Study of the Pluronic−Silica Interaction in Synthesis of Mesoporous Silica under Mild Acidic Conditions

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The interaction between silica and poly(ethylene oxide) (PEO) in water may appear trivial and it is generally stated that hydrogen bonding is responsible for the attraction. However, a literature search shows that there is not a consensus with respect to the mechanism behind the attractive interaction. Several papers claim that only hydrogen bonding is not sufficient to explain the binding. The silica−PEO interaction is interesting from an academic perspective and it is also exploited in the preparation of mesoporous silica, a material of considerable current interest. This study concerns the very early stage of synthesis of mesoporous silica under mild acidic conditions, pH 2−5, and the aim is to shed light on the interaction between silica and the PEO-containing structure directing agent. The synthesis comprises two steps. An organic silica source, tetraethylorthosilicate (TEOS), is first hydrolyzed and Pluronic P123, a poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) block copolymer, is subsequently added at different time periods following the hydrolysis of TEOS. It is shown that the interaction between the silica and the Pluronic is dependent both on the temperature and on the time between onset of TEOS hydrolysis and addition of the copolymer. The results show that the interaction is mainly driven by entropy. The effect of the synthesis temperature and of the time between hydrolysis and addition of the copolymer on the final material is also studied. The material with the highest degree of mesoorder was obtained when the reaction was performed at 20 °C and the copolymer was added 40 h after the start of TEOS hydrolysis. It is claimed that the reason for the good ordering of the silica is that whereas particle formation under these conditions is fast, the rate of silica condensation is relatively low.

Introduction

It is well-known that there is an attractive interaction between silica and poly(ethylene oxide) (PEO) or nonionic surfactants containing PEO.[1,2] For instance, alcohol ethoxylates (C_nEO_m) adsorb strongly at silica surfaces displaying a critical surface aggregation concentration about 1 order of magnitude lower than the critical micelle concentration (CMC) of the surfactant.[3,4] The fact that the silanol groups have been shown to be essential for the adsorption has led to the conclusion that hydrogen bonding between the ether oxygens in the PEO and the silanol groups is responsible for the adsorption.[2,5,6] It has also been suggested that the adsorption is favored by hydrophobic regions between the adsorption sites[2] and other authors are also of the opinion that hydrogen bonding alone cannot explain this interaction. They claim that hydrogen bonding between solutes and between a solute and a surface in aqueous solution will never be important because hydrogen bonding to water molecules will always dominate. Instead, it has been postulated that hydrophobic interaction between PEO and silica may be important.[7] The situation is far from clear and further studies are obviously needed.

Pluronics, the BASF trade name of nonionic amphiphiles composed of PEO and poly(propylene oxide) (PPO) arranged as a triblock copolymer (PEO−PPO−PEO), may in dilute water solution self-assemble into micelles and the CMC will depend on concentration and temperature. The temperature at which the first micelles are formed is called the critical micellar temperature (CMT) and is dependent on the concentration of the block copolymer. Since both the PEO and the PPO segments display a reverse solubility versus temperature relationship, that is, they become less water-soluble at higher temperature, the solution behavior of Pluronics is much more temperature dependent than that of normal nonionic surfactants of the C_nEO_m type. For instance, a change in temperature of 20° may cause a change in CMC for a Pluronic of 3 orders of magnitude.[8] For a C_nEO_m surfactant such a change in temperature only leads to a small change in CMC.[3] The micelle shape is governed by the ratio of PEO to PPO, in accordance with the critical packing parameter concept (CPP).[9] The micelles grow in size with increasing temperature. Pluronics also have a so-called cloud point, where a macroscopic phase separation occurs. The temperatures at which all these changes occur are also known to be affected by additives, such as inorganic salts and hydrophobic substances.[10−13]

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Water solutions of Pluronics have been studied extensively and there are several reviews summarizing the findings.[14−16]

Both the hydrophilic PEO and the hydrophobic PPO segments are highly polydisperse with a Poisson distribution of the homologues. The PEO−PPO−PEO block copolymer, consisting of three polydisperse segments, will therefore comprise a very broad mixture of polymers with respect to hydrophilic−lipophilic balance.[17,18] Molecules with a long PPO segment and short PEO segments will be hydrophobic and those with the reverse composition will be hydrophilic. This means that the solution properties, and specifically the aggregation behavior, of a PEO−PPO−PEO block copolymer will be more complex than for C_nEO_m surfactants in which the hydrophobic part, typically the alkyl chain of a fatty alcohol ethoxylate, is not so broad in homologue distribution. Both experimental results[17−23] and theoretical predictions[19,20] show that the first aggregates formed on raising the temperature of a solution of a Pluronic in water consist of molecules with a very high PPO to PEO ratio. A recent study in which pulsed field gradient nuclear magnetic resonance (PFG NMR) was used provided a semiquantitative description of the initial aggregation process.[21]

The fact that the first aggregates that form in solution are composed of block copolymers with longer PPO and shorter PEO segments than the average segment lengths of the Pluronic used will have consequences for the size and shape of these aggregates. Such copolymers will have a higher value of the CPP, which means that the micelles will be larger than those formed at higher temperatures, which are composed of an average of all the individual block copolymers. For some Pluronics the first aggregates formed may be vesicles, not micelles.

In this paper, the interaction between silica and PEO is investigated using Pluronic as PEO source. The interaction between silica and Pluronic is known to govern the synthesis of mesoporous silica and the mechanisms involved have been extensively studied since the first publications in 1998.[5,22] Several reports have shown that the synthesis temperature is very important and that it affects both the order and morphology of the final material.[23−28] Other synthesis parameters, such as pH, type of Pluronic, silica source, and concentration of the Pluronic and the silica have also been shown to influence the structure of the mesoporous material formed.[29] For instance, Kipkemboi et al. showed that provided the PPO block is approximately constant the length of the PEO blocks of the Pluronic is decisive of the type of geometry generated. They also found the cloud point of the

surfactant to be the limiting temperature for obtaining ordered material.[26]

In earlier reports, two similar syntheses of mesostructured silica have been presented.[30,31] The main difference between them is the silica sources used, a sodium silicate solution and tetraethylorthosilicate (TEOS), respectively. It was shown that the silica source has a strong influence on the rate of material formation and also on the structure of the final material. Most reported syntheses of mesostructured silica are based on alkoxide precursors, but a number of studies based on sodium silicate solutions have also been reported as summarized in a recent review.[32] The reason for the effect obtained when changing the silica source is the topic of a separate study, where the synthesis based on TEOS is used to illustrate the effect from changing silica source by varying the degree of condensation of the silica.[33] The synthesis is comprised of two steps. The TEOS is first hydrolyzed and the Pluronic is subsequently added at different times after the hydrolysis. The variation of the time between the hydrolysis and the addition of Pluronic is used to vary the degree of condensation of the silica source. An observation made in that study was that a clear solution of a mixture of silica and Pluronic may become turbid both on cooling and on heating from room temperature and that this process is reversible to a certain extent. There were also indications that this behavior influenced the outcome of the synthesis of mesostructured silica. The current work is a more in-depth study of the same synthesis and the aim is to gain insight into the mechanism of formation of the ordered mesoporous material with particular focus on the initial interaction between silica and Pluronic. In this study UV/vis spectroscopy and dynamic light scattering (DLS) are the main tools used. UV/vis spectroscopy was used to measure the turbidity of the solutions while DLS was used to determine average aggregate size and the two methods gave complementary results. A series of syntheses were also performed in order to assess the effect of temperature and aging of the silica source on the structure of the final material.

Experimental Section

The experiments in this work are divided in two parts. The first part concerns DLS and turbidity measurements focused on the initial stage of the synthesis of mesostructured silica. The second part is dedicated to syntheses of mesostructured silica. All experiments started with hydrolysis of TEOS (Aldrich, 98%) in Milli-Q water with pH set to 2.8 by a small addition of HCl and with a TEOS amount corresponding to a SiO_2 concentration of 3 wt % in the final solution. The solutions were stirred for 2 h and during this time they all changed from turbid to clear as a result of the hydrolysis of TEOS. The solutions were then stored under static conditions in room temperature before mixing with a water (Milli-Q) solution of the nonionic block copolymer Pluronic P123 (Aldrich, $EO_{20}PO_{70}EO_{20}$, where EO and PO refer to the ethylene oxide and propylene oxide repeat units, respectively) forming reaction solutions with the composition 1:2:100 (SiO_2/P123/H_2O) based on weight.

Dynamic Light Scattering and Turbidity Measurements. For the study using DLS and turbidity, both the prehydrolyzed TEOS solution and the Pluronic solution were cooled to 5 °C immediately before mixing the reactants. The reaction solutions were transferred into two plastic cuvettes, which were kept cool until the start of the DLS and absorbance measurements.

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Both analyses were initiated within 10 min after the mixing of the reactants. The time between the start of the hydrolysis of TEOS and the addition of the Pluronic solution was varied between 3 and 52 h. However, DLS measurements were only possible up to a storage time of 48 h. A reference sample of Pluronic P123 under the same conditions as used in the synthesis but without silica was also analyzed.

Synthesis of Mesostructured Silica. For the synthesis of mesostructured silica, the time between start of hydrolysis and the addition of the Pluronic was varied between 19, 28, and 40 h. The samples prepared after 19 h were mixed at 20 °C and then cooled or heated to a reaction temperature of 15, 25, or 35 °C. The samples synthesized after 28 h were prepared in the same way but using reaction temperatures of 15, 20, and 65 °C. For the samples prepared after 40 h, at 3, 20, and 25 °C, respectively the starting solutions were first heated or cooled to the reaction temperatures used before mixing. This procedure was used because the formation of the material at 20 °C was rapid. All samples were stored at the reaction temperature for at least 24 h followed by storage for 5 days at room temperature before the obtained products were separated by filtration and washed with Milli-Q water. The surfactant was removed by calcination at 500 °C for 4 h. The samples are named XX h-YY °C, where XX is the time between start of hydrolysis and addition of Pluronic and YY is the reaction temperature.

Analytical Methods. Turbidity of the reaction solutions was studied by measuring the absorbance as a function of temperature using a UV/vis spectrometer (GBC UV/vis 920). The measurements started at 5 °C and the temperature was then continually increased to 65 °C during a period of 30 min. The temperature was measured with a probe placed in a reference cell. The absorbance at the wavelength 700 nm was measured every 10th second during the temperature increase. This wavelength was chosen since the molecular absorbance of the system is low at this wavelength. This facilitates an accurate measurement of the amount of scattered light, that is, of the turbidity of the solution. Thus, the absorbance is used as a measurement of the turbidity, or scattering, of the sample. The results obtained up to a storage time of 28 h have been normalized to the lowest value obtained in each measurement. This was done since the plastic cuvettes used have an absorbance that varies slightly between different cuvettes. For the measurements carried out from 32 h and onward this small correction was considered insignificant.

DLS measurements were performed using a Zetasizer nano-ZS from Malvern Instruments. The collected correlation functions were analyzed using cumulant analysis[34] and CONTIN.[35] The two methods gave similar results and the reported values are z-average diameter obtained from calculations based on the first cumulant. For the cumulant analysis, the default setting with a cutoff level of 10% was used. This standard procedure did not give reliable results for all the measurements, indicated by high residuals for the cumulant fit. This occurred when the size of the aggregates increased and for the measurements close to the clouding of the system. The settings in the cumulant analysis were then changed. This comprised a systematic reduction of the amount of data used in the analysis by increasing the cutoff level. This procedure enables a study focused on the initial slope of the correlation function and lowered the influence from the relatively large aggregates, that may have formed in the solution, to the calculated average size. The residuals from the cumulant analysis were used to determine if the obtained z-average value was reliable or if a further reduction of the data used was necessary. The CONTIN analysis was also used to confirm the results. At high temperatures and for samples mixed after a long storage time, the aggregates studied were probably not always spherical. However, the calculation of the z-average diameter assumes a spherical shape of the aggregates. The values reported should therefore

mainly be used for comparing different samples and showing trends of changes, not as measures of absolute size. Measurements were carried out at selected temperatures between 5 and 70 °C, starting with 5 °C. The duration of a measurement series from 5 to 70 °C was approximately 1 h. The temperatures used are presented in Figure 2 and in the Results.

Small angle X-ray scattering (SAXS) measurements of the prepared material were performed using a Kratky camera (Hecus X-ray systems, Graz, Austria) with a position-sensitive detector (MBraun, Garching, Germany) containing 1024 channels. An X-ray generator operating at 50 kV and 40 mA (Philips, PW 1830/40, The Netherlands) was used to produce CuK_α radiation ($\lambda = 0.1542$ nm). The sample to detector distance was 282 mm and the exposure time was 30 min per sample.

The N_2 adsorption and desorption isotherms of the calcined powder products were collected at -196 °C using a Micromeritics Tristar. Prior to the measurements, the samples were dried in vacuum at 200 °C for 2 h. The pore size distribution of the materials was calculated using the adsorption isotherm and the Barrett, Joyner, Halenda (BJH) method.[36]

Transmission electron microscope (TEM) images were obtained with a JEOL JEM-1200 EX II TEM operated at 120 kV. The samples were prepared by dispersing a small amount of calcined product or reaction solution in ethanol and placing drops of the solution on a holey carbon-coated copper grid, followed by evaporation.

Results

The results are divided in two parts. The first part covers DLS and UV/vis experiments to study the silica—Pluronic interaction while the second part is focused on the materials obtained from the syntheses.

The Silica—Pluronic Interaction. The turbidity results obtained from the absorbance measurements are presented in Figure 1.

In Figure 1A, it can be seen that all the solutions behave in a similar way. Below 10 °C the absorbance is very low. As the temperature increases, the absorbance passes through a maximum at 15—18 °C. It then decreases and reaches a new level where the absorption is low but still higher than what is observed below 10 °C. At elevated temperature, there is a sudden strong increase in absorption. This increase appears at ca. 53 °C for the reference sample without silica and for the Pluronic—silica samples with short time between start of hydrolysis of TEOS and addition of Pluronic. For the samples with longer time between start of hydrolysis and addition of Pluronic, the increase in absorption starts at lower temperatures. In Figure 1B, this decrease of the temperature for the increased absorption is continued. Here it can also be seen that the increase is very strong from 24 h and onward, indicating a phase separation or clouding in the solution. At longer hydrolysis times, also the peak in the 15—18 °C range increases both in height and width and in the last measurement the sample is more or less turbid over the entire temperature range.

When analyzing these results it is important to remember that the molecular absorbance of the sample is not changed with temperature. The changes observed here are instead the result of changes in the amount of light scattered by the sample. In the discussion of the results, the changes in absorption will therefore be referred to as changes in turbidity. It is also important to remember that the intensity of the scattered light increases strongly with increasing size of the aggregates. This means that the size of the scattering object will have a much stronger impact on the intensity than the number of objects.

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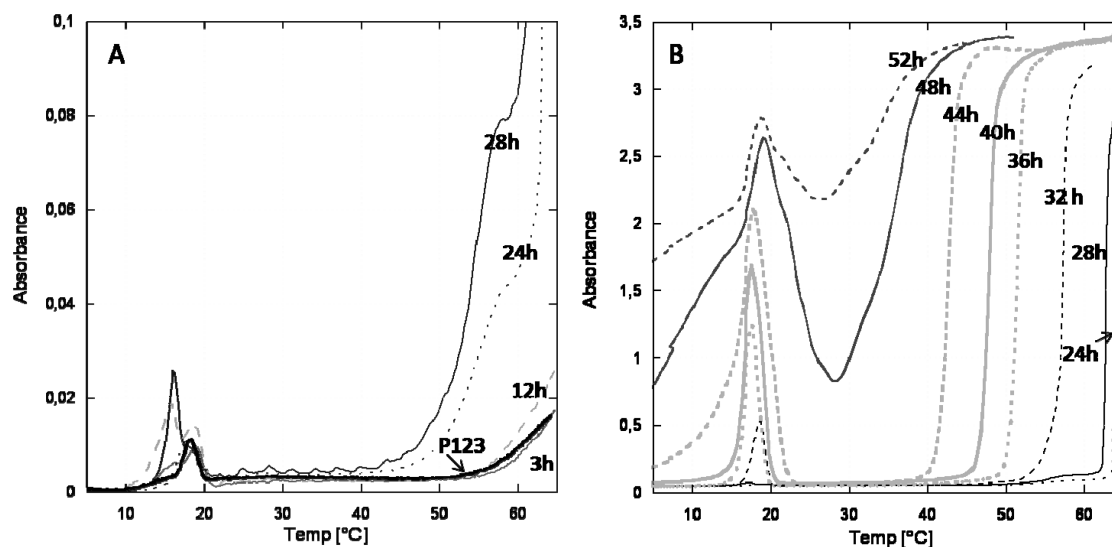
Figure 1. Turbidity as a function of temperature of mixtures of prehydrolyzed TEOS and P123 as detected by absorbance measurements at 700 nm. The labels represent time in hours between start of hydrolysis and addition of P123. Panel A shows the result for P123 (the thick line), which is a reference system without silica, and for samples 3−28 h. Panel B shows the results for samples 24−52 h. Note that different scales are used for the absorbance in the two figures.
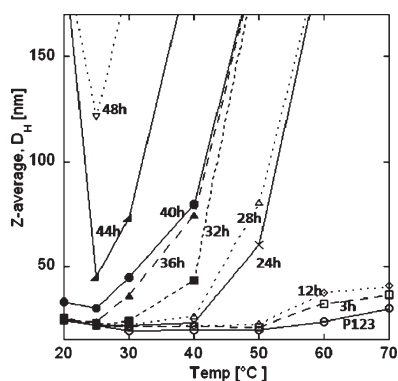
Figure 2. DLS results of measurements of mixtures of prehydro-lyzed TEOS and P123 with labels representing time in hours between start of hydrolysis and addition of P123. Values presented are z-averages (in nm) from cumulant analysis. The lines are only added to guide the eye. The strong increase in z-average with increasing temperature, seen for the 24−48 h samples, indicates clouding.

Experiments were also made to cool the samples after clouding (data not shown). It was found that when a sample was cooled within a few minutes from the onset of clouding, the solution became clear again. The same type of reversibility of aggregate formation on heating−cooling has been observed before in a study related to synthesis of SBA-15.[23]

The same reaction solutions that were studied using UV/vis absorbance were also analyzed by DLS. The results obtained are summarized in Figure 2.

The results from the DLS study correlate very well with the absorbance measurements presented in Figure 1. It can be seen that the size of the aggregates increases by the addition of the silica and by increasing the temperature. The aggregates also grow as the time between hydrolysis of TEOS and addition of Pluronic is increased. The clouding of the system, observed from 24 h and onward, is indicated by a strong increase in size. After this point it was not possible to determine an average size of the aggregates.

DLS measurements were also performed at 5, 10, 15, and 17.5 °C. At 5 and 10 °C the solutions mainly contain unimers of the Pluronic and the scattering was too low to give reliable estimates of average size. At 15 and 17.5 °C the samples scattered relatively strongly but also for these measurements it was not possible to obtain a reliable result from the cumulant analysis. The reason for this is probably that in this temperature range the dispersions are very polydisperse. The correlation functions for these measurements, not presented here, indicate presence of large aggregates. This correlates well with the turbidity measurements, which, as discussed above, showed an increase in absorbance in the range 15−18 °C. A sample prepared without P123, containing silica added 48 h after the hydrolysis, was also studied using DLS, results not shown. The scattering from this sample was very low indicating that the above-mentioned results are not due to only silica present in the solutions.

Synthesis of Mesoporous Silica. The second part of the Results section concerns the products obtained using different temperatures and different times between start of hydrolysis of TEOS and addition of the Pluronic. All products were calcined at 500 °C for 4 h before being analyzed. The results obtained from calculating the pore volume versus pore diameter from N_2-sorption, using the BJH method, are shown in Figure 3.

These results show that both the reaction temperature and the time between hydrolysis of TEOS and addition of the Pluronic are decisive of the porosity of the material. For the 19 h samples, it is clear that the synthesis performed at 15 °C gives a material with a very narrow pore size distribution while the materials prepared at 25 and 35 °C have a broader distribution of pore sizes. It is interesting to note that 15 °C is in the region where formation of aggregates was observed by both absorption measurements and DLS, as discussed above. Increasing the time to 28 h yields a narrow pore size distribution at both 15 and 20 °C but the sample prepared at 65 °C gave a broad distribution. The 40 h series exhibits a narrow pore size distribution for all the samples with the one prepared at 20 °C being the most narrow.

The SAXS results, shown in Figure 4, confirm the gas adsorp-tion results. The 40 h-20 °C sample seems to be the most ordered material, showing some indications of higher order peaks. It can
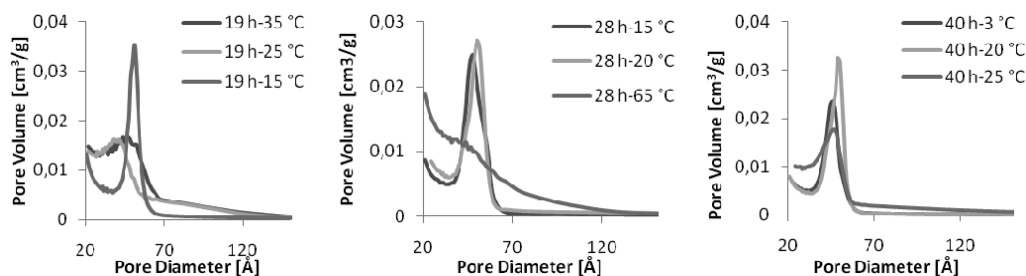
Figure 3. Pore volume vs pore diameter from the N_2-adsorption isotherm, obtained using the BJH method, of samples prepared using 19, 28, or 40 h of time between onset of hydrolysis and mixing with P123 and using different synthesis temperatures.
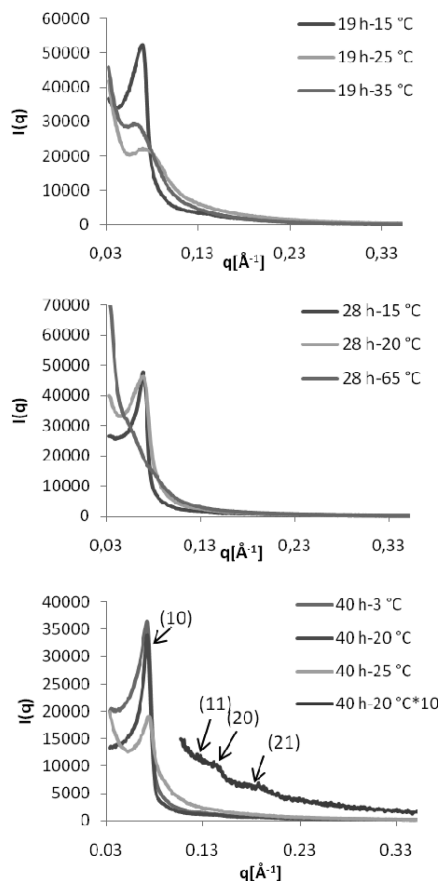
Figure 4. SAXS spectra of calcined samples prepared using 19, 28, or 40 h of time between onset of TEOS hydrolysis and addition of P123 and using different synthesis temperatures. The extra curve in the figure related to the 40 h experiments is the curve for the 40 h-25 °C sample multiplied by 10, showing indications of Bragg peaks (11), (20), and (21). The (10)-label indicates the position of the first Bragg peak.

also be noticed that a small increase of the temperature to 25 °C (the 40 h-25 °C sample) causes a substantial reduction of the order while a lowering of the temperature to 3 °C (the 40 h-3 °C sample) has a smaller influence on the order. The general trend of improved order with increasing time between onset of TEOS hydrolysis and addition of the Pluronic within the time span studied here is also shown by comparing the 19 h-25 °C and the 40 h-25 °C samples, as well as the 28 h-20 °C and the 40 h-20 °C samples. It can be concluded that the best ordered material in this study is obtained when a synthesis temperature between 15 and 20 °C is used.

The results from the SAXS and N_2-sorption measurements were largely confirmed by TEM analyses, shown in Figure 5. The degree of order was clearly influenced by both the reaction temperature and the time between hydrolysis of TEOS and addition of the Pluronic. The 40 h-3 °C, 40 h-20 °C, and 28 h-15 °C samples were well ordered while the 19 h-15 °C, 28 h-20 °C, and 40 h-25 °C samples were only partly ordered. The rest of the samples lacked mesoorder. From the TEM analyses and the SAXS spectra it is difficult to unambiguously distinguish between *p6m* and *Im3m* symmetries for some of the samples. Earlier studies on the same synthesis, performed at room temperature, show a hexagonal symmetry[31,33] and most results presented here also support this structure. However, there might also be influences of the cubic structure in some samples. More detailed structural studies are needed to unambiguously determine the structures obtained and whether or not the structure may change with temperature in this temperature range.

Discussion

The discussion of the results is divided into two parts. The first part deals primarily with the results from the turbidity and DLS measurements. Here the reference system based on only Pluronic is compared to the systems where Pluronic has been added to a solution of hydrolyzed TEOS. Special attention is paid to the effect of the time between onset of TEOS hydrolysis and addition of Pluronic on the aggregation. The second part concerns the formation of the mesostructured material.

Formation of Aggregates in Solution. The results from the absorption measurements by UV/vis and from the DLS correlate very well, and they obviously describe a rather complicated system. To reduce the complexity the reference system without silica is considered first. Below 15 °C, both the turbidity and the scattering are low, indicating that the Pluronic is only present as unimers. Pluronic is a PEO—PPO—PEO copolymer and it is well-known that as the temperature is increased the solubility of both the PPO and the PEO blocks is decreased. Pure PPO is however much less soluble in water than pure PEO. The low solubility of PPO induces formation of aggregates in the solution observed as an increase of scattering around 15 °C. The DLS measurement indicates formation of relatively large aggregates. This is further supported by the absorption measurements. The Pluronic is, as mentioned in the Introduction, highly polydisperse, composed of unimers covering a very broad span on the hydrophilicity—hydrophobicity scale. The aggregates formed around 15 °C are likely to be composed of the most hydrophobic unimers, that is, those with the highest PPO/PEO ratio. The PPO/PEO ratio also affects the structure of the aggregates formed, as can be explained by the CPP concept.[9] An increased ratio of the hydrophobic to the hydrophilic moiety in a surfactant means a higher CPP value, which, in turn, favors formation of larger aggregates.
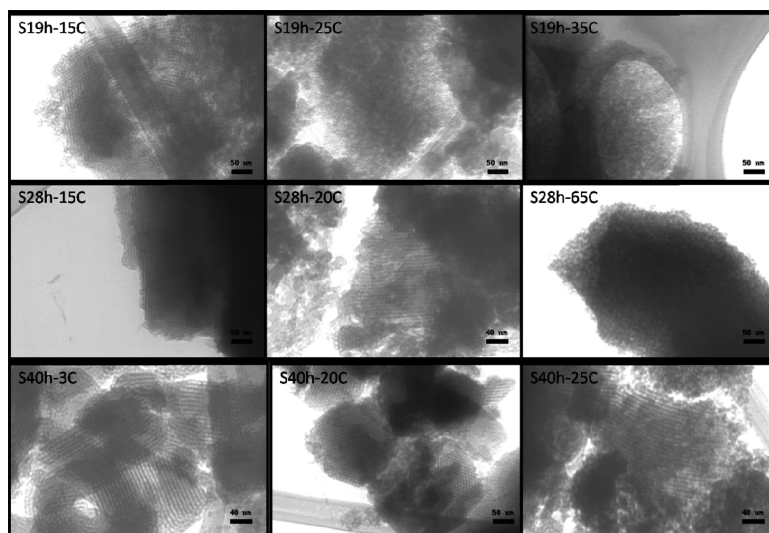
Figure 5. TEM micrographs of calcined samples using 19, 28, or 40 h of time between onset of TEOS hydrolysis and addition of P123 and using different synthesis temperatures.

Further increase of the temperature leads to decreased scattering of the solution. This can be explained by a more general self-assembly of the block copolymer in solution, which will lead to formation of ordinary spherical micelles. The unimers with high content of PPO will not form separate micelles but be incorporated into aggregates composed of unimers with widely varying PPO/PEO ratios. Technical nonionic surfactants, which are always composed of unimers with widely different hydrophilicity—hydrophobicity character, generally form mixed micelles rather than coexisting populations of micelles with different CPP values.[37] The large aggregates formed around 15 °C will therefore disintegrate, which is manifested by the decrease in the absorbance peak at around 18 °C. Since the aggregates formed above this temperature are much smaller, the total scattering of the solution will be less, as seen in the adsorption measurement. Our observations are in accordance with other studies of formation of aggregates in Pluronic systems[38–43] and other authors have also reported a CMT for 1−2.5% Pluronic P123 solutions in the 14−17 °C range.[8,44]

As the temperature is further increased the turbidity remains constant up to 53 °C, indicating that the micelle size does not change in this temperature interval. At higher temperature, the turbidity goes up. The DLS measurements of the P123 reference solution in this temperature range indicate that the micelles start to grow around 60 °C, which correlates well with the increase of the turbidity. This probably reflects a sphere-to-rod transition.[44,45] The increase in temperature causes a reduction of the amount of water in the PEO corona of the micelle, leading to a reduction of the headgroup area. This means an increase in the CPP value, which gives an increase in the number of surfactants per aggregate, and, thus, aggregate growth. A favorable overlap between the headgroup regions of micelles provides a mechanism for an attractive micelle—micelle interaction that at even higher temperatures triggers clouding.[46]

We now turn our attention to the Pluronic—silica system and we are, in particular, interested in how the presence of the silica changes the aggregation behavior. The temperatures where the sphere-to-rod transition and the cloud point occur are lowered by the presence of the silica. It can also be observed that increasing the time between onset of TEOS hydrolysis and addition of the Pluronic increases this effect. It is well-known that additives, such as salts, can lower both the sphere-to-rod transition temperature and the cloud point of Pluronics.[10,11] The added salt is believed to reduce the cloud point due to repulsion between the electrolytes and the PEO segments, creating a salt-deficient zone. This zone gives rise to an attractive component in the interaction between PEO segments, facilitating clouding.[10,47] This mechanism cannot be used to explain the observations presented here, however. It is well-known that PEO-containing polymers[2] and surfactants[1] adsorb on silica surfaces. Thus, the silica—PEO interaction is attractive and not repulsive as in the case of ordinary salts. Added silica will instead be concentrated around the PEO in the corona of the micelles. This will reduce the amount of water solvating the PEO and, as a consequence, lower the headgroup repulsion and size. A reduction of the headgroup will lead to a growth of the micelles, as discussed above to explain the effect of a temperature increase. Shrinkage of the headgroup will also lead to a lower temperature for the sphere-to-rod transition and to an increased attraction between micelles causing a decrease in the clouding temperature.

But how can the pronounced effect of the time between onset of hydrolysis of TEOS and addition of Pluronic on the turbidity be explained? Hydrolysis of TEOS at the pH used takes about 2 h and is indicated by a change from a turbid to a clear solution, then follows a spontaneous condensation of the hydrolyzed silica species. At pH 2.8 and a concentration of 3%, as used here,

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this reaction is relatively slow. During the time-span studied in this work (from 3 to 52 h), the average silica species in the solution will have changed from predominantly monomeric to fairly large oligomers.[48,49] Since the degree of condensation, or the average molar weight of the silica in solution, is the sole variable in the process, it can be concluded that this affects the silica–Pluronic interaction to a large extent. It can clearly be seen that the temperature for the sphere-to-rod transition, as well as the cloud point, decreases with an increase of the degree of silica condensation.

The effect of the size of the silica species on the interaction with PEO has been discussed in studies on how the sol–gel process is influenced by PEO-containing species. It was concluded that the interaction between PEO and silica arises only when the silica oligomers have reached a certain size.[50–52] The authors of those studies explain the results in the following way: When only small silica oligomers exist in the solution it is unfavorable for the PEO to destroy its hydrated structure in order to form only a few hydrogen bonds with silica. As the average molar weight of the silica oligomers increases a more continuous array of silanol sites becomes available, to which a greater fraction of the PEO can form hydrogen bonds.[50]

The influence of the degree of polymerization can be understood if the change in Gibbs free energy, expressed as $\Delta G = \Delta H - T\Delta S$, is considered. ΔH, describing the change of enthalpy, is affected by the bonds broken and formed. As mentioned earlier this can be expected to be of minor importance since both the number and the strength of the hydrogen bonds formed and broken are relatively equal. It will probably not be very dependent on the degree of polymerization of the silica. ΔS, describing the change of entropy of the system, is on the other hand to a large extent affected by the degree of polymerization of the silica. When the silica and the Pluronic aggregate, they will interact by hydrogen bonds. Before aggregation both the silica and the Pluronic are strongly hydrated with hydrogen-bonded water. During the aggregation these water molecules will be released, leaving a bonded stage with low entropy and entering a free state in the solution with high entropy. The higher the silica molecular weight, the more water molecules will be released, generating a greater change in entropy. By this rationale there will be an increasing attraction between the silica and the PEO as the degree of silica polymerization increases. The silica–Pluronic interaction can be seen as an example of an oligomer–polymer interaction, where the silica is the oligomer and the PEO is the polymer. These types of interactions are known to be very much affected by the number of interaction sites, which may be transformed into chain length of the oligomer. A critical chain length, at which the interaction strongly increases is often observed.[53]

Another interesting observation is that the temperature for the phase separation decreases with increasing time between hydrolysis and the addition of the Pluronic. The most straightforward way of explaining this is to use the conclusions made earlier; an increase in temperature induces clouding of the Pluronic, silica interacting with the Pluronic lowers the clouding temperature, and the storage time controls the amount of silica interacting with the Pluronic. A long storage time will then result in a high amount

of silica interacting with the Pluronic and therefore give a low cloud point. However, the amount of silica interacting with the Pluronic will also be influenced by the temperature since the Gibbs free energy of the system will change with temperature. The relative importance of the entropy will increase with increasing temperature. An increased amount of silica interacting with the Pluronic can thus be expected as the temperature is increased. This contributes to the temperature dependence of the observed system.

The large aggregates formed from solutions of Pluronic at low temperatures (15–18 °C in this work) are also affected by addition of silica and it is likely that the mechanism behind this influence is the same as for the aggregation at higher temperature. The change in aggregate size with increasing time between the start of TEOS hydrolysis and addition of the Pluronic could only be indirectly monitored by the change in turbidity as measured by absorption. The results show an increased turbidity, indicating that the aggregates grow either by size or number (or both) as the storage time is increased. It can also be observed that the temperature range at which the aggregation is observed is increased with a longer storage time. The presence of aggregates larger than normal micelles at low temperatures in the reference Pluronic solution has already been addressed. It was concluded that these aggregates were formed by the most hydrophobic fraction of the block copolymer. The fact that the aggregates are large, with a high CPP value, implies that only a small reduction of the headgroup repulsion may induce further aggregation. The absorption measurements show that added silica will indeed provide a substantial increase in the size also of these aggregates provided the silica solution has been allowed enough time between onset of the hydrolysis and addition of the Pluronic.

Formation of Mesostructured Materials. The second part of this study concerns the effects of the synthesis temperature and of the time between onset of TEOS hydrolysis and addition of Pluronic on the final material. It was found that ordered material is formed between 3 and 25 °C and that the most well-ordered material is obtained at 15–20 °C. The order also seems to be improved as the hydrolysis time is increased within the limits of the range of time studied here. The high degree of order at 15–20 °C is interesting since this is the temperature at which aggregates are formed in the reference solution without silica as well as in mixtures of Pluronic and condensed silica, as presented above. There is apparently a connection between aggregation in solution and degree of ordering of the mesoporous solid material.

A proposed formation mechanism can shortly be described as follows. First the silica oligomer and the PEO interact, leading to growth of the micellar aggregates and eventually to a micelle–micelle attraction, which induces the second step, the phase separation. The micellar aggregates form larger particles, rich in Pluronic and silica, dispersed in water. The third step involves formation of an ordered structure in these particles. This mechanism, which resembles many of the mechanisms presented in earlier studies,[7,23,28,54–60] is described in more detail in a separate

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study.[33] To obtain a well-ordered material, the rates of these three steps are crucial. The first and second step must be fast relative to the condensation of the silica in the corona of the micelles. Since the concentration of silica can be expected to be higher in the corona than in the bulk solution, it is reasonable to assume that the rate of condensation of the silica oligomers is higher in the corona. As the degree of silica polymerization increases, the material gradually solidifies. If the silica that has aggregated in the corona condenses too much and forms a solid structure before the particles are formed the structure of the material will be disordered because the order is obtained in the third step. This is in agreement with previously reported work on both mesoporous films[61] and precipitation-based methods.[59]

This proposed mechanism suggests that the optimal condition for obtaining an ordered material is a high rate of particle formation and a slow rate of silica condensation. The rate of particle formation will here be controlled by the temperature and by the time between start of the hydrolysis of the TEOS and addition of the Pluronic while the rate of the condensation reaction will increase with increasing temperature. The mechanism is supported by the results presented in this paper, as can be seen by comparing the degree of order of materials prepared under different reaction conditions.

Fast particle formation is expected for the syntheses 19 h-15 °C, 28 h-15 °C, 28 h-20 °C, 28 h-65 °C, and 40 h-20 °C because these are performed in a temperature range were aggregation, and thus particle formation, occurs quickly. Even if the first aggregates formed in the low temperature region, 15−20 °C, contain just a small fraction of the surfactant with a high PPO/PEO ratio, as discussed earlier, these aggregates will act as nuclei for further particle formation. Since the critical association concentration is lower than the CMC in systems with attractive interactions,[62] the surfactants with a lower PPO/PEO ratio, which in absence of silica would have been single unimers in the solution, will associate with the aggregates and induce further growth. The PEO segments of the surfactants will go to the surface of the aggregates and the silica will preferentially interact with these exposed and highly hydrated moieties. This leads to a situation where the particle formation proceeds relatively fast while the rate of the condensation reaction is comparatively low, due to the low temperature and pH. According to the proposed mechanism this is good conditions for obtaining ordered material and the best ordered material obtained in this study, 40 h-20 °C, is also formed under these conditions. Since a longer time between hydrolysis and mixing increases the rate of particle formation, the degree of order should improve when going from 19 h-15 °C to 28 h-15 °C and from 28 h-20 °C to 40 h-20 °C. This is consistent with the results presented earlier. The 28 h-65 °C sample illustrates that a low rate of silica condensation is needed in order to obtain a highly ordered material. In this synthesis, both the rate of particle formation and the rate of condensation are high and the material obtained is disordered.

For syntheses 19 h-25 °C, 19 h-35 °C, 40 h-3 °C, and 40 h-25 °C, the formation of particles is relatively slow. In accordance with the hypothesis, syntheses 19 h-25 °C and 19 h-35 °C result in disordered products. Increasing the time between hydrolysis and mixing, and thus increasing the rate of particle formation, seems to improve the order. This is illustrated by synthesis 40 h-25 °C, as compared to 19 h-25 °C. Synthesis 40 h-3 °C, resulting in a well-ordered material, illustrates that a relatively slow particle formation rate can be compensated for by a slow condensation rate, due to the low temperature used in this synthesis.

Conclusions

It is shown that the interaction between Pluronic P123 and silica is very dependent on the temperature and on the time allowed for condensation of the starting silica solution prior to addition of Pluronic. Studies of Pluronic in a solution without silica showed that the unimers form large aggregates at ca. 17 °C. Above 20 °C smaller spherical micelles are formed and at ca. 60 °C these micelles change from spherical to cylindrical. The addition of silica was found to lower the sphere-to-rod transition temperature, as well as the cloud point. The formation of larger aggregates at low temperatures was also accelerated by the presence of silica, resulting in a turbid solution. The effect caused by the silica became more pronounced as the time allowed for condensation of the silica prior to Pluronic addition was increased. Both the aggregation at low temperatures and the clouding were found to be partly reversible. The observations made suggest that the interaction between silica and Pluronic is mainly entropy-driven.

The effect of the reaction temperature and the time for condensation of the silica on the degree of order of the final material formed upon mixing of the silica solution with Pluronic was also studied. It was concluded that the order is affected by the relative rates of the different steps in the synthesis. The second step, formation of the particles, should be fast relative to the condensation of the silica. It was observed that the materials with the highest degree of mesoorder were obtained between 15 and 20 °C. This was explained by fast formation of particles in combination with a relatively slow rate of condensation. Increasing the time allowed for silica condensation also increased the degree of mesoorder, within the time span studied, as a result of faster particle formation.

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