volume ratio core-shell.

for 2 up to 12 h. For poly(methyl methacrylate) (PMMA), the latices were sintered (annealed) at 80 °C. For poly(methyl α -chloroacrylate) (PMCA) and poly(methyl α -bromoacrylate) (PMBA) core-shell latices, the sintering temperature was 110 °C. Without sintering, the colloids will redissolve in water.

The thickness of the opaline films was determined with a Dektak 3ST from Veeco, an instrument normally used to measure surface profiles of thin polymer films mechanically in photoresist technology.

Optical characterization was done using a UV-2102-PC UV-visible spectrometer from Shimadzu. The measurements were done in transmission (perpendicular to the (111)-plane) and reflection (almost perpendicular to the (111)-plane to be able to detect the reflected light) at a range from 300 to 900 nm using glass slides as substrate.

We determine the size of the particles from the position of the stop band (lattice constant of the fcc crystal). This value always agrees well with EM measurements.⁹ However, since the polymer opals are sensitive to E-beams, we consider the optical measurement to be more accurate. Light scattering measurements of the colloidal solutions give polydispersities of ~3%, which is rather low. This corresponds to a low half-bandwidth of the stop band of below 7% (perfect packing in the crystal).

Results and Discussion

Preparation of Monodisperse Colloids. Starting with our experience in monodisperse PMMA latices,²⁴ we worked on methods to prepare functional heterostructures with other spheres. From the chemical point of view, this requires the preparation of colloids with different refractive indexes (e.g., colloids from fluorinated monomers²⁵), colloids with different thermal

stability, and the preparation of colloids, which can be discriminated from each other independent of their size and colloids, that form water-stable photonic crystal films. There are different ways to make distinguishable colloids. One is to dope the latices with fluorescent dyes.⁹ Another way is to use methacrylate and acrylate derivatives with heavy atoms. In this case, it becomes possible to differentiate layers of different colloids with EDX. For the multilayer buildup, it is necessary to stabilize the photonic crystal film in such a way that it does not disintegrate (= redisperse) if dipped a second time into a colloidal suspension in water (this indeed happens with unannealed samples). To achieve this, the colloidal beads must fuse during annealing at their connecting point without a melting of the whole structure, which would destroy the photonic structure. The optimal way to achieve this is the use of slightly cross-linked colloids, which cannot melt into a homogeneous polymer film but which still get sticky, if heated close to their T_g value. For un-cross-linked colloids, this task is more difficult but can be achieved by limiting the annealing conditions to temperatures 20–30 °C below T_g . The combination of un-cross-linked and cross-linked colloids opens, in addition, the possibility to functional thermoswitchable structures.

For this purpose, we worked on the preparation of various un-cross-linked and cross-linked methacrylates, and we investigated especially MCA and MBA as monomers. Here the α -methyl group of MMA is exchanged by chlorine (MCA) or bromine (MBA). The accelerating voltage for chlorine in EDX is, for example, ~10 kV. This is in a range in which PMMA and PMCA latices stay stable in an E-beam if cross-linked and cooled.

During the polymerization experiments, we found that the surfactant-free emulsion homopolymerization does not work well with the less water soluble halogen-containing monomers MCA and MBA. Only in the case of MCA are colloids formed by this method. However, they are not as monodisperse as necessary. They can be crystallized, and the resulting films show some Bragg scattering of light, but the stop bands are broad and not very intense. For this reason, we started to synthesize core-shell latices. We used small MMA colloids as core and MCA or MBA as monomers for the shell. With this method, core-shell latices of high monodispersity and good optical properties are accessible from halogen-containing monomers. Latices synthesized with both methods (surfactant free emulsion homopolymerization and seed polymerization) are collected in Table 1.

Photonic Crystal Films. For the preparation of heterostructures from different photonic films, we used a drawing device, which allows lifting a substrate (normally glass) with a speed down to a few hundred nanometers per second out of a colloid suspension. This process results in homogeneous photonic crystal films with controllable thickness (see ref 22 for comparison) by the process sketched in Figure 1. To look closer into the process of crystallization, scanning electron microscopy (SEM) images were taken from the crystallized opaline films. At the beginning, a monolayer is formed in the meniscus. A second layer is crystallized on this

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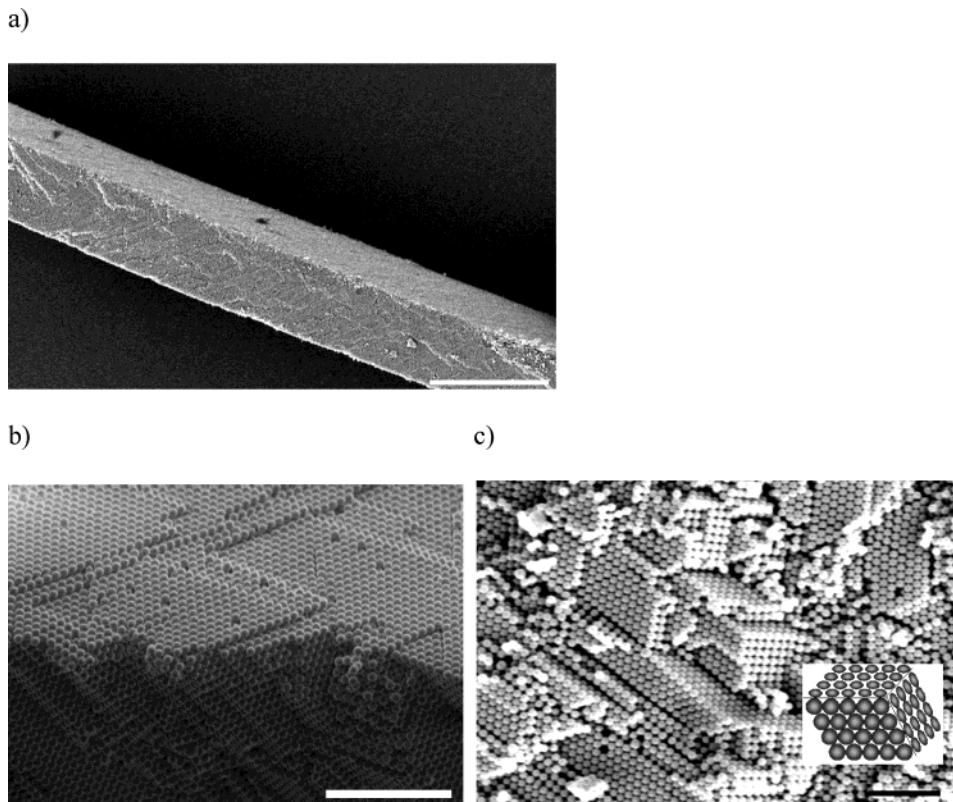


Figure 2. SEM images of photonic crystal films. (a) Clod of a PMMA film. Scale bar = 20 μm . (b) Top and side view of a PMCA film. Scale bar = 4 μm . (c) Different views on the fcc structure. Scale bar = 2 μm . The inset is a scheme of an fcc structure.

layer, and then the third, and so on. After a certain time, the crystallization in the meniscus comes to an equilibrium resulting in a film of homogeneous thickness and a smooth surface, which can macroscopically extend over an area of several square centimeters. Figure 2a shows a piece of such a film. In our case, concentrations of 3–4 wt % and drawing speeds of 200 nm/s or below are necessary to observe nice homogeneous films. If films of macroscopic dimensions are examined by optical microscopy, it turns out that they are broken in large crystallites with the size of 100–200 μm .²⁶ These crystallites have their (111)-plane parallel to the substrate. Inside the crystallites, the order is high and there are very few defects (Figure 2b). The film itself has a face-centered cubic (fcc) structure, which is nicely shown in Figure 2c, indicating different facets of the fcc packing.

Generally, the film thickness depends on such parameters as lifting speed, solution concentration, temperature, air humidity, and sphere size (see ref 22 for comparison). Keeping all parameters constant but the suspension concentration, we studied the effect upon the film thickness. The thickness was then measured mechanically (Experimental Section) in the part of the film with constant thickness. The film thickness as a function of the concentration is shown in Figure 3. It increases quite linearly with concentration but has a certain offset. That means that a critical concentration is necessary to build up a close-packed film on a substrate.

Heterostructured Opals. Multilayers of different opal films can be prepared by the procedure described

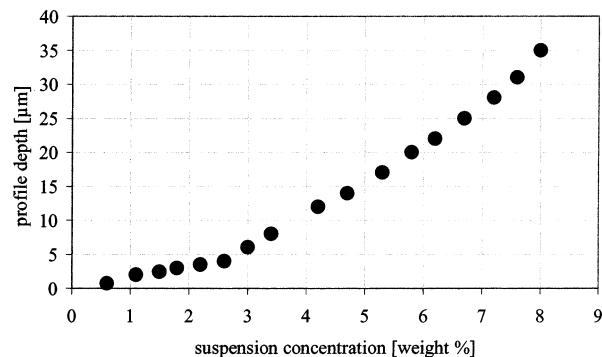


Figure 3. Dependence of the film thickness on the suspension concentration for PMMA latices with a diameter of 280 nm (**C3**). The drawing speed is 100 nm/s.

below. A hydrophilic glass substrate is put into a 3 wt % latices containing solution and pulled out with a speed of 200 nm/s. In this way, the deposition of films with constant thicknesses can be achieved. Directly after preparation, this film is very fragile and tends to be redispersed again if put into water or a second suspension of spheres. Therefore, the film has to be sintered (annealed) to glue the spheres together. The sintering was performed at 80 °C for PMMA and at 110 °C for PMCA and PMBA core–shell latices. During annealing, the cracks described above open a bit, but the quality inside the crystallites (100 μm) does not decrease.

Using spheres with different sizes, different refractive indexes, or both, the layers can be discriminated by UV–visible spectroscopy. Measurements were made in transmission and reflection modes. In Figure 4a are shown the transmission spectra of the double-layer opal consisting of poly(methyl methacrylate) (**C5**) with a

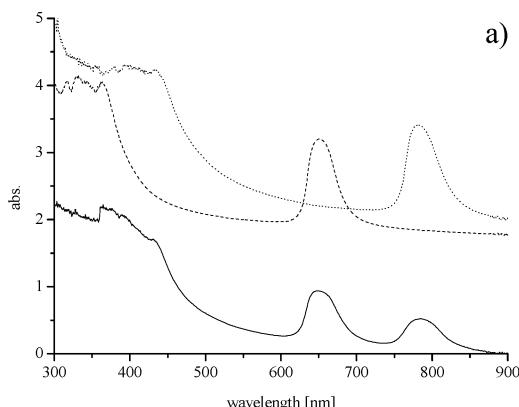


Figure 4. UV-visible spectra of a double layer composed of PMMA (290 nm, **C5**) at the bottom and PMBA (349 nm, **C19**) at the top. (a) Measurement in transmission. (b) Measurement in reflection.

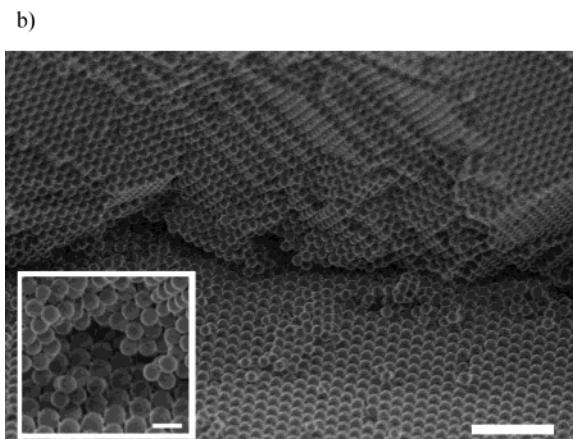
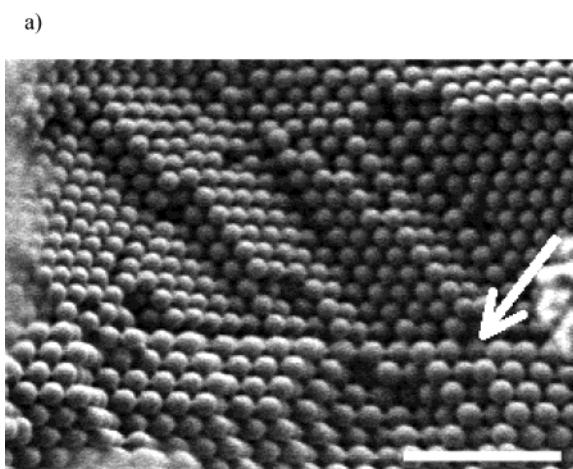
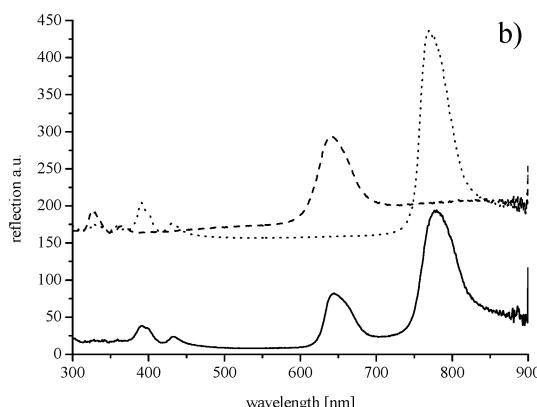


Figure 5. SEM images of a double layer consisting of a PMMA (344 nm, **C6**) layer at the bottom and a PMCA (303 nm, **C16**) layer at the top. (a) Arrow marks the interface. Scale bars: (a) 4 μ m; (b) 20 μ m and inset 200 nm.

diameter of 290 nm as bottom layer and colloids **C19** with a diameter of 349 nm as top layer.

Diffraction resonances from stacks of (111)-planes of both layers are visible as well as resonances at shorter wavelength of the top layer. These peaks correlate with the wavelength of the second band gap along the (111)-axis of opals. In Figure 4b, the reflection spectrum of the same double-layer opal is shown. In this case also, the resonances along the (111)-axis of both layers and the peaks of the second band gap along the (111)-axis of the opal film on top are visible. Usually, the resolution of optical resonances is better in reflection spectrum

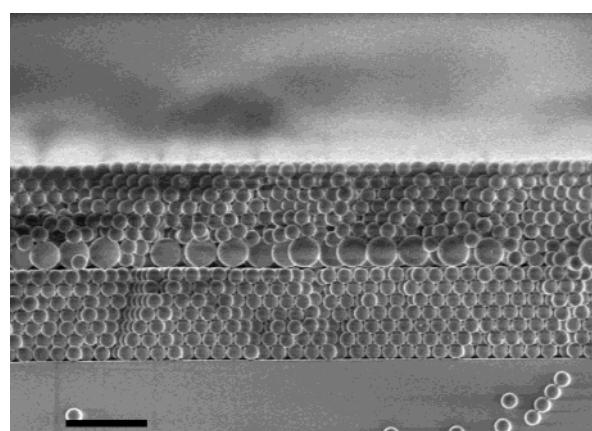


Figure 6. Monolayer of 804-nm PS beads in an ABA heterostructure surrounded by crystal films with beads with diameters of 398 nm (**C7**) (space bar = 2 μ m).

than in transmission. In transmission, the diffuse scattering due to the presence of packing defects along the optical path through the film contributes to the spectrum. In contrast, the reflection spectrum is dominated by the uppermost (111)-planes; i.e., the light path inside the opal is shorter and the contribution of defects is smaller. It is thus less sensible to defects in the volume.

To get a closer look at the heterostructures, EM investigations were made. Looking at different films, it seems that the cracks in successive opaline layers form independently from the cracks in the underlying sublayer. So cracks in the underlying films are—at least partially—covered by the new opaline film and new cracks form. To investigate the interface between two opal lattices, SEM pictures were taken from the cleaved edge. The results are shown in Figure 5. The double layer consists of a poly(methyl methacrylate) film (**C6**) with a bead diameter of 344 nm at the bottom and a poly(methyl α -chloroacrylate) film (**C16**) with a bead diameter of 303 nm at the top. In Figure 5a, a clear cut through both layers is visible. Figure 5b shows a film of the smaller colloids resting on a plane of the crystallized larger colloids. Both pictures indicate highly ordered opaline films and a homogeneous thickness of the structure. We also observed a sharp borderline between both opaline films on SEM images although the diameters of beads cannot be matched geometrically (the lattice constants are incommensurable). This allows us to treat opaline films as a planar substrate for the

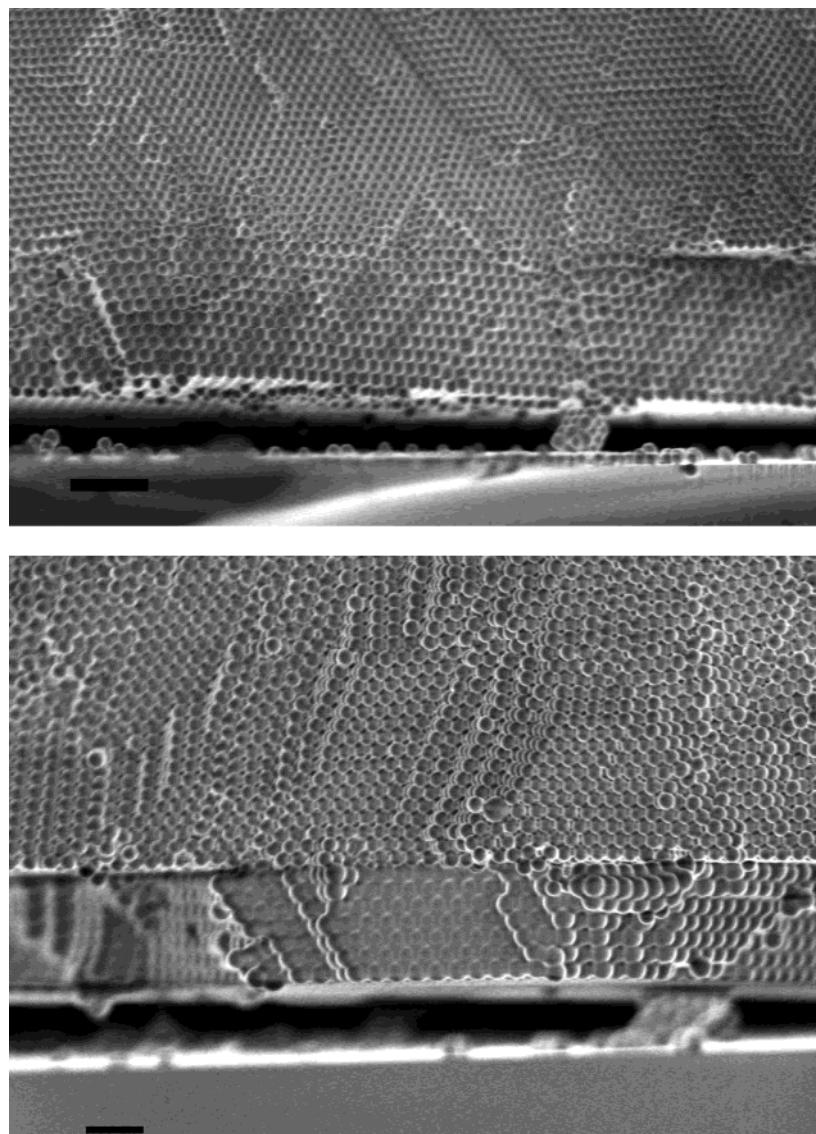


Figure 7. (a) Thermolabile double layer consisting of cross-linked **C13** (313 nm) and un-cross-linked **C7** (398 nm) at 140 °C (space bar = 1 μ m). (b) Thermolabile double layer consisting of cross-linked **C13** (313 nm) and un-cross-linked **C7** (398 nm) at 140 °C (space bar = 1 μ m).

preparation of a second film on top of it. Generally the interface between two opaline films is a mechanically weak point. Mechanical stress leads preferably to a breaking of the samples at this point (see also Figure 5b). We have, however, many pictures from the cleaved etch, which show both sublayers in intimate contact. So we suppose that they are formed in intimate contact after crystallization and annealing.

Using the dipping apparatus more complex structures can be created. Figure 6 shows, for example, a monolayer of polystyrene beads with a diameter of 804 nm resting between two opaline film sublayers of colloid **C7** (398 nm). This shows that a consecutive heterostructure buildup with more than two sublayers is possible even with monolayers.

The preparation of functional heterostructures is possible by using sublayers with fluorescent dyes or by using colloids of a different thermal stability, e.g., cross-linked and un-cross-linked ones. Figure 7 shows an example of this. Here un-cross-linked (thermolabile) PMMA colloids with a diameter of 398 nm (**C7**) have been crystallized on top of cross-linked PMMA colloids

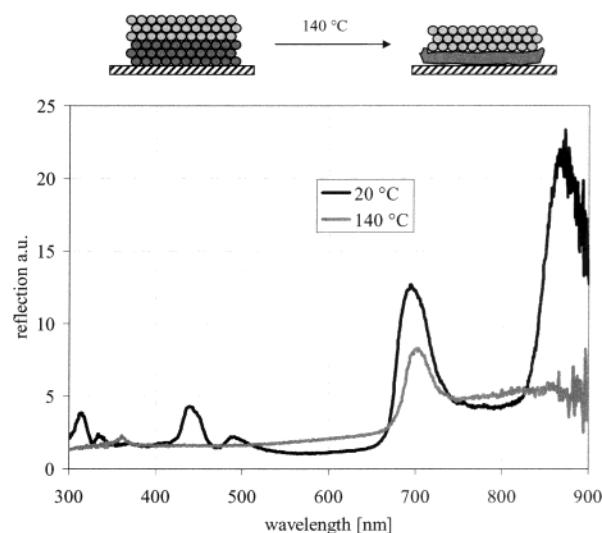


Figure 8. (a) Schematic illustration of the annealing process and (b) UV-visible spectra of the partially thermolabile heterostructures (**C7 + 13**) at 20 and 140 °C (also see Figure 7).

(C13) with a diameter of 313 nm. Annealing of this heterostructure below the T_g value of PMMA leads to a mechanically stable opaline heterostructure (see Figure 7a). Heating of this heterostructure for 15 min to 140 °C (above the T_g of PMMA) leads, however, to a melting of the un-cross-linked spheres and their fusion (see Figure 7b). The change in the optical properties associated with this process is presented in Figure 8. The UV spectrum shows a superposition of both stop bands (see

Figure 4 for comparison) prior to annealing. After annealing, the stop band of the thermolabile opaline sublayer has disappeared.

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