Evolution (Biogenesis)

Chemical synthesis of biomimetic forms

Jacques Livage

Chimie de la matière condensée, Collège de France, 11, place Marcelin-Berthelot, 75231 Paris, France

Abstract

The biogenic origin of the first traces of life is often based on the morphological analysis of microfossils. However life-like forms can also be obtained via chemical synthesis from purely inorganic precursors. Many examples can be found in literature that are mainly based on aqueous solution chemistry. Osmotic growth of gelatinous precipitates is observed during the formation of "chemical gardens". Point defects in surfactant mesophases lead to mesoporous silica with curved shapes. The oriented attachment of nanocrystals via hydrophilic polymers leads to mesocrystals that exhibit a large variety of unusual shapes. ***To cite this article: J. Livage, C. R. Palevol 8 (2009).***
© 2009 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Résumé

Synthèse chimique de formes biomimétiques. L'origine biogénique des premières traces fossiles est souvent basée sur une analyse morphologique. Il apparaît toutefois que des formes analogues peuvent être obtenues par synthèse chimique, à partir d'éléments purement minéraux. De nombreux exemples sont décrits dans la littérature, qui font intervenir le plus souvent la chimie des solutions aqueuses. Les processus de croissance osmotique de précipités gélatineux sont à l'origine de la formation des « jardins chimiques ». La présence de défauts ponctuels dans les mésophases de surfactants conduit à des silices mésoporeuses qui présentent des surfaces courbes. L'association contrôlée de nanocristaux via des polymères hydrophiles provoque la croissance de mésocristaux qui présentent des formes inhabituelles. ***Pour citer cet article : J. Livage, C. R. Palevol 8 (2009).***
© 2009 Académie des sciences. Publié par Elsevier Masson SAS. Tous droits réservés.

Keywords: Mesocrystals; Biomorph silica; Chemical garden

Mots clés : Mésocristaux ; Silice biomorphe ; Jardin chimique

1. Introduction

Fossilized remains have been studied for centuries and the search for the first traces of life has long been based on the shape of microfossils. Organic matter usually degrades quite fast so that only hard parts of a body (bones, shells, teeth...) or mineralized tissue can be found as fossils. New analytical technologies have been applied to fossil materials during the past decade in order to confirm their biogenic origin [32], but morphology is still one of the main parameters to decide whether microfossils could be considered as traces of life rather than just mineral forms.

Minerals usually exhibit regular crystalline shapes, while living organisms build much more sophisticated
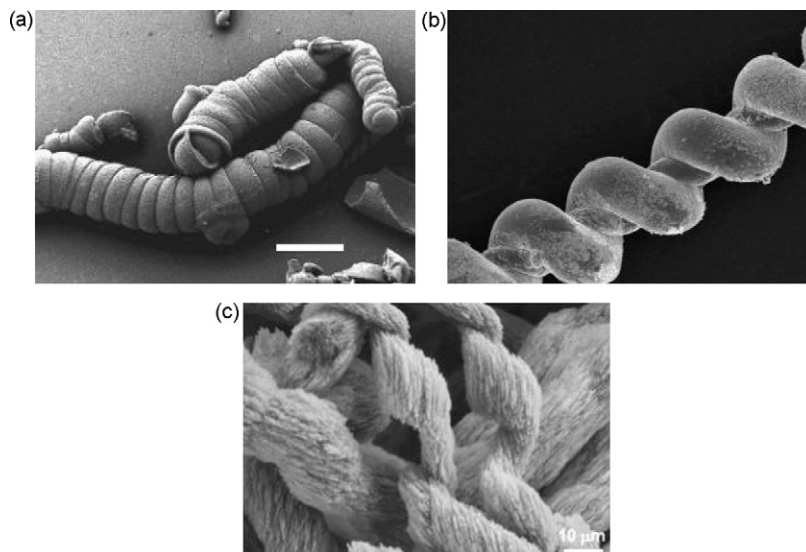
Fig. 1. Self-assembled nanocrystals obtained via chemical synthesis from inorganic precursors. a, b: silica–witherite (SiO_2–$BaCO_3$) biomorphs (from [7]); c: $BaCO_3$ helices induced by racemic block copolymers (from [8]).
Fig. 1. Auto-organisation de nanocristaux obtenus par synthèse chimique à partir de précurseurs inorganiques. a, b : biomorphes silice–witherite (SiO_2–$BaCO_3$) (d'après [7]) ; c : hélices de $BaCO_3$ obtenues en présence de copolymères blocs racémiques.

architectures. This can be easily illustrated by comparing quartz crystals with the shells of diatoms. Both are made of silica (SiO_2) but their shape is completely different. A similar comparison could also been made with calcium carbonate ($CaCO_3$), between aragonite crystals and coccolithe shells. These examples suggest that it should be quite straightforward to decide whether fossil traces are from biogenic origin. There is no doubt either about the biological nature of dinosaur bones or ammonite shells buried in ancient sediments. However, this is no longer the case when microorganisms such as bacteria are involved. Microfossils coming from the most ancient forms of life on Earth are often difficult to recognize and controversies based on the analysis of shapes can be often found in literature.

The biogenicity of most structures previously interpreted as Archean microfossils has been often questioned [35]. The controversy arises from the fact that natural abiotic processes have been shown to be able to lead to biological morphology. This can be well illustrated by the debate about the microbe-like filaments found in the Precambrian Warrawoona chert formation in western Australia. Schopf et al. reported that these were the earliest traces of life on Earth, due to cyanobateria about 3500 billion years old [31]. But, in the same issue of *Nature*, Brasier et al. showed that similar shapes could be formed from inorganic precursors under hydrothermal conditions [2] and a year later, Garcia-Ruiz et al. synthesized micron-sized silica-coated carbonate filaments exhibiting curved helical morphologies, reminiscent of biological forms. They were made upon heating $BaCl_2$ in alkaline sodium silicate solutions [12]. Self-assembled silica-carbonate aggregates have been obtained that exhibit strong resemblance to biogenic forms [15]. As pointed out by these authors, morphology should be considered as an ambiguous indicator of biogenicity [11,23] (Fig. 1).

The following question then arises. Is it possible via chemical morphogenesis to synthesize shapes usually typical of life? The synthesis of complex form by living organisms is a real challenge for chemists [24] and reproducing the forms of life has long been a dream for all chemists [34]! This article describes some examples of inorganic syntheses leading to the formation of biomorph solids.

2. Chemical gardens

One of the first chemical syntheses of living forms was reported about a century ago by Stephane Leduc. He showed that a spectacular plant-like growth occurs when crystals of metal salts ($FeCl_3$, $CuSO_4$, $Ni(NO_3)_2$, $CoCl_2$) are dropped into an aqueous solution of sodium silicate (water glass) [4]. Colorful plant-like extensions grow from the surface of each crystal giving rise to the so-called "chemical gardens" (Fig. 2). At that time Stephane Leduc thought he was able to create some
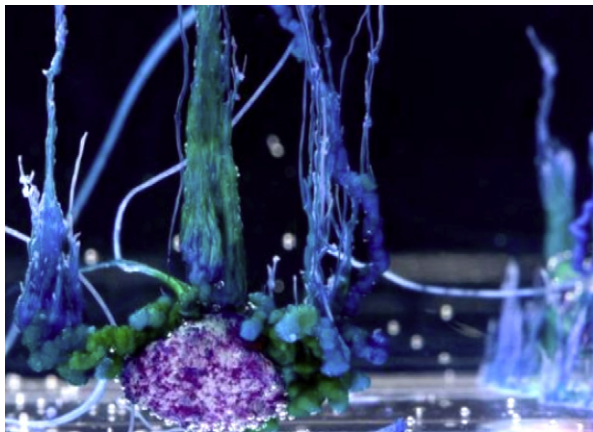
Fig. 2. Chemical gardens obtained by diping CoCl$_2$ crystals in a silicate solution (photo from Stéphane Querbes, for "les atomes crochus" and "Animascience").

Fig. 2. Jardin chimique obtenu en plongeant des cristaux de CoCl$_2$ dans une solution de silicate (photo de Stéphane Querbes pour « les atomes crochus » et « animascience »).

artificial life leading to the publication of many papers about the mechanism of life [19,20]!

Two physicochemical processes are actualy involved in the formation of these chemical gardens.

2.1. Precipitation of oxides or hydroxides from aqueous solutions of metal salts

The first one is the precipitation of oxides or hydroxides from aqueous solutions of metal salts. This process is mainly governed by the pH of the solution.

When dissolved in water, salts of low-valent metal cations (Cu^{2+}, Co^{2+}, Fe^{3+}...) give acid solutions in which metal cations are solvated by dipolar water molecules. Precipitation occurs by adding a base in order to increase the pH.

$$[Cu(OH_2)_6]^{2+} + 2OH^- \Rightarrow Cu(OH)_2 + 6H_2O$$
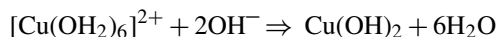
The reverse is observed for silica which is only soluble in an alkaline medium. The precipitation of silica from a silicate solution occurs by adding an acid to decrease the pH.

$$[SiO_4]^{4-} + 4H^+ \Rightarrow SiO_2 + 2H_2O$$
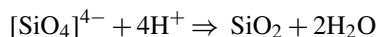
When a crystal of an acid metal salt is dropped into an alkaline silicate solution, the salt progressively dissolves and a strong pH gradient is formed between the acid solution surrounding the crystal and the basic silicate solution. Precipitation then occurs at the interface between both solutions.

2.2. Osmotic growth

The second process is called osmotic growth.

Actually a gelatinous precipitate of hydrous silicate is formed that behaves as a semi-permeable membrane [28]. The acid solution inside the membrane is much more concentrated than the basic silicate solution outside. An osmotic pressure is then established between both sides of the gelatinous precipitate inducing water diffusion through the membrane inward. The crystal continues to dissolve and the membrane to swell until it breaks. Some concentrated salt acid solution is then ejected into the basic silicate medium and a new precipitate immediately forms. Tubular fibres then develop from each point of rupture giving rise to the spectacular plant-like shape of the chemical gardens [1].

The physicochemical parameters leading to the formation of chemical gardens have been studied using more sophisticated analytical methods during the past decade in order to get a better understanding of this amazing reaction. NMR and ESCA experiments for instance show that aluminosilicates rather than hydroxides are formed with Al(NO$_3$)$_3$ crystals [10]. Hollow fibres actually grow from the crystal [27]. Bubbles are formed at the tip of these fibres guiding their tubular growth [36,37]. Gravity appears also to be involved so that chemical gardens have been grown in space [16].

3. Biomorph mesoporous silica

Biogenic silica has been used by planktonic microorganisms for their protection. Diatoms provide a wonderful example of the beautiful architectures made by life. These single-cell microalgeas are surrounded by a porous silica shell (frustule) that exhibits an increadible variety of shapes. Chemists are very interested by these microorganisms that are able to make silica glasses under ambiant conditions while high temperatures are required to make industrial glasses from molten silica. Therefore the soft solution synthesis of porous silica glasses is becoming a very popular field of research. It leads to the development of the so-called sol–gel process [3]. Sol–gel silica is made via the hydrolysis and condensation of molecular precursors such as silicon alkoxides Si(OR)$_4$ (R=CH$_3$, C$_2$H$_5$...) as follows:

$$Si(OR)_4 + 2H_2O \Rightarrow Si(OH)_4 + 4ROH$$

$$Si(OH)_4 \Rightarrow SiO_2 + 2H_2O$$
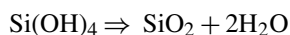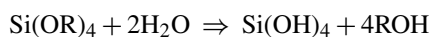
An hydrous silica gel is formed that transforms into a silica glass upon heating. One of the main advantages of the sol–gel route is to allow the powderless processing

of glasses and ceramics. It has been widely developped for the production of fibres and coatings [17].

The sol–gel route leads to the formation of porous silica gels, but their pore size cannot be accurately controlled. A real breakthrough occurred when scientists at Mobil showed that it was possible to get ordered mesoporous silica in the presence of surfactants such as cethyltrimethylammonium chloride (CTACl) [18].

Surfactant molecules are made of a long hydrophobic alkyl tail and a polar hydrophilic head. They self-assemble in polar solvents such as water to give micelles in which all polar heads are directed toward the outside aqueous medium. Mesophases are formed when surfactants are mixed with oil and water. Mesoporous silica is then obtained via a "liquid crystal templating" process. Depending on concentration, different mesophases (hexagonal, cubic, lamellar) are obtained that behave as templates for the synthesis of porous silica. Molecular precursors, alkoxides $Si(OR)_4$ or silicic acid $Si(OH)_4$ occupy the continuous water region. Condensation leads to the formation of silica walls between the surfactants assemblies. Organic surfactants are removed via calcination leaving a porous silica network. A periodic mesoporous structure can then be obtained leading to the development of mesoporous silicas which are nowadays extensively used in the field of catalysis.

Chemists are usually looking for defect free mesoporous structures. However, it is well known that
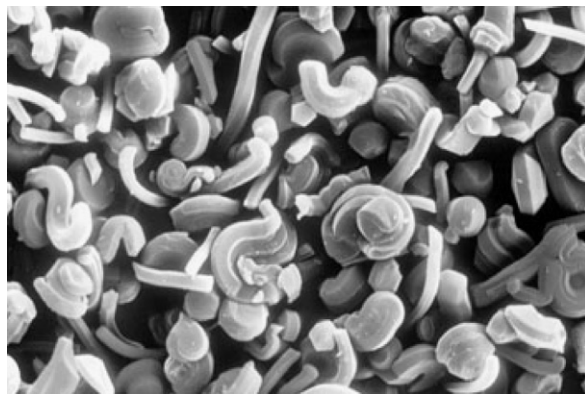

Fig. 3. Biomorph silica (from [5]).
Fig. 3. Silices biomorphes (d'après [5]).

topological defects, points, lines or planes can be observed during the formation of surfactant mesophases. The energy required to stabilize these defects is much smaller than in solid crystals. Large defects several micrometers in dimensions can be easily formed. The condensation of silica around these defects leads to curved shapes so that the resulting solid particles exhibit sophisticated curves that look like biogenic silica (Fig. 3) [13,14].

Hexagonal mesoporous silicas, MCM-41, have been extensively studied by Ozin. They are built of assemblies of rod-like 2D hexagonal array of surfactants. Topolog-
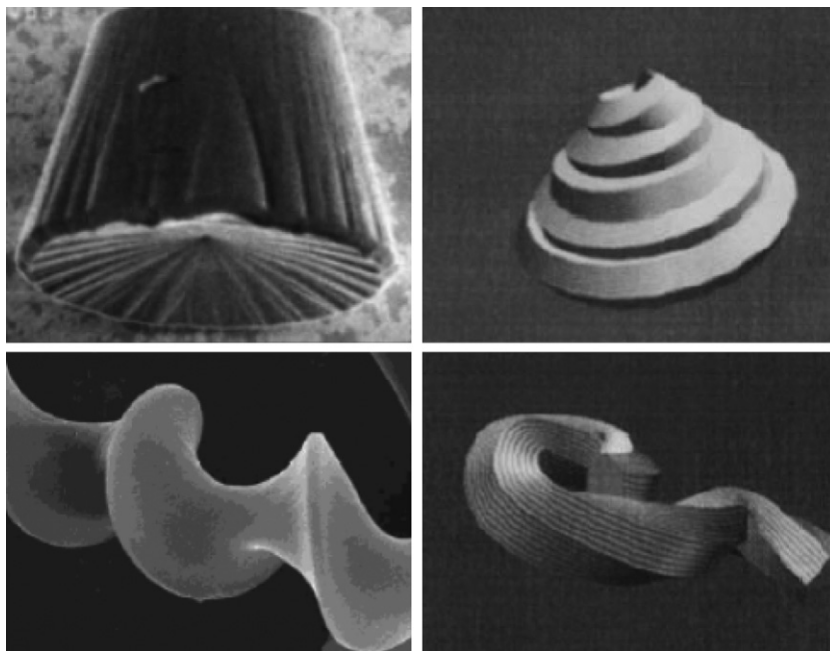

Fig. 4. The role of defects in the formation of mesoporous silica (from [26,27]).
Fig. 4. Rôle des défauts dans la formation de silices mésoporeuses (d'après [26,27]).
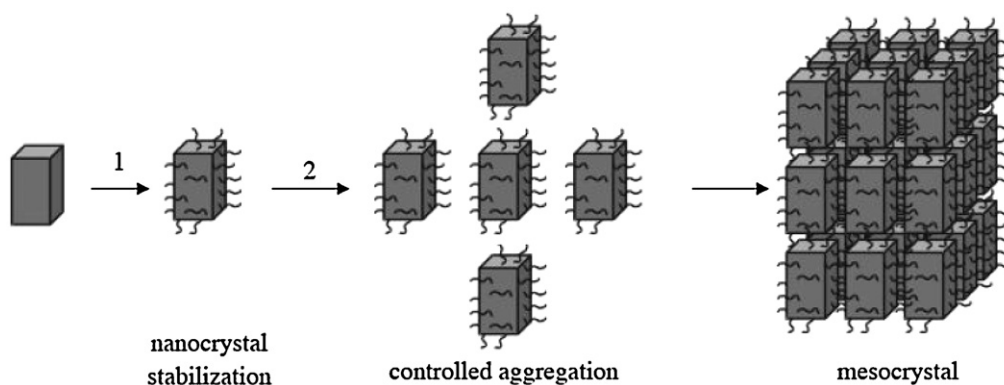
Fig. 5. Formation of mesocrystals in the presence of organic additives.
Fig. 5. Rôle des additifs organiques dans la formation des mésocristaux.

ical point defects change the orientation of the director field leading to the formation of curved structures that can initiate and direct the growth of particular forms of mesoporous silica: discoidal, toroidal, disk-like, spiral, spheroidal [25]. The condensation of silica mainly quenches the topological defect and its associated director field pattern. It is possible to draw a relation between a specific type of defect and a particular mesoporous silica shape [26]. Each morphology can be associated with a specific kind of dislocation or disclination defect (Fig. 4). Two defects can even combine to lead to more spohisticated morphologies (bagel, twisted toroid...).

4. Crystal tectonics and mesocrystals

Biomorph shapes have been mainly obtained with silica-based materials. Silica is a well known glass former that leads to amorphous solids. Curved surfaces are then much easier to form in the absence of crystallographic constraints. This is no longer the case when crystals are used as precursors. Flat surfaces corresponding to the crystallographic planes, with definite angles, are then usually observed. Curved surfaces could anyway be obtained via the controlled self-assembly of nanocrystals, leading to ordered superstructures called "mesocrystals" [8,9].

These mesocrystals somehow mimic the formation of biostructures found in the hammer-shaped building units of coccoliths or the skeletal plates of sea urchins.

Mesocrystals are formed via a bottom-up process that couples together chemical synthesis and self-assembly in order to produce complex superstructures. Syntheses are performed in the presence of organic additives that limit crystal growth and control their aggregation. Self-organization leads to single-crystalline structures with included organic additives as defects. Mesocrys-

tals could be considered as a special case of colloidal crystals in which building units are anistropic nanocrystals rather than spherical colloidal particles. They could be described as "crystals of crystals" in which the building units are nanocrystals rather than ions or molecules.

The formation of mesocrystals is a two-step reaction in which organic additives play a double role (Fig. 5):

- in the first step, organic additives bind to some crystalline faces. Crystal growth is then limited leading to
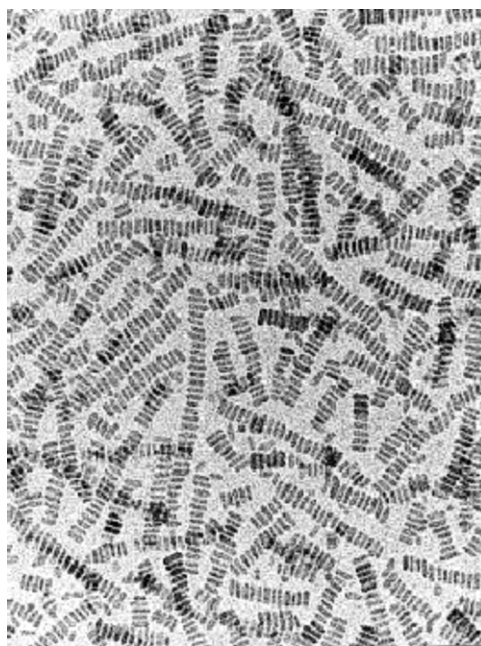

Fig. 6. Ordered chains of prismatic $BaCrO_4$ particles prepared in AOT microemulsions (from [30]).
Fig. 6. Formation de chaînes de particules prismatiques de $BaCrO_4$ au sein de microémulsions (d'après [30]).
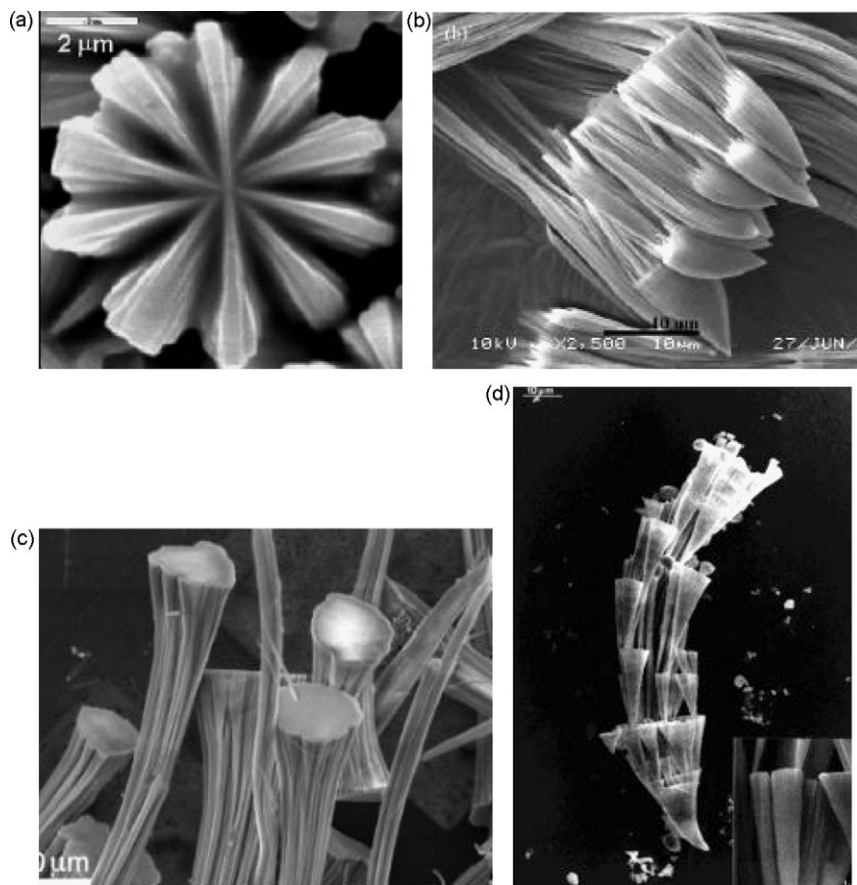
Fig. 7. Some examples of BaSO$_4$ mesocrystals prepared in the presence of double hydrophilic block copolymers (from [31,32,35–37]). Some examples of BaSO$_4$ mesocrystals grown in the presence of block copolymers. a: PEO-*b*-PEI–SO$_3$H (from ref. [7]); b: PEO-b-PMAA–PO$_3$H$_2$ (from ref. [22]); c: BaSO$_4$ fiber bundles with PEO-b-PMAA–PO$_3$H$_2$ (from ref. [29]); d: cone-shaped BaSO$_4$ particles with polyacrylate (from ref. [29]).
Fig. 7. Exemples de mésocristaux de BaSO$_4$ formés en présence de copolymères blocs hydrophiles (d'après [31,32,35–37]).

the formation of nanocrystals stabilized by the organic molecules adsorbed at their surface;

- in the second step, weak interactions between organic additives favor the controlled aggregation of the nanocrystalline building blocks, leading to ordered superstructures.

The synthesis of BaSO$_4$ (or CrO$_4$) mesocrystals provides a nice example of such a process. Linear chains of prismatic nanoparticles have been synthesized from a mixture of baryum sulfosuccinate reverse micelles and sodium sulfosuccinate microemulsions containing encapsulated sulfate or chromate anions. Slow exchange between these two components leads to the formation of BaSO$_4$ or BaCrO$_4$ nanoparticles [21]. The anionic groups (SO$_4$)$^{2-}$ or (CrO$_4$)$^{2-}$ preferentially bind to some faces of the crystals leading to the formation of prismatic nanoparticles. Interactions between organic chains of the surfactants then lead to the directed aggregation along the axis perpendicular to the larger faces in order to maximize the hydrophobic interactions. Nanocrystals within a chain are separated by a regular spacing of 2 nm corresponding to an interdigitated bilayer of surfactant molecules (Fig. 6).

Double hydrophilic block copolymers (DHBC) have been recently introduced to control the formation of mesocrystals [6,22]. They are made of two hydrophilic blocks. One is strongly interacting with the inorganic particles while the other one does not. In the PEG-b-PMAA block copolymer for instance, the carboxylic groups of the PolyMethAcrylic Acid (PMAA) strongly interacts with the inorganic particles while Polythylene Glycol (PEG) only provides solubility.

Complex morphologies have been obtained via the precipitation of BaSO$_4$ (or BaCrO$_4$) in the presence of the PEG-b-PMAA–PO$_3$H$_2$ block copolymer (Fig. 7) [33].

The complexing power of DHBC depends on the nature of the functional groups (–COOH, –PO$_3$H$_2$, –SO$_3$H) and their protonation state, i.e. on pH. A large variety of forms can be obtained [7,8]. Bundles of coiled single-crystalline BaSO$_4$ nanofilamnents are obtained in the presence of poly(ethylene oxide)-*block*-poly(methacrylic acid) (PEO-*b*-PMAA–PO$_3$H$_2$) [29,30].

5. Conclusion

Only a few examples have been described in this article. They show that chemical morphogenesis can lead to sophisticated structures. Preparing man-made materials with life-like forms becomes nowadays quite fashionable [23]. However, this is not the only aim of these research works. Shape is also very important for materials scientists. The properties of a given material often depend on its shape. Glass windows or fibres for instance are used for their transparency. Glass wool is used for its insulating properties and glass bottles as containers. Moreover, the development of nanotechnologies requires the synthesis of nanostructured materials. In this field, bio-materials provide a nice guide for the synthesis of bio-inspired materials.

References

[1] D. Balköse, F. Ozkan, U. Köktürk, S. Ulutan, S. Ulkü, G. Nisli, Characterization of hollow chemical garden fibers from metal salts and water glass, J. Sol-Gel Sci. Techn. 23 (2002) 253–263.

[2] M.D. Brasier, O.R. Green, A.P. Jephcoat, A.K. Kleppe, M.J. Van Kranendonk, J.F. Lindsay, A. Steele, N.V. Grassineau, Questioning the evidence for Earth's oldest fossils, Nature 416 (2002) 76–81.

[3] C.J. Brinker, G.W. Scherrer, Sol–gel science, Acad. Press, San Diego, CA., 1990.

[4] J.H.E. Cartwright, J.M. GarciRuiz, M.L. Novella, F. Otalora, Formation of chemical gardens, J. Colloid Interface Sci. 256 (2002) 351–362.

[5] H.B.S. Chan, P.M. Budd, T.V. Naylor, Control of mesostructured silica particle morphology, J. Mater. Chem. 11 (2001) 951–957.

[6] H. Cölfen, Double-hydrophilic block coplymers, synhtesis and application as novel surfactant and crystal growth modifiers, Macromol. Rapid Commun. 22 (2001) 219–252.

[7] H. Cölfen, L. Qi, Y. Mastal, L. Börger, Formation of unusual 10-petal BaSO$_4$ structure in the presence of polymeric additive, Cryst. Growth Design 2 (2002) 191–196.

[8] H. Cölfen, S. Mann, Higher-order organization by mesoscale self-assembly and transformation of hybrid nanostructures, Angew. Chem. Int. Ed. 42 (2003) 2350–2365.

[9] H. Cölfen, M. Antonietti, Mesocrystals: Inorganic superstructures made by highly parallel crystallization and controlled alignment, Angew. Chem. Int. Ed. 44 (2005) 5576–5591.

[10] C. Collins, G. Mann, E. Hoppe, T. Duggal, T.L. Barr, J. Klinowski, NMR and ESCA studies of the "silica garden" Brönsted acid catalyst, Phys. Chem. Chem. Phys. 1 (1999) 3685–3687.

[11] J.M. Garcia-Ruiz, A. Carnerup, A.G. Christy, N.J. Welham, S.T. Hyde, Morphology: an ambiguous indicator of biogenicity, Astrobiology 2 (2002) 353–370.

[12] J.M. Garcia-Ruiz, S.T. Hyde, A.M. Carnerup, A.G. Christy, M.J. Van Kranendonk, N.J. Welham, Self-assembled silica–carbonate structures and detection of ancient microfossils, Science 302 (2003) 1194–1197.

[13] Hong Yang, N. Coombs, G.A. Ozin, Morphogenesis of shapes and surface patterns in mesoporous silica, Nature 386 (1997) 692–695.

[14] Hong Yang, G.A. Ozin, C.T. Kresge, The role of defects in the formation of mesoporous silica fibers, films and curved shapes, Adv. Mater. 10 (1998) 883–887.

[15] S.T. Hyde, A.M. Carnerup, A.K. Larsson, A.G. Christy, J.M. Garcia-Ruiz, Self-assembly of carbonate–silica colloids: between living and non-living form, Physica A 339 (2004) 24–33.

[16] D.E.H. Jones, U. Walter, The silicate garden reaction in microgravity: a fluid interfacial instability, J. Colloid Interface Sci. 203 (1998) 286–293.

[17] L.C. Klein, Sol–gel technology for thin films, fibers, performs, electronics and speciality shapes, Noyes Pub. Park Ridge, NJ, 1988.

[18] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Ordered mesoporous molecular sieves synthesized by a liquid crystal template mechanism, Nature 359 (1992) 710–712.

[19] S. Leduc, Théorie physicochimique de la vie, A. Poinat Ed, 1910.

[20] S. Leduc, La biologie synthétique, A. Poinat Ed, 1912.

[21] M. Li, H. Schnablegger, S. Mann, Coupled synthesis and self-assembly of nanoparticles to give structures with controlled organization, Nature 402 (1999) 393–395.

[22] M. Li, H. Cölfen, S. Mann, Morphological control of BaSO$_4$ microstructures by double hydrophilic block copolymer mixtures, J. Mater. Chem. 14 (2004) 2269–2276.

[23] S. Mann, The chemistry of forms, Angew. Chem. Int. Ed. 39 (2000) 3393–3406.

[24] G.A. Ozin, Morphogenesis of biomineral and morphosynthesis of biomimetic forms, Acc. Chem. Res. 30 (1997) 17–27.

[25] G.A. Ozin, Curves in chemistry: supramolecular materials taking shape, Can. J. Chem. 77 (1999) 2001–2014.

[26] G.A. Ozin, C.T. Kresge, H. Yang, The role of defects in the formation of mesoporous silica fibers, films and curved shapes, Adv. Mater. 11 (1999) 883–887.

[27] J.J. Pagano, T. Bansagi, O. Steinbock, Tube formation in reverse silica gardens, J. Phys. Chem. C 111 (2007) 9324–9329.

[28] J.J. Pagano, S. Thouvenel-Romans, O. Steinbock, Compositional analysis of copper–silica precipitation tubes, Phys. Chem. Chem. Phys. 9 (2007) 110–116.

[29] L. Qi, H. Cölfen, M. Antonietti, Control of barite morphology by double-hydrophilic bock copolymers, Chem. Mater. 12 (2000) 2392–2403.

[30] L.M. Qi, H. Cölfen, M. Antonietti, M. Li, D. Hopwood, A.J. Ashley, S. Mann, Formation of BaSO4 fibres with morphological complexity in aqueous polymer solutions, Chem. Eur. J. 7 (2001) 3526–3532.

[31] J.W. Schopf, A.B. Kudryavtsev, D.G. Agresti, T.J. Wdowiak, A.D. Czaja, Laser-Raman imagery of Earth's earliest fossils, Nature 416 (2002) 73–76.

[32] M.H. Schweitzer, R. Avci, T. Collier, M.B. Goodwin, Microcopic, chemical and molecular methods for examining fossil preservation, C.R. Palevol 7 (2008) 159–184.

[33] Shu-Hong Yu, H. Cölfen, M. Antonietti, Control of the morphogenesis of baryum chromate by using double-hydrophilic block copolymers (DHBCs) as crystal growth modifiers, Chem. Eur. J. 8 (2002) 2937–2945.

[34] Shu-Hong Yu, H. Cölfen, K. Tauer, M. Antonietti, Tectonic arrangement of $BaCO_3$ nanocrystals into helices induced by a racemic block copolymer, Nat. Mater. 4 (2005) 51–55.

[35] K. Sugitani, K. Grey, A. Allwood, T. Nagaoka, K. Mimura, M. Minami, C.P. Marshall, M.J. Van Kranendonk, M.R. Walter, Diverse microstructures from Archean chert from the Mount Goldsworthy–Mount Grant area, Pilbara Craton, Western Australia: microfossils, dubiofossils or pseudofossils? Precambrian Res. 158 (2007) 228–262.

[36] S. Thouvenet-Romans, O. Steinbock, Oscillatory growth of silica tubes in chemical gardens, J. Am. Chem. Soc. 125 (2003) 4338–4341.

[37] S. Thouvenet-Romans, J.J. Pagano, O. Steinbock, Bubble guidance of tubular growth in reaction–precipitation systems, Phys. Chem. Chem. Phys. 7 (2005) 2610–2615.