Toward optimization of macroporous silica gels for application to capillary or microchip-based CEC and LC

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Abstract

Silica aerogels were prepared via the sol–gel process using tetramethoxysilane (TMOS) as the precursor and polyethylene oxide (PEO) of molecular weights 10,000 and 100,000 to provide a polymeric template for gelation. The experiments included eleven different formulations ranging from 100% 10,000 MW PEO to 100% 100,000 MW PEO in 10% increments. The total concentration of PEO was kept constant throughout the experiment. The gelation time of the wet-gel prepared using 10,000 MW PEO was 15.3 (±0.1) × 10^3 s, while gelation occurred almost 30 times faster by using long-chain 100,000 MW PEO. The surface area of aerogels prepared with 10,000 MW PEO was 40 m^2 g^1 and that of 100,000 MW PEO aerogels was more than an order of magnitude larger. The Young’s modulus of 10,000 MW PEO aerogels was 1.2 (±0.3) MPa while that for 100,000 MW PEO aerogels was almost four times larger. Estimated pore sizes for all types of gels were in the macroporous region. The estimated pore sizes for 10,000 MW PEO were an order of magnitude greater than those estimated for 100,000 MW PEO. The physical properties of silica aerogels such as gelation time, pore size, surface area, and Young’s modulus can be tailored to make them suitable for application as separation media in HPLC and CEC.

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1. Introduction

High-performance liquid chromatography (HPLC) is a widely used method to separate and analyze complex mixtures. In this method, a column is packed with a stationary phase, which can be a solid surface, or a liquid-coated surface, usually in the form of silica or polymer beads. A sample is loaded onto the column, and then passed through the column using a liquid mobile phase. The small size of the packing creates a large pressure drop through the columns, thus high pressure is usually required to flow the liquid phase through the column. The components in the sample pass through the column at varying rates due to differences in the partitioning between the mobile and stationary phases, or due to specific affinity interactions with the stationary phase [1]. Chromatographic interactions based on partitioning, such as reverse-phase separations, often use step or continuous gradients in two mobile-phase components in order to provide optimal separations. The use of capillaries as columns for HPLC separations has the advantage of enhanced performance and sensitivity in addition to savings in consumable materials. Another widely used form of analytical separation is electrophoresis, the transport of electrically charged particles or species in an electric field [2,3]. Separation occurs due to different electrophoretic mobilities of the components in the sample. By adjusting the buffer composition, the electrophoretic separation can be designed to separate on the
basis of size-to-charge ratio, size alone, or isoelectric point [4]. Separations can also be achieved via partitioning between two liquid phases in a method termed micellar electrokinetic chromatography (MEKC) [5]. Capillary electrochromatography (CEC) replaces the micelles with a stationary phase, such as those used in HPLC, providing a hybrid method that combines the principles of capillary HPLC and capillary electrophoresis. In CEC separations, an electric field rather than a pressure gradient is used to generate the flow of mobile phase through the packed column [6,7].

Conventionally, a bed of spherical particles forms the stationary phase in chromatography experiments. Theoretical analysis on the use of small diameter, spherical beads in packed beds as the stationary phase in capillary chromatography has shown that for molecular weight greater than $10^5$, maximum efficiency of the separation column is obtained using porous particles of about 1 $\mu$m diameter in the packing medium. But, problems with packing, column backpressure, dead volumes in detection instruments, and connecting tubes etc., make the concept of using very small beads impractical [8,9]. Replacing the packed bed with a monolithic, porous, column provides better separation properties, increased permeability, and reproducibility as well as advantages resulting from in-situ preparation within a capillary tube [10]. Macroporous, monolithic silica aerogels are such continuous, porous columns, and are being considered as an alternative to packed beds. Minakuchi et al. [11] and Ishizuka et al. [12] tested the potential of applying aerogels as separation media by preparing silica rods and enclosing them in heat-shrink PTFE tubing. Ishizuka et al. [12] and Wolfe et al. [13] performed experiments by directly forcing the liquid sol into capillary tubes. Silica aerogels showed results similar to that expected from monolithic, porous, columns.

Macroporous silica aerogels can be produced by using a combination of tetramethoxysilane (TMOS), polyethylene oxide (PEO), and 0.01 M acetic acid. Ishizuka et al. prepared silica aerogels by varying concentrations of TMOS and 10,000 MW PEO and found the diameter of the continuous solid phase, known as the gel skeleton, to range from 0.97–2.31 $\mu$m, and through-pore sizes from 1.26–3.39 $\mu$m [14]. The macroporous nature of these aerogels can be attributed to the presence of PEO as a template for gelation. The molecular structure of 10,000 MW PEO is $\text{HOCH}_2\text{CH}_2\text{OH}$, and that of 100,000 MW PEO is $\text{[-CH}_2\text{CH}_2\text{O-]}_n$. When mixed with water, PEO undergoes aggregation into liquid crystalline phases, which are stable over a wide range of composition and temperature. The PEO forms micelles when mixed with water or other suitable solvents. More complex aggregate structures are formed at higher polymer concentrations [15]. Furthermore, studies show that choosing a template with higher molecular concentra-

### 2. Experimental

The gels used for these experiments were made by varying a procedure developed by Ishizuka et al. [14]. The PEO (1.06 g) was dissolved in 0.01 M acetic acid (10 ml). The first batch of gels was made with 100,000 MW PEO. For subsequent batches, the weight of 100,000 MW PEO was reduced by 10% and made up by adding 10,000 MW PEO. The concentrations were changed in steps of 10% until the final batch had no 100,000 MW PEO and 100% of 10,000 MW PEO. The TMOS (3.5 ml) was added to this solution and the mixture was stirred at room temperature. To measure the gelation time, a variable transformer controlled torque motor set-up was used as shown in Fig. 1. One end of a shaft was connected to the torque motor and a paddle was attached to the other end of the shaft. By varying the input voltage to the torque motor, the paddle was rotated. Gelation in these experiments is defined as the point where the gel structure is strong enough to resist the spinning of the paddle. The time between addition of TMOS to the PEO solution and stopping of the
paddle due to gelation is then defined as the gelation time. Samples were prepared in glass beakers. The procedure adopted resulted in the samples being destroyed at the end of each trial.

Gelation time measurement being a destructive technique, the samples had to be prepared again for further study. Starting with the same chemicals and using the procedure described above, more sol was prepared and poured in 20ml cylindrical plastic molds. The samples were aged at room temperature for 24h, decast from the molds and repeatedly soaked in ethanol until all the interstitial fluid in the gels was replaced with ethanol. The completion of solvent exchange was verified by matching the refractive index of the fluid in which the samples were soaked with the refractive index of ethanol using a densitometer. The gels were then placed in an autoclave for supercritical drying by first replacing the ethanol with CO₂, and then increasing the temperature and pressure of the CO₂ to supercritical levels in order to avoid shrinkage of the aerogels due to development of capillary pressure, as demonstrated by Tewari et al. [20].

The microstructure of the aerogel samples was compared using a JEOL JXA-840A scanning electron microscope. The samples were coated with gold and images taken at a magnification of 4000x, accelerating voltage of 20kV, and a working distance of 14mm. The specific surface area was found by nitrogen physisorption using a Micromeritics 2010 Surface Area Analyzer and Brunauer–Emmett–Teller (BET) analysis of the isotherm. Finally, Young’s modulus measurements were made using the custom-built compression-testing device shown in Fig. 2. It uses a compressed nitrogen system to apply force to the sample through three Airpel™ low friction cylinders. A typical run consists of slowly increasing the gas pressure on the cylinders while monitoring the gas pressure and the position of the stage as it compresses the sample. Prior to testing, samples were ground flat on two parallel surfaces to assure pure compression and the dimensions were measured for normalization. This device was also used to study the mechanical properties of silica aerogels by varying the concentration of polyethylene glycol [21].

3. Results

For all combinations of TEOS plus PEO, the sol remained transparent while the final gel and aerogel were opaque and white, indicating large pore sizes. Volumetric shrinkage was observed in samples where the concentration of 10,000 MW PEO was 40% or more. The mean gelation time that was measured for five samples ranged between 0.50 (±0.01) × 10³ s for samples with no 10,000 MW PEO to 15.3 (±0.1) × 10³ s for samples with 100% 10,000 MW PEO, as shown in Table 1. The reported error is ± one standard deviation based on measurements of five samples.

An SEM micrograph of aerogel made with 100% 10,000 MW PEO is shown in Fig. 3. The micrograph reveals macroporous regions with diameters between ~5μm and 7μm. The micrograph also shows a uniform distribution of pores inside the aerogel. Aggregated arrays can be seen in the micrograph of aerogel made with 50% 10,000 MW and 50% 100,000 MW shown in Fig. 4, with estimated diameters ranging between 2μm and 4μm. Although macroporous, the pore
distribution is not as uniform as seen in Fig. 3 with certain regions having larger pores while other regions have smaller pores. In the micrograph of aerogel made with 100\% 100,000 MW PEO, shown in Fig. 5, the pore structure appears to be macroporous in nature, but the porosity is significantly less when compared to the aerogels in Fig. 3 and Fig. 4. The pore diameter is estimated to be in the range of 900 nm to 1 \mu m.

The surface area of the aerogels ranged between 520 m\(^2\)g\(^{-1}\) for samples with no 10,000 MW PEO to 380 m\(^2\)g\(^{-1}\) for samples with 50\% 10,000 MW and 50\% 100,000 MW PEO to 40 m\(^2\)g\(^{-1}\) for samples with 100\% 10,000 MW PEO. This trend indicates a decrease in the surface area of the gel with increasing polymer concentration.

A specially designed uniaxial compression test machine was used to perform mechanical testing. The Young's modulus was measured for samples consisting of 10,000 MW PEO in percentage quantities of 0\% (i.e., 100\% 100,000 MW PEO), 20\%, 40\%, 60\%, 80\% and 100\% (i.e., 0\% 100,000 MW PEO). The results are reported in Table 1 where it is seen that the Young's

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### Table 1
Concentrations of PEO in each batch\(^a\)

<table>
<thead>
<tr>
<th>Group no.</th>
<th>Percentage concentration of PEO</th>
<th>Gelation time x10(^3) (s)</th>
<th>Young's modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 100</td>
<td>0.50 (±0.01)</td>
<td>0.25 (±0.04)</td>
</tr>
<tr>
<td>2</td>
<td>10 90</td>
<td>0.60 (±0.01)</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>20 80</td>
<td>0.90 (±0.03)</td>
<td>0.20 (±0.04)</td>
</tr>
<tr>
<td>4</td>
<td>30 70</td>
<td>2.0 (±0.1)</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>40 60</td>
<td>3.0 (±0.3)</td>
<td>0.25 (±0.02)</td>
</tr>
<tr>
<td>6</td>
<td>50 50</td>
<td>3.5 (±0.1)</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>60 40</td>
<td>3.7 (±0.1)</td>
<td>0.39 (±0.02)</td>
</tr>
<tr>
<td>8</td>
<td>70 30</td>
<td>4.0 (±0.2)</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>80 20</td>
<td>4.1 (±0.2)</td>
<td>0.66 (±0.02)</td>
</tr>
<tr>
<td>10</td>
<td>90 10</td>
<td>5.3 (±0.1)</td>
<td>–</td>
</tr>
<tr>
<td>11</td>
<td>100 0</td>
<td>15.3 (±0.1)</td>
<td>1.2 (±0.3)</td>
</tr>
</tbody>
</table>

\(^a\) Gelation time and Young's modulus values are averaged over five samples and reported to ± one standard deviation.
modulus is $0.25 \pm 0.04$ MPa for samples with 0% 10,000 MW PEO, with no appreciable change until the concentration of 10,000 MW PEO is increased to 60%. The reported error is ± one standard deviation based on five samples. The maximum Young’s modulus was found for samples made with 100% 10,000 MW PEO at 1.2 ± 0.3 MPa.

4. Discussion

Since the polymer chains are longer for PEO of higher molecular weight, crosslinking occurs faster during the gelation of 100,000 MW PEO samples resulting in faster gelation times when compared to 10,000 MW PEO samples. The homogeneous distribution of the ethylene oxide chains in the inorganic matrix causes the considerably high porosity [16]. The increasing macro-porosity with increasing concentration of 10,000 MW PEO that is found in these experiments is consistent with published findings [22]. This transition is explained by an unspecified nanoscale-mixing phenomenon where the pores are more likely to be formed by more than one PEO chain [16]. Close-packed arrays seen in the SEM micrographs of 50% 10,000 MW and 50% 100,000 MW PEO are consistent with the observation of hexagonal arrays seen by Goltner et al. [23]. Surface area characterization by nitrogen adsorption shows decreasing surface area with increasing polymer concentration. Martin et al. [21] also report the lowest surface area for the highest polyethylene glycol concentration in their study. The quantity of PEO retained in the sample causes variation in surface area. PEO is insoluble in ethanol and liquid CO$_2$, which are the only two reagents that the templated gel is immersed in over extended periods of time in preparation for supercritical drying. The decreasing surface area of the aerogel with increasing concentration of PEO suggests that all the PEO added to the sample during gel preparation is retained in the aerogel. Thermogravimetric analysis would provide a better determination of the quantity of PEO retained, but was not performed on these samples. With increasing polymer concentration, condensation causes the formation of larger globules. The crosslinking of these large globules to form the three-dimensional network results in larger surface area for higher polymer concentrations. The presence of PEO significantly affected the Young’s modulus of the aerogels as indicated in Table 1. A function of the polymer is to provide reinforcement to the aerogel structure. As concentration increases, the aerogels become more dense and stronger, resulting in higher Young’s modulus values.

As mentioned earlier, monolithic, porous, silica columns are more advantageous when compared to packed beds for use as stationary phases in miniaturized HPLC columns. Using the methods described, it is possible to tailor the pore sizes of silica aerogels to make them application specific. Samples containing small components can be separated using aerogels prepared using 100% 100,000 MW PEO as stationary columns since their pore sizes are in the lower macro-porous region. Samples containing larger components can be separated using 10,000 MW PEO aerogels; these aerogels can also be used in high-pressure separation experiments owing to their higher Young’s modulus. Volumetric shrinkage of the aerogels after gelation results in voids between capillary walls and the stationary phase causing eluent plus mobile phase to flow via paths of lesser resistance, thereby reducing separation efficiency. This loss mechanism can be avoided by using aerogels made using 100,000 MW PEO, as these templated gels exhibit no volumetric shrinkage. However, due to their fast gelation times, the precursor sols are difficult to fill into capillary tubes before gelation. Using the concentrations given in Table 1, it is possible to prepare an aerogel with no volumetric shrinkage and desirable pore sizes, which offer sufficient time to fill capillaries before gelation.

5. Conclusion

This study shows that increasing the concentration of polymer in the manufacture of macroporous silica aerogels results in an increase in gelation time, porosity, and Young’s modulus, and a decrease in the specific surface area of the samples. By varying the concentrations of the 10,000 MW and 100,000 MW PEO used to template the gel, aerogels can be tailored to have desired pore sizes, surface areas, and mechanical strength. On the basis of the requirements of the specific application, these gels can be employed as stationary phases in capillary HPLC and microchip-based electrochromatography, as either wet gels or aerogels [13,24]. Further, size exclusion is one of the mechanisms employed to separate an analyte from a solvent in solid-phase extraction (SPE). Depending upon the size of the analyte to be separated, one of the above formulations can be used as an SPE column to facilitate separation in addition to the normal mechanisms, such as hydrogen bonding, polar interactions, Van der Waal’s forces, and anionic and cationic exchange [25].

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References