

# Amino-functionalization of large-pore mesoscopically ordered silica by a one-step hyperbranching polymerization of a surface-grown polyethyleneimine†

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**A simple method for surface functionalization of large-pore mesoporous silica by hyperbranching polymerization resulting in a high loading of amine groups is presented.**

Mesoporous and mesoscopically ordered silicas followed by a wide variety of other metal oxides have attracted vast scientific and technological attention after the first full reports of the synthesis and characterization of this interesting class of materials appeared in the early 90's.<sup>1</sup> This is due to their unique properties which include a narrow pore size distribution, high specific surface area and pore volume and tunable pore sizes and structures. The application prospects for these materials include catalysis, chromatography, sensing, controlled immobilization or release of biologically active molecules, and use as nanoreactors. In these applications, successful surface modification is often an integrated and crucial part of the material processing, and is the basis for the functionality of the material. One of the most attractive surface functionalities is the primary amino group, which is especially effective for the immobilization of various molecules of biological interest such as enzymes and antibodies, which typically contain functional groups which are able to strongly complex with amino functions.<sup>2</sup> Furthermore, aminopropyl-functionalized mesoporous silica has been found to be useful for some base-catalyzed reactions, further postsynthesis functionalization and as heavy metal sorbents.<sup>3,4</sup>

Typically, the surface modification of mesoporous silica is carried out according to two distinctively different approaches. The surface functionality can be introduced either by direct incorporation of organic groups through co-condensation of functional silanes or by grafting. However, certain drawbacks are associated with both methods. Whereas the postsynthesis grafting method typically results in an inhomogeneous surface coverage, the co-condensation approach has, by some research groups, been reported to enable a higher and more homogeneous distribution of organosilane functionalities<sup>5</sup> but generally at the expense of the mesoscopic ordering. Furthermore, co-condensation may also make an important fraction of the functional groups inaccessible and embedded in the silica network. The location and the

accessibility of the functional groups are typically not determined, and consequently only bulk values of the loading of groups are reported.

Motivated by the drawbacks of the two general routes for amino-silanization on the surface of mesoporous molecular sieves, we have utilized an acid-catalyzed hyperbranching polymerization approach<sup>6</sup> to produce reactive primary amino groups on the surface of mesoporous SBA-15 in the form of a surface-grown polyethyleneimine (PEI). The polymer is grown directly from the surface silanol groups utilizing a highly reactive, non-bulky monomer. Recently, surface functionalization of mesoporous, surfactant templated silica was performed by surface growth of dendrimers, where, however, a pre-functionalization of the silica surface with aminosilanes was required.<sup>7</sup> To the best of our knowledge, these are the only studies of this kind reported to date, even though adsorption of dendrimers on mesoporous silica has been documented before.<sup>8</sup> In our approach, the surface concentration of polymer is hence not dependent on the initial surface concentration of the aminosilane function. PEI in itself is the cationic polymer exhibiting the highest positive charge density when fully protonated in aqueous solution.<sup>9</sup> Due to the high quantity of primary amino groups providing a very high charge density, PEI in itself has been used in *e.g.* gene delivery<sup>10</sup> and as a polymeric film on cell adhesion substrates,<sup>11</sup> besides its potential as, for instance, an enzyme substrate for biocatalysis. For these kinds of applications the stability of the inorganic host is crucial, in combination with an open porosity allowing reagents and guest molecules to diffuse throughout the whole matrix. Two approaches were undertaken, firstly the functionalization of a pure siliceous SBA-15 where acetic acid was introduced into the mesoporous silica together with the monomer before polymerization, and in the second approach, carboxylic acid functionalized silica, denoted COOH-SBA-15, was used as the substrate for the polymerization in order to aid a complete surface functionalization. The amount of accessible amino groups was determined by imine-formation of the primary amino groups,<sup>12</sup> and compared with the total amount of polymer (amino groups), determined by thermogravimetry.

Aziridine was synthesized from aminoethylsulfuric acid (Aldrich) according to the procedure described in ref. 13, and subsequently the compound was positively identified by <sup>1</sup>H NMR. The mesoporous silica SBA-15 parent material was synthesized according to Choi *et al.*<sup>14</sup> Mesoporous silica SBA-15 functionalized with carboxylic acid groups was prepared according to the synthesis described by Yang *et al.* by a co-condensation-based synthesis of a cyano-functionalized hybrid material followed by

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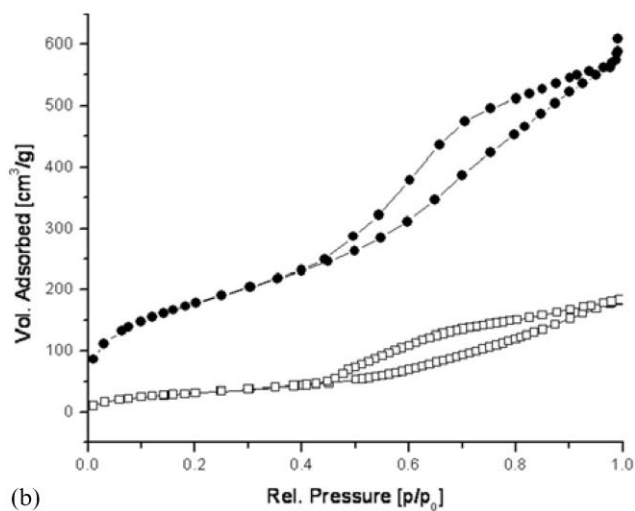
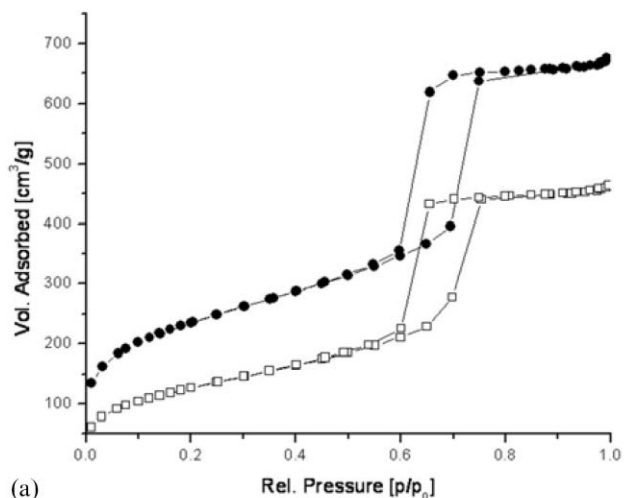
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treatment with sulfuric acid in order to remove the surfactant as well as hydrolyze the cyano groups.<sup>15</sup> The XRD patterns† of the synthesized materials were in good agreement with previous reports.

The surface polymerization of aziridine was performed with toluene as solvent, in which the SBA-15 substrate was suspended in the presence of catalytic amounts of acetic acid. The suspension was refluxed under an argon atmosphere overnight at 348 K, filtered, washed with toluene and dried *in vacuo* at 313 K.

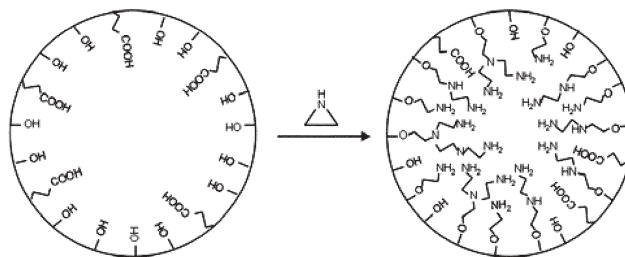
Nitrogen physisorption measurements were performed at 77 K using an ASAP 2010 sorptometer (Micromeritics, USA). The calcined SBA-15 materials were outgassed at 423 K prior to the measurements, whereas the functionalized materials were outgassed at 343 K. The NLDFT model (Autosorb 1 software, Quantachrome Instruments) developed for silica exhibiting a cylindrical pore geometry<sup>16</sup> was used for pores size and pore volume determination. For the SBA-15 the equilibrium model was used, while the adsorption branch was used for COOH-SBA-15. The sorption isotherms before and after functionalization are shown in Fig. 1, with the corresponding data in Table 1. The



**Fig. 1** a. Nitrogen sorption isotherms for siliceous SBA-15 (●) and PEI-SBA-15 (□). b. Nitrogen sorption isotherms for COOH-SBA-15 (●) and PEI-COOH-SBA-15 (□).

**Table 1** BET surface area,  $A_s$  and the corresponding  $C$ -value, total pore volume,  $V_p$ , and mesopore volume,  $V_{mp}$ , as calculated from the volume uptake in the relative pressure range corresponding to condensation of nitrogen in the surfactant templated mesopores, and mean mesopore diameter,  $d_p$ , for the studied materials as determined by  $N_2$  sorption at 77 K

Material	$A_s$ (BET)/ $m^2 g^{-1}$	$C$ -value (BET)	$V_p$ / $cm^3 g^{-1}$	$V_{mp}$ / $cm^3 g^{-1}$	$d_p$ / nm
SBA-15	845	150.5	0.997	0.48	7.03
PEI-SBA-15	468	63.7	0.687	0.36	7.03
COOH-SBA-15	654	71.1	0.857	0.50	6.08
PEI-COOH-SBA-15	122	36.3	0.269	0.20	5.88



**Fig. 2** Schematic of the polymerization proceeding in the mesopore.

polymerization process for COOH-SBA-15 is schematically illustrated in Fig. 2.

The great reduction in specific surface area and pore volume suggests a successful incorporation of the organic polymer. The lowering of the  $C$ -value also indicates organics present on the surface, as compared to the hydrophilic silica surface, of which the COOH-SBA-15 already to a certain extent also comprise of organic carboxyethyl-groups, as reflected in the  $C$ -value. Another important implication for a successful surface functionalization is that the lowering of the (meso)pore volume is much greater than what would be expected only from the increase in total mass due to the mass of the formed polymer, which indicates that the polymer is also situated inside on the mesopore walls and certainly not only on the external particle surface. In the case where the decrease would only originate from the increase in mass due to the polymeric function, the mesopore volumes of the functionalized samples should be about  $0.43 cm^3 g^{-1}$  and  $0.36 cm^3 g^{-1}$  for PEI-SBA-15 and PEI-COOH-SBA-15, respectively. Another indication of this is the disappearance of the microporosity for the siliceous SBA-15 (not present in the COOH-SBA-15 sample). Importantly, the nitrogen sorption isotherms reveal that the mesopores are still fully accessible after the functionalization due to the almost parallel adsorption and desorption branches (Fig. 1a). This implies that no pore blocking occurs, which is of utmost importance in applications, allowing facile access for the chemical reagents or guest molecules. The slight decrease in mesopore diameter upon functionalization for the COOH-material and the virtually unchanged mesopore diameter of the SBA-15 material may appear surprising. However, we note that the NLDFT kernel used for the mesopore size evaluation is not strictly valid for the surface functionalized materials, and thus the mesopore diameters determined for the PEI materials should not be taken as absolute, and the mesopore diameter variation should thus not be used as a direct measure of a successful surface functionalization.

**Table 2** Amino group content in the PEI functionalized materials. Total PEI amount determined by TGA respect to a reference sample, estimated<sup>a</sup> total concentration of amino groups, and the surface concentration of the accessible primary amino groups,  $\Gamma_{\text{NH}_2,\text{acc}}$ , as determined by imine-formation

Material	wt% PEI <sup>a</sup>	( $n_{\text{amino}}/w$ )/mmol g <sup>-1</sup>	$\Gamma_{\text{amino}}$ /μmol m <sup>-2</sup>	$\Gamma_{\text{NH}_2,\text{acc}}$ /μmol m <sup>-2</sup>
PEI-SBA-15	11	2.5	5.5	0.80
PEI-COOH-SBA-15	28	6.5	43	16.5

<sup>a</sup> as calculated from the  $M_w$  of aziridine.

The total loading of PEI was characterized by thermogravimetric analysis (Netzsch TGA 209). Additionally, the total amount of accessible primary amino groups was determined by a surface–imine formation procedure following the procedure of Moon *et al.*<sup>12</sup> with subsequent hydrolysis in aqueous solution. The regenerated 4-nitrobenzaldehyde-concentration was determined spectrophotometrically (Shimadzu) at  $\lambda = 269$  nm. The data is presented in Table 2. Fairly dramatic differences were observed for the two substrate materials. The values obtained for the accessible amino groups incorporated by addition of acetic acid as the catalyst for surface polymerization are in fact comparable to the ones obtained for conventionally aminosilanized SBA-15, as is the reduction in surface area. In contrast, the PEI-COOH-SBA-15 material exhibits a total mass loss of 42 wt%, of which the total PEI contribution accounts for 28 wt%. The rest of the weight loss is ascribed to the decomposition and combustion of carboxyethyl groups as well as water originating from silica condensation. This corresponds to a much higher total loading of amino groups of 6.5 mmol g<sup>-1</sup>. Furthermore, a much higher relative number of amino groups are accessible as judged by the imine method, which we ascribe to both a more homogeneous growth of PEI in this sample due to the presence of the catalytically active COOH function on the pore walls, as well as on the missing microporosity in the COOH-SBA-15 substrate material. This can for instance be compared to the values given in a very recent report regarding the co-condensation, where including as much as a 0.4 proportion of aminopropylsilane, lead to a amino group content of 2.36 mmol g<sup>-1</sup>.<sup>4</sup> Conclusively, with the catalytic groups distributed homogeneously throughout the whole matrix, the aziridine would be transported to the site of the catalyst before the reaction (polymerization) takes place, which enables a kinetic control of the polymerization and leads to a more dramatic increase in amino surface concentration as to the purely siliceous SBA-15. Furthermore, since the COOH-SBA-15 was solvent extracted compared to the calcined SBA-15, it contains a significantly higher amount of OH-groups, which are thought to serve as the sites from which the hyperbranched polymer is grown.<sup>6</sup> The covalent attachment of PEI to the silanols and the primary location of PEI in the mesopores is also supported by the TGA results,<sup>†</sup> where no PEI degradation was observed before 200 °C and continuing up to about 700 °C due to coke formation; while the PEI-function was reported to be rather thermally stable up to 70 °C on flat surfaces.<sup>6</sup>

Branching and several-generation growth characteristic of the polymer function, probably more pronounced on the outer surface of the silica particles, and some portion of inaccessible amino groups, can explain the smaller value determined by the

imine-formation route as compared that determined by TGA. The results also suggest that substantially more than first-generation growth of PEI on the siliceous SBA-15 sample, although no apparent improvement in the effective amino group surface concentration from the conventionally silane-grafted SBA-15 was achieved. However, in a confined environment as the mesopores, probably not all primary amino groups will be accessible for imine reaction due to spatial restriction. This could however reflect the real situation of the number of amine groups accessible for guest molecules in host–guest applications. Furthermore, for the COOH-SBA-15, as confirmed by FTIR analysis, some of the amino groups may be complexed with the COOH-groups as the imine reaction is performed in anhydrous methanol and hence not available for imine reaction.

This rather straightforward procedure is here shown to be applicable also to the surface functionalization of mesoporous materials. The direct linkage of the polymerization catalyst to the pore surfaces can be used to greatly enhance the surface coverage of the functional groups. We will return with a more detailed description of the surface properties of these composite materials shortly.

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