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Feature Article

Polymeric monolithic materials: Syntheses, properties, functionalization and applications

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Abstract

The synthetic particularities for the synthesis of polymer-based monolithic materials are summarized. In this context, monoliths prepared *via* thermal-, UV- or electron-beam triggered free radical polymerization, controlled TEMPO-mediated radical polymerization, polyaddition, polycondensation as well as living ring-opening metathesis polymerization (ROMP) will be covered. Particular attention is devoted to the aspects of controlling pore sizes, pore volumes and pore size distributions as well as functionalization of these supports. Finally, selected, recent applications in separation science, (bio-) catalysis and chip technology will be summarized.

Keywords: Monolithic materials; Polymer materials; Polymer synthesis

1. Introduction

Monolithic materials have rapidly developed during the last 15 years and nowadays hold an impressively strong position in separation science as well as in other areas of chemistry. As is true for any other ''mature'' technique, a number of reviews can be found on that topic [1–12], the book edited by F. Švec, T.B. Tennikova and Z. Deyl certainly being the most comprehensive and recent one [13]. In view of these reviews, this paper does *not* intend to give another comprehensive summary on the topic of monolithic materials, but to outline the aspects of polymer chemistry relevant to the *synthesis* of these materials in more detail. In due consequence, the applications of monolithic materials are only mentioned in a rather condensed way.

2. History

The history of monolithic materials goes back to the late 1960s. Kubín et al. were the first to investigate alternatives to packed columns based on beaded polymers or inorganic oxides [14]. They developed methacrylate-based hydrogel-type materials with low degrees of crosslinking, typically around 0.2%. Not unexpected, these materials were compressible and allowed only for comparatively low flow rates. A milestone in the development of these materials was the use of open-pore poly(urethane)-based materials which allowed for the separation of small analytes by means of HPLC [15–18]. Their use as GC columns was, however, restricted due to their insufficient thermal stability (<200 °C). Hjertén et al. published work on continuous beds consisting of acrylic acid and *N*,*N*-methylene bis(acrylamide) in the presence of a salt [19–21]. This material was then compressed within the confines of a chromatographic column and allowed for high flow rates. A comprehensive historical view can be found in Refs. [5,13]. Parallel work by Belenkii et al. [22,23] and Tennikova et al. [24] finally resulted in the birth of ''*monolithic*'' media (though the term ''monolithic'' was used at a later stage).

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Generally, the major advantage of monolithic supports, whether in chromatography or in heterogeneous catalysis, is the fast mass transport that is achieved between the monolithic support (stationary phase, catalyst bed) and the surrounding liquid (mobile phase, reaction mixture). These transport phenomena are nowadays quite well understood [25–34]. In the following, the synthetic concepts that have been elaborated for the realization of monolithic supports will be outlined.

3. Monolithic materials prepared by thermally triggered free radical polymerization

3.1. General considerations

In 1992, Švec and Fréchet published their first paper on "continuous rods", later referred to as "monoliths" [35]. Glycidyl methacrylate and ethylene glycol dimethacrylate were used as monomer and crosslinker, respectively; cyclohexanol and dodecanol were used as the macro- and microporogen. Polymerization was initiated thermally using AIBN as initiator. The epoxide moieties of glycidyl methacrylate were used for post-polymerization functionalization (*vide infra*) and converted into *vic*-diols, respectively were reacted with diethylamine. The first separations carried out with these supports were neither impressively efficient nor fast (35 min for myoglobin, ovalbumin, cytochrome C and lysozyme); however, they demonstrated the *principal applicability* of this approach for the first time. Unfortunately, or depending on the point of view, interestingly, the existing knowledge about pore formation in porous beads prepared by suspension polymerization could *not* be transferred at all to the synthesis of monoliths with continuous porosity [36]. As a result, the prediction of pore properties is hard and still rather strongly depends on experience than on real planning. One, yet certainly not the only valid explanation for the differences in porosity found between monolithic materials and beaded polymers prepared *via* suspension polymerization is the difference in interfacial tension [13]. In order to understand the relevant aspects of monolith synthesis, a few parameters need to be discussed. Fig. 1 gives an illustration of a monolith's composition. The monolithic unitary structure consists of interconnected microglobules of a certain average diameter d_p. These microglobules are formed during monolith synthesis from a large number of growing nuclei that become chemically bonded to each other. The larger the number of nuclei and the smaller their size is, the smaller the pores are and, in due consequence, the lower the pore volume between these nuclei becomes. The volume fraction of the void volume (ε_z) and the volume fraction of the pore volume (ε_p) sum up to the total porosity $\varepsilon_t = \varepsilon_z + \varepsilon_p$.

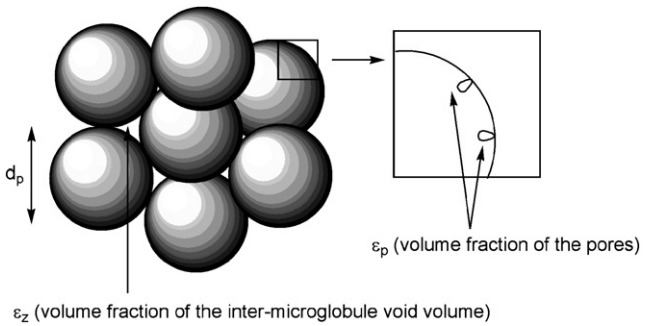


Fig. 1. Illustration of the physical meanings of d_p, ε_z, ε_p and schematic drawing of a monolith.

The most important parameters for monolith synthesis governing the microglobule diameter d_p, the volume fraction of void volume ε_z, the volume fraction of pore volume ε_p, the total porosity ε_t, the specific surface area σ and the apparent density ρ_{app}, are polymerization temperature T_p, weight or mole fraction of the initiator, the chemical nature (*i.e.* size polarity) of the monomer(s) and the crosslinker(s) as well as the polarity of the porogens. To realize a continuous, yet porous structure, the polymerization mixture should be based on at least a crosslinker, and two types of porogens, *i.e.* a macroporogen and a microporogen [1,37–39]. Addition of a further monomer helps to control the porous structure. The nature of these porogens strongly depends on the chemistry (*i.e.* polarity) of the monomer and the crosslinker. In the following, the role of each of these variables in a thermally triggered polymerization system relevant to the synthesis of monolithic systems shall be briefly outlined.

3.1.1. Polymerization temperature

The *polymerization temperature* is probable the most effective parameter to influence polymerization kinetics [40,41]. Thus, the half-time of decomposition of azobis(isobutyronitrile) (AIBN) in styrene is 5.7 h at 70 °C, while it is approximately 3.2 min at 110 °C. A more rapid decomposition of an initiator results in a larger number of growing polymer chains, and, as a consequence of the phase separation process, a larger number of growing nuclei [40,41]. This phase separation process may be triggered by both the amount and the nature of the *porogenic solvents* as well as by the amount of crosslinker present in the polymerization mixture (*vide infra*). "Good" polymer solvents usually serve as microporogens and "poor" polymer solvents as macroporogens.

3.1.2. Porogenic solvents

Phase separation may be initiated either at an early or comparably late stage of polymerization, depending on the solvent composition. In this context, the absence of any crosslinker and macroporogen may accidentally lead to glassy, transparent structures. In principle, the choice of porogens depends on the polarity of both the monomer(s) and the crosslinker(s). Polar, butyl methacrylate/ethylene glycol dimethacrylate-based monoliths are usually prepared in a mixture of cyclohexanol (microporogen) and dodecanol (macroporogen), however, other mixtures, *e.g.* dimethylsulfoxide and dodecanol or water, 1-propanol and 1,4-butandiol, methanol/THF, have been used, too [42–44]. Increasing amounts of alcohols result in monoliths containing larger pores. Acrylamide/*N*,*N*′-methylenbisacrylamide derived monoliths have been prepared in the presence of dimethylsulfoxide (microporogen) and 2-heptanol (macroporogen) [45]. In addition, various poly(ethylene glycols) have been used as template molecules in order to

increase the average pore size. Non-polar styrene/divinylbenzene (DVB)-based monoliths are accessible *via* utilization of a mixture of decanol (macroporogen) and (freshly distilled) THF (microporogen) [46], dodecanol (macroporogen) and toluene (microporogen) [47] or pure dodecanol (macroporogen) [48,49]. Non-polar norborn-2-ene- and cyclooctene-based monoliths [11,50–61] are prepared in the presence of mixtures of 2-propanol (macroporogen) and toluene (microporogen, *vide infra*). An interesting alternative to organic solvents is the use of supercritical CO_2, which was used as porogen in ethylene glycol dimethacrylate or trimethylolpropane trimethacrylate derived systems [62]. Phase separation was suggested to be solely governed by monomer concentration, thus offering access to pure macroporous as well as to macro- and mesoporous monoliths. In addition, the specific surface area was found to be dependant on the CO_2 pressure applied [63].

3.1.3. Structure formation

Once the polymerization has been started in the presence of (a) precipitant(s) acting as porogens, the polymers formed start to precipitate from the mixture and form insoluble nuclei. This is a result of both the crosslinking process and the lack of solubility of the polymer in the solvent mixture. Even at a comparably late stage of the polymerization, the remaining, unreacted monomer and crosslinker have a higher affinity to the growing polymer chains than to the porogen. They thus act as solvating agents for the polymer. In due consequence, the nuclei are monomer and crosslinker swollen throughout the entire polymerization process, *i.e.* a continuous back extraction of both the monomer and the crosslinker from the solution into the growing nuclei takes place. In this regard, this process is quite comparable to a seeded emulsion polymerization [64,65]. Furthermore, due to the high monomer concentration, polymerization proceeds by far faster within the nuclei than in solution. At least up to a certain size, branched and/or crosslinked polymers in a solution are recaptured by the nuclei, thus further increasing its size. At a comparably early stage, the nuclei associate and are connected (copolymerized) to each other by surface-localized reactive groups. Towards the end of the entire polymerization process, the small aggregates are large enough to form a continuous, interconnected phase consisting of microglobules, again chemically bound to each other. At the end, a monolithic system with large-diameter microglobules and large void volumes is formed. This void volume fraction ε_z, *i.e.* the volume of the macropores, approximately corresponds to the volume fraction of the porogens, however, significant deviations may be found in case monomer conversion is $\ll$100%.

Since the entire process of pore formation [37,38,66] is a result of the solubility of the growing polymer chains in the solvent mixture, it is not surprising at all that the *nature of the monomer*(*s*) has a similar effect on the porous structure. The same arguments in terms of solubility and phase separation, respectively, apply, yet the actual composition of a polymerization mixture necessary to achieve certain porosities and pore size distributions is still quite based on serendipity.

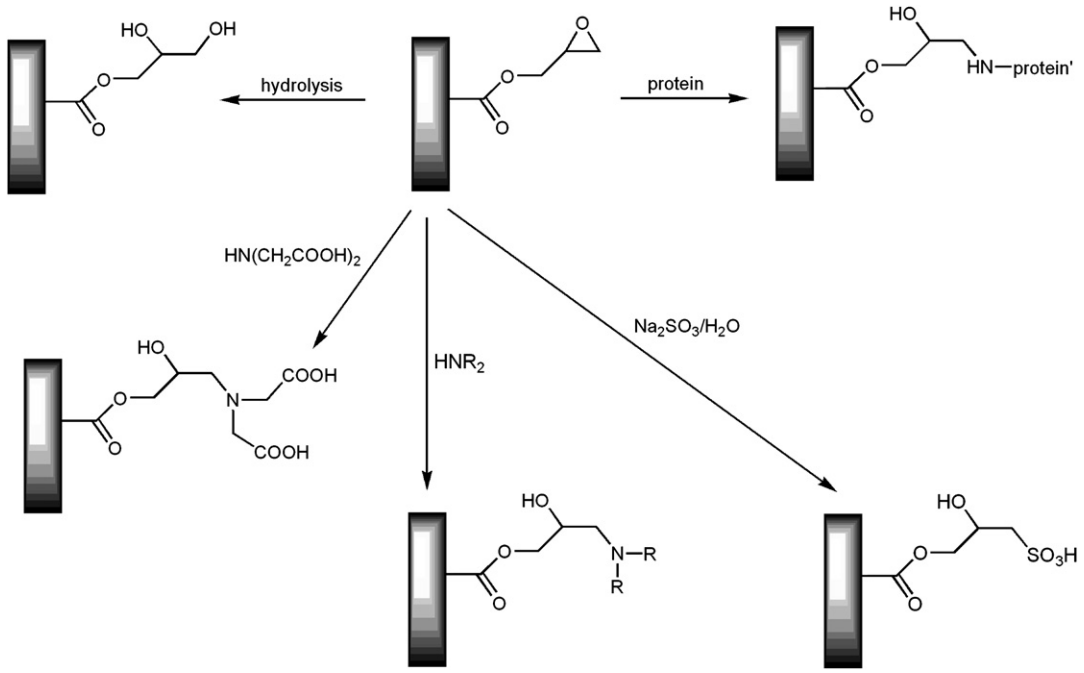
3.2. Control of porous properties

One parameter for the control of porosity of free radical polymerization derived monoliths is again polymerization temperature [41,67]. Generally, the higher the polymerization temperature is, the smaller the pores are. This holds true for both styrene/divinylbenzene as well as for methacrylate-based systems [68]. A valid explanation for this general rule is that an increase in temperature results in an increase in growing polymer chains, which ultimately form insoluble nuclei. The larger the number of nuclei is, the smaller they are and the smaller the void volumes in the final microglobules consisting of these nuclei are. In addition, the composition of the porogenic solvent plays a crucial role. The larger the fraction of macroporogen is, the larger the mean pore diameter becomes. Again, this may be counterbalanced by raising the temperature, leading to a better solvation of the growing polymer chains and in due consequence, to a reduction in pore diameter [41,67]. Finally, the ratio of mono-functional, *i.e.* monomer, over the difunctional compound, *i.e.* crosslinker, is of utmost significance. The more crosslinking agent is present, the higher the degree of crosslinking will be at early stages of the polymerization. This translates into early onsets of phase separation, into a large number of small nuclei as well as in a reduced capability of swelling of the formed nuclei with solvent and/or monomer. In due consequence, the smaller nuclei coalesce and form microglobules with small voids, *i.e.* pores [41,67]. In other words, heavily aggregated microglobules consisting of a larger number of nuclei are formed. This aggregation results in structure with high microporosity and thus high surface areas of up to 800 m^2/g [69,70].

A quite original approach to monolithic materials is the synthesis of polymerized high internal phase emulsion (polyHIPE) monoliths [71,72]. Such a system was reported by Krajnc et al. [73]. They prepared a highly porous, open cellular monolithic system from an oil-in-water high internal phase emulsion based on acrylic acid, *N*,*N*′-methylene bisacrylamide and water as the aqueous phase and from toluene serving as the oil phase. Pore sizes between 700 and 1100 nm were realized, being strongly dependant on the type of initiator used. The use of particle loaded monoliths was reported by Remcho et al. They imbedded silica particles with a styrene/divinylbenzene or butyl methacrylate/ethylene glycol dimethacrylate monolithic matrix [74]. The silica particles were removed yielding a templated macroporosity.

3.3. Functionalization

Though purely hydrocarbon or acrylate-based monoliths are excellent separation media, functionalization is of utmost importance for the use of monolithic systems for certain applications in separation science and particularly in heterogeneous catalysis (*vide infra*). In principle, functionalization may be achieved *via* three different procedures [1,8,13]: (i) copolymerization of functional monomers, (ii) post-polymerization functionalization or secondary functionalization including grafting [38], and (iii) imprinting [75–78].



Scheme 1. Post-synthesis functionalization of glycidyl methacrylate-based monolithic columns.

3.3.1. Copolymerization of functional monomers

The simplest approach to functional monoliths lies in the use of functional monomers that are copolymerized during monolith synthesis. In this context, methacrylic acid, 2-acrylamido-2-methyl-1-propanesulfonic acid [79–81], vinylsulfonic acid [82], zwitterionic sulfobetaines [83], 2-vinyl-4,4-dimethylazlactone [84,85], chiral quinidine-based monomers [86–88], dimethylaminoethyl methacrylate [89], or, in an approach for mimicking C-18 silica-based materials, octylmethacrylate [90] have been used. Even zwitterionic phases are accessible by the simultaneous use of both acidic and basic methacrylic monomers [91]. In divinylbenzene derived monolithic supports, vinylpyridine was used as comonomer [92].

Despite its simplicity, this approach entails several disadvantages. First, due to changes in polarity, the entire monolith synthesis must be elaborated for every particular monomer in order to obtain the desired structure in terms of porosity. Second, a major part of the functional monomer is located within the – in case of monoliths designed for fast separations – mostly non-porous microglobules. This may not only lead to unfavorable swelling characteristics, particularly in gradient separations, but is also uneconomical in case expensive and/or hardly synthesizable monomers are used [93]. The alternative lies in the use of functional monomers that are cheap and may easily be converted into other, more sophisticated groups. However, it should be emphasized that the problem of changing backpressures caused by changes in the mobile phase as necessary in gradient elution, remains.

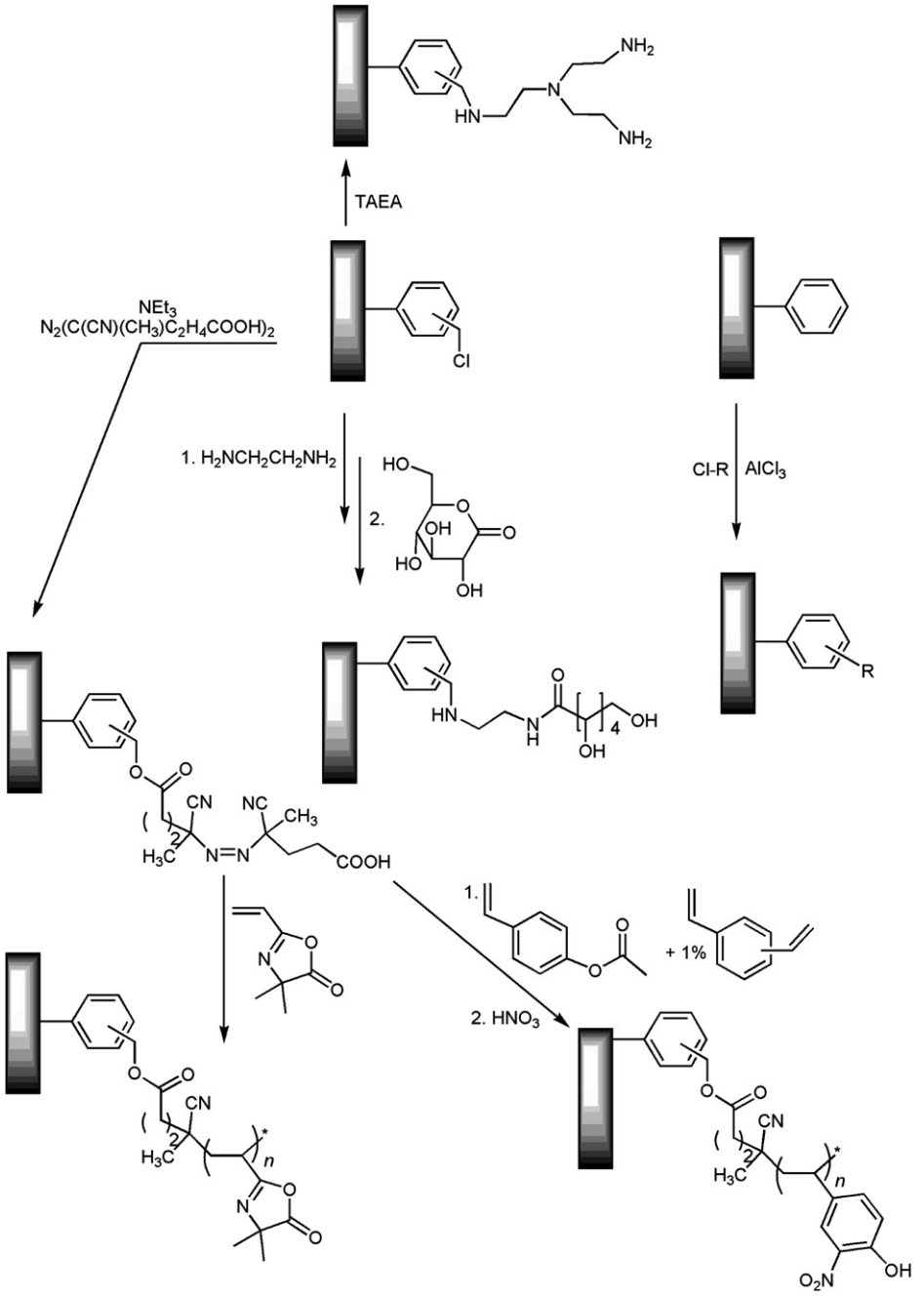
3.3.2. Post-polymerization functionalization

One of the first approaches within the context of post-polymerization functionalization was the use of glycidyl methacrylate, since it generally offers access to various functionalization reactions (Scheme 1).

Once monolith synthesis has been completed, this monomer may be simply hydrolyzed to give *vic*-diols or ring-opened with secondary amines, *e.g.* diethylamine, to yield amino hydroxyl-functionalized monoliths [94,95]. The thus surface modified monoliths have been used in ion-exchange chromatography of oligothymidylic acids [96]. If reacted with iminodiacetic acid, the monolith may be used in immobilized metal affinity chromatography [97]. The glycidyl groups may also be used for the immobilization of proteins *via* the ε-amino functionality [98–100]. Reaction with sodium sulfite yields the corresponding sulfonated phases [101,102]. In styrene-based monoliths, 4-chloromethylstyrene is the preferred monomer for post-polymerization functionalization (Scheme 2).

This monomer may be copolymerized with styrene since the copolymerization parameters are quite similar for both monomers. Reactions with amines [103] yield the corresponding amino or in the case of tertiary amines ammonium functionalized supports. Highly hydrophilic surfaces were created by reaction with 1,2-ethylene diamine and γ-glucuronolactone [104]. Alternatively, Friedel–Crafts alkylation reactions with α-chloroalkanes have been reported to yield the corresponding surface-alkylated stationary phases [105].

As an alternative to the transformation of copolymerized monomers, grafting techniques have been developed. Generally speaking, a major advantage of such grafting techniques is based on the fact that the parent monolithic system may be prepared from one (optimized) monomer/crosslinker/porogen system. In addition, the polarity of the monolithic support is *not* changed during the grafting procedure, which is of advantage particularly for applications in separation science. Photografting of butyl methacrylate/ethylene glycol dimethacrylate-based



Scheme 2. Functionalization of poly(styrene-*co*-divinylbenzene) derived supports. TAEA = tris(aminoethyl)amine.

monoliths has been reported, too [106,107]. Distinct areas of the monolith were functionalized with 2-vinyl-4,4-dimethyl-azlactone by the use of a mask. The graft polymer was then used for the immobilization of trypsin. The entire setup was realized in form of a microfluidic device within the tip of needle with an inner diameter of 50 μm and 25 mm in length. Use of this separation/reaction device in ESI-MS analysis allowed for efficient peptide mass mapping. In addition, photografting was used for the surface grafting of monolith-filled, 50 or 100 μm i.d. fused silica capillaries with 2-acrylamido-2-methyl-1-propanesulfonic acid. Photografting was also applied for the construction of shielded monolithic stationary phases for use in capillary electrochromatography (CEC) [108]. Thus, butyl methyacrylate/ethylene glycol dimethacrylate derived monolith was first grafted with an ionizable monomer, *i.e.* 2-acrylamido-2-methyl-1-propanesulfonic acid. This layer allowed for establishing the electroosmotic flow (EOF). Then, a second layer of a hydrophobic monomer, *i.e.* butylacrylate, was grafted on top of the first one. This protective layer prevented the ionic analytes from interacting with the ionic layer, thus allowing for their ultra-fast separation. Finally, a ring-opening metathesis polymerization (ROMP)-based *in situ* grafting approach was reported by our group and shall be outlined in Section 5.2.

3.3.3. Imprinting techniques

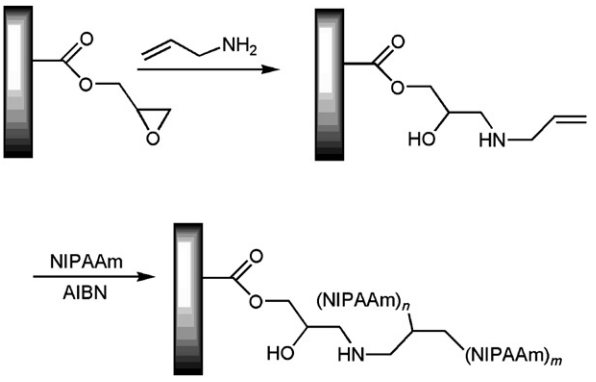
Imprinting techniques have been used for 2-trifluromethylacrylic acid/ethylene glycol dimethacrylate derived monoliths. 1-Dodecanol was used as macroporogen and cyclohexanol as microporogen. Both (−) cinchonidine and (+) cinchonine were used for imprinting. Selectivity values (α) between 1.21 and 1.86 were found for the separation of (−) cinchonidine and (+) cinchonine [78]. Acrylic acid/ethylene glycol dimethacrylate derived monoliths were imprinted with a series of chiral amines, *e.g.* phenylalanine anilide. The resulting stationary phases allowed for the separation of the corresponding enantiomers with selectivity factors between 1.4 and 1.7 [109]. In a similar system, pentamidine was imprinted, allowing for separation factors of 54 [110].

3.3.4. Pore size specific functionalization

In 1995, Sveć and Fréchet reported on a novel concept for the pore size specific modification of porous materials [111]. They reacted porous poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) beads with high molecular weight poly(styrenesulfonic acid) ($M = 1{,}200{,}000$). With this reagent only roughly 11% of the epoxide groups, *i.e.* those located within the large pores, were converted into *vic*-diols. The remaining glycidyl groups within the small pores were then converted into hydroxyamines *via* reaction with octadecylamine. This concept was later adopted to the pore specific modification of monolithic materials [112]. Finally, poly(glycidyl methacrylate) derived monoliths were reacted with allyl amine. The thus "vinylized" pores were then grafted with *N*-isopropylacrylamide) (NIPAAm). The thermosensitive graft polymer acted as a thermal valve for the opening/closing of the pores, thus controlling flow and surface polarity (Scheme 3) [113].

3.4. Pore size characterization

Structural data such as the microglobule diameter (d_p) are best determined by electron microscopy (REM) while inverse size exclusion chromatography (ISEC) allows for the determination of porosities (ε_z, ε_p, ε_t), the pore volume (V_p), the mean pore diameter as well as of the specific surface area (σ) [114,115]. Alternatively, mercury intrusion (mercury porosimetry) or nitrogen sorption (BET method) may be used, since they represent competitive alternatives for the analysis of porous systems. Particularly mercury intrusion is capable of providing data for the macropores (>1000 Å). Nevertheless, mercury intrusion and particularly BET turned out to be problematic. Thus, a major difference between the data obtained *via* ISEC and those retrieved from BET and mercury intrusion stem from the fact that the former measurement is carried out in the presence of a good polymer solvent, *e.g.* THF or chloroform, resulting in the swelling of the monolith. In contrast, BET as well as mercury intrusion measurements are carried out with dry samples, where micro- and mesopores often collapse. This difference in measuring conditions results in different results in terms of micro- and mesoporosity and specific surface area. Skinner et al. confirmed such differences in pore size characterization using both atomic force spectroscopy (AFM) and scanning electron microscopy (SEM) [116]. While no micro- or mesopores were visible in the SEM, mesopores were identified by AFM on an acetonitrile wetted sample. Recently, Irgum et al. reported on the computer-aided assessment of the macroporous structure of monolithic capillary columns by transmission electron microscopy (TEM) [117]. The results obtained were quite similar to those retrieved from mercury intrusion; however, TEM provided additional information on pore size and pore anisotropy.



Scheme 3. Synthesis of thermally responsive monoliths *via* grafting of *N*-(isopropylacrylamide) (NIPAAm).

4. Monolithic materials prepared by other polymerization techniques

4.1. UV- or γ-irradiation derived monoliths

Mixtures of glycidyl methacrylate and trimethylolpropane trimethacrylate in *i*-octane (macroporogen) and toluene (microporogen) were photocured in the presence of benzoin methyl ether within the confines of quartz columns [118]. UV-light with a main wavelength of 365 nm was used at ambient temperature, the intensity of the light that reached the polymerization zone was around 10 mW/cm^2. Mean pore diameters between 33 and 4500 nm, translating into specific surface areas between 8 and 165 m^2 were realized by varying the relative ratios of both the monomers and the solvents.

Diethylene glycol dimethacrylate was transformed into a highly crosslinked, porous monolithic structure using various solvents such as methanol, ethanol, 2-propanol, *tert*-butanol, acetone, ethyl acetate, acetonitrile, dioxane or THF. Initiation was accomplished in the absence of any photoinitiator and at ambient temperature using γ-irradiation, applying a dose rate of 10–40 kGy/h [119]. While the lower alcohols acted as macroporogens, solvents like acetone, ethyl acetate, acetonitrile, dioxane or THF acted as microporogens, a finding that may well be explained by the better solubility of the monomer in these solvents [41].

4.2. Monoliths prepared by electron-beam (EB) irradiation

Recently, our group reported on the EB-triggered synthesis of (meth)acrylate derived monolithic systems [120]. Variations

in the polymerization mixture's composition allowed for the realization of porous systems with average pore diameters in the range of 270–750 nm. Since the total dose necessary for complete curing can be applied over a longer period of time using pulsed EB curing, radicals can be generated over a longer period of time. This allows for efficient heat dissipation and, consequently, large-scale monoliths up to inner diameters of 2 cm with uniform pore size are easily accessible by this technique. Functionalization was realized so far by copolymerization of functional monomers. The novel supports have been successfully used for the fast semi-preparative separation of proteins as well as catalytic supports.

4.3. Polycondensation derived monoliths

A novel approach to monolithic media has been reported by Hosoya et al. [121]. They utilized the condensation reaction between tris(2,3-epoxypropyl) isocyanurate and various chiral amines, *i.e.* 4-[4-aminocyclohexal)methyl]cyclohexylamine and *trans*-1,2-diaminocyclohexanediamine, respectively, for the synthesis of the monolithic support. Poly(ethylene glycol) 200 and 300, respectively, were used as macroporogens. The resulting monolithic structure consisted of a macroporous network with virtually no micro- and low mesoporosity, translating into low specific surface areas of 2.7 m^2/g. Excellent separation efficiency was observed for low molecular weight analytes such as alkylbenzenes.

4.4. Polyaddition derived monoliths

Hosoya et al. reported on a polyaddition derived monolith prepared *via* reaction of bisphenol A diglycidyl ether with 4,4′-methylene-bis(cyclohexylamine) at temperatures between 80 and 160 °C [122]. Using various kinds of poly(ethylene glycol) as macroporogen, different macroporous monolithic matrices were obtained. Irgum et al. reported on the manufacture of monolithic columns in an oil-in-water emulsion process from epoxy monomers, *i.e.* 1,4-butanedioal diglycidyl ether and bisphenol A diglycidyl ether, and a diamine, *i.e.* 1,6-diaminohexane in the presence of diethylene glycol dibutyl ether and diethylene glycol diethyl ether, respectively [123]. Macroporous monoliths with specific surface areas <2 m^2 were obtained. Unfortunately, the rigidity was too low to make these materials suitable for HPLC applications.

4.5. Miscellaneous

Monoliths prepared from superagarose were reported to be useful materials for mini-reactors in flow injection systems [124]. Cyanobromide was used for activation, followed by reaction with lysozyme or *anti*-β-galactosidaseantibodies. The thus immobilized proteins allowed for the use of the monolithic devices for the on-line determination of glucose in cultivation broth and for the immunochemical quantification of intracellular β-glucosidase in *Escherichia coli*.

5. Monolithic materials prepared by ("quasi") living polymerization techniques

5.1. TEMPO derived monoliths

Poly(styrene-*co*-divinylbenzene)-based monoliths were prepared by the action of tetramethylpiperidyloxy (TEMPO). Controlled, *i.e.* comparably slow polymerization kinetics were observed, resulting in the formation of a homogeneous monolithic structure, even in case of large-diameter (50 mm) monoliths [125]. Important enough, this approach allows for the subsequent *in situ* surface modification of the monolithic structure as realized by the grafting of either 2-hydroxyethyl methacrylate or vinyl benzyl chloride. Based on these encouraging results, an entirely novel set of TEMPO derivatives was used for monolith synthesis. Mixtures of poly(ethylene glycol 400)/1-decanol as well as of higher aliphatic alcohols/toluene were used as porogens. For grafting, *tert*-butyl methacrylate, chloromethylstyrene and vinylpyridine were used. 3-Sulfopropylmethacrylate was used as graft monomer for the manufacture of monolithic supports suitable for the cation-exchange chromatography of proteins [126–128]. Another interesting feature of the TEMPO-mediated polymerization process is the absence of any Trommsdorff effect. This had already been postulated by George's group [129] in the mid-1990s of the last century and proved in fact valid also for monolith synthesis.

5.2. Ring-opening metathesis polymerization (ROMP)

5.2.1. Structure formation

Ring-opening metathesis polymerization (ROMP) is a transition-metal catalyzed polymerization technique. One of the major advantages of ROMP is the possibility to use functional monomers. This and the controlled, ''living'' [130,131] polymerization mechanism allow for a highly flexible yet reproducible polymerization setup. In course of our investigations to use ROMP for the synthesis of functional high-performance materials [132–136], we already combined this polymerization technique with grafting and precipitation techniques for the synthesis of functionalized separation media [132,134–139] and catalytic supports [140–144]. Due to the broad applicability of ROMP and the high definition of the resulting materials, we applied this polymerization technique to the synthesis of continuous polymeric supports.

In terms of monomers and crosslinkers, norborn-2-ene, 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*,*endo*-dimethanonaphthalene (DMNH-6), tris(norborn-5-ene-2-ylmethylenoxy)methylsilane as well as cyclooctene and tris(cyclooct-4-ene-1-yloxy)methylsilane were used. The poor polymer solvent 2-propanol revealed good macropore-forming properties; the good polymer solvents toluene, dichloromethane and dichloroethane were found to be capable of forming the desired microstructures in combination with 2-propanol.

As in any other polymerization-based monolith synthesis, initiator concentration represents a crucial point in the preparation of ROMP derived monoliths. Again, any uncontrolled,

highly exothermic reactions had to be strictly avoided. In a "living"[130,131] polymerization that is additionally characterized by the fast and quantitative reaction of the initiator with monomer, the number of growing polymer chains and in due consequence the number of growing nuclei that are responsible for phase separation and microglobule size is generated in a highly reproducible way. Important enough, transition metal catalyzed, living polymerizations differ from free radical polymerizations in that the total number of growing polymer chains is constant from the very beginning if initiation is quantitative and fast, thus providing a highly reproducible polymerization system. As a matter of fact, the initiation efficiency of the first generation Grubbs' catalyst $RuCl_2(PCy_3)_2(=CHPh)$ used for monolith synthesis is not quantitative yet sufficiently high [145] to allow for the realization of such a reproducible polymerization system. As observed for other polymerization systems (*vide supra*), an increase in polymerization temperature resulted in elevated polymerization kinetics and in due consequence in the formation of smaller microglobules. Microglobule *shape* was found to remain unaffected by an increase in T_p while the microglobule diameter increased with lower temperature. These findings were explained by the influence of polymerization temperature on polymerization kinetics. Thus, decreased polymerization temperatures *decreased* both polymerization kinetics and initiation efficiency of $RuCl_2(PCy_3)_2(=CHPh)$. This results in a reduced amount of (slower) growing nuclei, providing enough time for the monomer and crosslinker to accumulate within the growing nuclei, resulting in the formation of larger microglobules. *Vice versa*, elevated temperatures *increased* both initiation efficiency and polymerization kinetics and lead to the formation of a larger amount of growing nuclei and consequently to the formation of smaller microglobules [50,51].

Since Grubbs' catalyst-initiated metathesis polymerizations were shown to proceed *via* a dissociative mechanism [146,147], dissociation of one phosphine ligand is generally required in order to resume polymerization. Rebinding of the phosphine to the Ru-catalyst is competitive with olefin coordination under the chosen reaction conditions, therefore the presence of additional phosphine had a drastic effect on polymerization kinetics and in due consequence on the microstructure of the monolith. Thus, even small amounts (<10 μg/g) of PCy_3 drastically affected the synthesis of the rods, basically preventing its use. Instead, triphenyl phosphine was chosen [53]. Again, the presence of even small amounts of phosphine (20–80 μg/g) leads to a reduction in the volume fraction of pores (ε_p) and pore volume (V_p) while the volume fraction of the intermicroglobule void volume (ε_z) was enhanced [53]. In due consequence, values for the specific surface (σ) area were reduced by approximately a factor of 2. The presence of additional phosphine also affected the mean microglobule diameter. Values changed from 2 ± 1 to 4.5 ± 0.5 μm. These observations could be well explained by reduced overall polymerization rates, changing the setup from diffusion-controlled to propagation-controlled polymerization. Consequently, microglobules grow slowly and in a controlled way to a larger size [53].

In terms of monolith structure and stability, some important features of cyclooctene-based monoliths have to be mentioned. Thus, norborn-2-ene derived monomers result in polymer structures comprising *tert*. allylic carbons, which tend to be oxidized, resulting in reduced long-term stabilities of monolithic columns. However, cyclooctene-based monoliths revealed a significantly improved long-term stability, which was attributed to the *sec*-allylic structures present in each repeat unit [56]. The most striking feature of cyclooctene-based systems is their structural difference from norborn-2-ene derived ones. Monoliths differ significantly in that the cyclooctene-based structures exhibit significantly reduced values for ε_z, yet higher values for ε_p and V_p compared to their norborn-2-ene-based counterparts. This turned out to be a very important finding, since it has ultimate impact on separation issues [56].

5.2.2. Functionalization

Using the ROMP-based protocol, functionalization was achieved *in situ*. Thus, the "living" character [130,131,148–151] of ruthenium-catalyzed polymerizations offered a perfect access to functionalization. In fact, the active ruthenium-sites were successfully used for derivatization after rod-formation was complete. Ru-measurements by inductively coupled plasma optical emission spectroscopy (ICP-OES) investigations revealed that more than 98% of the initiator were located at the surface of the microglobules after the structure forming process [64]. This is in accordance with a micelle-based microglobule formation, where the polar catalytically active sites are located at the boundary between the non-polar solid and the polar liquid phase. Fortunately, besides some effects on the microglobule shape, no significant influences of initiator concentration within a range of 0.1–1% on the morphology in terms of pore and microglobule size of the continuous rods were observed. Important enough, the catalyst may be completely removed from the monolith either after monolith synthesis or functionalization, resulting in final Ru-concentrations of less than 10 μg Ru/g. Using the initiator covalently bound to the surface, a series of functional monomers were successfully grafted onto the monolith surface by simply passing solutions thereof through the mold [50,51]. For these purposes, various norborn-2-ene derivatives containing carboxylic acid, amino, hydroxyl, dipyrid-2-ylamido, β-cyclodextrin or imidazolium groups were used. Tentacle-like polymer chains attached to the surface were formed. The degree of this graft polymerization of functional monomers varied within almost two orders of magnitude, depending on their ROMP activity. Typical grafting yields were in the range of 0.5–5 wt.% of functional monomer. Post-synthesis grafting using $RuCl_2$(1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene)-$(PCy_3)(=CHC_6H_5)$ (2nd generation Grubbs' catalyst, Cy = cyclohexyl) allowed for grafting yields of up to 16.5 wt.% of functional monomer [59]. Generally, this "*in situ*, grafting-from" approach offered multiple advantages (*vide supra*). First, the structure of the parent monolith is not affected by the functional monomer and can be optimized regardless of the functional monomer used later. Second, solvents other than the porogens (*e.g.* methylene chloride, DMF) may be used for

"*in situ*" derivatization, depending on the solubility of the monomer.

6. Selected, recent applications in separation science and hyphenated techniques

Monolithic media are nowadays used for the separation of double stranded (ds-) DNA [57], proteins [7,10], oligo- [53] and polynucleotides [10], chip electrochromatography [9,152], polymer-supported reagents and scavengers [8]. In addition to applications in LC, monolithic supports have been used in capillary HPLC (μ-HPLC) [4,153], capillary electrochromatography [2,6,8,154,155], as well as for (on-chip) solid-phase extraction SPE [3,61] and thin layer chromatography followed by MALDI-TOF-MS [156]. In tube solid-phase microextraction was reported by Feng et al. [157]. Latex-coated monoliths prepared from sulfonated methacrylic monoliths and quaternary ammonium functionalized latex particles were used for both (micro) anion-exchange chromatography and in-line preconcentration of halogenides, thiocyanates and chromates [81, 158] as well as of saccharides [159]. An attractive hyphenated technique allowing for the separation and analysis of analytes in the ato-mol concentrations is μ-HPLC–MS(–MS) [46,105, 160–165]. More recently, monolithic discs have been used [166], however, these supports also already entered the field of semi-industrial processing [167,168]. However, it has to be lined out that large-diameter monoliths, *i.e.* those with i.d.s > 50 mm are not available [169]. As described above (Section 3.2), extensive heat formation occurs in any polymerization system. Since the polymerization temperature has a strong influence on the monolith's structure, no monolithic supports with a uniform structure have been realized so far. Thus, existing large-diameter systems have been prepared in a modular way from monolithic annuluses that are assembled after synthesis [170]. However, the use of EB curing (see Section 3.2) might well be a solution to that problem.

7. Selected, recent applications in (bio-) catalysis

A nice summary on applications of monolithic media in biocatalysis has been published a few years ago [10,171]. Therefore, only recent applications shall be mentioned. 2-Vinyl-4,4-dimethylazlactone-based monoliths were used for the immobilization of trypsin, thus serving as bioreactors [84,85]. In addition, 2-vinyl-4,4-dimethylazlactone were proposed as monolithic scavengers for the reactive filtration of amines [172]. A disc format has been suggested for these applications [173] as well as for a polymer bound acylating reagent [174]. In this context, the authors outlined the superiority of functional graft polymers over functional monoliths prepared *via* copolymerization of the functional monomer in terms of accessibility of the functional groups, thus underlining the general statements made in Section 3.3. Poly-HIPE derived monoliths prepared from chloromethylstyrene and divinylbenzene were reacted with 4-aminobutanol, tris(hydroxymethyl)-aminomethane, morpholine, hexamethylenetriamine and tris(aminoethyl)amine (TAEA) leading to a series of amino and hydroxyl-functionalized monolithic supports. A TAEA-functionalized support was used for scavenging excess 4-chlrobenzoylchloride from reaction mixtures [72].

Monolithic supports have also been used for the immobilization of metal clusters for catalytic applications [175]. $Mo_6Cl_{12}(EtOH)_2$ has been immobilized on pyridine functionalized monolithic materials prepared from 4-vinylpyridine and divinylbenzene using toluene and heptane as porogens. Initiation was achieved thermally using AIBN.

Particularly ROMP derived monolithic supports [11] have been extensively used for the immobilization of Pd-based Heck's catalysts [142], Schrock's catalysts [176] and Grubbs' catalysts [176–181]. Both continuous flow devices [177,179–181] as well as monolithic discs [176,178] were manufactured. Comprehensive reviews on this topic may be found in Refs. [143,144,182].

8. Summary

Monolithic columns have gone a long way. However, both the increasing demand for more and more specialized separation media, high-throughput supports or other polymeric devices and the still growing armor of tools for polymer synthesis are believed to further push this field towards new frontiers and applications. In this context, functionalization on the one hand and miniaturization as well as upscaling on the other will play an important role.

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