Polyhedral Silsesquioxanes

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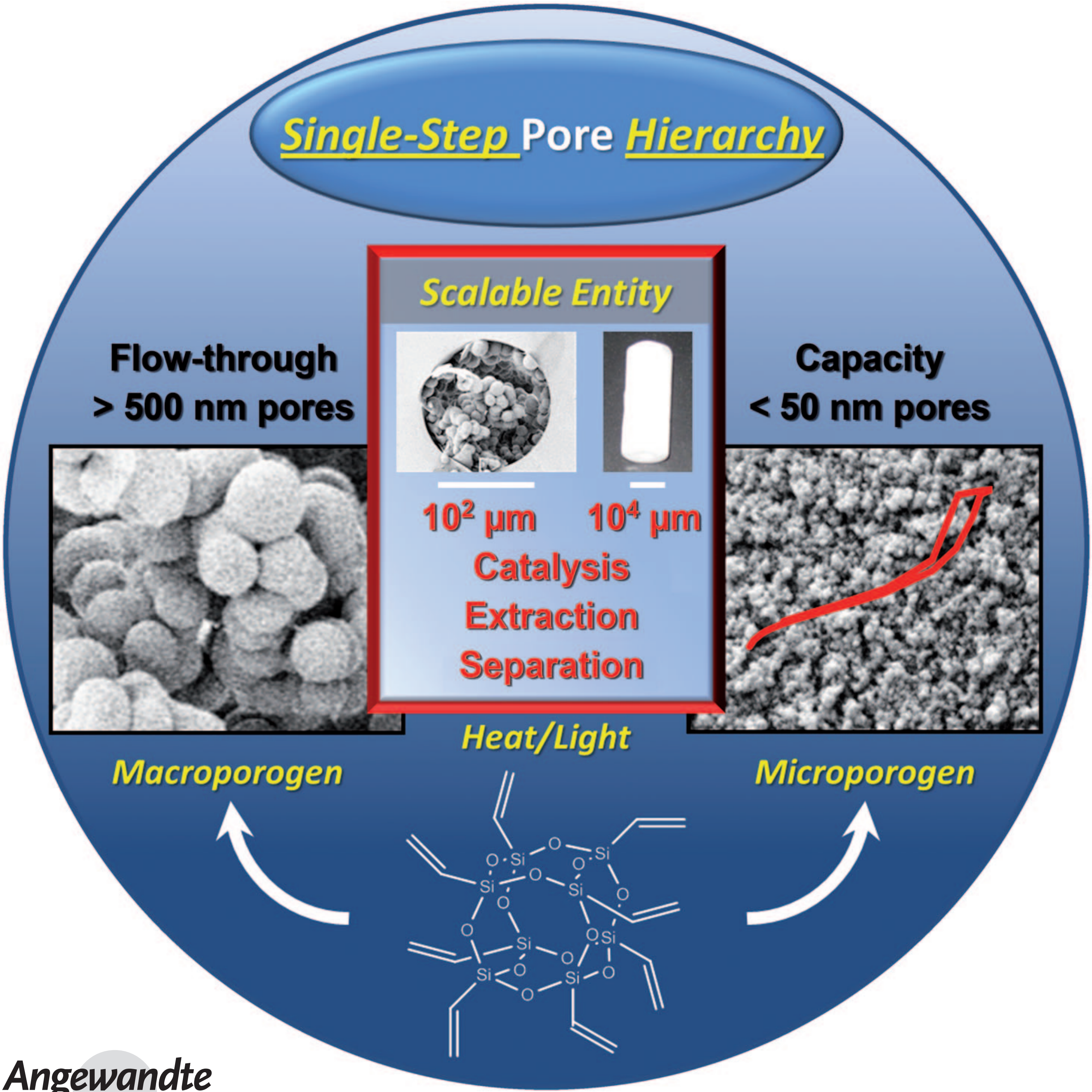
Facile, Single-Step Preparation of Versatile, High-Surface-Area, Hierarchically Structured Hybrid Materials**

Ivo Nischang, Oliver Brüggemann, and Ian Teasdale*



High-surface-area, porous adsorbents have a wide variety of applications including gas storage, catalysis, and as selectively permeable membranes, as well as in liquid chromatographic separations.[1] The rapidly developing field of microengineering demands an increase in surface-to-volume ratios of design elements in order to allow functionality such as loading, selectivity, and suitable flow-through properties. Porous, monolithic materials for such applications demand facile, repeatable, and relative ease of preparation. For flow-through applications, both in microfluidic and in larger dimensions, rigid, hierarchically structured silica monoliths offer a number of advantages including the high permeability to flow, and surface areas that are typically around 300 $m^2 g^{-1}$.[2] Attempts to derive hybrid inorganic/organic monoliths have also been successful.[3] However, the multistep sol–gel synthetic routes tend to be highly sensitive to operational variables.[2] Although they suffer from swelling and low surface area, polymer monoliths are technologically interesting platforms since they are easily derivable and functionalized, and possess good scaling capability to fill molds of a wide variety of shapes ranging from a centimeter to a single micrometer.[4]

Cubic polyhedral silsesquioxanes (POSS) with the basic structure $(RSiO_{3/2})_n$ ($n = 8$, 10, 12) are nanometer-sized inorganic/organic hybrid building blocks of interest in many areas and for applications that range from dendrimer synthesis to the reinforcement of high-performance polymer materials.[5] Microporous/mesoporous materials based on POSS precursors have been prepared by various chemical routes including hydrosilation methods,[6] thermolysis,[7] and copper-mediated coupling.[8]

Herein, we introduce a facile preparation of hierarchically structured adsorbents based on a radically initiated polymerization of polyhedral vinylsilsesquioxane in a single-step molding process that leads to porous monolithic three-dimensionally adhered entities. We also describe how their macroporosity (> 0.5 μm pore sizes, which are important for the flow-through mode) can be readily tailored whilst maintaining nanoporosity by the use of a suitable binary porogenic solvent mixture, and also detail the surface functionalization of the materials.

Polymerization of polyhedral vinylsilsesquioxane in THF resulted in a transparent, glassy polymer (Scheme 1). Nitrogen adsorption/desorption analysis (Figure 1 and Table 1) revealed a nanoporous structure with surface areas of approximately 800 $m^2 g^{-1}$ and a pore volume of 0.53 $cm^3 g^{-1}$, originating from micro (≤ 2 nm) and mesopores (< 10 nm; Figure 1). The high surface area originates from the assembly of the nanometer-sized, bulky rigid cages,[6a] which can only pack with a limited density. A significant pore space persists in the dry state. The introduction of mesopores and subsequently macropores into the monolithic material could be accomplished by replacement of specific portions of the THF with PEG200. The pore size increased as the fraction of PEG200 increased (Figure 1). This effect could be visually observed from bulk polymers (Figure S1 in the Supporting Information), in which a transition from transparent glassy materials to opaque materials was seen upon increasing the PEG200 fraction. As the macropore fraction of the polymers increased, their total surface area, which was probed by nitrogen adsorption/desorption, still exceeded 600 $m^2 g^{-1}$ at a maximum PEG200 fraction (Table 1). This result suggests that the observed high surface areas stem mostly from the microporous and mesoporous structure between the covalently adhered nanometer-sized, rigid building blocks.

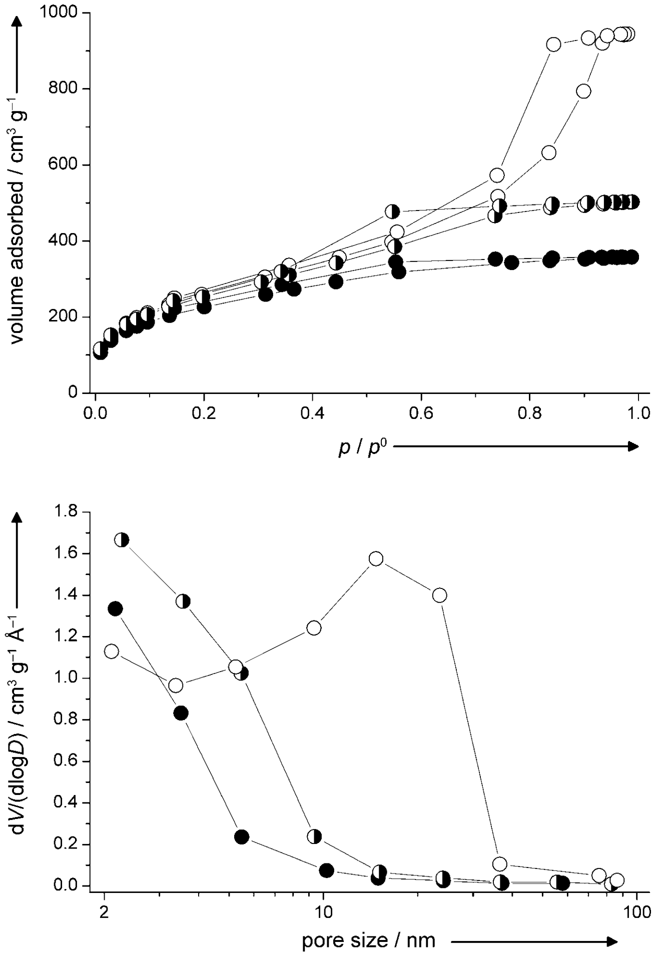


Figure 1. a) Nitrogen adsorption/desorption isotherms and b) pore-size distribution curves from adsorption according to Barrett–Joyner–Halenda (BJH) for polymer **1** (solid circles); polymer **2** (semifilled circles); polymer **3** (open circles). The isotherm with pure THF as porogen (polymer **1**) shows no hysteresis, increased amounts of PEG200 and reduced amounts of THF result in a pronounced hysteresis loop at relative pressures p/p^0 of 0.6–0.9, thus indicating a mesoporous structure (polymer **3**).

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[*] Dr. I. Nischang, Prof. O. Brüggemann, Dr. I. Teasdale
Institute of Polymer Chemistry, Johannes Kepler University Linz
Welser Strasse 42, 4060 Leonding (Austria)
Fax: (+43) 732-6715-4762
E-mail: ivo.nischang@jku.at

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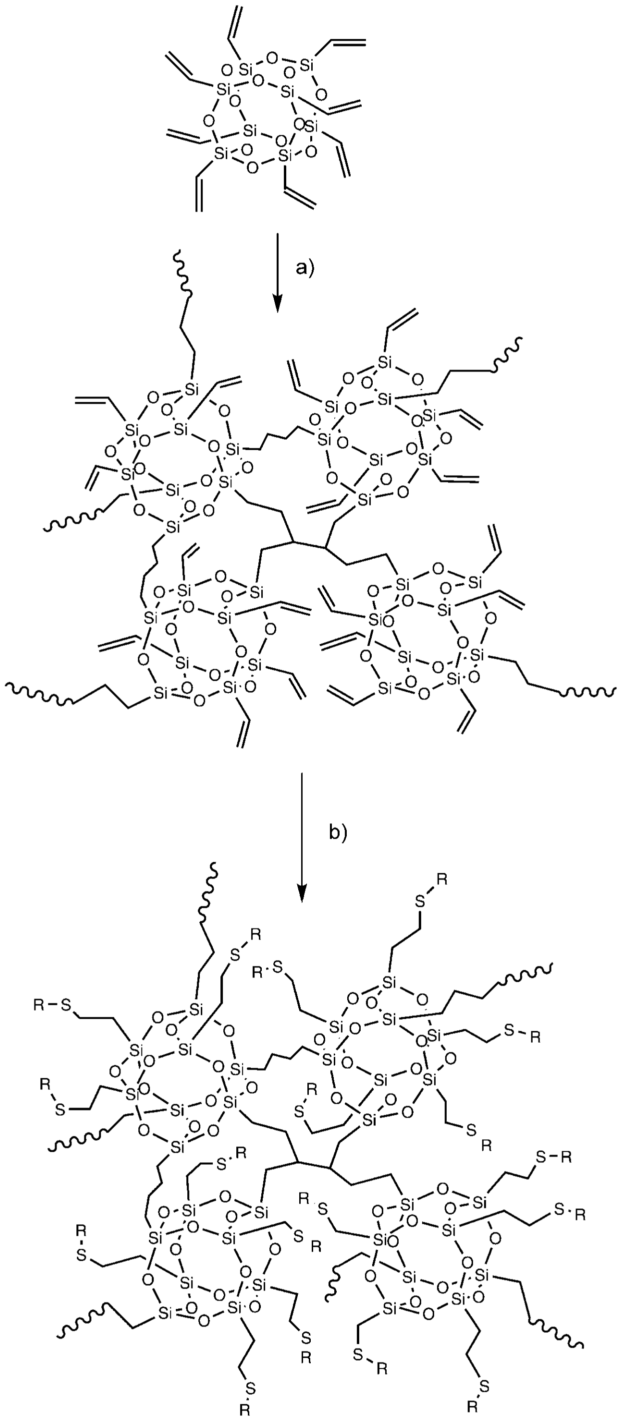

Scheme 1. Preparation of polyhedral vinylsilsesquioxane porous polymers $(RSiO_{3/2})_n$ (shown for $n=8$) and their functionalization: a) AIBN (16% w/w with respect to monomer), THF (40–80% w/w), PEG (0–40% w/w), 24 h, 60 °C. b) DMPA (1 wt% with respect to thiol), chloroform, R–SH, *hν*, 10 min. Polymer **4a**, $R=CH_2CH_2OCH_2CH_2OCH_2CH_2SH$; polymer **4b**, $R=CH_2COOH$. AIBN = azobisisobutyronitrile, DMPA = 2,2-dimethoxy-2-phenacetophenone, PEG = poly(ethylene glycol), THF = tetrahydrofuran.

Table 1: Porous properties of bulk polymers probed by nitrogen adsorption/desorption.

Polymer	Porogenic solvent PEG/THF[a]	BET surface area $[m^2 g^{-1}]$	Pore volume $[cm^3 g^{-1}]$[b]
1	0/80	782	0.53
2	10/70	868	0.88
3	20/60	891	1.53
4	30/50	743	0.36
5	40/40	680	0.16

[a] Values in w/w, solvent contains POSS 20% w/w. [b] BJH adsorption cumulative pore volume.

An inherent consequence of the polymerization of a multifunctional vinyl monomeric species is the existence of a number of residual vinyl groups (Scheme 1), even with the relatively high initiator concentration used in the reported experiments (16 wt% with respect to the monomer). FTIR spectroscopy (Figure 2, spectrum b) was used to confirm partial consumption of the vinyl groups of the multifunctional ($n \geq 8$) monomeric precursor. The appearance of new bands associated with the newly formed alkyl groups is also observed. This result is supported by solid-state ^{29}Si NMR spectroscopy (Figure 3, spectrum b), in which the shift of the neighboring silicon nuclei upon polymerization can be seen.

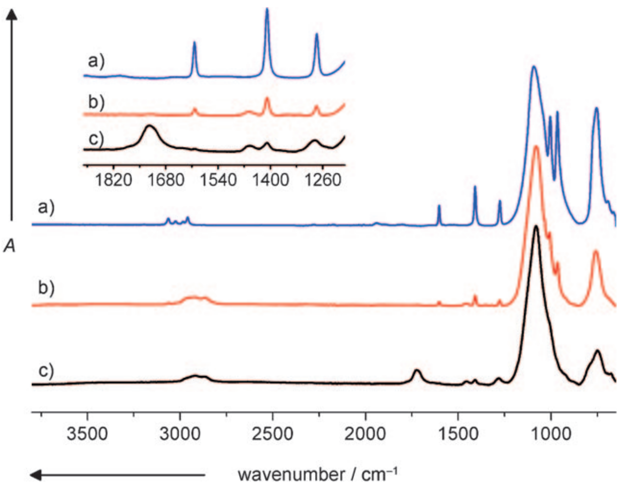

Figure 2. FTIR spectra of a) polyhedral vinylsilsesquioxane, b) polymer **4**, and c) polymer **4b** (modified with thioglycolic acid). The –Si–O–Si– stretching vibration (strong band at 1075 cm^{-1}) is preserved throughout the synthetic procedures, whilst the intensity of the peaks at 3050, 1600, 1410, and 1275 cm^{-1}, which are associated with the vinyl groups, decrease and that of the alkyl bands at 2900 cm^{-1} increase. An additional C=O stretching band at 1710 cm^{-1} is observed for the thioglycolic acid modified polymer.

Tailorability of the interface properties of the derived materials is desirable for final applications. Although many types of modification could be envisaged,[9] thiol–ene addition[10] provides a simple and effective route to tailor the surface properties of these porous hybrid polymers by thermally or photochemically induced functionalization of the residual vinyl groups. Whilst a wide range of substituents could be added to the surface by rapid and simple modifications, we demonstrate the versatility of the approach by modification with the dithiol 2,2′-(ethylenedioxy)diethanethiol (polymer **4a**) and with thioglycolic acid (polymer **4b**). The reaction could be thermally or photochemically initiated

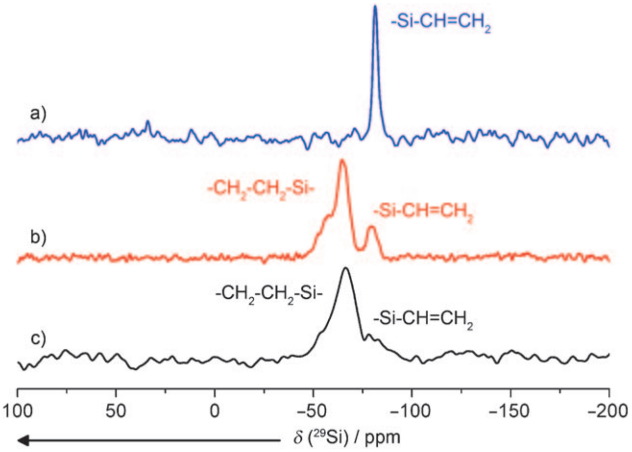

Figure 3. Solid-state ^{29}Si CP-MAS NMR spectra of a) polyhedral vinylsilsesquioxane monomer; b) polymer **4**; and c) polymer **4b** (modified with thioglycolic acid). The partial transformation of the vinyl groups to alkyl groups upon polymerization, followed by a further reduction upon modification, is reflected in the shift of the neighboring ^{29}Si nuclei.

and successful modification was confirmed by FTIR spectroscopy (Figure 2, spectrum c) for the bulk samples. Further reduction of the residual vinyl groups, as also evidenced by solid-state ^{29}Si NMR spectroscopy (Figure 3, spectrum c) is also observed. Additionally, reduced ceramic yields were indicated by thermogravimetric analysis (TGA) of the modified materials (Figure S2).

Viscous flow-through ability is a desirable property of these materials with respect to flow-through applications. The introduction of macropores into the materials increases the permeability for fluid flow and allows convective transport at low backpressures while maintaining the inherent high surface area. This property was realized by the polymerization of polyhedral vinylsilsesquioxane building blocks (polymer **4** in Table 1) in a fused-silica conduit (100 μm ID) with vinyl-functionalized walls (Figure 4).[4b] Pressure stability was confirmed up to the maximum flow rate of the instrument (resulting in 13MPa head-on pressure), and is enabled by the covalent wall anchorage and three-dimensional interadherence (Figure 4 and Figures S1 and S3).

Figure 4. Scanning electron microscopy images of polymer **4** prepared in situ in a fused-silica mold (100 μm ID) with pendant vinyl groups: left, cross-section; center, bulk region; right, wall region.

Alongside the porous properties in microfluidic conduits, the interface properties could open avenues to a wide variety of applications. In initial studies, the hydrophobic materials in the 100 μm ID conduit (Figure 4) could be successfully rendered hydrophilic by modification with the dithiol moiety (polymer **4a**). Whilst hydrophobic molecules are selectively retained on the hydrophobic precursor material, they show much less interaction upon modification (Figure S4). We are currently working on modifying these materials and testing their suitability for liquid chromatographic, extractive, and catalytic applications by tailoring pore-structural properties and interface chemistry.

In summary, we have demonstrated a facile, single-step preparation of a functionalizable high-surface-area material with a hierarchical pore space. This novel and highly flexible route to porous materials from a centimeter scale (Figure S1) to a micrometer scale (Figure 4) may emerge for a wide variety of applications in which high capacity and high surface areas are required.

Experimental Section

Polyhedral vinylsilsesquioxane was dissolved in the desired amount of THF and varying amounts of PEG200 were added while maintaining a constant weight fraction of monomer to porogenic solvent (20% w/w). The precursor mixture was then added to AIBN (16 wt% with respect to the monomer mass). The solution was deoxygenated by bubbling with N_2 for 10 min, followed by polymerization at 60°C for 24 h. After polymerization, the bulk polymers were cut into smaller pieces, extracted with THF for 16 h in a Soxhlet apparatus and dried in a vacuum oven overnight. For molding experiments in 100 μm ID capillaries, the previously vinylized fused-silica capillaries[4b] were filled with the polymerization mixture using a syringe, sealed with rubber stoppers, and immersed in a water bath at 60°C for 24 h. After monolith preparation, the capillaries were flushed with THF. In a sample modification, a polymer sample (0.2 g) was suspended in a solution containing thioglycolic acid (0.7 g, 7.6 mmol) and 2,2-dimethoxy-2-phenylacetophenone (1 wt% with respect to thiol) in chloroform (1 mL) and irradiated with UV light for 10 min under cooling and stirring. For capillary modifications, the reaction solution was continuously pumped through the capillary and irradiated at 4°C for 10 min. The materials were then washed repeatedly with chloroform and THF before drying or use. Further experimental details are provided in the Supporting Information.

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[1] a) M. E. Davis, *Nature* **2002**, *417*, 813; b) B. M. L. Dioos, I. F. J. Vankelecom, P. A. Jacobs, *Adv. Synth. Catal.* **2006**, *348*, 1413; c) N. B. McKeown, P. M. Budd, *Chem. Soc. Rev.* **2006**, *35*, 675; d) F. Svec, J. Germain, J. M. J. Fréchet, *Small* **2009**, *5*, 1098; e) K. K. Unger, R. Ditz, E. Machtejevas, R. Skudas, *Angew. Chem.* **2010**, *122*, 2350; *Angew. Chem. Int. Ed.* **2010**, *49*, 2300; f) M. R. Buchmeiser, *Polymeric Materials in Organic Synthesis and Catalysis*, Wiley-VCH, Weinheim, **2003**.

[2] a) N. Tanaka, H. Kobayashi, K. Nakanishi, H. Minakuchi, N. Ishizuka, *Anal. Chem.* **2001**, *73*, 420A; b) A. M. Siouffi, *J. Chromatogr. A* **2003**, *1000*, 801.

[3] K. Nakanishi, K. Kanamori, *J. Mater. Chem.* **2005**, *15*, 3776.

[4] a) F. Svec, J. M. J. Fréchet, *Science* **1996**, *273*, 205; b) I. Nischang, F. Svec, J. M. J. Fréchet, *Anal. Chem.* **2009**, *81*, 7390.

[5] a) D. B. Cordes, P. D. Lickiss, F. Rataboul, *Chem. Rev.* **2010**, *110*, 2081; b) G. Kickelbick, *Prog. Polym. Sci.* **2003**, *28*, 83.

[6] a) C. X. Zhang, F. Babonneau, C. Bonhomme, R. M. Laine, C. L. Soles, H. A. Hristov, A. F. Yee, *J. Am. Chem. Soc.* **1998**, *120*, 8380; b) J. J. Morrison, C. J. Love, B. W. Manson, I. J. Shannon, R. E. Morris, *J. Mater. Chem.* **2002**, *12*, 3208; c) P. G. Harrison, R. Kannengiesser, *Chem. Commun.* **1996**, 415; d) L. Zhang, H. C. L. Abbenhuis, Q. H. Yang, Y. M. Wang, P. Magusin, B. Mezari, R. A. van Santen, C. Li, *Angew. Chem.* **2007**, *119*, 5091; *Angew. Chem. Int. Ed.* **2007**, *46*, 5003.

[7] M. F. Roll, J. W. Kampf, Y. Kim, E. Yi, R. M. Laine, *J. Am. Chem. Soc.* **2010**, *132*, 10171.

[8] Y. Kim, K. Koh, M. F. Roll, R. M. Laine, A. J. Matzger, *Macromolecules* **2010**, *43*, 6995.

[9] G. Cheng, N. R. Vautravers, R. E. Morris, D. J. Cole-Hamilton, *Org. Biomol. Chem.* **2008**, *6*, 4662.

[10] a) A. B. Lowe, *Polym. Chem.* **2010**, *1*, 17; b) C. E. Hoyle, C. N. Bowman, *Angew. Chem.* **2010**, *122*, 1584; *Angew. Chem. Int. Ed.* **2010**, *49*, 1540.