Hard Templates for Soft Materials: Creating Nanostructured Organic Materials[†]

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This review describes the possibilities of using hard templates to create nanostructured “soft” materials, for example, polymer networks, carbon nitrides, or carbonaceous materials, that is, materials which are still organic in their nature. Examples are given for the whole range of hard templates described in the literature, starting from silica nanoparticles, zeolites, and periodic mesoporous silicas to aluminum oxide membranes and colloidal crystals.

1. Introduction

“Templating” essentially involves the replication of one structure into another under structural inversion. For example, the replication of single molecules is used for the generation of the pores in microporous zeolites (pore size $<$2 nm), while molecular aggregates such as micelles are used as templates for the fabrication of mesoporous silicas (pore size 2–50 nm). Thus, in the context of material chemistry, a template, in its most general definition, is a structure-directing agent. In case of direct or “true” templating, the templated material is a 1:1 (but inverse) copy of the template structure, and no changes in order or length scale of the template structure occur. Templating therefore is a versatile technique for the formation of nanostructured or porous materials, as size and shape of the resulting pore structures can be easily tuned by choosing the appropriate template structures.

Materials properties in general can exceptionally profit from the introduction of nanosized dimensions to their overall structure, and thus material nanostructuring has become a field on its own in material science. However, most of the reported nanostructured materials prepared via templating are inorganic, such as silica, metal oxides, or carbon, respectively. This holds for nanoparticles as well as for meso- or microporous materials, and numerous reviews describe their synthesis, properties, and applications.[1–8]

In contrast to nanostructured inorganic materials, the introduction of a nanostructure into organic, “soft” materials is much more restricted and imposes strict requirements on the resulting framework. In general, thermodynamics works against the formation of pores and tiny structural details, and surface areas of materials are normally kept at a minimum: the pores close by plastic deformation of the walls. Thus, polymer chains generally pack space efficiently, because the macromolecules can bend and twist to maximize intermolecular interactions. Therefore, the maintenance of, for example, an interconnected meso- or microporosity in an organic material normally requires a stiff and highly cross-linked polymer system, as it is found in activated carbons[9] or hyper-cross-linked polymer resins.[10]

Another general hindrance for the nanostructuration of chain molecules or polymers is depletion, that is, the entropic restriction of conformations in the nanoconfinement of particles and thin walls. This is why direct templating is usually not obtained via a polymerization reaction: the final structures are interesting but far from the starting situation adjusted with the monomer.[11,12]

Nevertheless, despite these obstacles it is attractive to construct nanostructured soft materials, as the resulting materials combine the properties of organic materials, for example, functionality or lightweight, with those usually attributed to inorganic nanostructures, such as high surface areas and chemical reactivity. Thus, nanostructured organic materials have great potential in catalysis, in membrane science, or as separation, optical, or dielectric materials.[11,13]

This paper intends to review the current status of fabrication of organic, soft materials replica mesostructures by direct templating techniques. It will be shown that successful replication along sufficiently flexible recipes is usually based on hard templates, where kinetic effects can be suppressed. Various nanostructures from different materials such as polymer resins, functional engineering plastics, carbons, and carbon nitrides are described, and the synthetic flexibility depending on the template structure is summarized.

2. “Soft” Materials

In the present context the term “soft” is introduced mainly to differentiate the materials described here from “hard”, that is, inorganic matter and metals. It will turn out that soft is, however, not to be restricted to the classical organic materials, alone, as the transition from engineering polymers to cross-linked pitches, carbonaceous materials, and carbon nitrides is rather continuous. Although polymers, from linear polymer chains to highly cross-linked organic networks, will play a prominent role, these are the borderline cases which are highly interesting for modern material science. For example, as-synthesized graphitic carbon nitride with its real, nonideal structure is not easily categorized as organic or

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inorganic material; rather, it fills the gap between highly cross-linked polymers (organic) and graphite (inorganic). Even more complicated is the classification of some of the intermediates observed during carbonization of molecular or polymeric precursors toward graphite. Often just described as "carbon" in the literature, depending on carbonization temperature a wide variety of intermediate compounds can be considered, which cannot be classified satisfactorily to one or the other term, organic or inorganic. For instance, phenolic resins are often used as precursors for carbonaceous materials, but while samples heat treated at 500 °C are still described as cross-linked polymers, further heat treatment results in species defined as carbon, even though graphitic structures are scarcely pronounced.

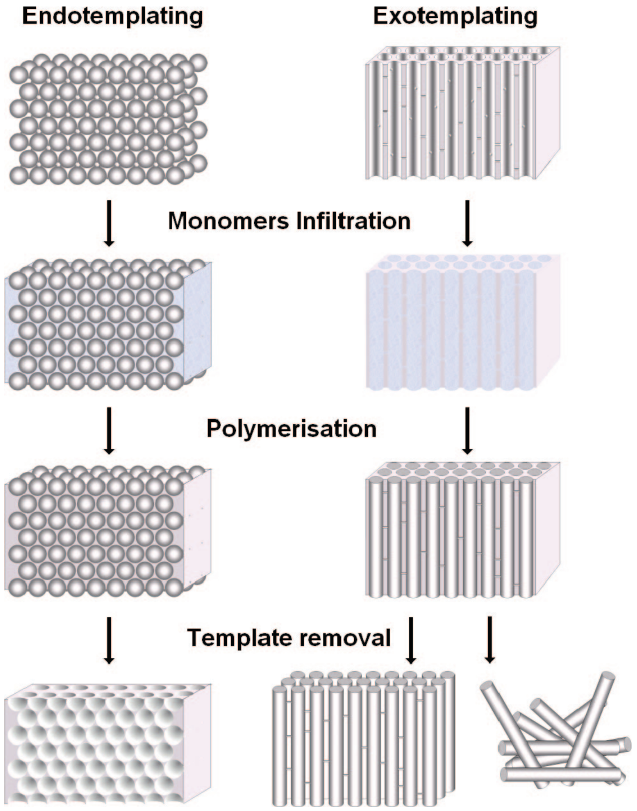
As excellent reviews exist describing the fabrication of mesoporous carbons via templating techniques,[9,14,15] this review will not cover carbons fabricated via pyrolysis. However, when carbonaceous materials are made along polymerization-like, typical soft matter processes, such as, for examples, carbons prepared via hydrothermal carbonization (HTC),[16,17] they will be considered. Such carbonaceous materials can still contain high amounts of heteroatoms and exhibit pronounced and adjustable surface functionality but also show throughout synthesis the typical problems of templating of polymers. This is why we classify them in the present context as "soft materials".

3. Soft Materials and Inorganic Templates

Many attempts to use soft templates for soft materials have been reported in literature, but with some very specific exceptions (e.g., molecular imprinting of hyper-cross-linked networks),[18] they essentially failed. The thermodynamic and physicochemical reasons for this failure as well as a comprehensive list of the diverse soft/soft approaches are summarized in recent reviews.[11,19,20] This is why the focus has shifted to the use of inorganic templates to prepare nanostructured soft materials. Often the template, for example, the porous system of ordered mesoporous silicas, is used to confine, isolate, or align molecules or macromolecules. The topic of inclusion compounds and organic materials in confinement is treated in a number of reviews.[21,22] In these approaches the removal of the template would unquestionably result in the collapse of the organic structure formed in the channels. However, the first step of the preparation of such inorganic/organic host materials is conceptually the same as for the template assisted preparation of nanostructured polymeric materials, so one can learn from those experiments.

The most straightforward process would just involve a simple mixing of the organic compound with the inorganic template; however, this approach has several drawbacks. First of all, the threading of larger molecules into porous systems is experimentally very difficult, because of the associated loss of entropy.[23] Even more problematic is retention of the desired nanostructure which requires most often cross-linked polymeric structures, which naturally excludes infiltration approaches. Thus, in most cases host/guest polymerization reactions are used: Here the template is mixed together with a monomer melt or solution, yielding either a suspension of the template in the monomers (endotemplates) or the incorporation of the monomers in the pores of the template (exotemplate)[24] (Scheme 1).

Scheme 1. Schematic Presentation of Templating Approaches Toward Nanostructured Soft Materials Using Endo and Exotemplates



Polymerization of the monomers can be subsequently carried out by thermal, chemical, electro- or photochemical polymerization (or a combination of those). The templating process does normally imply the removal of the template, here the inorganic phase. As in most examples where silica or alumina templates are used, the removal of these templates can be easily achieved using hydrofluoric acid and strong bases or acids, respectively. The replication of one nanostructure into another can yield a three-dimensional (3D) negative of the respective template structure (transcriptive synthesis).[25] Thus, a mesoporous structure can act as template for the generation of nanoparticles, or when continuous pore systems are used as templates, a replica of the channel system is obtained. Vice versa, nanoparticles as templates can be used for the generation of mesoporous frameworks, with pores reflecting size and morphology of the inserted particles (Scheme 1).

The resulting nanostructures of the organic materials can be analyzed by electron microscopy and, if porous organic materials are prepared, nitrogen sorption measurements. However, often polymers synthesized in confinement also exhibit higher molecular weights, longer conjugation length, higher glass transition temperatures, or higher crystallinity,[26–28] which can be analyzed by spectroscopic, scattering, and chromatographic methods.

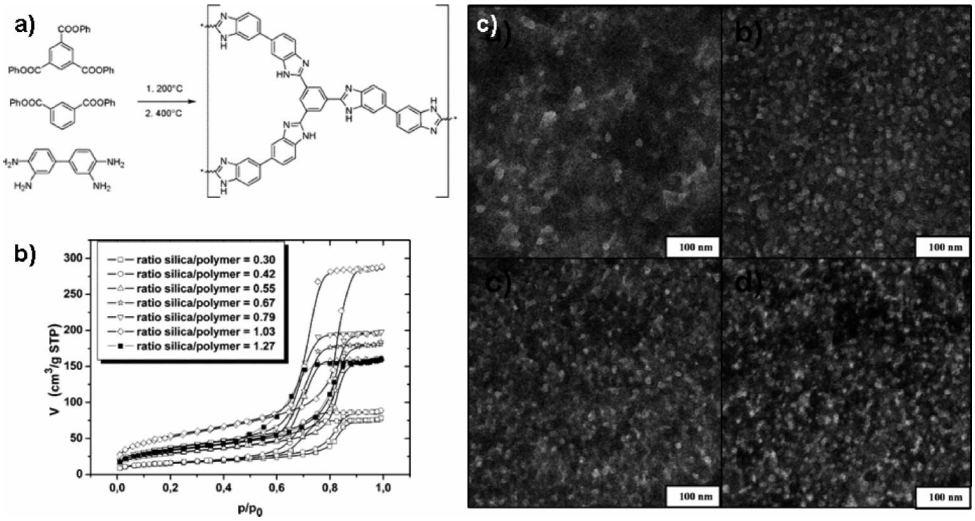


Figure 1. (a) Schematic presentation of the synthesis and chemical structure of cross-linked PBI, (b) sorption isotherms, and (c) TEM pictures of mp-PBI depending on the silica/polymer ratio. Reprinted with permission from ref 35. Copyright 2007 American Chemical Society.

4. Endotemplates

4.1. Silica Nanoparticles. The inclusion of inorganic nanoparticles into polymers as fillers is frequently used to enhance the mechanical properties of the respective polymer phase. Silica but also crystalline inorganic nanoparticles were incorporated into polymer resins, yielding materials with improved hardness, scratch resistance, or flame retardance.[29–32] Templating approaches using nanoparticles conceptually follow the same synthetic routes, just that an additional step to remove the template is required. Thus, to create mesoporous organic materials, silica templates have to be used, whose size fits to the desired pore size and whose surface functionality allows an intermingling with the polymer phase. Fortunately, using the well-known Stöber process (or modified processes therefrom), a wide variety of monodispere silica particles with diameters ranging from 10 to 500 nm can be prepared.[33]

In a pioneering work, Mallouk et al. showed that silica particles indeed can be used to create even ordered mesoporous polymers.[34] In this approach, silica nanoparticles with diameters of approximately 35 nm were used as template. Pellets pressed from these particles were infiltrated with solutions of either pure divinylbenzene (DVB) or ethyleneglycol dimethacrylate (EDMA) monomers or mixtures thereof, together with a free radical initiator. These mixtures filled by capillarity the void spaces between the silica nanoparticles and were subsequently polymerized by heating the composites to 60 °C. After removal of the silica template ordered mesoporous polymers were observed, which perfectly replicated the structure of the inorganic template, as long as DVB was used as the monomer. Interestingly, when the mole fraction of EDMA increases, it was observed that the mean pore size became smaller, decreasing to 15 nm for the pure polyEDMA.

These experiments nicely illustrate some of the basic principles and problems which have to be considered preparing "soft" nanostructured materials: If the introduction of the nanostructure is accompanied with a considerable surface area, the softness and elasticity of most polymeric or organic materials will follow the emerging high interface energies, yielding in an elastic reduction or, finally, the collapse of the pore system. Thus, either high cross-linking densities have to be applied, or the polymers should exhibit stiff main chains. In the present example, both networks are highly cross-linked, but polyEDMA forms more flexible networks than polyDVB, which results in a remarkable shrinkage of the whole system together with an overall decrease in surface area. A second, positive point is that hard templates, when densely packed, indeed work: a potential demixing of the template during the polymerization process is suppressed by the immobile character of the template structure: the polymer simply has to adapt to the given situation.

A detailed study investigating the interplay of porosity, polymer stiffness, and cross-linking density was recently presented with the aim of producing proton conducting polymer membranes. Here, a similar approach was used as described above, however, using smaller silica particles (12 nm) as a template and polybenzimidazole (PBI) as the organic component.[35] The silica particles where dispersed in monomer melts composed of 3,3′-diaminobenzidine and diphenylisophtalate. Here, the aminic character of one of the co-monomers was very beneficial to provide a homogeneous, transparent dispersion of bare unfunctionalized silica nanoparticles. The mixture was then heated to form linear PBIs via melt polycondensation at 400 °C.[36] In some experiments diphenylisophtalate was replaced to a certain extend by a tricarboxylic acid triphenylester, enabling different densities of cross-linking in the resulting PBIs. After removal of the silica templates the resulting porosities and surface areas of the mesoporous PBIs were analyzed by BET, small-angle X-ray scattering (SAXS), and electron microscopy measurements (Figure 1).

Even though PBI is known as a stiff and rigid polymer, no porosity could be observed in the samples prepared without cross-linker, that is, all pores collapse after template removal due to the ductile flow even well below the glass transition of the polymer (i.e., even glassy PBI is "soft").

For polymers containing cross-linking units in every tenth repeating unit, the onset of a preserved inner surface area is observed (76 m^2/g), while the highest surface area is found for the fully cross-linked samples (188 m^2/g). However, already the introduction of the cross-linker in every fifth repeating unit yields surface areas with comparable high values (152 m^2/g); that is, this amount is sufficient to stabilize the hard and mechanically robust framework against ductile flow, ensuring an adequate replication of the hard templates. Interestingly, the pores sizes in this example are nearly independent of the amount of cross-linker, which indicates that in this case no overall shrinkage of the pores is observed but that rather some pores collapse and others do not. This can be explained by a slightly inhomogeneous cross-linking density of the PBI networks.

Several examples can be found in the literature describing the infiltration of phenol−formaldehyde resins with silica nanoparticles.[37,38] However, the aim of these reports was the synthesis of mesoporous carbons; thus, the composites were carbonized at high temperatures, and no attention was paid to the polymer intermediates.

Another interesting example for the preparation of mesoporous polymer networks using silica nanoparticles as template was described by Caruso and co-workers.[39] Layer-by-layer (LbL) self-assembly was combined with templating approaches to produce nanoporous polyelectrolyte polymer thin films. In a first step, a hybrid multilayer assembled from poly(allylamine hydrochloride) (PAH) in alternation with a blend of silica nanoparticles and poly(acrylic acid) (PAA) was produced, which were subsequently cross-linked using a carbodiimide. Removal of the silica template then resulted in mesoporous thin films, with pores reflecting the size of the silica nanoparticles used. These films show better permeability as demonstrated by an increasing amount of bovine serum albumin (BSA) adsorbed compared to cross-linked, but not template-organized, films.

Another “soft” material, which recently was subjected to nanostructuring via templating of silica particles, is graphitic carbon nitride, g-C_3N_4. Graphitic carbon nitride is produced via simple heating of cyanamide, dicyanamide or melamine to 600 °C, resulting in the condensation of these compounds first into single tri-*s*-triazine units (“melem”), polymeric tri-*s*-triazine (“melon”), and finally a more or less condensed graphitic C_3N_4.[40] (It should be noted that Schnick and co-workers recently showed that one of the condensation intermediates, the polymeric melon, in fact is composed of linear connected tri-*s*-triazine units and features X-ray diffraction (XRD) patterns which are close to these expected for the perfect graphitic carbon nitride.)[41] As g-C_3N_4 synthesis is a high-temperature procedure, appropriate templates that withstand 600 °C for at least 12 h are needed for the scaffolding of the mesoporous system, and silica nanoparticles were used as hard templates. The monomer, cyanamide, is melting close to room temperature, and because of its aminic character, bare silica nanoparticles of 12 nm in diameter could be homogeneously dispersed. Heating to 550 °C and subsequent removal of the silica template yielded a mesoporous graphitic carbon nitride (mpg-C_3N_4) with disordered pore systems of spherical pores with a mean diameter of 12 nm, thus obtaining the negative image of the structure of the silica sol. In addition, the retention of the graphitic structure was proven by selected area electron diffraction and XRD measurements. Furthermore the overall pore volume and surface area could easily be tailored by the amount of silica used in respect to the starting monomer, cyanamide.[42]

The above described examples show that silica nanoparticles are suitable hard templates for soft materials. Major advantages are that they are available in almost every size, starting form 10 nm up to the micrometer range by easy and well described processes. Also many silica particles with various sizes are commercially available, as they have found widespread use in industry. However, some major drawbacks are also associated with these templates: First of all, silica nanoparticles tend to aggregate and can subsequently segregate from the emerging polymeric networks. Thus, the right surface chemistry has to be addressed to ensure a homogeneous dispersion of these templates in the preceding monomer melt or solution and resulting polymeric networks. Additionally, while spherical silica nanoparticles are easy to prepare, the fabrication of other template morphologies is not a trivial task. Thus mesoporous materials with cylindrical instead of spherical pores would require the use of silica nanorods as template, which are not commonly available.

4.2. Colloidal Crystals. Colloidal crystals, 3D periodic structures formed from monodisperse colloids, have stimulated wide interest in recent years owing mainly to their interesting optical applications.[43–45] Most often silica or polymer spheres, exhibiting diameters of several hundred nanometers, are used to assemble such colloidal crystals. Therefore, these nanoparticles can be easily distinguished from the templates described in section 4.1 as their replication typically results in macroporous materials (pore sizes >50 nm).

A replication of an ordered colloidal array results in so-called “inverse opals” which conceptually exhibit the same optical properties, such as a photonic band gap, as the colloidal crystal template. As a consequence colloidal crystals have been frequently used as templates for silica, metal oxides, metals, metal chalcogenides, organosilicas, carbon, and also polymers.[46]

Inverse opals made from polymers are attractive as they extend the use of diffractive optics into applications that require lightweight and low cost. Also, because of little volume shrinkage during polymer curing in comparison to inorganic systems, large area samples can be prepared. However, for optical applications it should be noted that the refractive index of polymers is considerably lower than those of most inorganic materials, thus yielding a low dielectric contrast (polymer/air).

The use of colloidal crystals as templates usually follows three steps: In the first step the colloidal crystal is formed by packing uniform spheres into 3D arrays. In the second step the interstitial space between the spheres is filled with molten or dissolved monomers, which are subsequently polymerized. In the final step the template is removed either chemically or by thermal treatment of the composite, yielding macroporous polymers.

Xia et al. described the use of latex and silica spheres as templates for 3D macroporous poly(urethane) membranes.[47–49] In the case of latex spheres the template was removed by dissolution of the polystyrene (PS) in toluene. A variety of conventional polymers, including PS, poly(methyl methacrylate) (PMMA), or epoxy resins were templated with colloidal silica spheres to yield macroporous polymers.[50] Other porous polymeric materials synthesized by colloidal crystal templating include poly(acrylate−methacrylate) copolymer,[49] polypyrrole and polythiophene,[51] polyaniline (PANI),[52,53] polymer/nanoparticles composites,[54] hydrogels,[55–57] phenol−formaldehyde resins,[58,59] and graphitic carbon nitrides.[60]

An interesting application of macroporous polymers made from colloidal crystal templates was described by Colvin et al.[61] In this report the polymer frameworks were used as template by themselves for the preparation of a variety of monodisperse colloids. In a first step colloidal crystals assembled from silica spheres were replicated into either PMMA or PS inverse opals. The replicas could be refilled with metal or metal oxide precursors to form spherical colloids, principally generating direct copies of the first used silica particles. However, not only inorganic materials were replicated but also polypyrrole and poly(phenylenevinylene) colloidal spheres were synthesized using this approach. Intriguingly, the authors further used the mechanical property, that is, the "softness", of their polymeric materials to produce rather unusual exotemplates: By heating the macroporous polymers above their glass transition and stretching the films by a uniaxial or biaxial force, elongated pore structures were produced. Cooling to room temperature fixed these structures in the then glassy, inflexible polymer. Thus, depending whether on one- or two-dimensional extension was applied, ellipsoidal or oblate pores were observed, which could be nicely replicated into, for example, TiO_2 ellipsoidal colloidal crystals.[61]

A feasible large scale fabrication of macroporous polymers using colloidal crystal templates was recently accomplished by essentially combining steps 1 and 2 in the above sketched preparation. In this report a dispersion of monodisperse silica colloids in a triacrylate monomer together with a photoinitiator were spin-coated on substrates, leading to shear induced ordering of the silica particles. The composite films were subsequently exposed to ultraviolet light inducing the polymerization. Removal of the silica yielded large-area macroporous polymers with controllable thickness (Figure 2).[62]

In summary, colloidal crystals are feasible templates for the generation of macroporous polymers. These polymers can find interesting optical applications as they act as diffractive optics for visible light. However, several other applications can be envisaged, for example, as catalytic surfaces and supports and separation and adsorption media and in chemical sensing and biosensing.

4.3. Coating Endotemplates. Colloidal particles of several hundred nanometers in size have been frequently used for the nanoengineering of polymer and organic/inorganic hybrid hollow spheres using LbL self-assembly.[63,64] Particles, which can in principle also assemble into colloidal crystals, are here used in dispersion rather than in bulk. Consequently, not the voids of crystals are replicated, but a coating onto the template particles is formed, yielding isolated hollow objects after removal of the template. Mainly silica or PS latex particles were used as template for this approach. Oppositely charged polymers but also nanoparticles, lipids, or multivalent dyes are then consecutively adsorbed on their surface, forming multilayer coated particles and hollow objects after template removal. As a result, the buildup of the capsule wall is modular in terms of its composition, whereby each one of the wall components adds functionality to the multilayered capsules.[65] Shell thickness is determined by the number of layers but typically measures a few nanometres. The variable size of the capsules can be fully controlled from 50 nm to tens of micrometers. In terms of the new development of LbL capsules, one domain that will be strongly addressed in the future concerns biological applications.[66,67] Polyelectrolyte capsules have now become a field on its own in material science; thus ,a comprehensive overview over this field is out of the scope of this review. However, there are several reviews found in the literature containing more information about this special templating technique.[65,68–72]

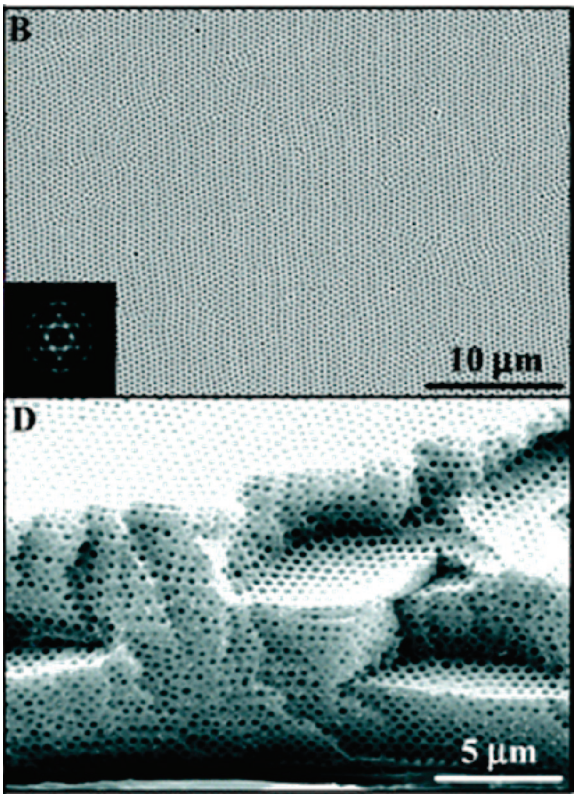


Figure 2. Self-standing macroporous polymer replica after removal of silica spheres by wet etching: top-view (top) and side view (bottom) SEM image and its Fourier transform (inset). Reprinted with permission from ref 62. Copyright 2004 American Chemical Society.

Leaving the spherical templates, Qian et al. used tellurium nanowires as template in HTCs.[73] Te nanowires were dispersed in water, and then glucose was added to the dispersion. Subsequent heating of the mixtures in closed autoclaves resulted in the formation of carbon coated tellurium wires. The nanostructured were placed in 5% H_2O_2 to remove the tellurium core, yielding uniform carbon fibers under soft collapse of the primary nanowires hole. A similar approach was conducted using silver or copper nanowires as templates, however with the crucial difference that these nanowires are formed in situ during the HTC.[74,75]

5. Exotemplates

Besides putting particles within a monomer melt to react around (i.e., "endotemplating"), also the inverse situation can be envisaged. Here, the monomer mixture is filled within a nano- or microstructured, hard reaction environment (the "exotemplate"). For this purpose, many inorganic matrices are suitable, which are discussed in the following paragraphs.

5.1. Zeolites. Zeolites and related molecular sieves are typically synthesized by hydrothermal (or solvothermal) methods. They are crystalline, feature a narrow distribution in pore size, and the topology of interconnections between those pores is well-defined. Zeolites in general exhibit pore sizes smaller 2 nm; that is, they are "microporous". As an important industrial product they are commercially available, but also a vast variety of synthetic schemes toward zeolites with various pore structures are described in the literature.[76,77] Because of the very small size of their cages and channels, with dimensions ranging those of organic molecules, zeolites feature an interesting and extreme case for testing the versatility of the described replication strategies.[78]

Several groups studied the polymerization reaction in zeolites and the properties of the resulting polymers incorporated in the cage structures. Zeolite-inclusion compounds of PS,[79] PMMA,[80] poly(ethylacrylate),[81] poly(acrylnitril),[82] and poly(vinylethers)[23,83] have been reported. Also conducting polymers such as poly(methylacetylenes),[84] polypyrrole,[85,86] poyaniline,[87–89] and polythiophene[90] were successfully incorporated into zeolites by aligning and connecting precursor molecules in the pores, yielding in isolated "molecular wires".[28,91] However, as in these examples where mainly linear polymers were formed, the preservation of an inverted porous structure into the polymer without pore collapse could not be expected and was not the aim of these studies.

The first replication of the porous structure of zeolites into polymers was described by Mallouk and co-workers.[78] Three zeolites, exhibiting different pore network topologies, were used as the hard template. Infiltration of the pores with phenol and formaldehyde yielded first in an acid catalyzed formation of a phenolic resin polymer, which was subsequently thermally cross-linked at 500 °C. Depending on the type of zeolite used as template, the formation of microporous polymers was observed, which however lacked the long-range order of the pores observed in zeolite framework. As thermal cross-linking was carried out at higher temperatures, elemental analysis of the organic replica showed that carbonaceous cross-linked polymer rather than graphitic carbon was formed.

Another recent attempt to confine and direct the growth of a polymer using zeolite templates yielded in unexpected polymer morphologies.[92] Styrene, methyl methacrylate (MMA), or DVB monomers where infiltrated into zeolites using a supercritical fluid inclusion technique and thermally polymerized. However, removal of the zeolite did not yield replica structures but flowerlike polymer microstructures. It was stated that these structures were actually formed during zeolite removal with HF, because of assembly of the polymer and the intermediately formed Na_2SiF_6 crystals. Interestingly, this was also described for DVB monomers, which should actually result in highly cross-linked networks. This example shows that, besides infiltration of monomers into small pores, polymerization in confinement, and the preservation of the porosity against high capillary pressures, the removal of the templates can also play a crucial role and have to be optimized for the successful fabrication of mesostructured soft networks.

Several other attempts describing polymerization within zeolite nanocages are found in the literature. However, in these reports the incorporated polymers are carbonized prior to template removal to fabricate microporous carbons.[93–95]

5.2. Periodic Mesoporous Silicas. Since the first report on periodic mesoporous silica, MCM-41, rapid development could be observed regarding the synthesis of mesoporous materials with various structures and compositions. A great variety of mesoporous materials have been synthesized using micelles of surfactants or block copolymers as template, yielding various morphologies, for example, ordered hexagonal or cubic pore structures. In general, mesoporous materials feature pore sizes in the range 2–50 nm. Thus large molecules are much easier to incorporate into the porous structure compared to microporous materials, such as zeolites. Consequently, a large variety of polymers have been incorporated into mesoporous silicas and metal oxides. In many of those reports, the pore channels act as nanoreactor or nanoconfinement, to align linear polymer chains.[21,22,28,96,97] We will focus here on "real" replication approaches, that is, where, at least, parts of the structural characteristics of the mesoporous materials are transferred into the pure polymer phase.

For the generation of structured polymeric materials via templating approaches, two cases can be distinguished: In the first case, polymerization is carried out in the confinement of the mesopore, but the growing polymer chain is extruded from the template structure. Thus, the template has not to be removed to observe the pure polymer. Kageyama et al. described the synthesis of crystalline nanofibers of ultrahigh molecular weight polyethylene by extrusion polymerization from mesoporous silica fibers.[98] For this, ethene was polymerized with Cp_2TiCl_2 grafted on the interior of the mesoporous silica fiber using MAO (methyl aluminooxane) as a cocatalyst. Scanning electron microscopy (SEM) revealed the formation of 30–50 nm fibers with a very high crystal density, pointing to highly aligned polymer chains within the fibers. Subsequent to this first report on nanoextrusion polymerization, further investigations on this fabrication technique has been described in the literature. Thus polyethylene and polypropylene nanofibers were prepared from MCM-41 and SBA-15 supported titanocene and zirconocene catalysts.[99–101]

In a first report about the use of mesoporous silicas to form nanostructured polymeric materials, Mallouk, Ozin, and

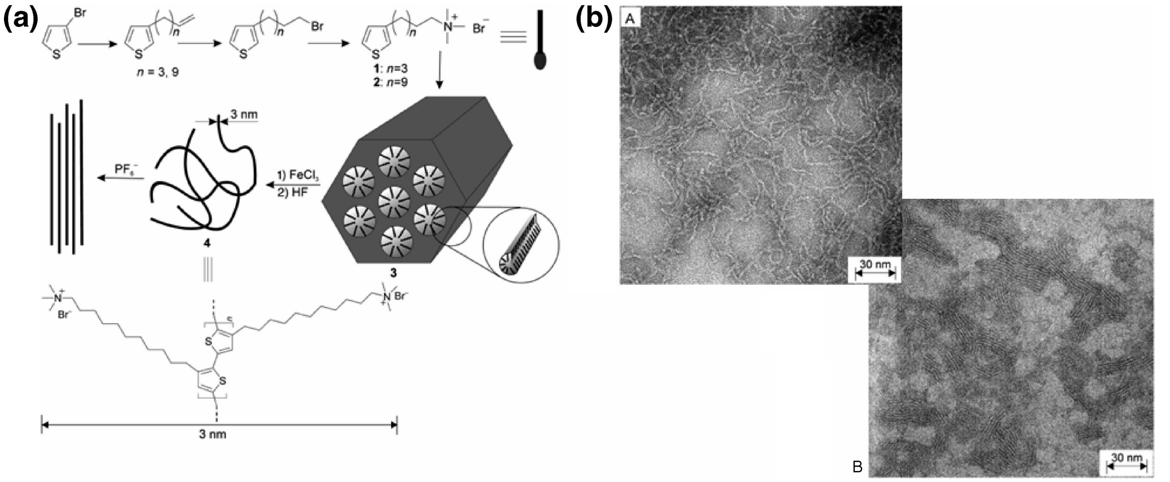


Figure 3. (a) Schematic presentation of the fabrication and organization of conjugated polythiophene molecular wires with mesoporous silica MCM-41. (b) TEM images of (A) the conjugated molecular wires from the polymerization of **2** and (B) the organized wires upon the addition of PF_6^- ions. Reprinted with permission from ref 104. Copyright 2003 Wiley-VCH.

co-workers[102] described the synthesis of poly(phenolformaldehyde) mesofibers using MCM-41 silica as a mold. Phenol and formaldehyde were incorporated into the channel structure of the silica and submitted to HCl vapor to initiate an acid catalyzed polymerization and then heat treated to 500 °C for 12 h to induce cross-linking. After removal of the silica via HF treatment, polymer mesofibers were observed, showing diameters which are comparable to the pore diameter of the template.

An intriguing approach toward functional polymer nanofibers was introduced by Fuhrhop et al.[103,104] and Aida et al.:[105] Here the monomers acted first as organic template for the generation of the mesoporous silica, which then served in a second step as a hard template for the polymerization toward polymer nanofibers. This was achieved by using pyrrole, thiophene, or styrene containing surfactants, which could be assembled (similar to the classical MCM-41 synthesis) into monomer/silica composites, with the monomer molecules aligned in the cylindrical mesochannel. Polymerization of the monomers then occurred under retention of the assembled structures, providing polymer silica nanocomposites. Removal of the silica template yielded PS or conjugated molecular polythiophene wires, respectively (Figure 3).

Taking replication one step further, Goltner et al. reported for the first time on the synthesis of mesoporous polymers.[106] A mesoporous silica monolith was used as template. A mixture of the monomer (MMA), cross-linker (EDMA), and initiator (azobisisobutyronitrile, AIBN) was soaked into the monolith, and polymerization was initiated by heating the samples to 65 °C for 2 days. After removal of the silica, the organic polymers maintained the original shape of the monolith. SAXS measurements on the monolith further revealed that the higher order reflections originating from the hexagonal symmetry were transferred to the polymer structure.

Curiously, interest in the polymeric replica from mesoporous silica seemed to vanish for some time, probably because it was overwhelmed by the successes achieved synthesizing mesoporous carbon replicas. Thus, although several polymers, for example, poly(furfurylalcohol) or phenolic resins, were synthesized inside various mesoporous silicas, the resulting the composites were always directly subjected to pyrolysis to generate mesoporous carbon. Nevertheless, some time later Kim et al. reported on the synthesis of highly ordered mesoporous polymer networks.[107] MCM-48 (cubic) and SBA-15 (hexagonal) silicas were used as templates, and DVB was used as the monomer. Infiltration of the monomer solution together with the initiator AIBN and heating yielded silica−polyDVB composites and, after removal of the silica, ordered polymer networks, which perfectly reflected the structure of the preceding silica templates (Figure 4).

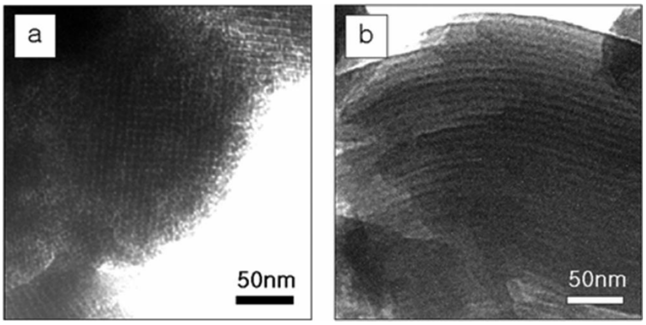


Figure 4. TEM images of thin sections of mesoporous polyDVB networks obtained by replication of calcined silica (a) MCM-48 and (b) SBA-15. Reprinted with permission from ref 107. Copyright 2001 Royal Society of Chemistry.

Furthermore, nitrogen sorption measurements showed that at least parts of the mesoporous structure were retained in the polymer replica, which revealed high surface areas of 610 m^2/g and 410 m^2/g, respectively.

The cylindrical pores of SBA-15 were also used as nanoreactor for the fabrication of polymer composite nanostructures: Polypyrrole/PMMA coaxial nanocables where fabricated using a two-step approach: First MMA was polymerized inside the SBA-15 channels, however at a concentration yielding PMMA tubular structures covering the pore wall of the silica. Pyrrole was subsequently infiltrated into the tubular holes of the PMMA/SBA-15 composite followed by oxidative polymerization using $FeCl_3$ solution. After removal of the silica, orientated and unidi-

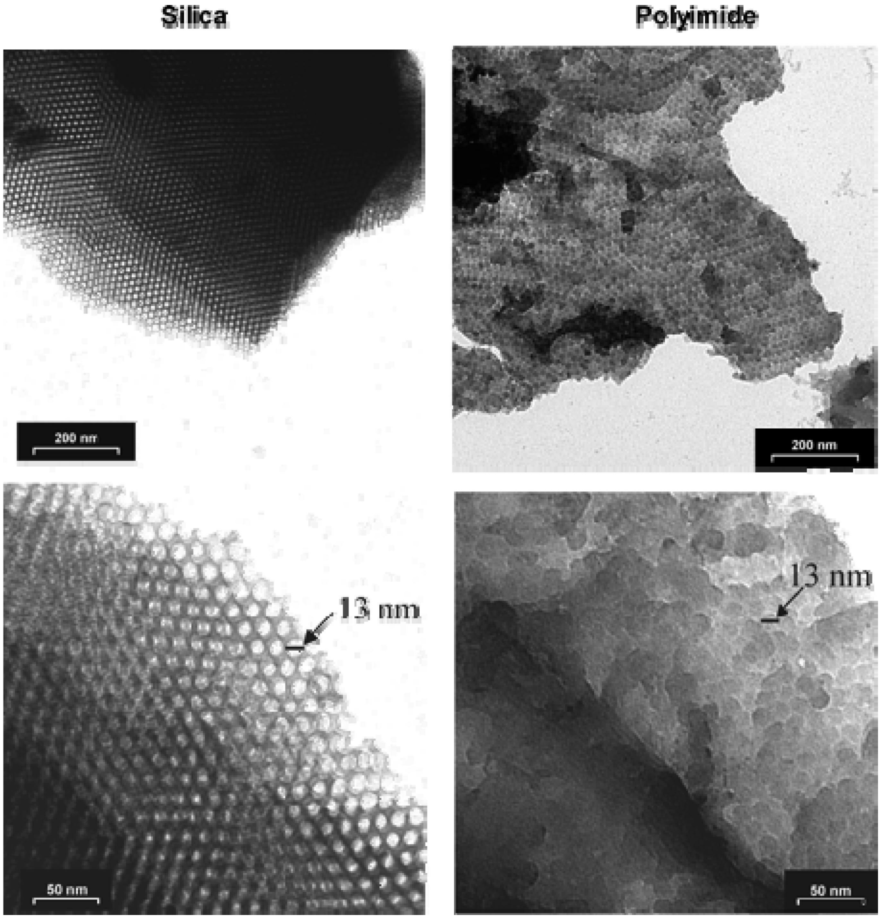


Figure 5. TEM micrographs of the pore structure of the silicas synthesized with block copolymer micelles as template (left) and the resulting polyimide replicas (right), Reprinted with permission from ref 110. Copyright 2004 American Chemical Society.

rectional structures of the polypyrrole/PMMA composite were observed, evidenced by atomic force microscopy (AFM) measurements, which was claimed to be a result from the template synthesis inside the regular hexagonal arranged mesopores of SBA-15.[108]

Nanoparticles made of a high performance polymer, aromatic polyimide, were prepared in a silica monolith exhibiting spherical pores assembled in a fcc-type arrangement.[109] Aromatic polyimide is synthesized via polycondensation of *p*-phenylenediamine and pyromellithic dianhydride. Solutions of these two monomers in dimethylformamide where cooled to −60 °C (to avoid bulk polymerization in solution) and mixed together, and the silica monolith was added. After separating the monolith from the solution, stepwise polymerization of the monomers occurred inside the pores, first at room temperature, to a poly(diamic acid), and then after heat treatment at 300 °C, to the fully condensed polyimide. After template removal, transmission electron microscopy (TEM) measurements clearly indicated that the spherical shape and the diameter of the pores (13 nm) were replicated into polyimide nanoparticles (Figure 5).[110] However, AFM measurements evidenced that replication was limited to the mesopores, while the micropores, that is, the pore interconnections, were not replicated. The process therefore yielded polyimide nanoparticles rather than the interconnected mesoporous polyimide replicas. That replication of smaller structures failed is probably due to the stiffness of the polyimide chains, making replication of very small and probably contorted micropores impossible to achieve. As micropores feature diameters smaller than 2 nm, they would also allow just a few, if not just a single, polymer chains to accommodate, which is probably too small to secure covalent linkage throughout.

A similar observation was made when mesoporous silicas exhibiting the same type of pore arrangement were used as templates for an even more rigid polymeric structure, graphitic-carbon nitrides. Condensation of cyanamide was carried out in the spherical pores of different mesoporous silicas, exhibiting pore diameters of 5, 13, and 60 nm, respectively. Isolated C_3N_4 particles were observed after removal of the silica template, reflecting the size of the spherical mesopores.[111] In none of the resulting carbon nitride replicas were interconnections between the particles found. Also here the authors assign this to the special architecture of the templated material: g-C_3N_4 is composed of tri-*s*-triazine units approximately 1 nm in size; that is, these motifs are simply too big to form in the micropores.

Using templating, mesoporous carbon nitrides with compositions differing from the ideal stoichiometry C_3N_4 have also been prepared. Vinu and co-workers reported on the use of SBA-15 mesoporous silica as template for a mesoporous carbon nitride.[112] The silica template was added to a mixture of ethylenediamine and carbon tetrachloride, and the obtained composite was heat treated in a nitrogen flow.

Removal of the silica yielded a material with high surface area (505 m^2/g) and regular porosity, replicating the structural features of the SBA-15 template. However, it was shown that the resulting material features a composition closer to "C_5N" and that the internal structure is amorphous, which makes the term "nitrogen doped carbon" probably more suitable to describe the material. Interestingly, micropores of the silica material in this example were perfectly replicated, showing that crystallinity and rigidity of the resulting material can have crucial influence on the outcome of the templating procedure and final mesostructure.

SBA-15 was also used as a template for the preparation of a mesoporous carbonaceous material produced via HTC. The HTC comprises the heating of carbohydrates and water in closed containers to 180 °C for several hours. Meanwhile, several articles have shown the versatility of this method for the production of micrometer sized carbon spheres or carbon core/metal oxide shell structures.[16,75,113] The internal structure of the carbonaceous materials observed after HTC, however, differs strongly from the carbons prepared via pyrolysis. Thus, still a high amount of oxygen and hydrogen is found in the samples (carbon content 70–80%), which makes the carbons "hydrophilic", that is, dispersable in or wettable with water. The abundance of chemical reactive oxygen groups in the material together with a templating approach was used from Titirici et al. to prepare mesoporous ordered hydrophilic carbons (OHC):[114] The pores of SBA-15 silica, showing a carefully adjusted surface chemistry and polarity using temperature treatment, were completely of partially filled with 2-furaldehyde (furfural). The resulting furfural/SBA-15 wet sands were placed in autoclaves followed by heating them at 180 °C for 24 h. After template removal the observed carbonaceous materials showed a carbon content of approximately 70%. It was shown that the remaining functional groups were accessible for further chemical reactions. Thus, a one-step functionalization with 3-chloropropylamine yielded an aminated carbon with extremely high amine content. The mesostructure of the materials prepared using different filling rates of the carbon precursor were accessed using nitrogen sorption isotherms, SAXS, and TEM measurements. It was shown that a completely filled SBA-15 template yielded materials comparable to the well-known CMK-3 mesoporous carbons, that is, a complete replication of the porous system of SBA-15 can be assumed.[115] However, some interesting structural features were observed for the carbon prepared by partial filling of the template. It could be assumed that such an approach should yield a carbon structure similar to CMK-5,[116] that is, a bimodal mesoporous material. The bimodality in CMK-5 arises form an incomplete filling of the cylindrical mesopores of SBA-15, yielding interconnected carbon nanopipes. Thus two pore sizes are observed, first from the replication of the silica pore walls and second from the inner pipe diameter. However, for the OHC material, no bimodal pore size distribution was observed, as the smaller pore sizes, which would be attributed to the replication of the silica pore walls, were missing. On the other side, the pore diameter attributable to the inner pipe diameter was considerably larger and even almost reached the pore diameter of the preceding silica. Thus a significant restructuring after removal of the template due to the softness of the carbon was assumed. Nondirectional pore collapsing, that is, simple shrinkage of the whole system, could be excluded by SAXS analysis, as no shift in the (100) reflection was observed. It is therefore more likely that the smaller pores do collapse while the larger pores expand at the same time, a localized version of Ostwald ripening we regard as typical for soft mesoporous materials. This assumption was backed by the finding that the pore size of the pure carbon compared with the composite increases by approximately 1 nm.

To summarize this chapter, periodic mesoporous silicas have been proven to be versatile hard templates for the nanostructuring of soft materials. However, there are several aspects which have to be considered using this approach, which play just minor roles replicating hard materials. First of all, to make the structure of the template correlate with the chemical structure of the replica, rigid, stiff, or multiple cross-linked structures have to be chosen. Interestingly, the micropore system, which is needed to empty and fill the mesopores with monomers, is lost when the structure generated by polymerization is not compatible with the pore structure. Thus, it was shown that stiff, aromatic polymer chains or nitride frameworks composed of bulky building units are unable to replicate the micropores. That way, often separated nanoparticles, -sheets, or -rods are obtained.

On the other hand, also restructuring of the material after template removal can occur because of the softness, yielding in mesostructures which can differ in relevant details from the structure of the original template.

5.3. Other Porous Silicas. Periodic mesoporous silicas are the standard exotemplates and have undoubted advantages considering their defined pore structures and monodisperse pore sizes. However, one has to admit that periodicity in applications is sometimes overrated[117] and actually only justified when properties of the materials are exceptionally enhanced by introducing order. Otherwise, the expenses associated with the preparation of periodic mesoporous materials rule out these materials for mass applications. More importantly, those regular structures are in fact in the sense of the word "minimal structures"; that is, they offer the minimal surface area and the maximal diffusion or transport resistance for a given length scale, so exactly what no one wants for a real life application. On the contrary, porous materials with multiple, hierarchical pore structures are beneficial, where the larger pores simplify transport while the smaller pores provide the system with the required large surface areas for exchange.[118] Therefore, turning to cheap and easy producible hard templates with appropriate structural morphology is, in an applied view, certainly a step in the right direction. Commercially available silica nanosols, discussed in section 4.1, can serve as an example. However, porous materials, which can act as suitable templates, are also commercially available or easy to produce from cheap precursors. An abundance of such materials is provided from the field of chromatography and separation. Indeed the stationary phases of HPLC columns are often composed of porous silica spheres,[119,120] and experimentalists can choose between various average pore sizes and particle diameters.

Furthermore, as there is a lasting interest in the development and improvement of such phases, throughout the literature there are several reports concerning synthesis of these porous silica beads.[121,122] Thus, it was not surprising that such porous silica beads were used as template for polymers, which then were likewise applied as stationary phase material.

Several authors did not restrict themselves to a simple templating approach but rather used an intriguing combination of hard templating and molecular imprinting. Molecular imprinting uses small molecules as template and thus structures polymers on a molecular scale.[123–125] The synthesis is usually performed by copolymerization of functional and cross-linking monomers in the presence of a molecular template (imprint molecule) and additional solvents as porogenes. The functional monomers have to interact with the template molecules by covalent or noncovalent bonding. After polymerization the template molecules are removed by extraction or chemical cleavage leaving molecular imprinted cavities according to the shape and chemical structure of the imprint molecules. Several reviews are available in the literature discussing the synthesis of molecular imprinted polymers (MIPs) and also their application in separation and sensing.[18,126,127] Molecular imprinting of small molecules has been carried out mainly with the template (imprint) molecules in free solution. Mosbach and co-workers presented a novel imprinting method based on oriented immobilization of the template onto a solid support, thus combining soft and hard templating.[128] As a hard template, a commercially available amino functionalized silica gel was used. The drug theophylline was immobilized by covalent bonding on this solid support, and then the pores were filled with a prepolymerized mixture of trifluoromethylacrylic acid (TFMAA) and DVB, together with an azo-initiator. The mixture was then allowed to polymerize. Removal of the solid support generated a polymer with uniform macropores with the selective binding sites well positioned on the surface of the pores. This was proven by readsorption of the drug theophylline. Indeed the imprinted polymers showed a higher capacity for the drug than a control polymer made by templating of an unfunctionalized silica gel.

Not much later this approach was expanded to porous silica beads as template, which then not only provided the porosity but also the morphology and microstructure directly suitable for a chromatographic column.[129,130] A prepolymerized imprinting mixture containing the functional monomer, an initiator, and the print molecule was infiltrated into the silica beads and subsequently polymerized.[129] Alternatively, the print molecules were immobilized first on the silica beads, and subsequently the monomer mixture was polymerized, replicating the porous structure and the print molecule (Figure 6).[130] Both approaches yielded polymer structures and morphologies similar to the mirror image of the original silica template and showed their feasibility in the imprinting and recognition of small molecules, more precisely small drugs in the first case and nucleotide bases in the second. This combination of hard templating and imprinting was also demonstrated to be particularly interesting, as a narrow pore size distribution was observed in the resulting polymers, which is in stark contrast to the broad distribution observed for the conventional bulk materials prepared without the use of a hard template.[131]

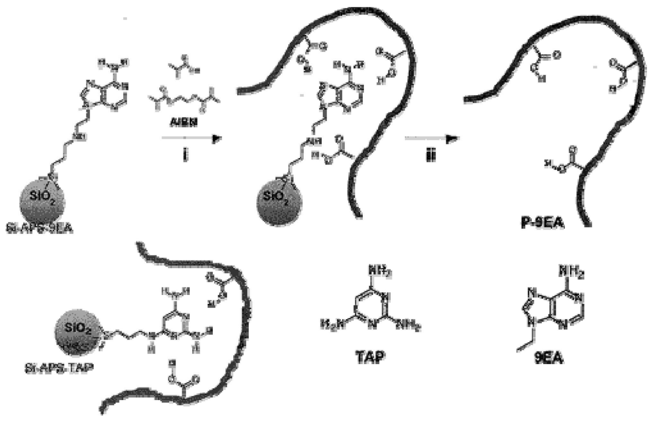


Figure 6. Approach used to prepare surface-confined templated sites for structures containing the adenine or triaminopyrimidine functionality. Reprinted with permission from ref 130. Copyright 2002 American Chemical Society.

In a related approach, Titirici et al. expanded this concept to peptide recognition.[132] Peptides were synthesized using a standard Merrifield chemistry with an aminopropylsilica (APS) with an average pore size of 11.5 nm as a common support material. Support and peptide were then used as template by filling the pores with the monomer/initiator mixture. Polymerization and removal of the template resulted in organic polymer beads with a size and morphology reflecting those of the original silica mold, with surface areas of approximately 200 m^2/g and average pore diameter of 5.4 nm. The polymers where thereafter directly used as stationary phase and showed enhanced retention factors for amino acid derivatives and peptides. Most importantly, the retention and imprinting factors far exceeded those observed using conventional bulk imprinted materials, evidencing the positive influence of the defined porosity introduced via templating.

Caruso and co-workers used LbL self-assembly inside the pores of a mesoporous silica sphere to obtain micrometer sized nanoporous polyelectrolyte spheres.[133] The surface of a bimodal mesoporous silica (pore sizes 2–3 nm and 10–40 nm) was functionalized with aminopropyltriethoxysilane (APTS), and subsequently LbL deposition was carried out with oppositely charged PEs (PAA and PAH). It is important to note that cross-linking of each PE layer was performed by heating the samples, forming amide bonds between the carboxylic acid and amine groups of the polymers. This treatment enhanced the structural stability of the layers. No cross-linking on the other hand yielded partial desorption of the polymers from the mesopores. It can be assumed that the cross-linking also has a crucial influence on the retention of the resulting pore structure in the polymer. Thus after removal of the template, free-standing polymer microspheres were observed featuring an interconnected polyelectrolyte network, with pores ranging from 5 to 50 nm. The diameter of the spheres was shown to be dependent on the number of polyelectrolyte layers, so polymer spheres made from a higher number of layers underwent less shrinkage. The spheres showed excellent capacity for the immobilization of enzymes. Not much later, a similar approach was reported to prepare enzyme-loaded, biocompatible microcapsules.[134] Here the enzyme was first immobilized on the mesoporous silica sphere which was subsequently loaded with poly (lysine) and poly(glutamic acid) by LbL technique. After removal of the silica template, it was shown that the enzyme (catalase) can be released by pH- or salt-induced permeability changes in the PLL/PGA microcapsules.

Beside structure and size of the template also its surface chemistry can have a crucial influence on the outcome of a templating reaction, as it controls wetting and binding. This was recently demonstrated by using mesoporous silica spheres as templates for carbons prepared via HTC.[135] In principle, all reactions were carried out from a dispersion of the silica spheres in aqueous solutions of the monomer (furfural) and subsequent HTC of these dispersions in autoclaves at 180 °C for several hours. However, mesoporous silica spheres with different surface polarities where applied as templates, yielding different micro- and mesostructured carbon replicas. Refluxing of the silica particles in HCl yields silica surfaces with abundant −OH groups, which was denoted as "very hydrophilic". For this template, a complete demixing of the monomer and the silica template was observed, that is, the carbonization completely occurred in the water phase and not in the pores of the template. The reaction of the hydroxyl groups with trimethylchlorosilane, on the other hand, yielded silicas with "very hydrophobic" surfaces. Also these spheres failed to act as a molecular template, as the water/monomer mixture could not penetrate the pore system. The silica particles were then floating at the surface of the carbon precursor solution, and monolithic carbonaceous layers with mesoporous silica beads being embedded in its surface were observed. Silica spheres where about half of the silanol groups were methylated ("moderate hydrophobic") yield mesoporous hollow carbon spheres, indicating an incomplete penetration of the micrometer sized spheres by the monomeric and polymeric intermediates. Optimal results in terms of replication were observed only for high-temperature treated, dehydroxylated silicas ("moderate hydrophobic"). This template yielded mesoporous carbon replicas with surface areas of 200 m^2/g and average pore sizes of 4.5 nm. It is interesting to note that such different carbonaceous structures can be accomplished with exactly the same reaction procedures, just by changing the polarity of the template surface.

Beside chromatographic beads, also monolithic chromatographic columns can be used as an exotemplate. These porous silicas are prepared according to the Nakanishi process[136,137] and can easily adopt crack-free outer shapes of 30 cm in length and a few centimeters in diameter. Those monoliths were for instance used for the Fe-catalyzed polymerization of the mesophase pitch toward soft, carbonaceous replicas for electrochemical purposes.[138] The quality of this replication process is depicted in Figure 7.

Those empirically optimized silica monoliths exhibit a continuous, sponge-like transport porosity on the 2–5 μm scale, while each of the crossbars itself is porous and contains the chromatographic active mesoporosity. As only those are filled by capillarity by the pitch monomer, structural inversion occurs on the level of the crossbars only, while the structure looks the same at the micrometer scale. Cross-linking the pitch to a ductile carbon turned out to be essential for the preservation of mesoporosity, while extensive carbonization turned out to be unfavorable for the desired electrochemical properties. This is why a temperature treatment of up to 700 °C to stimulate polymerization but to avoid extensive carbonization turned out to be beneficial.

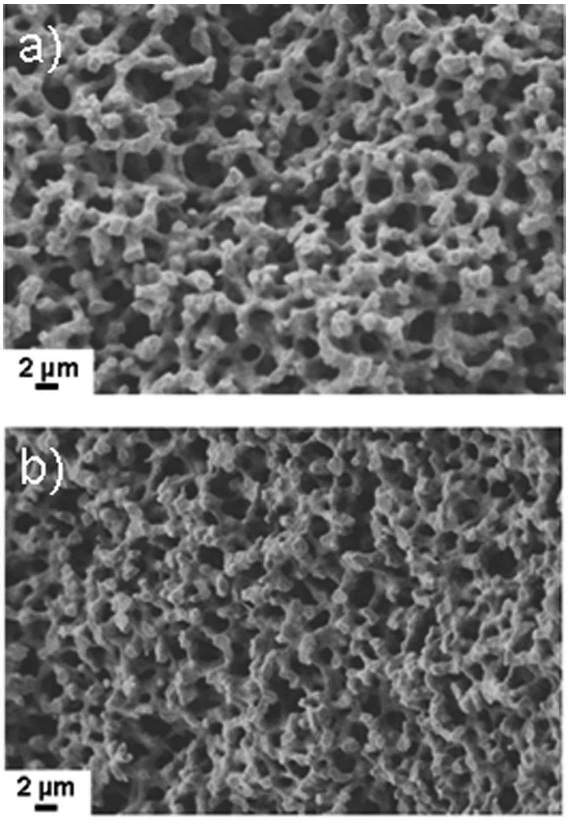


Figure 7. Replication of a continuous silica monolith for chromatography (a) in a polymerized mesophase pitch (b). Reprinted with permission from ref 138. Copyright 2007 Wiley-VCH.

It is also mentioned that the precursor coated silica monolith is also an ideal reactive "green body" to generate the corresponding ceramic SiC structure by simple heating (synthesis and characterization of SiC materials with hierarchical porosity obtained by replication techniques).[139] This use of mixed soft mesoporous systems as precursors to ceramic materials will however be discussed in more detail below.

5.4. Alumina Membranes. Nanoporous alumina membranes are formed by potentiostatic anodization of aluminum. Under certain conditions, a film of aluminum oxide with rather homogeneous pores can be observed. Applying a two-step process, also self-organized pore structures can be produced, in which cylindrical pores form hexagonal lattices with optical quality.[140] The distance between the centers of the pores can be further controlled by the conditions of the process. Subsequent selective etching of the aluminum oxide facilitates the adjustment of pore sizes from 15 to 100 nm. This pore size is especially interesting as it expands the scope of hexagonal mesoporous silicas to the larger size range. While it can not be expected that conformations of single polymer chains are affected by this confinement, it was shown that polymer assembly can be strongly influenced. Thus, interesting mesostructures were observed from block copolymers confined in the channels of anodized aluminum oxide (AAO) membranes, differing strongly from the mesophases observed in the bulk.[141–144]

As an exotemplate, AAO membranes have found widespread application for the generation of nanotubes and -rods from inorganic, organic, and composite materials. Several recent and comprehensive reviews deal with the topic of the generation of polymeric and organic tubes or rods in AAO membranes.[145–147] Therefore, this section should be restricted to a short listing of soft materials prepared in AAO membranes, while the reader is referred to the cited literature for further information.

Often polymer nanostructures are produced in AAO templates by controlled wetting of polymer melts or solutions in the nanochannels,[146–148] but also electrodeposition[149,150] and LbL deposition[151,152] were described.

The first reports on the replication of polymers in AAO membranes dealt with the preparation of PMMA membranes, which then were used as templates themselves for the generation of ordered metal nanohole arrays.[140] Several semiconducting polymers, such as polypyrrole, poly(3-methylthiophene), and PANI, were nanostructured using AAO templates. Oxidative polymerization of the corresponding monomers were carried out in the channels either electrochemically or by using chemical oxidizing agents.[149,150,153–155] In a similar approach, segmented metal/polymer composite rods consisting of a gold and a polypyrrole block were produced by first an electrodeposition of gold into the porous alumina template followed by electrochemical polymerization of polypyrrole. Thus, rods consisting of hydrophilic hard and hydrophobic soft domains were produced, which assembled into mesoscopic aggregates obeying the rules of the packing parameter for block copolymers, and different aggregate structures were observed depending on the length of the gold part in comparison to the polypyrrole part.[156] Template wetting was used to prepare PS, polytetrafluoroethylene (PTFE), and PMMA filaments.[148] Hyperbranched polyphenylenes were synthesized by Diels–Alder reactions of tetraphenylcyclopentadienes in the nanochannels of the membranes, which formed porous carbon nanotubes after carbonization.[157] Poly(*N*-isopropylacrylamide) (PNIPAM) as well as PNIPAM-*co*-MBBA (*N*,*N*′-methylenebisacrylamide) copolymer nanotubes were fabricated by attaching an ATRP initiator on the surface of the alumina channels. Surface initiated atom transfer radical polymerization yielded polymer nanotubes with wall thicknesses controlled via the monomer concentration.[158,159] Recently, even DNA and protein nanotubes were prepared using AAO templates and LbL approaches.[160,161]

Besides macromolecules, several organic molecular crystals have been assembled in the channels of the membranes and also showed retention of the tubular or rod-like structure after removal of the template. For example, organic nanotubes and nanorods composed of liquid crystals,[162] polycyclic aromatic hydrocarbons,[163,164] phtalocyanines,[165,166] and even smaller molecules[167–169] have been reported.

6. Applications of Templated Soft Materials

Physicists have known that for more than a century, actually, that size matters; that is, the typical length scale of a material strongly affects its physical properties. A textbook example of this phenomenon is visible to the eye; bulk gold is yellowish, while gold nanoparticle suspensions feature a strong coloration ranging from deep purple to red.[170] Similarly, nanostructuring organic materials can impact their features and thus increase the range of their potential applications. Soft materials have been widely used, for example, for photonic applications, for separation purposes, for catalysis, or for the elaboration of composite materials. Comprehensively reviewing these applications is thus far out of the scope of this part, and we would rather pinpoint some of those we find particularly promising.

6.1. Chromatography. Chromatography is a rather old technique but a continuously evolving research field. There is thus an increasing demand for new, more effective stationary phases. Because of high requirements on thermal and mechanical stability of these stationary phases, oxides have long been the only suited material. Nevertheless, recent progresses in the synthesis of stable organic nanostructured materials open a land of opportunities in this field. For example, the replication of mesoporous silica beads into hydrothermal carbon yielded pressure withstanding hydrophilic particles which proved to be effective in HPLC applications.[135]

Another promising approach is the use of MIPs. In such systems the polymer is built up around a templating target molecule, which is further removed. These polymers retain specific interactions with their guest and can then “recognize” later on.[18,126,127] Several reports showed that polymers templated at two length scales, that is, the molecular and the mesoscopic level, synthesized by hard exotemplating, featured improved properties.[128–130,132,171] These approaches showed that narrow pore size distributions were observed in the resulting polymers, while conventional bulk synthesis of these polymers yields very broad pore size distributions. This controlled and narrow porosity proved to be beneficial, as retention and imprinting factors far exceeding those observed from bulk imprinted materials can be observed.

A breakthrough in chromatography was established using monolithic stationary phases exhibiting a bimodal or hierarchical porosity, that is, macropores (>50 nm) beside mesopores (2–50 nm).[172,173] In such materials the mesopores ensure a large area of interaction (surface area), while the macropores allow an easy access to the mesopores and allow liquid to flow through these materials under low pressure even at high flow rates. The preparation of organic polymer monoliths is relatively simple and straightforward[174] compared to that of silica rods, mainly because of problems involving shrinking and cracking.[172] However, in comparison to polymeric materials, porosity in silicas can be much better controlled. The use of particle loaded monoliths was reported by Chirica and Remcho. They imbedded silica particles with a styrene/DVB or butyl methacrylate/EDMA monolithic matrix.[175] The silica particles were removed yielding a templated macroporosity. Using silica monolith as hard templates, several other polymeric monolith materials can be envisaged which exhibit superior control over the hierarchical porosity.

6.2. Sensing. As a result of the increasing number of biological and environmental issues, reliable, sensitive, selective, and user-friendly chemical sensors have become more and more attractive.[176] Many sensing devices are based on optical detection. As previously mentioned, nanostructuration strongly impacts the optical properties of materials and thus can increase their interest for sensing applications. Zhao et al. for instance reported on the strong fluorescence of bibenzoylmethane nanotubes, while the parent molecule is almost not fluorescent at all.[169] This system is very promising for realizing sensing devices, as fluorescence is very sensitive to tiny modifications in the environment of molecules and β-diketones are known to be good ligands for a large variety of metals. On the other hand, polymer based photonic crystals have already been shown to have their optical properties modified by the presence volatile organic compounds (VOC)[177] or biomolecules.[178]

6.3. Catalysis. Micro- and mesoporous metal oxides are one of the great success stories of modern catalysis, either as catalyst support or directly as active phase.[179–182] Mesoporous soft materials have at least the big opportunity to follow the same line. It is obvious that the surface chemistry of nanostructured soft materials can be much more complex than the one of mesoporous oxides, say, silica. It is the vision that heterogeneous catalysis with soft mesoporous materials may close the gap between classical heterogeneous catalysis and the related enzymatic/antibody catalysis.[183] It is usually the "porous" surface of an antibody which is catalytically active, and the binding of the substrate and the stabilization of the transition state is promoted by a multiple array of functional sites along the surface. Similar structures can in principle be established in soft mesoporous systems, and the single binding sites of classical inorganic catalysis might be expanded to an appropriately designed catalytic region or functional array.

This is still a long way to go, but first experiments indicate the unusual potential of such catalysts. For instance, mesoporous C_3N_4 can feature uncondensed amino functions, aromatic nitrogen atoms, and tri-*s*-triazine rings at its surface, and the various nitrogen species are obviously Lewis and Brönsted basic. Moreover, the aromatic rings are electron rich and may activate suited substrates via electron donation, while by polarization, the aromatic character of the system will result in developed transition states with multiple charge patterns. Finally, the alternation of carbon and nitrogen gives rise to very specific and regular termination sites, which, in a lock−key mechanism, can interact specifically with given substrates via H-bonding. All these functionalities may intervene in very different activation mechanisms. This makes the chemistry of these catalysts very complex but extremely rich.

In good agreement with these expectations, mesoporous graphitic C_3N_4 was shown to be able to catalyze various reactions such as Friedel–Crafts type reactions[42,184] or the cyclization of nitriles or alkynes.[185] Most unexpectedly (and directly related to the N−C−N− binding pattern), the same catalyst was able to activate CO_2; in the described reaction, benzene was oxidized to phenol while CO_2 turned into CO.[186] We believe that this "metal-free" catalysis based on an "all-organic coordination" has the potential to become one of the hot topics in the field.

6.4. Fuel Cells. Fuel cells are, in terms of economic and environmental concerns, an innovative alternative to existing power sources, because they combine high efficiency with the usage of renewable fuels. Because of their low operating temperatures, Polymer Exchange Membranes Fuel Cells (PEMFCs) are interesting for applications in transportation and portable electronics. To optimize the efficiency of the PEMFC, high demands are put on the polymer membrane, for example, a high conductivity should be ensured in a wide temperature window. The proton conductivity in polymer membranes benefits from a biphasic structure, as it is found in hydrated sulfonated polymers (e.g., Nafion or sulfonated PEEK).[187] The biphasic structure with nanometer sized channels supports the proton transport in the liquid phase because of undisturbed transportation pathways, while the second polymer phase supports the mechanical stability of the system. Mecerreyes et al. presented an approach toward macroporous PBI membranes prepared by leaching out a low molecular weight porogen, which enables high acid uptakes and increased proton conductivity.[188] However, as stated by the authors, only ill-defined macropores were obtained. In contrast, using hard templating approaches with silica nanoparticles as template mesoporous PBIs with defined pore sizes and porosities could be prepared.[35] It was shown that the introduction of a nanosized biphasic structure into the PBI/H_3PO_4 system leads to a distinct enhancement of the proton conductivity compared to linear PBI, while the conductivity values could be tuned by varying the porosity and cross-linker content of the resulting network. Thus, membranes exhibiting high proton conductivities at high temperatures (~180 °C) even under zero humidity can be prepared.[189]

It is interesting to note that several carbon based electrode materials for fuel cells are reported in the literature, which exhibited enhanced performance because of introduction of a nanostructure using hard templating.[190–192] Thus it is not implausible that all components of the future fuel cells will actually consist of materials prepared via hard templating.

6.5. Soft to Hard: Soft Mesoporous Materials as "Reactive Templates" for Ceramics. Sol–gel chemistry enabled material scientists to synthesize a large variety of well defined nanostructured metal oxides. However, this chemistry was not directly helpful for accessing other types of nanostructured ceramics, such as carbides or nitrides. It is actually possible to convert oxides into the corresponding carbides or nitrides, but the required reaction conditions are rather harsh,[139] the conversion is often partial, and the nanostructure is not always well preserved.[193] An alternative approach, using nanostructured soft materials as templates and nanoreactor, was suggested by works of Colvin et al.[61] These authors indeed show that a PMMA inversed opal could be used as a nanoreactor to synthesize a TiO_2 colloidal crystal. Going one step further, Fischer et al. used mesoporous carbon nitride as both a nanoreactor and a nitrogen source to produce

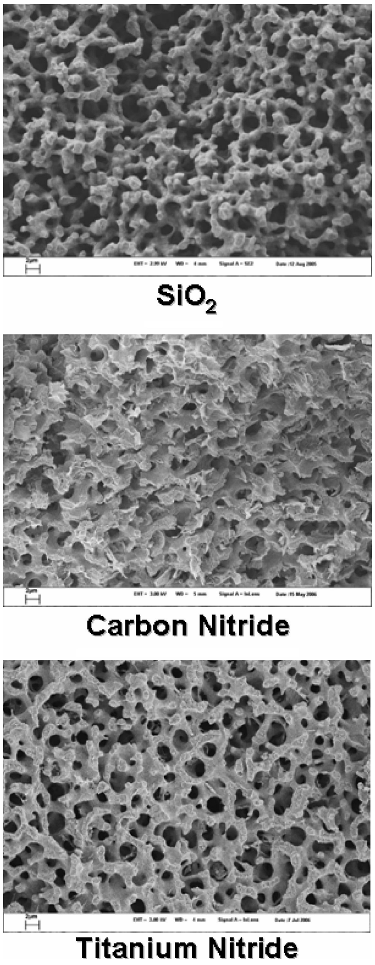


Figure 8. SEM images of a macro-/mesoporous silica template, its carbon nitride replica, and a titanium nitride replica derived therefrom.

pure and mixed metal nitrides nanoparticles.[194] To do so, mesoporous C_3N_4 was infiltrated with the desired metal precursors. The obtained powder was then heated to the decomposition temperature of the carbon nitride. Upon degradation C_3N_4 provided the required N atoms, while confining the nanoparticles preventing their sintering. Thus, crystalline metal nitride nanoparticles with well controlled sizes were obtained.

This approach can easily be expanded to other nanostructures. Thus, a hierarchical silica material, exhibiting a defined meso- and macroporosity, was used as template for graphitic carbon nitride, followed by removal of the silica. The porous carbon nitride was then infiltrated with a titanium precursor ($Ti(OEt_4)$), which under air converts in an amorphous TiO_2/C_3N_4 composite. Upon heating to 800 °C the C_3N_4 scaffold decomposes and donates nitrogens to the TiO_2 network, eventually yielding a meso/macroporous titanium nitride (Figure 8).

An, in principle, similar approach was used for the generation of porous silicon carbides. Here silica templates were filled with carbon precursors, such as mesophase pitch[139] or furfurylalcohol,[195] and heated to temperatures where the precursor polymerized and subsequently carbonized. However, those composites did not have to be freed from the silica template, as heating to high temperatures and inert gas atmosphere directly yielded the mesostructured silicon carbide.

6.6. Dielectric Insulators. Currently there is some need for materials exhibiting a very low dielectric constant. This would enable new intermetal dielectric layers (IMD) with lower dielectric constants to reduce the signal delays, drive voltages, and power consumptions of today's high powered integrated circuits.[196,197] Especially polyimides have attracted the attention of several research groups as low-k material because of its many favorable properties such as high thermal stability, good processability, and very good electric properties (low dielectric constant, high resistivity, high breakdown voltage). Beside chemical approaches toward low dielectric constant materials, an alternative approach toward lowering a polymer's bulk dielectric constant is to introduce nanoscopic porosity into the polymer film. Indeed, the generation of a porous dielectric substantially reduces the dielectric constant while maintaining the desired thermal and mechanical properties required for the rigorous manufacturing environment. The reduction in the dielectric constant is simply achieved by incorporating air (or, for very small pores, vacuum) voids that have a dielectric constant of 1. Nanoporous polyimide films are mainly prepared via a so-called phase-separated block-copolymer route.[197,198] Here, block copolymers consisting of a highly temperature-stable block and a thermally labile block are used. Pore formation can be accomplished by thermolysis of the labile blocks, which leaves pores of sizes and shapes corresponding to those present in the initial copolymer's morphology. Recently also a templating procedure for the generation of porous polyimides using hybrid poly(ethylene oxide)−polyhedral oligosilsesquioxane (PEO-POSS) nanoparticles as templates has been reported.[199] On the other hand, the introduction of defined mesoporosities in organosilicas has been shown to yield very promising low-k materials.[200] Thus, it can be assumed that hard templating of (presumably cross-linked) polyimides should yield materials with very small pores, high porosities, and thus very low dielectric constants.

6.7. Electrode Materials. A promising application of high surface area, conducting carbonaceous materials is as an anode in lithium batteries. The monoliths made of a polymerized mesophase pitch described in Figure 7, for instance, have been tested as an anode material for lithium batteries. The resulting electrochemical cycling behavior is depicted in Figure 9 a,b. After formation of a solid electrolyte interphase in the first four cycles, a remarkably high, fully reversible capacity of >800 mA h g^{-1} is found, clearly exceeding any commercial anode material. The real benefit of the hierarchical monolithic pore structure is reflected in Figure 9b. The materials can be cycled for hundreds of cycles at extreme cycle rates of 60 C, without any loss of battery performance. (60 C corresponds to loading with 1 mol of electrons/structural unit in 1 min, which is complete loading and unloading in 1 min.) This example illustrates the extreme benefits for material performance when both the chemical and the pore structure of an active mesoporous material are optimized.

It is no wonder that the same mesoporous polymerized mesophase pitch, when additionally covered with another

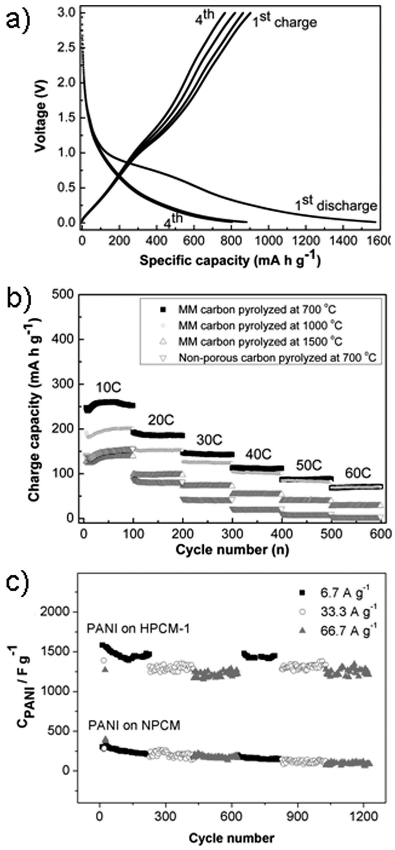


Figure 9. Electrochemical performance of monolithic mesophase pitch in two applications. (a) Lithium insertion behavior at 1 C, indicating that the material passivates in the first four cycles, and then is very stable. (b) Accelerated ageing protocol involving also extremely high cycling rates, indicating no loss of performance over 600 load cycles. (c) PANI modified monolith of polymerized mesophase pitch in a supercapacity run. The material exhibits a very high supercapacitance of ca. 1250 F/g PANI which is in addition practically free of detoriation, at least over 1200 cycles. Reprinted with permission from refs 138 and 201. Copyright 2007 Wiley-VCH.

layer of PANI, also sets record values for supercapacitance (high electroactivity of PANI in supercapacitors by using hierarchically porous carbon monolith as a support,[201] see Figure 9c).

The material (PANI on HPCM-1) shows a cycle-stable supercapacitance of above 1250 F/g PANI even at high current densities, while a corresponding nanocarbon/PANI hybrid of similar chemical composition (PANI on NPCM) only shows a much lower supercapacitance, which in addition detoriates with time. Again, the advantages of the rational setup of a porous nanostructure become immediately obvious.

Even in those storage applications, there is still much potential for improvement, especially when the potential variation of the chemistry of soft mesoporous materials is considered. For instance, nitrogen rich materials seem to be very promising for further improving hydrogen and lithium storage.[202,203]

7. Nanostructured Organic Materials: Hard Templates, Soft Templates, or No Templates at All?

Soft organic nanostructured materials certainly complement the well-known nanostructured metal oxides and provide new opportunities in emerging technological areas. For example, heterogeneous materials with tunable pore size and high surface areas can be envisaged, which allow an exquisite control over the chemical nature of their large accessible surface areas as well as the physical properties of the resulting networks. A wide variety of possible functionalities (acid/base, aromatic, hydrophilic/hydrophobic, chiral, and so on) can be imagined to be part of an organic nanostructure, which are not available within inorganic materials. The organic surface area is usually accessible, and thus functionalities can be easily converted using the versatility of organic chemistry. Furthermore, recognition sites in the form of organic ligands can possibly be introduced into the organic nanostructures; complexing metals on these structures could therefore yield the highly desired target of heterogenizing metal−organic catalysis. Research in the direction of soft mesoporous materials can furthermore lead to systems exhibiting light weight, a low dielectric constant, low refractive index, and ultralow heat conductivity combined with attractive mechanical properties of soft materials, such as, for example, ductility, toughness, or elasticity.

Porous soft matter is a very classic research field full of mature products. For the introduction of macrostructures (>50 nm) into polymers several methods exist, such as foaming, phase separations, HIPE (high internal phase emulsion) polymerizations, or micellar imprinting[11] which in principle all rely on templating of soft materials, such as gases, liquids, or other polymers. However, attempts to prepare meso- or microstructured organic materials using these approaches most often had failed. As shown in this report, hard templating can be a versatile method to achieve the preparation of nanostructured organic materials. Hard templating has the indisputable advantage that direct copies of the template structure can be achieved easily. As a variety of inorganic nanostructures are meanwhile available, using these as templates has resulted in a wide range of organic replicas. Thus, many organic meso- and microstructures have been produced over the last years, ranging from meso- and microporous materials to nanoparticles, nanorods, and nanotubes. Several organic, polymeric, or carbonaceous structures have been reported.

However, all of the materials have in common that their chemical composition has to provide some degree of rigidity to withstand the emerging high capillary pressures, once pores and the accompanying increasing surface areas have been created. Naturally, the rigidity of the organic networks has to increase with increasing surface areas and decreasing wall thicknesses to retain the nanostructure after template removal.

It should be noted that several recent reports showed that in some cases also soft templates are able to introduce nanostructures into materials. Mesoporous polymer networks were produced using block copolymers, such as, for example, poly(ethylenoxide)/(propylenoxide) triblockcopolymers or poly(styrene)-*block*-(4-vinylpyridine).[204–206] Just as for mesoporous silicas, mesoporous polymers with cubic or hexagonal periodicity could be prepared. Furthermore, this approach avoids the use of hydrofluoric acid, perhaps the biggest disadvantage when working with silica hard templates. Simple calcination or extraction of the polymer template is sufficient to remove it from the organic network.

So far this approach was just applied for the generation of mesoporous phenol−formaldehyde resins (Bakelite), but there is some hope that there are other mesoporous polymer networks still to be made. Nevertheless, the general restrictions of this approach still hold true, and mutual compatibility of the template with both the monomer and the polymer phase is just one of the many problems to be addressed.

Interestingly, there seems to be also a "template-free" path to porous polymers, as exemplified by new intriguing materials called "polymers with intrinsic microporosities".[207,208] These polymers consist of stiff and rigid chains but do not have to be cross-linked to exhibit high porosities and high surface areas. This is accomplished by introducing a rigid, angular, structure breaking motif (for example, spiro-compounds) as a monomer into the otherwise linear polymer chain. The resulting polymers exhibit a highly rigid but contorted molecular structure, which makes them soluble but prevents space-efficient packing in the solid state. The same concept can be applied for organic networks, and these cross-linked PIMs exhibit surface areas of >1000 m^2/g, already comparable to that of inorganic zeolites.[209–212] Such a formation of nanostructures from molecular design is of course highly desirable. Yaghi and co-workers have recently set the performance limit even higher, preparing covalently bound, crystalline porous materials, which in fact can be described as "organic zeolites".[213,214]

Such template-free approaches (where solvents may take the role of the template) toward microporous organic materials do have the unquestionable advantage that they are one-step processes (the synthesis of the structure generating organic building blocks not counted), as the porosity is formed inherently during polymerization. Any template synthesis and removal thus can be avoided, and no waste is produced. Regarding these results, will templates be needed at all to create the future nanostructured organic materials? Certainly, especially regarding the length scales on which molecular self-assembly can occur. Hard templates simply are very versatile, are available in different geometries, and cover length scales from a few nanometers over the micro- to the macroscale, enabling also the construction of hierarchical pore architectures by simultaneous application of more than one template at the same time.[215,216] It is, at the end, the task which defines the tool.

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