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Template synthesis of functionalized polystyrene in ordered silicate channels†

Guangtao Li,*[ab] Sheshanath Bhosale,[b] Sidhanath Bhosale,[b] Fengting Li,[a] Yihe Zhang,[a] Ruirong Guo,[a] Hesun Zhu[a] and Jurgen-Hinrich Fuhrhop*[b]

[a] *Department of Chemistry, Tsinghua University, 100084 Beijing, P.R. China.*
E-mail: LGT@mail.tsinghua.edu.cn; Fax: +86 10 62785967; Tel: +86 10 62785369
[b] *Freie Universitaet Berlin, Institut fuer Organische Chemie, Takustr. 3, D-14195 Berlin, Germany.*
E-mail: fuhrhop@chemie.fu-berlin.de; Fax: +49 30 83855589; Tel: +49 30 83855394

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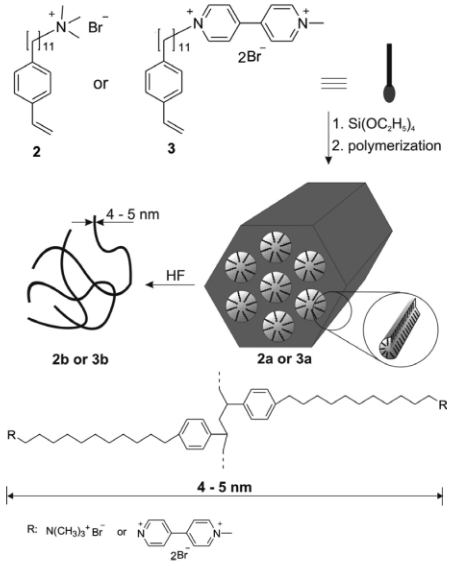
A mesostructured nanocomposite was fabricated by using a novel electroactive, polymerizable surfactant as a template in a sol–gel process, and the first example of well-resolved polystyrene with redoxactive functional group synthesized in silicate matrices was provided.

A highly ordered hexagonal channel structure and uniform tunable pore size make the mesoporous silicate MCM-41 very attractive as an ideal host for rational nanomanufacturing,[1–5] especially as a synthetic scaffold for controlled polymerization.[6–8] Inspired by the pioneering work of Bein and coworkers,[9] the polymerization of various monomers, such as styrene, alkynes, ethylene and methacrylates, have been reported within MCM-41.[6–8,10]

Recently, following the *in-situ* polymerization strategy developed by Brinker and Aida groups,[11–12] we employed a template with a terminal thiophene group, which functions both as structure-directing agent and monomer, for MCM-41 framework synthesis using tetraethoxysilane (TEOS) in the sol–gel process. After the MCM-41 formation the densely packed template monomers were directly polymerized in a controllable fashion, and submicrometer long, separated polythiophene molecular wires were fabricated in gram scale.[13] In this study, we report two new surfactants bearing polymerizable styrene units. Besides the quaternary ammonium group, an electroactive viologen moiety was induced as polar head group in surfactant synthesis. It is found that, although viologen has a large volume, the synthesized surfactant is still suitable as a template for the construction of a well-defined hexagonal channel structure under certain conditions. Using the same strategy described above (see scheme), the water-soluble polystyrene molecular wire with electroactive functional group was produced for the first time in ordered silicate channels.

The synthesis of surfactant monomers **2** and **3** started with a Li_2CuCl_4 mediated Grignard coupling of 1-chloromethyl-4-vinylbenzene with 1,10-dibromodecane. The obtained bromide was subsequently transformed into the desired products by the reaction with trimethylamine and 1-methyl-4,4′-bipyridinyl-1-ium, respectively. Hexagonal mesoporous silica powders were prepared by hydrolyzing TEOS in the presence of polymerizable surfactant **2** or **3** and NH_4OH (28%). In a typical synthesis, 1.0 g of tetraethoxysilane (TEOS) was added to an aqueous solution of NH_4OH containing styrene derivative **2** or **3** under stirring. The molar ratio of 1.0 Si : 114 H_2O : 8.0 NH_4OH : 0.12 styrene **2** was established in the reaction mixture. In the case of styrene **3**, a lower molar ratio (0.10) was used. After 60 min stirring at room temperature, the resulting viscous gels were left to condense at 90 °C for 5 h in a closed polyethylene bottle. A white powder **2a** (in the case of **2**) or a yellow powder **3a** (in the case of **3**) was collected by filtration, and washed thoroughly with water and acetone. The samples were dried in air at room temperature.

X-ray diffraction (XRD) of the sample from **2** shows the characteristic well-resolved pattern with an intense (100) reflection at low angle and three more weak intensities corresponding to (110), (200) and (210) reflections of the hexagonal structure. Unexpectedly, surfactant **3** with a large polar head group is also very suitable for forming a well-ordered hexagonal mesoporous solid. Three typical diffraction peaks indexed as (100), (110), and (200) were detected for the sample **3a**. The *d* spacing of **2a** and **3a**, calculated from the position of the intense peak, is 2.4 nm and 3.1 nm respectively, which is near to the value expected for the diameter of rod micelles from **2** and **3**. Complementary to the XRD data, the images of transmission electron microscopy (TEM) of both samples **2a** and **3a** display a hexagonal array of mesopores throughout the sample. A typical TEM image of the mesoporous structure formed from **3** as monomer template was depicted in Fig. 1.



The polymerization of the densely filled styrene monomers in silicate channels was performed in a sealed Schlenck tube under nitrogen atmosphere. 10 ml of a toluene dispersion containing 2 g of synthesized silica powder and 2 ml of 0.05 M AIBN in toluene were mixed and stirred at 60 °C for 72 h. After the removal of the solvent and washing with dichloromethane, the residue was then dispersed in 20 ml of 0.2 M HF aqueous solution. In both cases of silicate **2a** and **3a**, an orange precipitate was formed, collected by filtration, washed carefully with water, and dried in air. Generally, we obtained about 500 mg polymer from 2 g of silicate powder.

As expected, both obtained polymers **2b** and **3b** were very soluble in water. TEM provided direct visualization of the formed polystyrene wires. A representative TEM image of sample **3b** stained by 1% phosphotungstate is shown in Fig. 1b. It is clear that massive, coiled, individual polymer wires or strands are distributed over large areas (Fig. 1, also in supporting information†). These wires or strands have a tendency to entangle with each other. Attempts to obtain separated single wire or strands by dilution and to detect clear-cut ending and thus determine the length of individual wire failed. These wires or strands, however, have a uniform width of about 6 nm, as deduced from the measurement of

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† Electronic supplementary information (ESI) available: TEM image of sample **3b**. See http://www.rsc.org/suppdata/cc/b4/b402794a/

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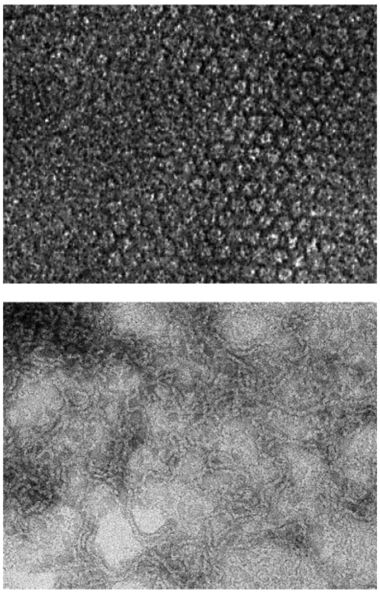

Fig. 1 TEM images of synthesized mesoporous silicate using surfactant **3** as structure-directing agent (top) and the viologen functionalized polystyrene molecular wires from the polymerisation of **3** in silicate channels (bottom).

the width of ten distinguishable strands. This value corresponds to the width of styrene repeating units in the all-*trans* conformation in a micellar double strand. Similar results were also observed in the case of sample **2b** and in our previous work.[13] These observations suggest that the *in-situ* polymerization in mesoporous silicate allows the fabrication of separated molecular wires.

Attempts to determine the molecule weight of synthesized polystyrene by size-exclusion chromatography experiments are unsuccessful, presumably because of the strong electrostatic interaction of the positive charged polystyrene with columnar statuary phase. MALDI-TOF spectroscopic measurements also gave no positive results.

Fig. 2 shows the cyclic voltammograms of polymer **2b** and **3b** modified ITO electrodes, prepared by a spin-coating approach from aqueous solution, in dichloromethane solution containing 0.1 M $TBNPF_6$. As expected, polystyrene **2b** with the usual quaternary ammonium groups did not display any electroactivity, and only a typical background wave was observed (dotted line in Fig. 2). In contrast, in the case of polymer **3b**, a much broader redox wave, producing presumably the viologen radical cation, was detected at a potential of $E_{1/2} = -0.82$ V [$E_{1/2} = (E_{pa} + E_{pc})/2$ *vs*. Ag/AgCl, dashed line in Fig. 2]. The peak currents scale linearly with the scan rate, showing that the electroactive polymer is in contact with the electrode and the charge transfer is controlled by a diffusion process. Cathodic–anodic peak potential separation for this wave is *ca*. 230 mV at 100 mV s^{-1}. In accordance with the general observations in redox polymer-coated electrodes, these values are significantly larger than those found for the polymer in solution, indicating also kinetic limitation in charge transport through this type of redox films.

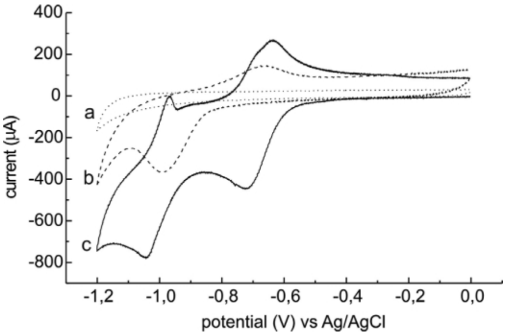

Fig. 2 Cyclic voltammograms of the polymer-coated ITO-electrodes in 0.1 M $TBAPF_6/CH_2Cl_2$ at 100 mV s^{-1}, curve a: polymer **2b**; curve b: polymer **3b**; curve c: polymer **3b** with embedded gold nanoparticles.

Charge transport rate limitations in redox polymer film can in principle be minimized by admixture of the redox polymer with new film components which process high electron mobility.[14] In our case, small gold particles (13 nm) were incorporated in the polymer film using layer-by-layer approach (alternative deposition of positively-charged polymer and negatively-charged gold particles on the electrode surface). Indeed, the electrochemical behavior of synthesized polystyrene is qualitatively improved. The redox process characteristic of viologen with a moderate peak potential splitting as well as the large peak currents is clearly detected for electrode film consisting of small gold particles embedded in the viologen functionalized polystyrene **3b** (solid line in Fig. 2). By integrating the area under the first viologen reduction peak in Fig. 2, we obtained a surface coverage of viologen (9.6×10^{-8} mol cm^{-2}). This experiment further confirms that after sol–gel, *in-situ* polymerization, and etching processes the functional viologen groups are correctly retained

In conclusion, we succeeded in the fabrication of a mesostructured nanocomposite using a novel electroactive, polymerizable surfactant as template in a sol–gel process, and provided, to the best of our knowledge, the first example of well-resolved, polymer wires with redoxactive functional groups synthesized in silicate matrices. Since the quaternary ammonium bromide can be replaced by other polar head groups such as PEG and phosphonate for MCM-41 synthesis, different functionalized polystyrene molecular wires should also be accessible using our method. This related work is currently being undertaken in our lab.

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Notes and references

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 F. Schuth and W. Schmidt, *Adv. Mater.*, 2002, **14**, 629.
3 J. Y. Ying, C. P. Mehnert and M. S. Wong, *Angew. Chem. Int. Ed.*, 1999, **38**, 56.
4 P. Yang, D. Zhao, D. I. Margolese, B. F. Chmekla and G. D. Stucky, *Nature*, 1998, **396**, 152.
5 C. E. Fowler, B. Lebean and S. Mann, *Chem. Commun.*, 1998, 1825.
6 K. Moller and T. Bein, *Chem. Mater.*, 1998, **10**, 2950.
7 S. Spange, *Angew. Chem. Int. Ed.*, 2003, **42**, 4430and references therein.
8 K. Tajima and T. Aida, *Chem. Commun.*, 2000, 2399.
9 (*a*) C. G. Wu and T. Bein, *Science*, 1994, **264**, 1757; (*b*) C. G. Wu and T. Bein, *Science*, 1994, **266**, 1013.
10 (*a*) S. A. Johnson, D. Khushalani, N. Coombs, T. E. Mallouk and G. A. Ozin, *J. Mater. Chem.*, 1998, **10**, 144; (*b*) M. J. MacLachlan, P. Aroca, N. Coombs, I. Manners and G. A. Ozin, *Adv. Mater.*, 1998, **10**, 144; (*c*) K. Kageyama, J. Tamazawa and T. Aida, *Science*, 1999, **285**, 2113.
11 Y. Lu, Y. Yang, A. Sellinger, M. Lu, J. Huang, H. Fan, R. Haddad, G. Lopez, A. R. Burns, D. Y. Sasaki, J. Shelnutt and C. J. Brinker, *Nature*, 2001, **410**, 913.
12 T. Aida and K. Tajima, *Angew. Chem. Int. Ed.*, 2001, **40**, 3803.
13 G. Li, S. Bhosale, T. Wang, Y. Zhang, H. Zhu and J. H. Fuhrhop, *Angew. Chem. Int. Ed.*, 2003, **42**, 3818.
14 P. Burgmayer and R. W. Murray, *J. Electroanal. Chem.*, 1982, **135**, 335.