New Ways to Porous Monolithic Materials with Uniform Pore Size Distribution

Michael R. Buchmeiser*

Basics of porous monolithic materials

Porosity represents an important structural feature of many inorganic and organic materials. It may be used to vary important material roperties such as electrical and thermal conductivity, refractive index, density, mechanical strength, and toughness. Additionally, porosity may be used for any kind of transport process as well as for molecular recognition. Both inorganic and organic porous materials, for example in the form of membranes,[1] find broad application in many areas of separation science such as membrane filtration for the clean up of biologically relevant compounds and fluids, (haemodialysis),[2] for the clean up of gases,[3, 4] and as ion-selective membranes.[5] Membranes for these applications usually consist of either isolated polymer netwerks or porous polymer films.[6] With the exception of materials for gas separation, there are comparably low demands on the pore size distribution. Organic, porous monolithic materials are of particular interest because of their intriguing properties in many areas of materials research.[7] The term "monolith" refers to unibody structures composed of interconnected repeating cells or channels.[8]

Compared to their mesoporous analogues, macroporous monoliths are easily accessible by copolymerization of different monomers such as glycidyl methacrylate and ethylene dimethacrylates. Derivatization is accomplished by a polymer transformation, for example, of the epoxide group. Such surface compatibilizations are of particular importance in various bioapplications, since they reduce or even prevent nonspecific surface adsorption. Monolithic media are used mainly as separation media in particular for macromolecules and biopolymers, but also as bioreactors.[9] In particular, systems based on polymers (PS-DVB or (meth)acrylates) mainly developed by Fréchet et al.[10] as well as those based on rigid rods composed of silica represent new benchmarks in separation science. Generally, the microstructure of such materials is characterized by a comparably broad distribution of micro- and macropores. It is generated by means of solvent-induced phase separation. Access to a broad range of functionalization was achieved by imprinting techniques,[11] a more generally applicable route was established by a transition metal catalyzed monolith synthesis which entailed a subsequent surface graft–polymerization.[12, 13]

Materials with defined porosity

Compared to the synthesis of materials with a continuous pore size distribution, the synthesis of mesoporous analogues with a *uniform pore size distribution* is definitely not trivial. If such a *defined* porosity could be generated within materials with dimensions of at least a few micrometers, these would possess enormous potential as "advanced materials" for many high-tech applications such as (parallel-)microelectrophoresis.[14–19] Additionally, because of their (thermal) degradability, defined organic pore structures may be used in the template-assisted syntheses of metals, semiconductors, etc. with nano- and mesoscopic dimensions.[20, 21] On the other hand, because of their high-temperature resistance, inorganic supports with defined porosity are already used in catalysis.[22–25] They may be accessed in a comparably easy way by template-assisted syntheses. Thus, inorganic metal oxides with a large variety of mesoscopic morphologies such as hexagonally packed cylinders may be prepared.[26, 27] Organic polymers, which can be removed thermally, serve as templates. Mesoporous structures based on carbon may be prepared in an analogous way.[28]

In contrast, for organic materials the inorganic domains were introduced in the system either in the form of uniform inorganic particles or by sol–gel techniques.[29] Unfortunately, volume contraction of the polymer as well as "chemical defects" within the remaining polymer domain after template removal (e.g. silica) may cause problems, which severely impede a uniform porosity.[30] In addition, insufficient amounts of template surrounding the polymer may result in coagulation of the template, thus leading to the formation of large pores. Consequently, synthetic strategies are applied that are based on the pore generation by the selective chemical destruction and removal of single organic polymer domains. For this purpose, low polydispersity block copolymers with well-defined blocks were synthesized, which were, for example, (spin-)coated onto a support and annealed to allow self-organization. In the course of this process, prepositioning of the pore precursors (one polymer block) and consequently of the pores is accomplished. Poly(methylmethacrylate-*b*-styrene), poly(isoprene-*b*-pentamethyldisilylstyrene-*b*-isoprene), poly(styrene-*b*-isoprene), poly(styrene-*b*-butadiene), and poly(*tert*-butylacrylate-*b*-2-cinnamoylmethylmethacrylate) have been applied as di- and triblock copolymers.[31–34]

In this context, the ability to undergo phase separation represents a crucial requirement. During pore generation, generally, the larger polymer block undergoes cross-linking, while the smaller one is destroyed (thermally or chemically) and removed. Among other methods, the use of MeOH/OsO_4 has application, in particular with poly(butadiene)- and poly(isoprenes) respectively.[35–37] This method may be applied

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[*] A. Univ.-Prof. Mag. Dr. M. R. Buchmeiser
Institute of Analytical Chemistry and Radiochemistry
University of Innsbruck
Innrain 52a, 6020 Innsbruck (Austria)
Fax: (+43) 512-507-2677
E-mail: michael.r.buchmeiser@uibk.ac.at

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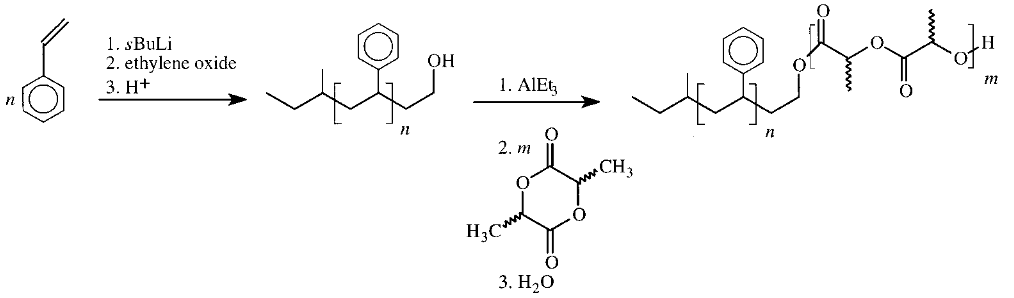
to the synthesis of thin porous polymeric layers, yet is not applicable to the generation of a defined bulk porosity within thicker materials. These problems must be attributed mainly to the oxidation process which is hard to control within the interior of highly cross-linked material. Furthermore, a controlled and broad functionalization of the surface is generally difficult to achieve by this method.

A Breakthrough?

Recently, an interesting approach to the synthesis of mesoporous monoliths from poly(styrene-*b*-lactic acid) (P(S-*b*-LA)) precursors has been described.[38] The synthesis of these block copolymers is based on an anionically initiated styrene polymerization. The living polymerization is terminated with ethylene oxide. Work-up of the hydroxy telechelic polystyrene (PS) and subsequent reaction with $AlEt_3$ allows the ring-opening polymerization (ROP) of lactic acid (Scheme 1).



Scheme 1. Synthesis of P(S-*b*-LA).

The excellent control over block size in terms of average degree of polymerization and polydispersity are prerequirements for the subsequent use as a monolith building matrix. The polylactic acid (PLA) segments form cylindrical domains which are rearranged into an (almost) perfect parallel arrangement. Basic hydrolysis of the PLA units above the glass temperature (T_g) of the PLA segments, yet below the T_g of the PS segment ($T_{hydrolysis} = 65\,^{\circ}C$) results in the formation of a PS monolith with defined porosity. The careful choice of the degradation temperature avoids softening of the PS segments, which would result in matrix deformation. On the other hand, a sufficient softness of the PLA segments is achieved and provides sufficient flexibility of the PLA segments to facilitate hydrolysis.

Despite a few structural defects, the comparably mild conditions used for the pore-generating step as well as the high uniformity of the surface functional groups generated in course of this process (primary hydroxyl groups) make this approach highly attractive. These advantages justify the fact that the concept is a priori subject to the same restrictions as found in standard leaching procedures and that the pore size is predetermined to a large extent by the block size of the PLA segment. The efficient transversal penetration of the monolith by (colored) solvent such as methanol suggests a sufficient porosity. Nevertheless, in view of the mechanical and chemical instability of non-cross-linked polymer structures, *cross-linking* appears highly favorable to gain access to some of the above-mentioned applications. Since the authors underline the advantages of the non-cross-linked matrix, which may be removed easily, applications of these materials can be expected mainly in the area of template synthesis.

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