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Preparation and characterisation of silica monoliths using a triblock copolymer (F68) as porogen

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ABSTRACT

Silica-based monoliths with co-continuous structure were successfully prepared through a sol–gel process in the presence of a poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (F68). The triblock copolymer was compared to the classical PEG, in the formation of silica monoliths and was demonstrated to lead to co-continuous structures in a wider composition range, presenting smaller through pores. Moreover, mesoporous structures templated at the sol–gel transition were assumed to occur at the surface of the silica skeleton while PEG exhibited no mesopore templating.

1. Introduction

Monolithic columns have been attracting the chromatographists' attention due to their little loss of separation efficiency when operated at high flow rate, with the advantage of a low operating pressure and a higher permeability. They can provide better performance than particle packed columns under fast operating conditions [1]. The preparation of these monolithic silica columns have been described extensively by Nakanishi et al. [2,3] and applied in chromatography by Minakuchi et al. [4–6], while the only commercially available column is the efficient Chromolith by MERCK.

As described by Nakanishi et al. [6], the formation of silica monoliths is due to two essential and competitive events, i.e. the phase separation and the sol–gel transition. Those events take place simultaneously and a spinodal decomposition occurs which leads to the formation of two phases, one being a silica rich phase, the other a solvent rich phase. When the sol–gel transition occurs, the transient morphology of the phase separation is frozen within the gel-network, and the macropore network is thus formed. By controlling the initial conditions, the speed of both events can be controlled and consequently the domain size (sum of the macropore size and the skeleton size). Polyethylene glycol is usually used as both phase separation inducer and porogen. Minor modifications in the composition of the starting mixture result in different monolith physical characteristics (macropore and skeleton size). Desmet et al. [7] reported simulation experiments that demonstrate that a monolith with a smaller domain size is more efficient in chromatographic separations than larger ones; in contrast the smaller domain size is more heterogeneous [8]. Investigations to optimize the characteristics of the monoliths for chromatographic applications are still in progress, since commercial columns are only available with a single macropore size and skeleton size (2 μm and 1.5 μm, respectively). To obtain smaller domain sizes and better homogeneities and thus better expected chromatographic performances, several authors used different approaches; the most common one being the variation of the concentration of the polymer. Hara et al. [9] reported the preparation of what they have called the second-generation monolithic silica columns using PEG as template; they obtained very good chromatographic performances by increasing the silica phase ratio thus decreasing the domain sizes, attributed to an increased homogeneity of the monoliths compared to previous monolithic silica columns.

Alternatively, the variation of the polymer's nature was also explored. In order to improve the homogeneity of the domain size, Saito et al. [10,11] studied the formation of the silica network by comparing two polymers, PEG and a more hydrophobic polymer, HPAA (polyacrylic acid), but came to contradictory conclusions regarding the homogeneity of the systems. Sun et al. [12] studied the effect of the PEG molecular weight on the formation of silica monoliths. They reported three types of morphologies depending on the molecular weight of PEG: under 2000 they obtained a particle aggregate morphology, between 2000 and 8000, they found network morphologies and above 8000 they reported a mixed type where the network has larger pores. Moreover, several non-ionic surfactants such as Pluronic P123 [13], Pluronic F127 [14] or polyoxyethylene nonylphenylethers [15] were used as phase separation inducers.

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In addition, triblock copolymers especially Pluronic P123 and Pluronic F127 were also used as a mesopore templates [12–14,16–21]. The addition of trimethylbenzene (TMB) is assumed to enhance the self-organisation of the Pluronics to transform the mesopore system from random to ordered [22]. An ordered mesopore network was also obtained with P123 and a greater amount of water [16] or F127 block copolymer [14]. Nakanishi et al. [15] also reported the preparation of silica monoliths using non-ionic surfactants as porogens and found that the cumulative pore volume (of the mesopores) increased with the decrease of the alkyl chain length of the surfactant.

The present paper describes the preparation of silica monolith according to the phase separation strategy using a triblock copolymer Pluronic F68 ($EO_{80}PO_{30}EO_{80}$). This polymer is relatively close to PEG but differs in its amphiphilic properties. It was used as a phase separation inducer in the formation of the silica network and as a mesopore template and compared to PEG.

2. Materials and methods

2.1. Chemicals

Tetramethoxysilane (TMOS) from Sigma–Aldrich was used as a silica source. Polyethylene glycol (PEG) having an average molecular weight of 10,000 was purchased from Fluka and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) F68: $(EO)_{80}$–$(PO)_{30}$–$(EO)_{80}$ with an average molecular weight of 8400 (HLB > 24) was purchased from Sigma–Aldrich. Acetic acid (Carlo Erba – SDS) was used as a catalyst for hydrolysis. Aqueous ammonia (Carlo Erba) was used for the generation of mesopores. Nitric acid (Fluka) and ethanol (Carlo Erba) were used for washing the monoliths before the drying step.

2.2. Preparation of silica rods

The silica monoliths preparation was adapted from the procedure described by Nakanishi et al. [2,23]. TMOS was added to 25 mL of a 0.01 M acetic acid solution in the presence of either F68 or PEG and the mixture was magnetically stirred in an ice bath for 30 min. The quantities of both TMOS and polymer were varied in order to obtain silica monoliths with different physical characteristics. The resulting mixture was then poured into cylindrical moulds and kept for gelation and aging for 48 h at 40 °C using a thermostated water bath. Wet silica rods thus formed were washed with ultra pure water and treated with 0.01 M ammonium hydroxide at 120 °C for 6 h to generate the mesoporosity. The gels were immersed in 0.1 M nitric acid then in a 25:75 ethanol:water (v:v) mixture and dried at 50 °C for 3 days. Finally, they were heat treated, with a temperature ramp of 1 $°C\ min^{-1}$ and kept for 2 h at 600 °C, to remove the organic polymer and stabilize the surface of the silica.

2.3. Characterisation of silica rods

The resulting silica rods were characterised by mercury porosimetry with a Micromeritics Pore sizer 9320 instrument for total pore volume and macropore size determinations using the Washburn equation $r_p = (2\gamma \cos\theta)/P$ where γ is the mercury surface tension and θ the contact angle. A JEOL JSM 6700F scanning electron microscope (SEM) was used for both observations and estimations of the skeletal size by taking the average thickness of at least 50 narrow portions between branching points [5]. The monoliths were fixed on the stub by silver lacquer and then coated with iridium by a home made sputter (IPCMS Strasbourg, France). The domain size was calculated by summing the skeletal size and the macropore size. Nitrogen adsorption/desorption isotherms were recorded at 77 K using a Sorptomatic 1990 (Thermoquest, CE instruments). The adsorption branch was used to estimate the average pore size and the pore size distribution using the Barrett–Joyner–Halenda (BJH) method [24], whereas the cumulative pore volume (V_c (cm^3/g)) was obtained by the summation of the pores' volumes between 2.5 and 50 nm diameter. Surface areas were achieved by the Brunauer–Emmett–Teller (BET) method [25]. Small angle X-ray scattering (SAXS) experiments were performed using Cu Kα radiation (1.54 Å wavelength) using a Nanostar from Bruker AXS (operating at 40 kV, 40 mA). The scattering intensities and patterns were detected by a 2D position-sensitive detector (Bruker AXS) with 512 × 512 channels. The measured wave vector (q) range was $0.05\ Å^{-1} < q < 1\ Å^{-1}$.

3. Results and discussion

As the phase separation results in the formation of two phases, one silica rich and one solvent rich, various transient structures of phase separation can be frozen-in as gel morphologies when the sol–gel transition occurs. When the transient structure possesses comparable volume fractions of the conjugate phases, a co-continuous gel is obtained (Fig. 1a). In this case, the phase separation and the sol–gel transition occur concurrently. When either the phase separation occurs earlier or the sol–gel transition is retarded, a "particle aggregate" morphology is obtained (Fig. 1b). This structure is obtained either when the polymer concentration is low or when the ratio of silica/water is low. When higher concentrations of either polymer or TMOS are used, the phase separation is decelerated (or the sol–gel transition accelerated) and a "nanoporous structure" is obtained (Fig. 1c).

For both polymers, i.e. F68 and PEG, the morphologies mentioned above were observed under SEM when varying the initial composition. The ternary diagrams (Fig. 2) show the relation between the calculated final composition and the morphology of the silica monoliths. The solvent composition represents the sum of water, acetic acid and methanol resulting from the hydrolysis of TMOS. Calculations were made by assuming that one mole of TMOS consumes two moles of water and generates four moles of methanol [26].

With F68, the interconnected macroporous structure was obtained in a wider but similar composition region than with PEG, i.e. between 4% and 9% of F68 and between 5% and 8% of PEG, the silica fraction varying between 10% and 14% for both polymers using the appropriate solvent fraction (81–83%). It is worth noting that phase diagrams reported with other non-ionic surfactants indicate the formation of the interconnected region for different compositions, especially regarding to the solvent fraction, i.e. 68–72% of solvent, 14–17% of surfactant and 15–16% of silica for P123 [13] or 76–82% of solvent and 5–12% of polymer while the silica region is limited between 12% and 13% of NS210 [22].

A mechanism based on two competitive events can be assumed to explain these behaviours.

On the one hand, the hydrogen bonds created between the ether functions of the polymer and the surface silanols will decrease the polycondensation extent. This leads to an increase of the gel time which constitutes a favourable factor to the formation of larger domains.

On the other hand, these interactions will improve the miscibility of the two phases, slowing down their separation and favouring then the formation of smaller domains.

When the hydrophobic character of the polymer increases, the formation of aggregates or even micelles can occur through hydrophobic interactions. These aggregates will limit the hydrogen bonds formation, affecting then the miscibility and to a lesser ex-