Crystal Branching and Spherulite Formation: Similar Shapes ↔ Different Mechanisms

Elena Rosseeva, Paul Simon, and Rüdiger Kniep

The phenomena of crystal branching and spherulite formation are wide and diverse. This kind of morphogenesis is found in biological, geological (e. g. sediments), and in synthetic systems as well [1]. Furthermore, the formation of spherulites has been reported for a large variety of materials [1–3]. The amazing architecture of natural and synthetic spherulites has attracted much interest although the mechanism of their formation is not yet definitely clear. One of the first studies on spherulites was published already in 1888 by *Lehmann* [2], who described them as radially arranged fibrillar aggregates. Since that time, a number of reviews and textbooks have been devoted to the description of spherulites formation and their properties [2,3]. Most of these contributions are devoted to the understanding of crystal branching of "pure" compounds, crystallized according to so-called "classical" crystal growth mechanisms (crystal growth by ion-by-ion or molecule attachment to a primary particle). In this case, additives which may be present in the medium and which are incorporated into the growing crystal act as impurities. These can, e.g., induce stress and defects or modify the anisotropy of crystal growth. Thus, the formation of spherulites can be explained within the well developed theory of "non-crystallographic" crystal branching (generally associated with fast crystal growth and caused by the existence of internal crystal strain (defects) and high supersaturation of the surrounding medium (with a small kinetic coefficient of the growing crystal faces)) [3]. However, the situation becomes even more complex if a branching aggregate consists of a well-ordered inorganic-organic nanocomposite with complex structure and hierarchical arrangement (mesocrystals) [4a, b]. For such materials, besides the "classical" concept of crystal growth, alternative models are based on "non-classical" crystallization processes which have been developed and investigated only recently [4]. These new models involve particle-mediated pathways and include special mechanisms such as oriented attachment of subunits [4d, e], mesoscale transformations of nanoparticles from amorphous precursors [4f], and the formation of mesocrystals by "brick-by-brick" self-assembly processes [4g, h]. The branching mechanisms of such aggregates seem to be also different from "non-crystallographic" crystal branching as proposed for the "classical" crystals.
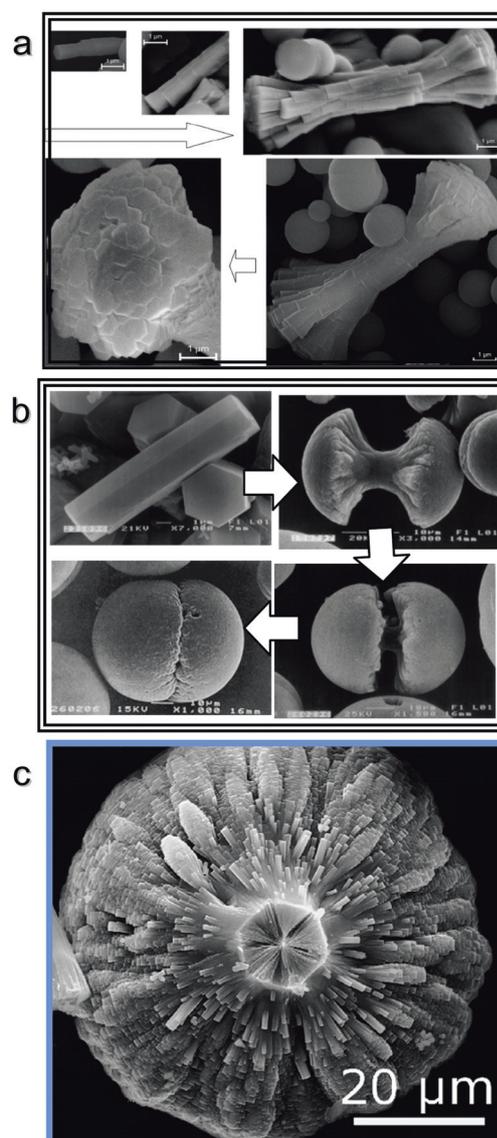

Fig. 1: SEM images of subsequent states of spherulite formation of (a) fluorapatite [1h] and (b) fluorapatite-gelatine nanocomposites (from the fractal series) [5]. (c) Half of a dumbbell of a fluorapatite-gelatine nanocomposite aggregate showing the principles of self-similarity and hierarchy.

Our particular interest in this problem is focused on the investigation of crystal branching and spherulite formation of fluorapatite-gelatine nanocomposites (from the so-called fractal series) [5]. The biomimetic system fluorapatite-gelatine bears strong resemblance to the biosystem hydroxy-apatite-collagen which plays a decisive role in the human body as functional material in the form of bone and teeth. In our former investigations, the shape development of the fluorapatite-gelatine nanocomposites from the nano- to micrometer-scale was studied in detail. The shape development starts with the mineralization of triple-helical fibre protein bundles, followed by the formation of aggregates with approximately parallel alignment of elongated nanoboards. This process then gives rise to the formation of a hexagonal prismatic seed with perfect parallel alignment of the nanoboards. Finally, the growth process leads to the development of a notched sphere via several growing dumbbell states (Fig. 1b). An analogous morphological evolution starting from a hexagonal prismatic crystal to a notched sphere was also observed for fluorapatite aggregates grown without any additive (Fig. 1a) [1h]. The splitting mechanism of these aggregates can be easily explained based on the "non-crystallographic" crystal branching scenario. However, the question arises whether the same mechanism is valid for the shape development of fluorapatite-gelatine nanocomposite aggregates representing a higher level of complexity.

In nature, there are a lot of examples illustrating that objects of similar shape may have nothing in common. As shown in Figure 2, the butterfly *Kallima inachus* with closed wings looks like a dry leaf with dark veins, however it belongs to a completely different form of organisms and even on a significantly higher level of complexity [6]. Coming back to the subject under consideration, the hierarchical pattern of the fluorapatite-gelatine-nanocomposite aggregate from the fractal growth series as shown in Figure 1c can hardly be grown from a "pure" inorganic system, even if "non-crystallographic" branching and geometrical selection process are assumed. Thus, based on experimental observations on the shape development of nanocomposite superstructures, an alternative mechanism for crystal branching must be present.
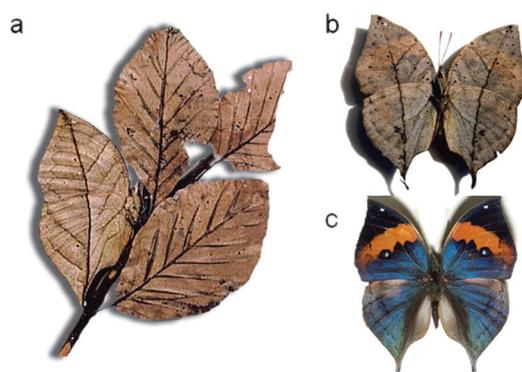

Fig. 2: (a) One of the leaves is a butterfly. Which one?* (b) Underside view of a Kallima inachus butterfly with opened wings appearing like a leaf with dark veins. (c) Colorful inner side of the same butterfly [6].

Recently, several phenomenological descriptions of spherulite formation based on "non-classical" crystallization processes were reported [4b, 4c; 7]. However, the mechanisms and driving forces controlling the formation of these hierarchical superstructures still remain only poorly understood.

Here, we briefly summarize and comparatively discuss mechanisms of spherulite formation based on the concept of "non-crystallographic" crystal branching and "non-classical crystallization", including nanocomposite controlled mechanisms of shape development. Furthermore, the range of applicability of these mechanisms for different systems is discussed.

Several reviews [3] are available, considering processes of crystal branching based on the "classical crystallization" model in great detail. The presence of impurities and high supersaturation in the surrounding medium are most often emphasized as essential prerequisites for this phenomenon [3a-d]. However, many of the experimental results showed that branching can be observed even in a system without impurities [3e]. Summarizing all the experimental observations available up to now, *Yu. Punin* and *A. Shtukenberg* [3f, g] suggested that internal stress generated during crystal growth is the most important factor for crystal branching. Specifically, internal stress can be induced by incorporation of impurities, mechanical stress, formation of crystal inhomogeneities, defects and others.
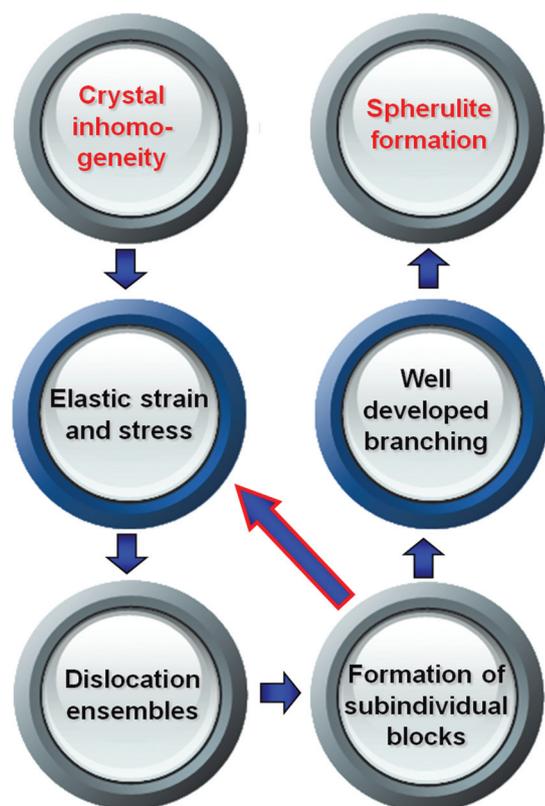
_____
* *Bottom left.*

Fig. 3: General scheme of subsequent states during "non-crystallographic" crystal branching and spherulite formation [3g].
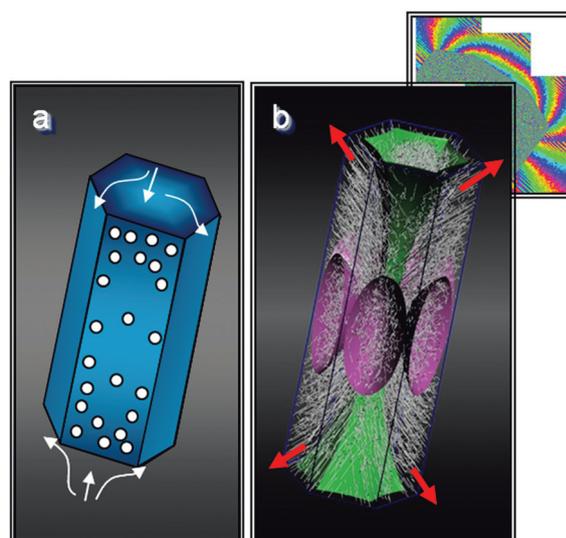

Fig. 4: (a) Distribution of possible nucleation points (accidental events) for the development of subindividuals from the prism faces of a hexagonal prismatic crystal according to "non-crystallographic" branching [3g] (conditions: high anisotropy of growth; growth regime close to diffusion control; white arrows indicate flux directions). (b) Three-dimensional representation of the inner architecture of a hexagonal-prismatic fluorapatite-gelatine nanocomposite crystal illustrating the distribution of additional hierarchical gelatine fibril pattern [5n] (Red arrows indicate some of the well-defined areas for further branching). (Upper inset) Retrieved phase image of an electron hologram showing the electric potential distribution around the nanocomposite crystal [5g, i, l]. **General message: Accidental branching (a) vs. well-defined (coded) branching (b).**

In accordance with this model, "non-crystallographic branching" is the driving force for spherulite formation. Phenomenologically, this model can be described as follows (Fig. 3). The process starts with the formation of inhomogeneities in the growing crystal inducing a long-range stress field. In order to reduce elastic energy, stress relaxation occurs via nucleation, multiplication, and motion of dislocations. This process then leads to the formation of ordered dislocation ensembles and further primary subindividual crystals, which can be slightly misoriented with respect to the primary crystal matrix. This step can be assumed as an early stage of branching. In the next step the subindividuals are isolated and grow independently. Furthermore, the formation of subindividuals induces additional stress in the growing crystal and initiates the multiplication of subindividuals. Thus, further crystal branching can be described as an autocatalytic process. If branching is strong enough one can expect the formation of a spherulite. Geometrical selection processes play a major role in this stage. Finally, it should be noted

that the process of formation of subindividuals within a crystal matrix is a stochastic event (Fig. 4a) and their growth is independently controlled by external conditions only (supersaturating, additives, temperature etc.).

However, the situation becomes completely different in the case of nanocomposite superstructures. Our recent investigations on the "embryonic states" [5l] of fluorapatite-gelatine nanocomposites (from the fractal series) confirmed that their morphogenesis is driven by the development of an intrinsic electric field which is induced by an ordered "board-by-board" self-assembly of nanocomposite subunits. During this kind of morphogenesis an intrinsic electric dipole field is generated by parallel alignment of the calcified triple-helical protein molecules within the nanoboards. Finally, the hexagonal prismatic seed (which can be described as highly mosaic controlled super-structure) is surrounded by an ideal electric dipole

field as visualized by electron holography (Fig. 4b). In addition it was also shown by detailed TEM investigations that the 3D nanocomposite super-structure of the hexagonal prismatic seeds is distinctively overlaid by a pattern consisting of gelatine microfibrils with diameters scaling around 10 nm. The orientation of the microfibrils can be assumed to be controlled by the intrinsic electric field generated by the nanocomposite superstructure.

This implies that even the very first "embryonic states" and the final hexagonal prismatic seed already bear the intrinsic conception for their future shape development on the μm-scale (via dumbbell states to slightly notched spheres). In order to prove this concept and to additionally get more detailed information on the orientational relations of microfibrils within the complex nanocomposite system, the pattern formation process (of the microfibrils) up to the μm-scale was simulated [5m, n]. The results of the simulations showed an excellent agreement with the experimental (TEM) data (not shown) and therefore support the concept of an intrinsic electric-field-driven morphogenesis of the fluorapatite-gelatine nanocomposites. In addition, the results of the simulations directly illustrate that after several aggregation cycles the Coulomb energy potential strongly increases around the hexagonal prismatic composite seed at the prismatic faces in areas close to its top and bottom [5m]. This finding supports our suggestion, that a branching process takes place in those areas where the Coulomb forces are strongest. Thus, in contrast to "non-crystallographic" branching processes, the positions of splittings in the nanocomposite aggregate are not accidental but significantly controlled by the intrinsic electric dipole field and the orientation of polar gelatine fibrils emerging from the prismatic seed (Fig. 4b). This shape development is far from classical growth and branching processes known for crystalline individuals. Obviously, these two completely different mechanisms of branching can result in the formation of spherulites with similar shapes (Fig. 1). Therefore, the branching mechanism can not simply be derived from the outer shape of an aggregate. Detailed knowledge about chemical composition, inner architecture and properties of the branching aggregates is rather necessary.
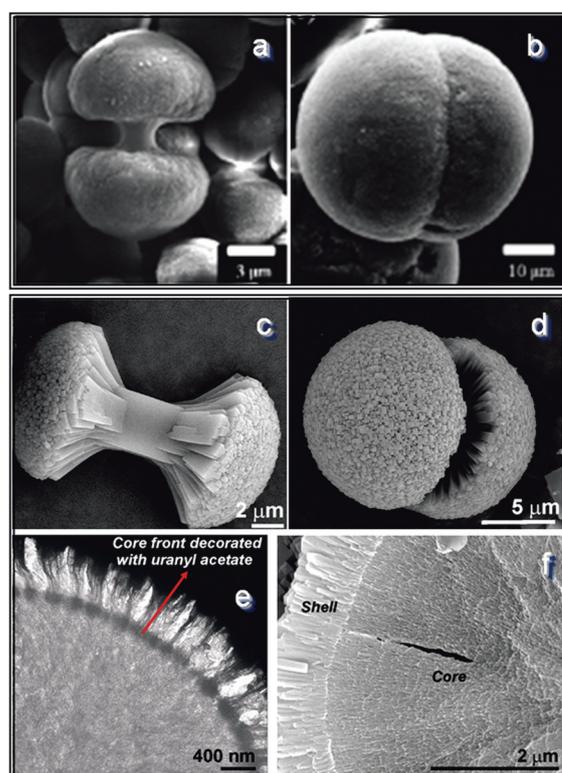

Fig. 5: SEM images of dumbbell- and spherulite-shaped aggregates of (a, b) fluorapatite grown in the presence of citric acid [7e] and (c, d) calcium oxalate dihydrate grown in the presence of polyacrylic acid [8]. (e, f) Inner structure of a calcium oxalate dihydrate dumbbell: (left) TEM image of a FIB cut (stained with 1% uranyl acetate) illustrating that the core front (dark area) is enriched with the organic component; (right) SEM image of the fracture area of a dumbbell showing the core-shell junction region. The core consists of smaller crystals compared with the shell individuals.

As shown in Figure 5a and 5b, fluorapatite aggregates grown in presence of citric acid exhibit nearly the same outer shape as the fluorapatite-gelatine-nanocomposites (Fig. 1b) [7e]. However, there is no evidence, that citric acid drives the morphogenesis of fluorapatite aggregates in a similar way as gelatine macromolecules do. Furthermore, our recent investigations [8] demonstrated, that calcium oxalate dihydrate grown in the presence of polyacrylic acid (PAA) also follows the scenario of "non-crystallographic" crystal branching by formation of dumbbells and spherulites (Fig. 5c, d). The investigation of the inner architecture of the aggregates did not give any evidence for the formation of a well-ordered nanocomposite superstructure. However, the inner architecture of the dumbbell-shaped aggregates is additionally characterized by development of a core-shell arrangement. At the

same time, it has been shown that the core-shell junction region is enriched by the organic component (Fig. 5e, f). Thus, in addition to "non-crystallographic" branching, which mostly takes place on the prismatic faces of initial crystals, new subindividuals can also grow from areas enriched by polyacrylic acid leading to secondary nucleation events.

Summary

Besides classical "non-crystallographic" crystal branching (accidental, stochastic, see Fig. 4a), a second mechanism of spherulite formation is based on "nanocomposite-controlled" scenarios (coded, see Fig. 4b). The latter can be applied to describe spherulite formation of well-ordered complex systems including trends for the development of even higher hierarchies. However, both mechanisms may contribute to the shape development of composite systems giving rise to additional flexibility and generation of even more complex morphologies. Deeper understanding of the general principles including the organization of bio-related nanocomposite superstructures will be a challenge for the near future.

References

[1] (a) *D. P. Grigor'ev*, Ontogeny of Minerals; Israel Program for Scientific Translations: Jerusalem, 1965. (b) *C. Buczinsky and H. Chafetz*, J. Sed. Petr. **61** (1991) 226; (c) *M. Diaz-Espineira, E. Escoalr, J. Bellanato, and J. A. Medina,* Scanning Micr. **9** (1995) 1071; (d) *L. Fernandez-Diaz, A. Putnis, M. Prieto, and C. V. Putnis,* J. Sed. Res. **66** (1996) 482; (e) *R. Warthmann, Y. van Lith, C. Vasconcelos, J. A. McKenzie, and A. M. Karpoff,* Geology, **28** (2000) 1091; (f) *T. Jung , W. S. Kim, and C. K. Choi,* J. Cryst. Growth **279** (2005) 154; (f) *P. Kasparova, M. Antoneitti, and H. Cölfen,* Coll. Surf. A **250** (2004) 153. (g) *J. Tang and A. P. Alivisatos*, Nano Lett. **6(12)** (2006) 2701; (h) *O. Prymak, V. Sokolova, T. Peitsch, and M. Epple,* Cryst. Growth & Design **6** (2006) 498.

[2] *O. Lehmann* "Molecularphysik" Wilhelm Guglemann, Leipzig, Vol. 1., 1888.

[3] (a) *M. N. Maleev*, TNPM Tschcrmaks Min. Petr. Mitt. **18** (1972) 1; (b) *N. Goldenfeld*, J. of Cryst. Growth. **84** (1987) 601; (c) *J. H. Magill* and J. of Mater. Sci. **36** (2001) 3143; (d) *H. D. Keith and F. J. Padden Jr.,* J. Appl. Phys. **34(8)** (1963) 2409; (e) *L. Gránásy, T. Pusztai, G. Tegze, J.A. Warren, and J. F. Douglas,* Phys. Rev. **E 72** (2005) 011605; (f) *Yu. O. Punin,* ZVMO. **110(6)** (1981) 666 (in Russian); (g) *Yu. O. Punin and A. G. Shtukenberg*, Autodeformation

Defects in Crystals; St. Petersburg Univ. Press: St. Petersburg, 2008 (in Russian).

[4] (a) *H. Cölfen and M. Antonietti,* Angew. Chem. **117** (2005) 5714; Angew. Chem. Int. Ed. **44** (2005) 5576; (b) *H. Cölfen and M. Antonietti,* Mesocrystals and Nonclassical Crystallization, Wiley, 2008. (c) *R.-Q. Song, H. Cölfen,* Adv. Mater. **22** (2010) 1301; *(d) R. L. Penn, J. F. Banfield,* Science **281** (1998) 969; (e) *A. Chemseddine and T. Moritz,* Eur. J. Inorg. Chem. **2** (1999) 235; (f) *S. Weiner, I. Sagi, and L. Addadi,* Science **309** (2005) 1027; (g) *O. Pujol, P. Bowen, P. A. Stadelmann, and H. Hofmann*, J. Phys. Chem. B **108** (2004) 13128; (h) *L. C. Soare, P. L. Bowen, J. Lemaitre, and H. Hofmann,* J. Phys. Chem. B **110** (2006) 17763.

[5] (a) *R. Kniep and S. Busch,* Angew. Chem. **108** (1996) 2787; Angew. Chem. Int. Ed. **35** (1996) 2624; (b) *S. Busch, H. Dolhaine, A. DuChesne, S. Heinz, O. Hochrein, F. Laeri, O. Podebrand, U. Vietze, T. Weiland, and R. Kniep,* Europ. J. Inorg. Chem. **10** (1999) 1643. (c) *S. Busch, U. Schwarz, and R. Kniep*, Chem. Mater. **13** (2001) 3260; (d) *S. Busch, U. Schwarz, and R. Kniep,* Adv. Funct. Mater. **13** (2003) 189; (e) *P. Simon, W. Carrillo-Cabrera, P. Formanek, C. Göbel, D. Geiger, R. Ramlau, H. Tlatlik, J. Buder, and R. Kniep*, J. Mater. Chem. **14** (2004) 2218; (f) *P. Simon, U. Schwarz, and R. Kniep*, J. Mater. Chem. **15** (2005) 4992; (g) *P. Simon, D. Zahn, H. Lichte, and R. Kniep,* Angew. Chem. **118** (2006) 1945; Angew. Chem. Int. Ed. **45** (2006) 1911; (h) *H. Tlatlik, P. Simon, A. Kawska, D. Zahn, and R. Kniep,* Angew. Chem. **118** (2006) 1939; Angew. Chem. Int. Ed. **45** (2006) 1905; (i) *R. Kniep, and P. Simon,* in Top. Curr. Chem.: Biomineralisation I, II (Ed.: K. Naka), Springer, Heidelberg, 2007, vol. I, p.73; (j) R. *Kniep, and P. Simon*, Angew. Chem. **120** (2008) 1427; Angew. Chem. Int. Ed. **47** (2008) 1405; (k) A. *Kawska, O. Hochrein, J. Brickmann, R. Kniep, and D. Zahn,* Angew. Chem. **120** (2008) 5060; Angew. Chem. Int. Ed. **47** (2008) 4982; (l) *P. Simon, E. Rosseeva, J. Buder, W. Carrillo-Cabrera, and R. Kniep,* Adv. Funct. Mater. **19** (2009) 3596; (m) *R. Paparcone, R. Kniep, and J. Brickmann,* Phys. Chem. Chem. Phys., **11** (2009) 2186; (n) *J. Brickmann, R. Paparcone, S. Kokolakis, D. Zahn, P. Duchstein, W. Carrillo-Cabrera, P. Simon, and R. Kniep*, Chem. Phys. Chem. **11** (2010) 1851.

[6] http:// en (ru).wikipedia.org/wiki/Kallima

[7] (a) *T. Wang, J. Mitchell, H. Börner, H. Cölfen, and M. Antonietti,* Phys. Chem. Chem. Phys. **12** (2010) 11984; (b) *Z. Liu, X. D. Wen, X. L. Wu, Y. J. Gao, H. T. Chen, J. Zhu, and P. K. Chu*, J. Am. Chem. Soc. **131** (2009) 9405; (c) *G.-Y. Chen, B. Dneg, G.-B. Cai, T.-K. Zhang, W.-F. Dong, W.-X. Zhang, and A.-W. Xu,* J. Phys. Chem. C, **112 (3)** (2008) 672 (d) *N. Sasaki, Y. Murakami, D. Shindo, and T. Sugimoto,* J. of Colloid and Interface Science **213** (1999) 121 (e) *Y.-J. Wu, Y.-H. Tseng, and J. C. C. Chan* ,Crystal Growth & Design, **10(10)** (2010) 4240.

[8] (a) *A. Thomas*, Techn. Univ. Dresden, Fak. Mathematik und Naturwiss., Diss., 2009; (b) *A. Thomas*, W. Carrillo-Cabrera, P. Duchstein, O. Hochrein, P. Simon, E. Rosseeva, D. Zahn, and R. Kniep,* Chem. Europ. J., submitted.