ACCOUNTS
of chemical research

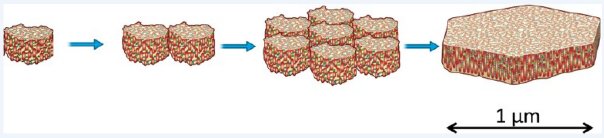
Article

pubs.acs.org/accounts

The Dynamic Association Processes Leading from a Silica Precursor to a Mesoporous SBA-15 Material

Viveka Alfredsson and Håkan Wennerström*

Division of Physical Chemistry, Department of Chemistry, Lund University P.O.Box 124, SE 22100 Lund, Sweden



CONSPECTUS: During the last two decades, the synthesis of silica with an ordered mesoporous structure has been thoroughly explored. The basis of the synthesis is to let silica monomers polymerize in the presence of an amphiphilic template component. In the first studies, cationic surfactants were used as structure inducer. Later it was shown that pluronic copolymers also could have the role. One advantage with the pluronics copolymers is that they allow for a wider variation in the radius of pores in the resulting silica material. Another advantage lies in the higher stability resulting from the thicker walls between the pores. Mesoporous silica has a very high area to volume ratio, and the ordered structure ensures surface homogeneity. There are a number of applications of this type of material. It can be used as support for catalysts, as templates to produces other mesoporous inorganic materials, or in controlled release applications.

The synthesis of mesoporous silica is, from a practical point of view, simple, but there are significant possibilities to vary synthesis conditions with a concomitant effect on the properties of the resulting material. It is clear that the structural properties on the nanometer scale are determined by the self-assembly properties of the amphiphile, and this knowledge has been used to optimize pore geometry and pore size. To have a practical functional material it is desirable to also control the structure on a micrometer scale and larger. In practice, one has largely taken an empirical approach in optimizing reaction conditions, paying less attention to underlying chemical and physicochemical mechanisms that lead from starting conditions to the final product. In this Account, we present our systematic studies of the processes involved not only in the formation of the mesoporous structure as such, but also of the formation of structures on the micrometer scale. The main point is to show how the ongoing silica polymerization triggers a sequence of structural changes through the action of colloidal interactions.

Our approach is to use a multitude of experimental methods to characterize the time evolution of the same highly reproducible synthesis process. It is the silica polymerization reactions that set the time scale, and the block copolymer self-assembly responds to the progress of the polymerization through a basically hydrophobic interaction between silica and ethylene oxide units. The progression of the silica polymerization leads to an increased hydrophobicity triggering an aggregation process resulting in the formation of silica–copolymer composite particles of increasing size. The particle growth occurs in a stepwise way caused by intricate shifts between colloidal stability and instability. By tuning reaction conditions one can have an end product of hexagonal prism composite particles with single crystal 2D hexagonal order.

INTRODUCTION

The synthesis of mesoporous silica has been a field of intense research for the last two decades. In the first reports[1,2] mesostructured materials with pore diameter of 2–3 nm were produced based on silica formation in a basic medium using cationic tetraalkylammonium surfactants as templating agents. Stucky and co-workers generalized the concept by templating through self-associating block copolymers in an acid medium, which produced materials with clearly larger pore sizes and thicker silica walls.[3] The concept has also been generalized to the formation of other inorganic mesoporous materials.[4,5] The basic principle of the synthesis is simple. One starts with an aqueous solution of appropriate pH and a templating agent in micellar form. To this one adds a silica precursor, and after some time a silica–amphiphile composite material has formed. This is easily separated from the reaction solution and can then be calcined to yield the mesoporous inorganic material. Even though the basic features of the synthesis are straightforward, the specific reaction conditions can be varied with respect to silica source, templating agent, reaction temperature, pH, salt content, etc. Using these degrees of freedom, one has the possibility to tune the product toward specific desired properties. An overview of the multitude of possibilities that has been explored can found in the reviews, refs 6–8.

Most papers in the field concentrate on the material science aspects of the synthesis, while fewer deal with the chemical mechanisms leading from the initial reactants to the final mesoporous product. In a series of papers, we have studied specific stages in the synthesis of a mesoporous material, with the goal of obtaining a coherent description of the combined chemical and structural transformations occurring during the synthesis. We have chosen to focus on one of the most well-known materials, SBA-15[3] (SBA stands for Santa Barbara Amorphous), which has a 2D hexagonal structure. The material is synthesized using pluronic block copolymers as structure inducers. This work has been progressing over a range of years,[9−15] and we are now at a point where we can present a

Received: March 30, 2015
Published: June 24, 2015

DOI: 10.1021/acs.accounts.5b00165
Acc. Chem. Res. 2015, 48, 1891−1900

Table 1. Synthesis Conditions

(a) Reactants and Concentrations for Our Typical Synthesis[11]			
	templating agent	silica source	acid
components	Pluronic P104, $(EO)_{27}(PO)_{61}(EO)_{27}$	TMOS, $Si(OCH_3)_4$	HCl
concentration	2.5 wt %	0.26 M	1.6 M
(b) Synthesis Procedure[11]			
	formation of composite particles, continuous stirring	hydrothermal treatment, static conditions	calcination
temp, °C	55	80	500
time, h	24	24	6

Table 2. Properties of the Material[11,24]

lattice parameter, nm	BET, m^2/g	pore diameter, nm	particle morphology	particle diameter, nm	particle height, nm
10.0	1000	6.6	hexagonal prism	1000	400

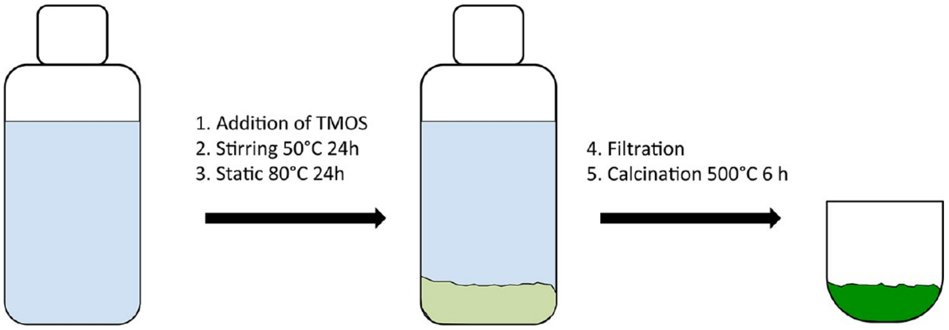


Figure 1. Synthesis procedure for SBA-15. The acid solution containing the micellar structure director is heated to 55 °C. The silica source, TMOS, is added, and the solution is left on the bench for a total of 24 h at this temperature. The solution is constantly stirred but with stronger stirring for a minute at the time of TMOS addition. The reagent flask is then transferred to an oven, held at 80°, and left for another 24 h. The powder is subsequently separated from the solution by filtration and washed with water. Finally the materials is calcined for 6 h at 500 °C.

coherent account of the different steps leading from reactants to the final product. The formation mechanism of SBA-15 material has also been studied by several other groups using mainly scattering[16−21] but also other techniques.[22,23]

REACTION CONDITIONS

The outcome of a specific synthesis of a mesoporous silica material is determined by a combination of generic and specific features. For us, the focus is primarily on the generic aspects, with the aim to control the specifics through an understanding of the underlying generic features. We have made the strategic choice of concentrating on a specific set of reaction conditions and to follow the time evolution of that reaction in as much detail as possible using a multitude of experimental methods. Table 1a,b specifies the conditions of our reference reaction. The resulting SBA-15 material has pores organized in a 2D ordered hexagonal packing with a pore diameter of 6.6 nm. The properties of the material are summarized in Table 2.

The synthesis procedure is illustrated in Figure 1.

The silica precursor, tetramethyl orthosilicate (TMOS, $Si(OCH_3)_4$) is rapidly hydrolyzed under the strongly acidic conditions and a sequence of polymerization reactions starts during the first minutes. Scheme 1 illustrates the reactions.

It is the progression of these reactions that is the basic factor determining the time evolution of the system. In the absence of the block copolymer, the silica polymerization would ultimately lead to the formation of a silica gel. The presence of the pluronic polymer does not have a major effect on the silica polymerization reactions (Scheme 1, reactions b−d) as such, but it has a dramatic influence on the structure of the resulting silica network.

Scheme 1[a]

Hydrolysis reaction:

a) $$Si(OCH_3)_4 + 4H_2O \longrightarrow Si(OH)_4 + 4CH_3OH$$

Silica polymerization reactions:

all equivalent to $\equiv Si\text{-}OH + HO\text{-}Si\equiv \longrightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$

b) $$Si(OH)_4 + SP_n(k) \longrightarrow SP_{n+1}(k+2) + H_2O$$

c) $$SP_n(k) + SP_m(l) \longrightarrow SP_{n+m}(k+l-2) + H_2O$$

d) $$SP_n(k) \longrightarrow SP_n(k-2) + H_2O$$

[a] The following notation is used: $SP_n(k)$, silica polymer with n Si atoms and k $Si{-}OH/Si{-}OH_2^+$ groups.

OVERVIEW OF REACTION STAGES

By monitoring the progress of the reaction in real time using several methods, it is clear that it follows a perfectly reproducible time sequence. We have been able to identify 12 different stages in the process from reactants to the final product. Similar sequences have been observed by others.[20] Figure 2 shows an overview of the progression of the formation of the composite particles.

Stage 1: Hydrolysis of the silica source into $Si(OH)_4$ and alcohol[25] ($t \leq 1$ min) (Scheme 1, reaction a).

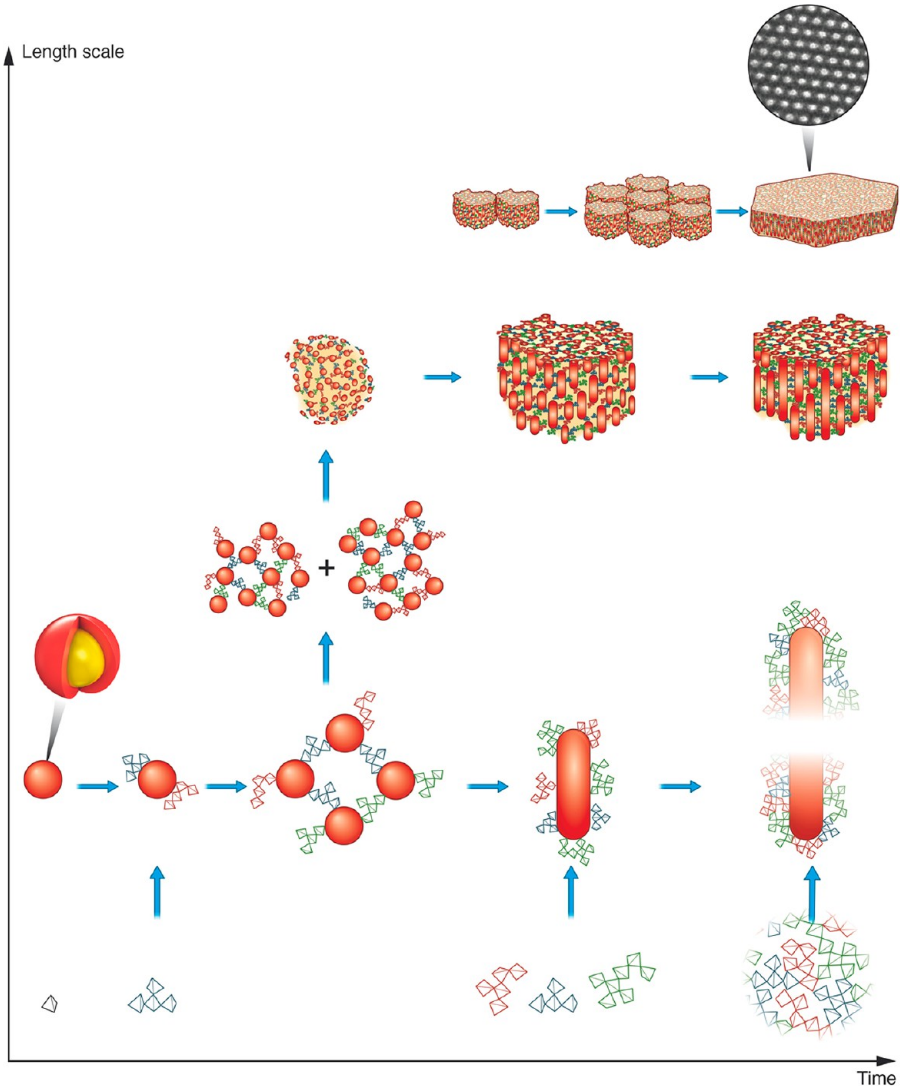


Figure 2. Schematic overview of the evolution of formation events. The tetrahedra illustrate SiO_4 units. The Pluronic micelles are depicted as red spheres and cylinders. The micelles have a core (yellow)−corona (red) structure. On the atomic length scale (bottom row), the silica polymerizes from $Si(OH)_4$ to oligomers, polymers, and finally a connected network. On the micellar length scale (second row), the spherical micelles transform gradually into extended cylindrical micelles. On the next level (third row), small flocs associate and the larger flocs thus formed (forth row) transform from an isotropic to an anisotropic shape (primary particles). The anisotropic flocs associate in a 7-mer (fifth row) creating the final particle.

Stage 2: Growth of a silica polymer by monomer addition. Monomer consumed after around 10 min[26] ($t < 10$ min) (Scheme 1, reaction b).

Stage 3: Adsorption of silica oligomers/polymers on pluronic micelles (∼2 min < t < ∼10 min).[12]

Stage 4: Association of pluronic micelles with adsorbed silica into flocs with a polydisperse size (diameter ∼50−200 nm, 9 min < t < 13 min).[14]

Stage 5: Micelles start to deviate from globular micelles at around 8 min with an ongoing one-dimensional growth in size until around 30 min.[12]

Stage 6: Association of flocs to nearly monodisperse primary particles with diameter ∼400 nm (11 min < t < 14 min).

Stage 7: Transformation of the globular isotropic particles containing cylindrical micelles into anisotropic particles of liquid crystalline internal order with ultimately 2D hexagonal symmetry (14 < t < 20 min).[12,27]

Stage 8: In-plane association of anisotropic particles into 7-mer particles of width ∼1 μm and height 400 nm (14 < t < 16 min).[11,14]

Stage 9: Annealing of 7-mer particle into single crystal 2D hexagonal order and hexagonal prism shape (15 < t < 30 min).[14]

Stage 10: Additional formation of Si−O−Si bonds producing a coherent silica network throughout the hexagonal particle (30 min < t < 24 h) (Scheme 1, reaction c).

Stage 11: Consolidation of the silica network by incubation of particles at an elevated temperature (80 °C). Additionally some sintering of particles occurs (24 < t < 48 h) (Scheme 1, reaction d).

Stage 12: Calcination of particles at 500 °C for 6 h burns out the organic polymer components, and the silica network is further strengthened.

DOI: 10.1021/acs.accounts.5b00165
Acc. Chem. Res. 2015, 48, 1891−1900

Below we will discuss in more detail the molecular mechanism of the crucial steps in the synthesis. A main point is to demonstrate that it requires a combination of experimental methods and an understanding of colloidal interactions to arrive at a coherent picture. Figure 3 shows a schematic representation of the results obtain from an in situ X-ray scattering study of our system at four different synthesis temperatures.[12] The time sequence for each synthesis is highly reproducible and although the overall appearance is similar the difference in timing leads to largely different morphologies of the product. The temperature also affects the lattice parameter of the 2D hexagonal structure.

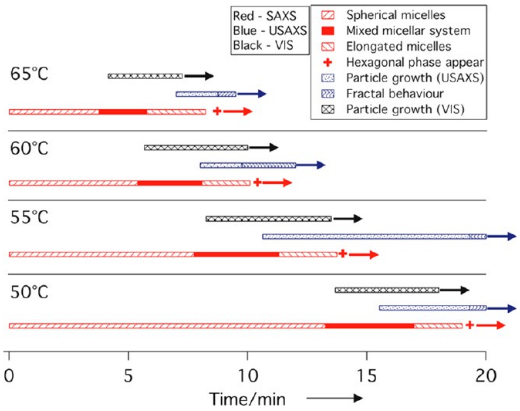


Figure 3. Time evolution for the formation of SBA-15 at four temperatures. The figure is based on observations from X-ray scattering and UV–vis.[12]

DETAILS ON THE FORMATION STAGES

Silica Polymerization, Its Adsorption on Micelles and Association of Micelles (Stages 1–4)

The initial silica polymerization leads to the formation of branched growing oligomers. They contain an increasing amount of O–Si–O links, turning the originally hydrophilic monomer into a more and more hydrophobic species. It is, for example, well documented that cavities in zeolites grow more hydrophobic the higher the fraction of O–Si–O links.[28] The pluronic micelles of the reaction solution have a core of poly(propylene oxide) ($(\mathrm{PO})_x$) chains and a corona consisting of poly(ethylene oxide) ($(\mathrm{EO})_y$) groups. Although the EO chains are sufficiently hydrophilic to ensure an amphiphilic character to the pluronic block copolymer, the EO corona is less polar than the aqueous environment. This has the result that there is a weak attractive interaction of a hydrophobic character between the O–Si–O groups of the silica and the EO groups of the micellar corona. Once the silica oligomers have grown to a certain size, they can make sufficient molecular contacts with the micellar corona to cause an adsorption of the silica oligomer or polymer on the surface of the micelle. That such a coupling occurs is well documented for the case of adsorption of EO-based nonionic surfactant and block copolymer micelles on silica surfaces.[29−31] In explaining the silica adsorption, there is thus no need to invoke a coupling based on the basically hydrophobic adsorption of anions to the nonionic micelles[32] and a subsequent electrostatic coupling to the, in the highly acidic medium, protonated silica polymer micelles.[3]

Once the silica oligomer or polymer is adsorbed on a micelle, it also exposes O–Si–O groups to the solution. As long as the silica oligomers or polymers are not in excess with respect to micelles, there will be free patches of micellar surface that can interact with silica moieties already attached to another micelle. The result is bridging association[33,34] leading to the formation of flocs of micelles. These are observable in the solution after 9 min. Figure 4 shows two experimental observations demonstrating the appearance of such flocs. There is a strong increase in turbidity, shown in Figure 4a, an increase in ^{1}H proton NMR line width[9] (see below), and an increase in the small-angle X-ray scattering (SAXS) at low values of the scattering vector (see below).[12] In cryo-transmission electron microscopy (cryo-TEM), we observe flocs of a polydisperse size of radius 80 ± 30 nm as shown in Figure 4b.[14]

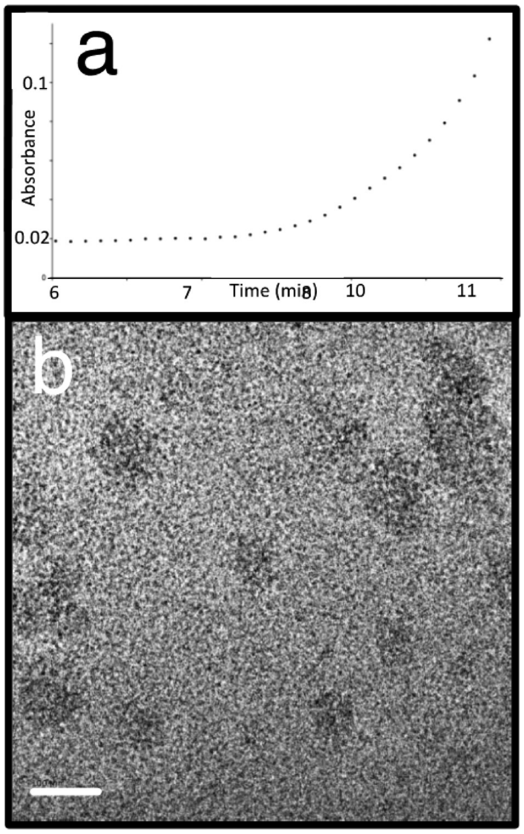


Figure 4. (a) Absorbace (UV–vis) measurement of the synthesis. The absorbance starts increasing at 9 min. (b) Cryo-TEM sample extracted at the same time shows the existence of flocs.[14] Scalebar 100 nm.

The formation of flocs is virtually completed after 14 min, and at this stage the majority of the silica monomers are incorporated into silica oligomers or polymers. Additionally most micelles have been incorporated into the flocs.[9] Provided there is an appropriate balance between the original amount of silica and of pluronic polymer, the flocs are temporarily kinetically stable toward coalescence through a steric entropic stabilization[34] (p 394 in ref 34). If there is too little silica, the flocs can continue the bridging association, while if there is too little block copolymer, individual micelles can be saturated with silica polymers and they remain kinetically stable until ongoing covalent Si–O–Si coupling has resulted in bad solvent conditions for the silica polymers.

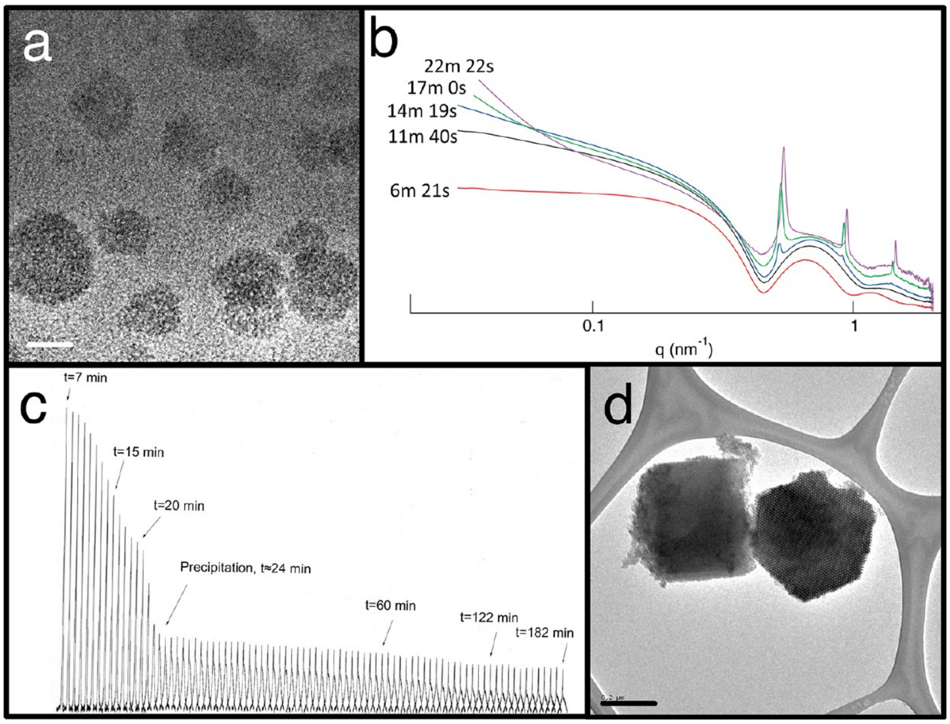


Figure 5. (a) Cryo-TEM image where the sample was extracted at 13 min after addition of TMOS.[14] Compare with the sample extracted at 9 min shown in Figure 4 b. Scalebar 100 nm. (b) In-situ SAXS data from the synthesis showing the data from the time interval of 6 to 22 min.[12] The first appearance of the Bragg peak is at 14 min. (c) NMR data from an equivalent synthesis system. Here P123 was used as structure director and the synthesis was performed at 35 °C.[9] The *x*-axis shows the time evolution (starting from $t = 7$ min) of the ^{1}H signal of the protons of the PO methyl group (one spectrum every minute for the first hour, followed by one spectrum every 5 min), and the *y*-axis shows the intensity of the NMR-signal. (d) Electron micrograph of resulting material of a typical synthesis that has been modified to prevent the oriented aggregation. The flocs have evolved to primary hexagonal prismatic particles with a uniform height to width ratio.[11] Scalebar 200 nm.

Particle Formation, Micellar Shape Change, and Transition to Hexagonal Packing (Stages 5–7)

Once the silica monomers are consumed, the evolution of the system is driven by the polymerization reactions c and d in Scheme 1. When these reactions dominate over reaction b, there is a gradual increase in both the branching ratio of the silica polymer and the occurrence of O–Si–O groups relative to that of the more polar the –Si–OH form. Consequently the silica polymer, polydisperse with respect to both size and branching ratio, is exposed to an increasingly poorer solvent. The result is a decreased stabilization of the flocs, and when two of these coalesce, there is an internal reorganization and the less branched, more hydrophilic silica polymers tend to accumulate on the surface of the newly formed floc. Having on average a more polar silica polymer on the surface, this larger floc is relatively more stable toward association than the smaller one. The presence of block copolymers on the surface is likely to have a contributing effect on the stabilization.[14] It has been clearly demonstrated that for a kinetic association scheme, where the association rate constants decrease with increasing aggregate size, there is a convergence to a nearly uniform size.[35] Figure 5a (cf. Figure 4b), showing the synthesis solution 13 min after TMOS addition, illustrates an intermediate stage of the flocs where still a considerable size variation is apparent. For our system, size converges toward a diameter of 400 nm as illustrated in Figure 5d. This stage is completed 15 min after the start of the reaction.

At the same time as the flocs associate in the larger particles, there also occurs a shape transformation of the pluronic micelles. Association of globular micelles into elongated or cylindrical shape is commonly found. There are four common causes for such a shape change. Additives decreasing the effective area volume ratio have this effect.[33] A strong increase in concentration promotes the transformation through a repulsive packing effect.[36] For amphiphiles, like the pluronics, where the polar group is built from EO residues, an increase in temperature can cause such a transformation.[37] This effect is clearly relevant for our system when we compare the synthesis results at different temperatures. However, the most important effect in the present case is the fourth possibility that an effectively attractive interaction between micelles promotes the spherical to cylindrical transition. Furthermore, an attraction is necessary to stabilize a compact assembly of micelles relative to dilution.[38] As the reactions c and d of Scheme 1 progress, there is an increasing strength of the coupling between the pluronic micelles and the silica polymers. At some point, starting at approximately 8 min for our system, the coupling is strong enough to promote a gradual globular to cylinder transformation. It is expected that the relatively stiff cylindrical aggregates give rise to a nematic order within the 400 nm particles. However, we have not been able to unequivocally characterize such a state. From $t \geq 14$ min, we observe the development of a liquid crystalline 2D hexagonal order in the particles as demonstrated by SAXS in Figure 5b and by NMR in Figure 5c. The anisotropic order makes the surface tension anisotropic, and the particles adopt an anisotropic shape with a hexagonal prism shown in the EM picture of Figure 5d as the final form. The transformation occurs at constant volume, and the height to width ratio is determined by minimizing the surface free energy.[39] By varying the reaction temperature, one obtains a variation in this ratio in a way that reflects the temperature dependence of the molecular packing in pluronic micelles.

The observation that the particles can rearrange internally to adopt their equilibrium structure shows that the particle has a liquid crystalline character allowing for free mobility of individual molecules. For this to happen, silica needs to be present in the form of individual silica polymer molecules of limited size rather than as a single percolated network, which is the final state of the polymerization process.

Formation of 7-mers and the Consolidation of the Silica Network (Stages 8–12)

Once they have adopted an anisotropic form the $d \approx 400$ nm primary particles can either remain stable for sufficient time so that they can be separated from the reaction mixture or undergo continued association. Figure 5d shows a system where the synthesis has been changed at $t = 15$ min to produce primary particles. However, if one keeps reaction conditions constant, the primary particles start to associate with one another. Since the particles are anisotropic, there are several modes of association as illustrated in Figure 6. For our reference reaction conditions at $T = 55$ °C, the association is primarily edge–edge (Figure 6a), that is, perpendicular to the 001 faces. In this situation, we observe the additional effect that there is a cooperativity in the association such that a primary particle associates more easily to a dimer than to another monomer (see Figure 6 a). There is, for example, an additional van der Waals contribution present for the trimer. It is remarkable that the main product of this association step is 7-mers of primary particles (Figure 7 a,b). For $T = 65$ °C, the particles form stacks (see Figure 6b) with a flat side–flat side (along the 001 faces) association. At this temperature, the primary particles have a higher length to width ratio.[11]

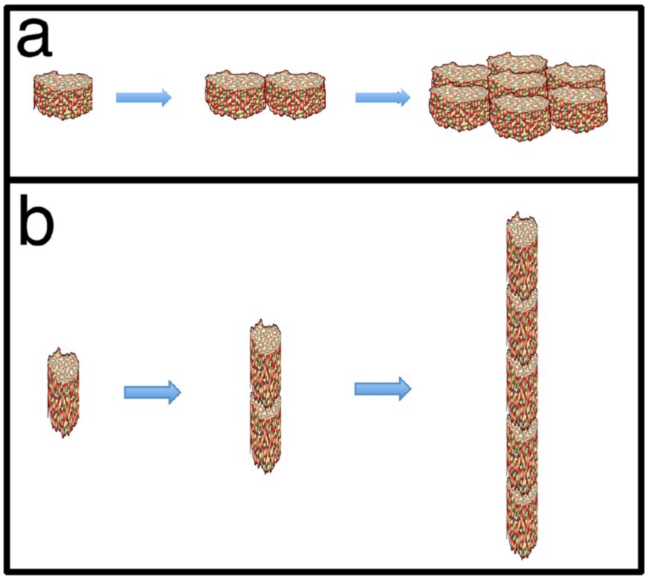


Figure 6. Primary particles in this system aggregate into (a) 7-mers under the typical synthesis conditions (55 °C), but at higher temperatures, (b) the aggregation leads to stacking along the *c*-axis. A higher temperature also induces a slightly different aspect ratio of the primary particles, with a higher length to width ratio than in the 55 °C synthesis.

The edge–edge association (Figure 6a) leads to a particle of a rather irregular shape. The equilibrium shape should be close to that of the primary particles with the same height to width ratio and with a uniform 2D hexagonal structure.[39] We observe an annealing of the structure through in plane diffusion of cylindrical micelles. Voids inside the composite particle are filled and the outer sides of the particle become straight. Then a single crystal hexagonal order is established throughout. In a final step, defects in the hexagonal order are eliminated. Figure 8 shows illustrative examples of cases where these processes have not been fully completed. During these annealing processes, the thickness of the 7-mer is kept the same as for the primary particle, even though this is not the equilibrium thickness. In contrast to the case for the smaller primary particles, the surface tension force is in this case apparently not strong enough to overcome the barrier involved in the reorganization to a less wide and thicker 7-mer. Both the sluggish in plane rearrangements and the absence of the more global shape change indicate that at this stage there has been substantial silica cross-linking and that one is close to the dynamical arrest[40] associated with a percolation of the silica network.

The formation of the 7-mers is complete after 30 min,[14] but in practice we keep reaction conditions constant for another 24 h. During this time there is a consolidation of the silica network. Less than 30 min into the reaction, the product is present as a precipitate consisting of a silica–block copolymer composite material. After 24 h stirring, the precipitate is matured at 80 °C for another 24 h in its mother liquor, resulting in an even more cross-linked silica network. This is followed by filtration and washing with water. In a final step, the organic polymer material is removed by calcination producing a silica material with ordered pores of diameter 6 nm as the final product. During the thermal treatment there is some sintering of the 7-mer particles, but when the product is redispersed in water, the sintering bonds can be broken by ultrasonic treatment and one can obtain reasonably monodisperse flat hexagonal particles of width 1.0 μm (typically the width varies from 0.75 to 1.25 μm),[14] and the height appears constant at 400 nm (±10%) as shown in Figure 9a.[41,42] The uniform size and chemical homogeneity of the pores is also reflected in the step-like capillary condensation of water[43] occurring at the relative humidity (RH) of RH = 70% as shown in Figure 9b.

■ FROM THE SPECIFICS TO THE GENERAL

Above we have in detail described the molecular events resulting in the synthesis of a specific mesoporous silica material. The experimental observations have revealed a fascinating interplay between the progress of the silica polymerization and the molecular organization controlled by colloidal interactions. There is a range of parameters that determine the reaction conditions, and there is similarly a range of possible properties of the products of the synthesis. It is our ambition that the careful study of a particular case also provides insights into general features of the synthesis.

It is our conclusion that it is the progression of the silica polymerization that drives the system and sets the time scale of the synthesis. With a clearly more rapid polymerization, one would have a percolated silica network before the pluronic system had responded to the changing conditions. With a slower silica condensation, it is difficult to accomplish the final stages in the coupling reaction, where the steric barriers are

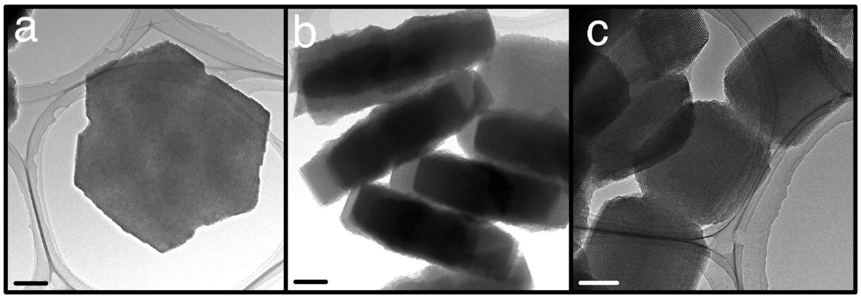


Figure 7. Transmission electron micrographs of platelet particles resulting from the 7-mer growth (cf. Figure 6a) from the 55 °C synthesis (a) aligned with the *c*-axis along the beam direction and (b) perpendicular to the beam direction. (c) Particles from a synthesis in which particles aggregate by stacking along the *c*-axis (cf. Figure 6b). In this particular case, the stacking was induced by addition of 1 M NaCl to the normal synthesis; the same stacking behavior is seen if the normal synthesis is performed at 65 °C. Scalebar 200 nm.

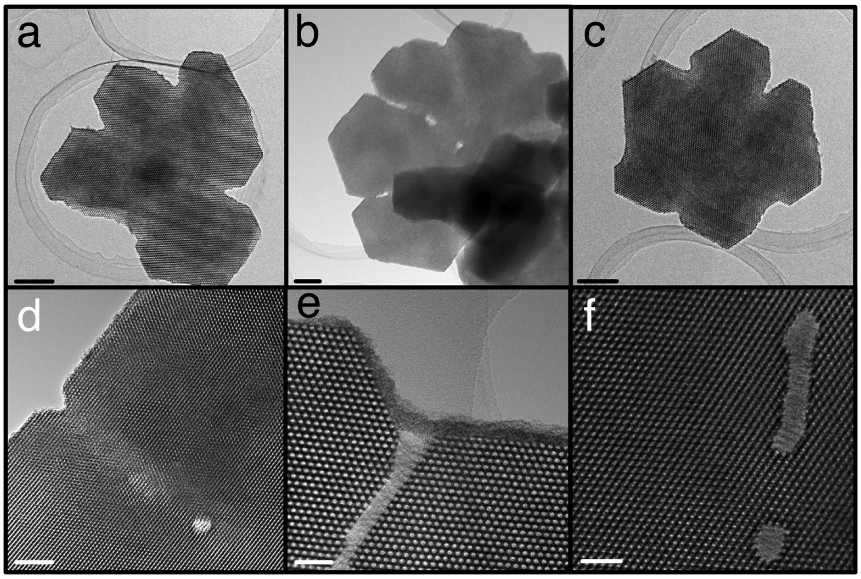


Figure 8. Examples of defects typically occurring within the platelet particles formed via the oriented aggregation. Scalebar (a−c) 200 nm, (d) 100 nm, and (e, f) 50 nm.

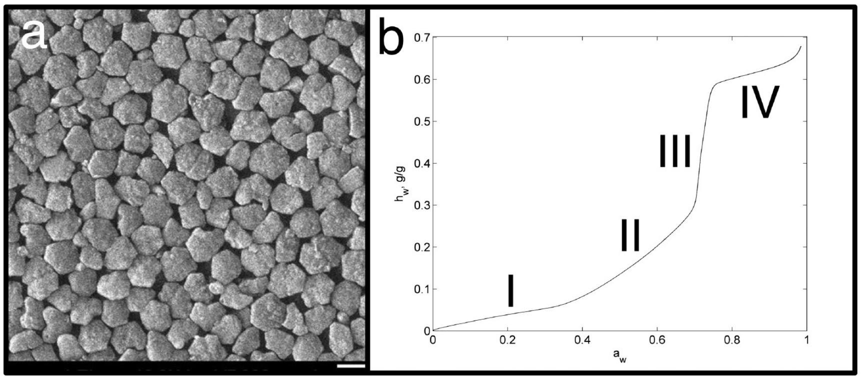


Figure 9. (a) A monolayer of SBA-15 particles deposited on a surface (scalebar 1 μm).[42] (b) Water sorption isotherm of SBA-15 measured using water sorption calorimetry.[43] The isotherm shows four distinct regimes: surface adsorption (I), filling of intrawall pores (II), capillary condensation in primary mesopores (III), and postcapillary condensation uptake of water (IV). The pore size of 6 nm leads to the sharp capillary condensation observed at water activity of 0.7.

substantial. The basic rates of the polymerization reactions of Scheme 1 are primarily determined by pH and temperature.

The liquid crystalline structure of the primary particles is determined by the pluronic amphiphile. The self-assembly properties of the block copolymers can be tuned by varying the length of the blocks in the polymer, and the phase behavior of different pluronic systems in water has been extensively studied.[44] It is also well-known that the preferred curvature of the self-assembly aggregates becomes smaller with increasing temperature. This effect can be used to fine-tune the result of a synthesis. The silica source is typically of the structure Si-(O-alkyl)$_4$, which after rapid hydrolysis produces an alcohol component in the reaction mixture. The longer the alkyl chain, the more the alcohol will partition into the micelles resulting in a change of the preferred curvature of the aggregate.[37,45] For our reference reaction, there was a transformation to a 2D hexagonal liquid crystalline structure. For other conditions, one can have ordered micellar or bicontinuous cubic liquid crystalline structures,[46] with profound effects on the properties of the resulting mesoporous material.[3,47,48]

We have chosen to describe the silica in terms of a branched polymer. By adopting the polymer perspective, it is possible to understand the interplay between colloidal stability and instability occurring throughout the synthesis. These time dependent changes between stability and instability are generic and should be occurring well beyond our specific reference reaction system. The first step involving an attraction between polymeric silica and a nonionic micelle induced by a weak hydrophobic interaction is well documented[34] (pages 29−31 in ref 34). Bridging flocculation by a polymer in low supply is commonly used in practice.[34] For a surface saturated with adsorbing polymer, one has the commonly occurring steric entropic stabilization. In this case, the repulsion is more effective the longer and more flexible the polymer chain and the better the solvent quality. It is highly relevant to realize that as the silica polymer changes through reactions c and d of Scheme 1, the flexibility is reduced and the solvent−monomer interaction becomes more unfavorable due to the increase in the number of O−Si−O bonds.

The ongoing silica polymerization causes the thermodynamic conditions to change continuously in the system. It is a crucial question to assess which molecular degrees of freedom can respond rapidly enough and which lag behind or are caught in metastable states. The properties of the system progress on a time scale of minutes, and a minute is a very long time in a molecular perspective. For amphiphile aggregates, a minute is often, but not always, longer than structural relaxation times. For a kinetically stabilized colloidal particle, a minute can be anything from very long to very short. The structural relaxation time that varies most dramatically during the synthesis is that of the silica system. For oligomers and short silica polymers the silica molecules respond rapidly to changes, but as the silica polymer becomes more branched and approaches percolation, resulting in a covalent network of mesoscopic dimensions, structural changes become more sluggish and one has finally a state of dynamical arrest. At this point, major structural changes are no longer possible. It is a crucial aspect of the design of the synthesis that the dynamical arrest sets in at a stage where one has established the desired structure in the system.

Above we have discussed the variation in synthesis in terms of the conditions at the start, $t = 0$. We conclude by pointing out that having a detailed description of the time evolution of the reaction provides the possibility of interfering at a chosen point in time and affecting the further progress by additions of reactants or inhibitors or by changing other reaction conditions. Because this strategy allows targeting of specific formation steps, it has clear advantages compared with changing the initial synthesis components. The latter could affect many, if not all, of the formation steps, such as the interaction between silica and micelles, floc formation, and aggregation, whereas the former is more discriminating and thereby more precise.

The synthesis of mesoporous silica discussed in this Account exemplifies a dimension of synthetic chemistry that has grown in importance in recent years. The challenge is not only to control the breaking and the making of covalent bonds but also to control the structure of the product on a mesoscopic scale. To meet this challenge, new elements need to be added to the toolbox of the synthetic chemist. Above we have demonstrated how it is essential to have a detailed knowledge of interactions on the colloidal scale in order to understand the mechanisms leading to the formation of mesoporous silica particles of given size and shape. We are convinced that this type of knowledge, taken in a broader context, is an essential ingredient when applying synthetic chemistry to the problems of nanotechnology. It is, with a long-term perspective, more efficient to choose the synthesis conditions based on an understanding of the molecular mechanisms rather than adopting an essential empirical approach. When combining chemical reactions with molecular self-assembly processes, the possibilities are simply too many.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

Biographies

Viveka Alfredsson, division of Physical Chemistry, Lund University, Sweden, graduated with a Master of Science degree from Lund University 1988 and received her Ph.D. in Inorganic Chemistry from the same university in 1994. In 1995−1996, she was a Post Doctoral fellow at UMIST in Manchester, U.K. After a short period in industry, she returned to Lund University in 1998. She was promoted to Professor in December 2011.

Håken Wennerström was born 30th August 1946 in Grycksbo, Sweden. He was a chemical engineer in 1970 at Lund University, earned a Ph.D. in Physical Chemistry at Lund University in 1974, was Professor in Physical Chemistry at Stockholm University in 1980 and Professor in Theoretical Physical Chemistry at Lund University in 1989. Since 2013, he has been Senior Professor Physical Chemistry at Lund University. Major research areas include NMR relaxation theory, amphiphile self-assembly and phase behavior, intermolecular interactions, and forces in colloidal systems. He is coauthor with D. F. Evans of the book *The Colloidal Domain, Where Physics, Chemistry, Biology and Technology Meet.* He was a member of the Nobel committee for chemistry 1997−2009 and its chairman 2006−2008.

■ ACKNOWLEDGMENTS

We are indebted to our former co-workers at Lund University; Katarina Flodström, Peter Linton, Juanfang Ruan, Tomas Kjellman, and Yana Znamenskaya, as well as our other coauthors. Financial support from the Swedish Research council, particularly via the Linneaus grant “Organizing Molecular Matter”, and the Swedish Foundation for Strategic Research is acknowledged.

■ REFERENCES

(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism. *Nature* **1992**, *359*, 710−712.

(2) Inagaki, S.; Fukushima, Y.; Kuroda, K. Synthesis of Highly Ordered Mesoporous Materials from a Layered Polysilicate. *J. Chem. Soc., Chem. Commun.* **1993**, *8*, 680−682.

(3) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. Nonionic Triblock and Star Diblock Copolymer and Oligomeric Surfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures. *J. Am. Chem. Soc.* **1998**, *120*, 6024−6036.

(4) Huo, Q. S.; Margolese, D. I.; Ciesla, U.; Feng, P. Y.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schuth, F.; Stucky, G. D. Generalized Synthesis of Periodic Surfactant Inorganic Composite-Materials. *Nature* **1994**, *368*, 317−321.

(5) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. Generalized Syntheses of Large-Pore Mesoporous Metal Oxides with Semicrystalline Frameworks. *Nature* **1998**, *396*, 152−155.

(6) Han, L.; Che, S. Anionic Surfactant Templated Mesoporous Silicas (AMSs). *Chem. Soc. Rev.* **2013**, *42*, 3740−3752.

(7) Soler-Illia, G. J. d. A. A.; Sanchez, C.; Lebeau, B.; Patarin, J. Chemical Strategies To Design Textured Materials: From Microporous and Mesoporous Oxides to Nanonetworks and Hierarchical Structures. *Chem. Rev.* **2002**, *102*, 4093−4138.

(8) Deng, Y.; Wei, J.; Sun, Z.; Zhao, D. Large-Pore Ordered Mesoporous Materials Templated from Non-Pluronic Amphiphilic Block Copolymers. *Chem. Soc. Rev.* **2013**, *42*, 4054−4070.

(9) Flodstrom, K.; Wennerstrom, H.; Alfredsson, V. Mechanism of Mesoporous Silica Formation. A Time-Resolved NMR and TEM Study of Silica-Block Copolymer Aggregation. *Langmuir* **2004**, *20*, 680−688.

(10) Flodstrom, K.; Teixeira, C. V.; Amenitsch, H.; Alfredsson, V.; Linden, M. In Situ Synchrotron Small-angle X-ray Scattering/X-ray Diffraction Study of the Formation of SBA-15 Mesoporous Silica. *Langmuir* **2004**, *20*, 4885−4891.

(11) Linton, P.; Alfredsson, V. Growth and Morphology of Mesoporous SBA-15 Particles. *Chem. Mater.* **2008**, *20*, 2878−2880.

(12) Linton, P.; Rennie, A. R.; Zackrisson, M.; Alfredsson, V. In Situ Observation of the Genesis of Mesoporous Silica SBA-15: Dynamics on Length Scales from 1 nm to 1 μm. *Langmuir* **2009**, *25*, 4685−4691.

(13) Teixeira, C. V.; Amenitsch, H.; Linton, P.; Linden, M.; Alfredsson, V. The Role Played by Salts in the Formation of SBA-15, an in Situ Small-Angle X-ray Scattering/Diffraction Study. *Langmuir* **2011**, *27*, 7121−7131.

(14) Ruan, J.; Kjellman, T.; Sakamoto, Y.; Alfredsson, V. Transient Colloidal Stability Controls the Particle Formation of SBA-15. *Langmuir* **2012**, *28*, 11567−11574.

(15) Kjellman, T.; Asahina, S.; Schmitt, J.; Impéror-Clerc, M.; Terasaki, O.; Alfredsson, V. Direct Observation of Plugs and Intrawall Pores in SBA-15 Using Low Voltage High Resolution SEM and the Influence of Solvent Properties on Plug-Formation. *Chem. Mater.* **2013**, *25*, 4105−4112.

(16) Sundblom, A.; Oliveira, C. L. P.; Palmqvist, A. E. C.; Pedersen, J. S. Modeling in Situ Small-Angle X-ray Scattering Measurements Following the Formation of Mesostructured Silica. *J. Phys. Chem. C* **2009**, *113*, 7706−7713.

(17) Sundblom, A.; Oliveira, C. L. P.; Pedersen, J. S.; Palmqvist, A. E. C. On the Formation Mechanism of Pluronic-Templated Mesostructured Silica. *J. Phys. Chem. C* **2010**, *114*, 3483−3492.

(18) Sundblom, A.; Palmqvist, A. E. C.; Holmberg, K. Study of the Pluronic-Silica Interaction in Synthesis of Mesoporous Silica under Mild Acidic Conditions. *Langmuir* **2010**, *26*, 1983−1990.

(19) Khodakov, A. Y.; Zholobenko, V. L.; Imperor-Clerc, M.; Durand, D. Characterisation of the Initial Stages of SBA-15 Synthesis by in Situ Time-Resolved Small-Angle X-ray Scattering. *J. Phys. Chem. B* **2005**, *109*, 22780−22790.

(20) Manet, S.; Schmitt, J.; Imperor-Clerc, M.; Zholobenko, V.; Durand, D.; Oliveira, C. L. P.; Pedersen, J. S.; Gervais, C.; Baccile, N.; Babonneau, F.; Grillo, I.; Meneau, F.; Rochas, C. Kinetics of the Formation of 2D-Hexagonal Silica Nanostructured Materials by Nonionic Block Copolymer Templating in Solution. *J. Phys. Chem. B* **2011**, *115*, 11330−11344.

(21) Impéror-Clerc, M.; Grillo, I.; Khodakov, A. Y.; Durand, D.; Zholobenko, V. L. New Insights into the Initial Steps of the Formation of SBA-15 Materials: An in-Situ Small Angle Neutron Scattering Investigation. *Chem. Commun.* **2007**, 834−836.

(22) Ruthstein, S.; Schmidt, J.; Kesselman, E.; Talmon, Y.; Goldfarb, D. Resolving Intermediate Solution Structures during the Formation of Mesoporous SBA-15. *J. Am. Chem. Soc.* **2006**, *128*, 3366−3374.

(23) Ruthstein, S.; Frydman, V.; Kababya, S.; Landau, M.; Goldfarb, D. Study of the Formation of Mesoporous Material SBA-15 by EPR Spectroscopy. *J. Phys. Chem. B* **2003**, *107*, 1739−1748.

(24) Kjellman, T.; Reichhardt, N.; Sakeye, M.; Smått, J.-H.; Lindén, M.; Alfredsson, V. Independent Fine-Tuning of the Intrawall Porosity and Primary Mesoporosity of SBA-15. *Chem. Mater.* **2013**, *25*, 1989−1997.

(25) Assink, R. A.; Kay, B. D. Sol-Gel Kinetics I. Functional Group Kinetics. *J. Non-Cryst. Solids* **1988**, *99*, 359−370.

(26) Iler, R. K. *The Chemistry of Silica*; Wiley-Interscience: New York, 1979.

(27) Linton, P.; Rennie, A. R.; Alfredsson, V. Evolution of Structure and Composition during the Synthesis of Mesoporous Silica SBA-15 Studied by Small-Angle Neutron Scattering. *Solid State Sci.* **2011**, *13*, 793−799.

(28) Zhang, K.; Lively, R. P.; Noel, J. D.; Dose, M. E.; McCool, B. A.; Chance, R. R.; Koros, W. J. Adsorption of Water and Ethanol in MFI-Type Zeolites. *Langmuir* **2012**, *28*, 8664−8673.

(29) Eskilsson, K.; Grant, L. M.; Hansson, P.; Tiberg, F. Self-Aggregation of Triblock Copolymers at the Solid Silica−Water Interface. *Langmuir* **1999**, *15*, 5150−5157.

(30) Tiberg, F.; Brinck, J.; Grant, L. Adsorption and Surface-Induced Self-Assembly of Surfactants at the Solid-Aqueous Interface. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 411−419.

(31) Grant, L. M.; Ederth, T.; Tiberg, F. Influence of Surface Hydrophobicity on the Layer Properties of Adsorbed Nonionic Surfactants. *Langmuir* **2000**, *16*, 2285−2291.

(32) Lindman, B.; Wennerstrom, H.; Forsen, S. Halide Ion Quadrupole Relaxation in Aqueous-Solutions Containing Organic Cations. *J. Phys. Chem.* **1992**, *96*, 5669−5670.

(33) Israelachvilli, J. *Intermolecular and Surface Forces*, 3rd ed.; Elsevier: London, 2006.

(34) Evans, D. F.; Wennerström, H. *The Colloidal Domain: Where Physics, Chemistry and Biology Meet*, 2nd ed.; Wiley-VCH: New York, Chichester, Weinheim, Brisbane, Singapore, Toronto, 1999.

(35) Roger, K.; Botet, R.; Cabane, B. Coalescence of Repelling Colloidal Droplets: A Route to Monodisperse Populations. *Langmuir* **2013**, *29*, 5689−5700.

(36) Jönsson, B.; Wennerstrom, H. Thermodynamics of Ionic Amphiphile—Water Systems. *J. Colloid Interface Sci.* **1981**, *80*, 482−496.

(37) Alexandridis, P.; Holmqvist, P.; Lindman, B. Poly(ethylene oxide)-Containing Amphiphilic Block Copolymers in Ternary Mixtures with Water and Organic Solvent: Effect of Copolymer and Solvent Type on Phase Behavior and Structure. *Colloids Surf., A* **1997**, *129*−*130*, 3−21.

(38) Wennerström, H. The Relation between Micelle Size and Shape and the Stability of Liquid Crystalline Phases in Surfactant Systems. *J. Colloid Interface Sci.* **1979**, *68*, 589−590.

(39) Linton, P.; Hernandez-Garrido, J. C.; Midgley, P. A.; Wennerstrom, H.; Alfredsson, V. Morphology of SBA-15-Directed by Association Processes and Surface Energies. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10973−10982.

(40) Götze, W. *Complex Dynamics of Glass Forming Liquids. A Mode-Coupling Theory*; Oxford University Press: Oxford, 2009.

(41) Kjellman, T.; Bodén, N.; Wennerström, H.; Edler, K. J.; Alfredsson, V. Orientation Specific Deposition of Mesoporous Particles. *APL Mater.* **2014**, *2*, No. 113305.

(42) Znamenskaya, Y.; Björklund, S.; Wennerström, H.; Kocherbitov, V.; Alfredsson, V. Effect of hydration on the properties of SBA-15 films studied by QCM-D. **2015**, manuscript in preparation.

(43) Kocherbitov, V.; Alfredsson, V. Assessment of Porosities of SBA-15 and MCM-41 Using Water Sorption Calorimetry. *Langmuir* **2011**, *27*, 3889−3897.

(44) Alexandridis, P. Poly(ethylene oxide)/poly(propylene oxide) block copolymer surfactants. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 478−489.

(45) Holmqvist, P.; Alexandridis, P.; Lindman, B. Phase Behavior and Structure of Ternary Amphiphilic Block Copolymer-Alkanol-Water

Systems: Comparison of Poly(ethylene oxide)/Poly(propylene oxide) to Poly(ethylene oxide)/Poly(tetrahydrofuran) Copolymers. *Langmuir* **1997**, *13*, 2471−2479.

(46) Flodstrom, K.; Wennerstrom, H.; Teixeira, C. V.; Amenitsch, H.; Linden, M.; Alfredsson, V. Time-Resolved in Situ Studies of the Formation of Cubic Mesoporous Silica Formed with Triblock Copolymers. *Langmuir* **2004**, *20*, 10311−10316.

(47) Flodstrom, K.; Alfredsson, V.; Kallrot, N. Formation of a New $Ia\overline{3}d$ Cubic Meso-Structured Silica via Triblock Copolymer-Assisted Synthesis. *J. Am. Chem. Soc.* **2003**, *125*, 4402−4403.

(48) Kim, T.-W.; Kleitz, F.; Paul, B.; Ryoo, R. MCM-48 Like Large Mesoporous Silicas with Tailored Pore Structure: Facile Synthesis Domain in a Ternary Triblock Copolymer−Butanol−Water System. *J. Am. Chem. Soc.* **2005**, *127*, 7601−7610.