

Formation of a New $Ia\bar{3}d$ Cubic Meso-Structured Silica via Triblock Copolymer-Assisted Synthesis

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Silica with meso-ordered structures has no true crystalline order; however, on the mesoscopic length scale they are highly ordered. This type of materials are synthesized via a surfactant-assisted formation process which can proceed either in concentrated¹ or in dilute^{2–4} surfactant solutions. In this work the latter method is employed. A large variety of surfactants, including block copolymers, can be used as structure directors. In the two pioneering works in this field, cationic surfactants were used to produce meso-ordered silica.^{2,3} Although Kresge et al.² reported a cubic phase, it was the hexagonal phases, FSM-16, and, in particular, MCM-41, that most attracted the interest of the scientific community. The cubic phase, MCM-48, however, has for many applications a more appealing structure. It has a $Ia\bar{3}d$ cubic symmetry with the center of the silica wall situated on the gyroid infinite periodic minimal surface (IPMS).^{5–7} This furnishes MCM-48 with a very open framework with two sets of pores of opposite handedness. Perhaps the more restricted synthesis condition is the cause for fewer reports having been published on MCM-48 than on MCM-41.

The first paper on structures formed with block copolymers appeared in 1998.⁸ These have the attractive properties of larger pore diameters, thicker walls, and higher stability than the M41S family of structures. Examples of these are SBA-15 ($p6mm$) and SBA-16 ($Im\bar{3}m$).⁴ It was later found that the hexagonal form SBA-15, structurally similar to MCM-41 ($p6mm$), apart from the large mesopores, also contained smaller pores interconnecting the large channels.⁹

Block copolymers are used in the synthesis of many of the SBA-materials. Especially versatile in these syntheses are the triblock copolymers Pluronics. These polymers have a central polypropylene block surrounded by polyethylene blocks $((EO)_x-(PO)_y-(EO)_x)$. Also for the SBA materials it is the hexagonal form that has attracted the largest interest.

Pluronics show an anomalous temperature behavior,¹⁰ which is manifested as an increase in the hydrophobicity of the polymer as the temperature is raised. This will, in an aqueous solution, eventually lead to association of the polymers and phase separation. The synthesis conditions in mesoporous silica formation vary depending on the chain lengths of the different polymer blocks of the Pluronics. Also, the chain lengths dictate the conditions for the type of meso-structure that will form.^{4,11} An important synthesis parameter is the temperature, largely due to the temperature sensitivity of the polymers.^{4,12} A raise in temperature can for certain Pluronics alter the behavior to such an extent that the resulting silica will have a different structure. This has been shown to occur for Pluronic P123 and P103, which normally will assist in forming a 2D hexagonal structure but at higher temperature will direct the structure toward a multilamellar vesicle-like phase.^{11,12}

Recently it was reported that inorganic salts have a strong influence on the outcome of the polymer-assisted synthesis. Yu et al.^{13,14} showed that the addition of alkali sulfates and/or chlorides provides the means for lowering the temperature of a successful

synthesis. Further, polymers that would not function as structure directors could in fact be used, provided an inorganic salt was added to the solution.¹³ Also, large single crystals of $Im\bar{3}m$ symmetry could be synthesized in the presence of inorganic salts.¹⁴ In a recent article by Leontidis,¹⁵ the effect of Hofmeister anions ($SO_4^{2-} > HPO_4^{2-} > F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^-$) on the formation of mesoporous solids is reviewed.

Here, we report that an inorganic salt can have such a strong influence that it can trigger the formation of a different structure. This structure is related to MCM-48 in the same way as SBA-15 is related to MCM-41. The structure is cubic with $Ia\bar{3}d$ symmetry, and judging from TEM micrographs the silica lies on the gyroid IPMS. MCM-48 has a unit cell around 100 Å. This new material, on the other hand, can have unit cell dimensions of up to 257 Å in the as-synthesized form. After submitting this article, we became aware of two newly published papers that also describe the synthesis of large $Ia\bar{3}d$ structures ($a = 182$ Å¹⁶ and $a = 188$ Å,¹⁷ respectively, in the calcined form). However, the methods of syntheses differ from ours. We believe our approach to be a simpler procedure for obtaining this cubic structure.

The Pluronics used in these syntheses are Pluronic P103, $(EO)_{17}-(PO)_{59}-(EO)_{17}$, and Pluronic P123, $(EO)_{20}-(PO)_{70}-(EO)_{20}$. The syntheses were prepared as the nonsalt mediated synthesis reported earlier,^{11,12} with the exception that sodium iodide was added and dissolved together with the polymer. Pluronic (1.92 g) and 11.24 g of NaI were dissolved in 45 g of Millipore water and 30 g of 4 M HCl in a Teflon bottle (leading to a 1 M NaI solution). After dissolution, the temperature was adjusted to 55 °C, and 4.0 g of the silica precursor tetraethyl orthosilicate (TEOS) was added under vigorous stirring for 1 min after which the stirring rate was lowered. Precipitation started almost directly after the TEOS addition. The mixture was stirred for 24 h, after which it was put in an 80 °C oven for another 24 h. The product was filtered and washed with water. The polymer was removed by calcination in air at 500 °C for 6 h.

The samples were examined by small-angle X-ray scattering, transmission electron microscopy (400kV), and nitrogen adsorption/desorption measurements (at 77 K).

The X-ray diffractogram for the material obtained with Pluronic P103 is shown in Figure 1a. The material is highly ordered; however, due to the small domain sizes (see Figure 2a), the peaks in the diffractograms are broad. Consequently, the diffractogram is not very distinct, but still the locations of the broad peaks fit clearly with the $Ia\bar{3}d$ space group (see Figure 1b) resulting in $a = 202$ Å for the calcined material. The uncalcined material has a lattice parameter of 232 Å. For the material obtained with the longer polymer Pluronic P123, the lattice parameter is 257 Å before calcination and 222 Å after. This can be compared to a lattice parameter of 85 Å for a calcined MCM-48 material.⁶ The electron micrographs show the structure along different directions. In Figure 2a the central domain is aligned along $[311]$ and in Figure 2b the

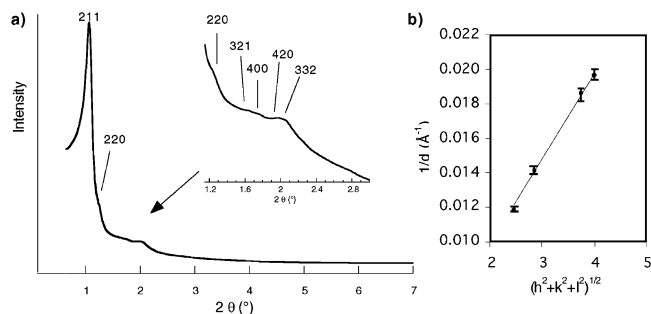


Figure 1. (a) X-ray diffraction pattern from cubic silica (calcined) formed with Pluronic P103. The diffractogram is indexed according to $Ia\bar{3}d$. The magnified part has log scale on the intensity axes. (b) Plot of $1/d$ versus $(h^2 + k^2 + l^2)^{1/2}$. Only the first four peaks are used as the 420 and 332 reflections are smeared out into one broad peak.

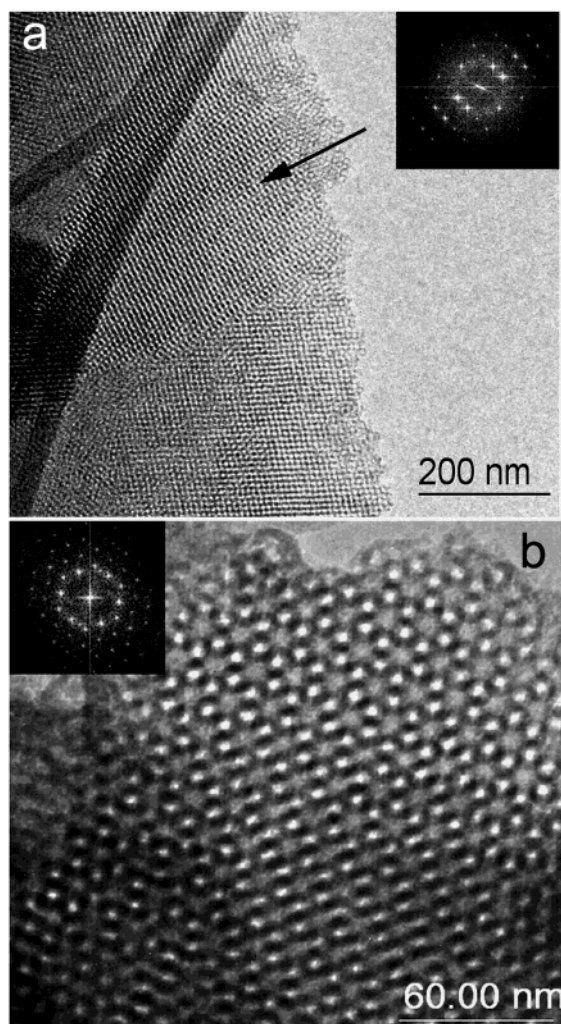


Figure 2. Transmission electron micrographs of cubic silica (calcined), formed with Pluronic P103. (a) Micrograph recorded along the [311]-direction for the central domain and (b) micrograph recorded along the [111]-direction. The corresponding Fourier transforms are inserted.

material is viewed along the [111]-direction. These micrographs reveal typical patterns for a material possessing a structure lying on the gyroid IPMS (cf. MCM-48). A BET surface area of 780 m²/g was achieved for the P103 sample and 630 m²/g for the P123 sample.

Inorganic salts influence the phase behavior of block copolymers. In several reports,^{18,19} it is concluded that the addition of, for

example, NaCl dehydrates the polyethylene units, making the polymer behave as a more hydrophobic amphiphile. This behavior is in agreement with the results published by Yu et al.¹³ In that report the synthesis could be performed at lower temperatures when NaCl was added. As a temperature increase causes a more hydrophobic behavior, the addition of chloride and sulfate salts will effectively induce a similar behavior.

In our case we have used NaI, which have been shown to have properties dissimilar to NaCl. Kabalnov et al.¹⁸ explained this as ions being either adsorbed (NaI, NaSCN) or depleted (NaF, NaCl, NaBr) in the surfactant monolayer. This implies that the two groups of ions affect the spontaneous curvature of the amphiphilic aggregates in opposite ways. The spontaneous curvature of the bicontinuous cubic structure (V_1) lies between that of the lamellar and the 2D hexagonal structure. However, generally the bicontinuous cubic structure is stable only in a narrow range. At the temperatures that were used here, the synthesis without NaI addition results in the formation of structures with an appearance similar to multilamellar vesicles, coexisting with the normal hexagonal structure. Addition of the iodide salt opens up the new structural window situated between the lamellar and the 2D hexagonal phases.

In conclusion, the relative lengths of the polymer blocks act as a coarse adjustment of the silica mesophase.¹¹ The temperature as well as the presence of inorganic salts on the other hand provides means of fine adjustment. In this case we have been able to achieve the bicontinuous cubic $Ia\bar{3}d$ structure through the addition of sodium iodide.

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