

Ethenylene-bridged periodic mesoporous organosilicas with ultra-large mesopores†

Carl Vercaemst,*^a Petra E. de Jongh,^b Johannes D. Meeldijk,^b Bart Goderis,^c Francis Verpoort^a and Pascal Van Der Voort*^a

Received (in Cambridge, UK) 15th April 2009, Accepted 11th May 2009

First published as an Advance Article on the web 1st June 2009

DOI: 10.1039/b907631j

***E*-configured ethenylene-bridged periodic mesoporous organosilicas with ultra-large mesopores and unprecedented pore volumes have been developed for the first time.**

Periodic mesoporous organosilicas (PMOs) are a relatively novel group of organic–inorganic hybrid materials in which the organic groups are not located in the pores, but rather are an intrinsic part of the pore walls.¹ They are prepared *via* the direct condensation of bridged organosilanes, most commonly of the type (RO)₃Si–R'–Si(OR)₃, in the presence of a structure directing agent. This way nanocomposites with a high organic content can be obtained while preserving the pore ordering and uniformity. Ethenylene-bridged PMOs are especially interesting as they are easily modified by means of olefin chemistry.² Due to their structural rigidity and controllable hydrophobic character, PMOs are of great interest for applications in catalysis,³ environmental technology^{4,5} and chromatography.⁶ However, the applicability of PMOs is often limited by their pore sizes, which typically range between 2 and 8 nm. In some applications, such as in biocatalysis or controlled drug release, larger mesopores are required to allow the diffusion, adsorption or immobilization of large biomolecules such as enzymes, proteins or drugs. To date, the synthesis of ethenylene-bridged PMOs with mesopores larger than 15 nm has not been reported, so with this goal in mind, we probed the possibility of adapting pluronic P123 as a template, in combination with 1,3,5-trimethylbenzene (TMB) as a sweller.

Recently we reported a novel synthesis of diastereoisomeric, hexagonally ordered ethenylene-bridged PMOs.^{7,8} Here we report on a new and easy method to develop ultra-large pore isomeric PMOs with unprecedented pore volumes consisting of various pore systems, including foam-like pore structures with uniformly sized mesopores, 3D stacked spherical pores

and nodular strings, *i.e.* cylinders built from linearly connected spheres. In a typical synthesis, 1.0 g of P123 was diluted in a solution containing 48.7 ml of H₂O, 1.2 ml of *n*-butanol and 2.1 ml of concentrated HCl. The mixture was stirred at room temperature until P123 was fully dissolved, after which a varying amount of TMB was added. This solution was stirred for 0.5 h, after which 1.86 ml of the homemade *E*-1,2-bis-(triethoxysilyl)ethene was added.⁷ Finally, the mixture was stirred for 3 h at 35 °C and aged for 24 h in an autoclave at 100 °C. The PMO was filtrated and the template removed by means of extraction with acetone. Following this procedure a series of 4 PMOs were synthesized by varying the amount of TMB, while keeping all other parameters constant. The results are given in Table 1.

By varying the amount of TMB, the pore size can be engineered from approximately 8.1 to 28.3 nm. Moreover, by increasing the amount of TMB, PMOs with extremely high pore volumes can be attained. When employing 7.76 mmol of TMB, a PMO with a pore diameter of 28.3 nm and a total pore volume of 2.25 cm³ g⁻¹ was acquired, which, to the best of our knowledge, is the largest pore size and volume ever reported for a PMO material. These hybrid materials also have relatively high micropore volumes (up to 0.2 cm³ g⁻¹), which were attained by using a mild extraction procedure. Fig. 1 shows the nitrogen adsorption–desorption isotherms of EBP-1, EBP-2, EBP-3 and EBP-4, which illustrate the impact of the swelling agent on the physisorption properties of the PMOs. The capillary condensation step in the isotherms of these PMOs is very sharp and occurs at very high relative pressures, indicating very uniform and ultra-large mesopores. The delayed nitrogen desorption of the PMOs synthesized with TMB suggests that the pores are confined.

Usually, the use of swelling agents, such as TMB, results in materials with very poor or no structural ordering, especially when materials with very large pores are attained. In fact, only a few reports on ultra-large pore PMOs exist.^{9,10}

^a Department of Inorganic and Physical Chemistry, Centre for Ordered Materials, Organometallics and Catalysis, University of Ghent, Krijgslaan 281, Building S3, 9000 Ghent, Belgium. E-mail: carl.vercaemst@ugent.be; Fax: +32 9264 4983; Tel: +32 9264 4442

^b Department of Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

^c Department of Chemistry, Division of Molecular and Nanomaterials, Catholic University of Leuven (K. U. Leuven), Celestijnenlaan 200F, 3001 Heverlee, Belgium

† Electronic Supplementary Information (ESI) available: TEM images, BJH pore size distributions, plot of the relative adsorption as a function of relative pressure, nitrogen isotherms of EBP-5. See DOI: 10.1039/b907631j/

Table 1 Properties of ethenylene-bridged PMOs

Sample	[TMB]/mmol	<i>S</i> /m ² g ⁻¹	<i>V</i> _t /cm ³ g ^{-1a}	<i>V</i> _{mic} /cm ³ g ^{-1b}	<i>D</i> _p /nm ^c
EBP-1	0	1018	1.03	0.1	8.1
EBP-2	1.73	783	1.23	0.1	18.5
EBP-3	2.59	819	1.50	0.1	21.3
EBP-4	7.76	944	2.25	0.2	28.3

^a Total pore volume. ^b Micropore volume (from *t*-plot). ^c Pore diameter determined by BJH method on the adsorption isotherm.

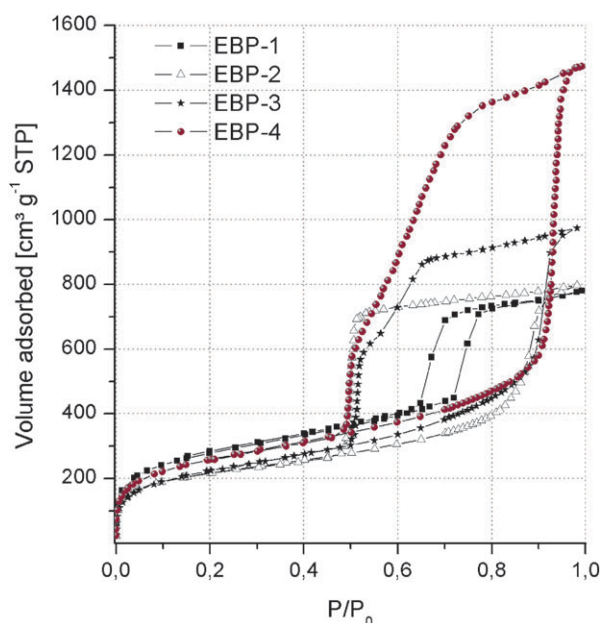


Fig. 1 Nitrogen adsorption-desorption isotherms of EBP-1, EBP-2, EBP-3 and EBP-4.

By using *E*-1,2-bis(triethoxysilyl)ethane according to the above described procedure, ordered ultra-large pore ethenylene-bridged PMOs were attained, as illustrated by the small-angle X-ray scattering (SAXS) plots in Fig. 2. However, the addition of TMB clearly has an effect on the long-range ordering of the materials. EBP-1 shows three well-resolved peaks which can be assigned to the (100), (110) and (200) reflections of a 2D hexagonal well-ordered structure. Due to lattice distortions and the presence of different mesophases, the assignment of the reflections in the SAXS patterns of EBP-2, EBP-3 and EBP-4 is not straightforward. Assuming that the maxima are caused by next neighbour correlations, a predominant hexagonal arrangement can be derived when

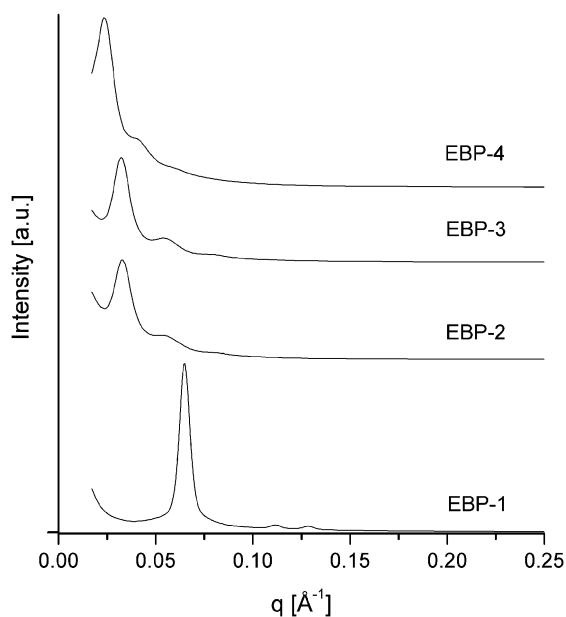


Fig. 2 SAXS plots of EBP-1, EBP-2, EBP-3 and EBP-4.

relying on the position of the first two peaks. Correlating the first peak with the (100) reflection and assuming a close packed arrangement of spheres, one can calculate sphere diameters of 20.0, 22.2 and 30.4 nm, respectively. Looking at the local ordering with TEM, the ultra-large pore PMOs reveal different mesophases, as illustrated by Fig. 3. Locally, mesostructures which consist of linearly connected spherical pores (nodular strings), are present. In addition, very large domains of foam-like, uniformly sized mesopores are found with a local hexagonal packing (Fig. 3b). A third type of mesophase consists of 3D highly ordered spherical pores, as illustrated by the TEM images in the tilt-series in Fig. 4. Herein the spheres seem to have a face-centered cubic structure.

The phase transition induced by TMB is caused by an alteration in the interfacial curvature of the surfactant micelles. Hereby, TMB influences the hydrophilic-hydrophobic volume ratio of the surfactant. By adding TMB, the rod-like surfactant-organosilica composite micelles transform into spherical micelles, which leads to the formation of spherical pores. This rod-to-sphere transition accounts for the different mesostructures observed by TEM and explains the change in the nitrogen desorption behaviour of the ultra-large pore PMOs when compared to EBP-1 (Fig. 1). The delayed

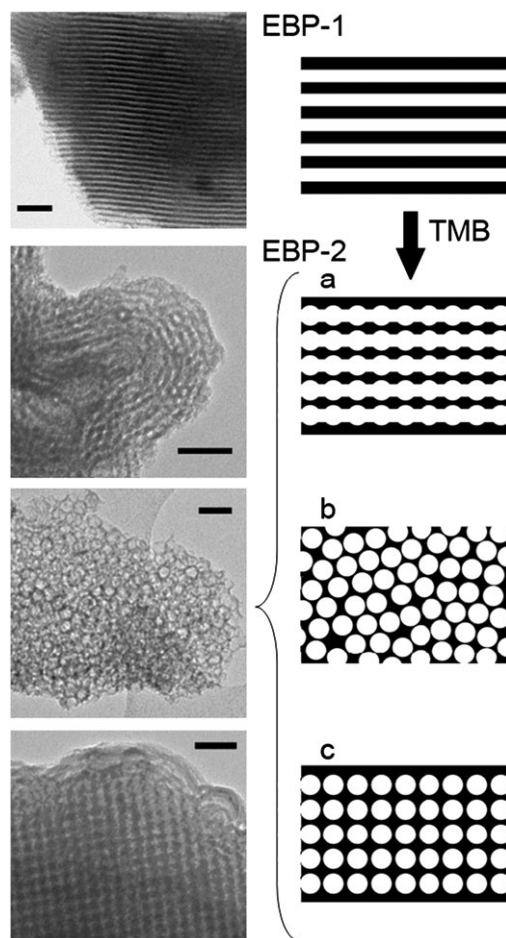


Fig. 3 TEM images of EBP-1 and EBP-2 (scale bars are 50 nm), illustrating the phase transformation induced by TMB and a schematic representations of (a) nodular strings, (b) foam-like mesophase and (c) ordered spherical pores.

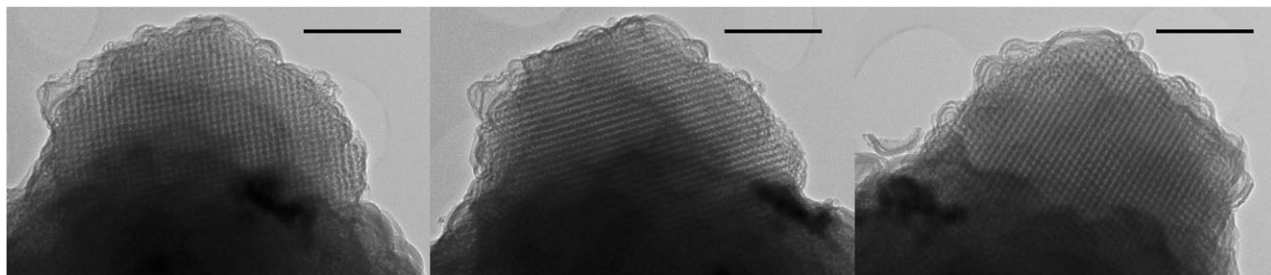


Fig. 4 TEM images of EBP-2. The specimen was tilted to 18.7°, 35° and -24° (left to right). The scale bars are 200 nm.

nitrogen desorption in the desorption isotherms of EBP-2, EBP-3 and EBP-4 is caused by the confinement of nitrogen in the mesopores.

Besides PMOs with monomodal pore size distributions, PMOs with bimodal pore size distributions can be developed by slightly changing the reaction conditions described above. By using the same molar composition as for EBP-3, but performing the aging step at atmospheric pressure and at 90 °C, a PMO with a bimodal pore size distribution is obtained, as illustrated by Fig. 5a. This bimodal PMO, abbreviated to EBP-5, has pores of both 21.3 nm (like EBP-3) and 8.1 nm

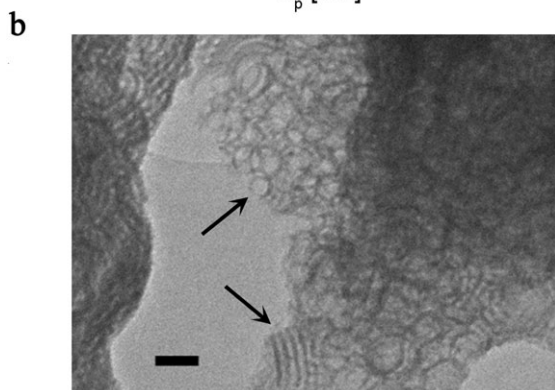
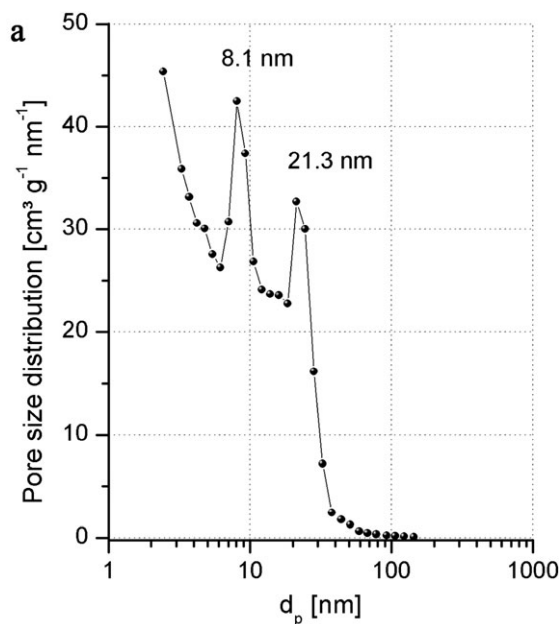


Fig. 5 (a) Bimodal BJH pore size distribution of EBP-5, calculated for the adsorption isotherm. (b) TEM image of EBP-5, showing both pore systems (scale bar is 50 nm).

(like EBP-1). A two-step adsorption isotherm, related to the bimodal pore size distribution, is clearly visible (see ESI†). To uncover the morphological composition, the sample was studied with TEM. The TEM images clearly show that both pore systems are present within a single particle, excluding the possibility of there being two separate mesophases with two different pore size distributions (see Fig. 5b).

These types of hybrid materials with unprecedented pore sizes may be of interest for applications requiring large pore volumes such as in catalysis, environmental technology and nanoelectronics. The easily modifiable ethenylene-bridges give a means to immobilize catalysts or heavy metal scavengers *via* carbon-carbon or carbon-metal bond formation as opposed to the commonly used and often less stable siloxane bond, while the large pore cavities when sealed can be potentially interesting in designing low-*k* materials by air-trapping.

In conclusion, isomeric ethenylene-bridged PMOs with ultra-large pores have been synthesized for the first time by employing P123 as a template in combination with TMB as a sweller. The addition of TMB causes a transition in the pore structure from cylinders to foams, nodular strings and ordered spheres. A novel and straightforward method to obtain ethenylene-bridged PMOs with bimodal pore size distributions has also been presented.

The authors gratefully acknowledge the staff of the Dutch-Belgian Beam Line (DUBBLE) at the ESRF in France for SAXS measurements, Heiner Friedrich for TEM measurements and Frederik Van Schelvergem and Joachim D'hooge for experimental aid.

Notes and references

- 1 T. Asefa, M. J. MacLachan, N. Coombs and G. A. Ozin, *Nature*, 1999, **402**, 867.
- 2 K. Nakajima, I. Tomita, M. Hara, S. Hayashi, K. Domen and J. N. Kondo, *Catal. Today*, 2006, **116**, 151.
- 3 C. Baleizao, B. Gigante, D. Das, M. Alvaro, H. Garcia and A. Corma, *Chem. Commun.*, 2003, 1860.
- 4 O. Olkhoviyk and M. Jaroniec, *J. Am. Chem. Soc.*, 2005, **127**, 60.
- 5 L. X. Zhang, W. H. Zhang, J. L. Shi, Z. Hua, Y. S. Li and J. Yan, *Chem. Commun.*, 2003, 210.
- 6 V. Rebbin, R. Schmidt and M. Froba, *Angew. Chem., Int. Ed.*, 2006, **45**, 5210.
- 7 C. Vercaemst, M. Ide, B. Allaert, N. Ledoux, F. Verpoort and P. Van der Voort, *Chem. Commun.*, 2007, 2261.
- 8 C. Vercaemst, H. Friedrich, P. E. de Jongh, A. V. Neimark, B. Goderis, F. Verpoort and P. Van Der Voort, *J. Phys. Chem. C*, 2009, **113**, 5556.
- 9 M. C. Burleigh, M. A. Markowitz, E. M. Wong, J. S. Lin and B. P. Gaber, *Chem. Mater.*, 2001, **13**, 4411.
- 10 X. F. Zhou, S. Z. Qiao, N. Hao, X. L. Wang, C. Z. Yu, L. Z. Wang, D. Y. Zhao and G. Q. Lu, *Chem. Mater.*, 2007, **19**, 1870.