Supporting Information

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Graphical abstract

Experimental section

Materials

4,4’-isopropylidenediphenol (bisphenol A), paraformaldehyde (96%), aniline, p-toluenesulfonic acid monohydrate (TsOH•H₂O), dimethyl sulfoxide (DMSO) were obtained from Sigma-Aldrich. All reagents and solvents were used as received.

Synthesis of benoxazine monomer

Bisphenol A, aniline, and paraformaldehyde (molar ratio of 1:2:4) were added to a beaker and placed in a preheated oil bath at 130 °C. The ingredients were mixed for 1 h and the mixture turned into yellow, viscous liquid. The products solidified upon cooling to room temperature and were ground into powder form for further use.

Preparation of polybenzoxazine aerogel

0.5 g benoxazine (BZ) monomer powder and 0.01 g TsOH were added in 1.82 mL solvent and stirred at room temperature for 15 min to obtain BZ sol (0.275 g/mL). The BZ sol was placed inside an oven at two temperatures – 90 °C and 130 °C – to obtain the gel. All organogels were aged at the gelation temperature for duration of four times the
gel time. The aged organolgels were washed in acetone four times over a period of 12 h. The washed gels were dried under supercritical condition in carbon dioxide.

**Determination of gel time**

The gel time of BZ sols was determined using Cole-Parmer basic viscometer. The viscosity of 10 g sol kept at the gel temperature in an oil bath was monitored over a period of time (Figure S1). The gel time was determined as the time when the viscosity ($\eta$) increased dramatically. This was achieved by plotting $1/\eta$ vs. time and noting down the time as the quantity $1/\eta$ became negligibly small.

**Characterization**

The morphology of aerogels was probed using scanning electron microscopy (SEM; JEOL JSM5310) with operating voltage 8 kV. Brunauer–Emmett–Teller (BET) surface area and pore size distribution of aerogel specimens were obtained from N$_2$-sorption isotherms at 77 K, analyzed using a Micromeritics Tristar II 3020 analyzer. The aerogel specimens were sectioned and placed in designated chamber followed by degassing at 60 °C for 12 h before collecting data.

The bulk density $\rho_b$ of aerogels was obtained from the weight and volume of cylindrical aerogel specimens. The skeletal density $\rho_s$ was measured using an Accupyc 1340 helium pycnometer (Micromeritics). The skeletal density can be used in conjunction with the bulk density to calculate porosity $p$. The diameter shrinkage $\delta_d$ was determined from the difference of diameter of the aerogel ($D$) and the diameter of the corresponding gel specimen before supercritical drying ($D_0$). The bulk density ($\rho_b$), porosity ($p$), and diameter shrinkage ($\delta_d$) of the aerogel specimens were calculated using the following relationships:

\[
\rho_b = \frac{4m}{\pi D^2h} \quad (1)
\]

\[
p = \left(1 - \frac{\rho_b}{\rho_s}\right) \times 100\% \quad (2)
\]
\[ \delta_d = \left(1 - \frac{D}{D_0}\right) \times 100\% \quad (3) \]

Infrared (IR) spectra were recorded on a Brucker FT-IR Alpha spectrophotometer using a Platinum ATR accessory. Attenuated Total Reflection (ATR) was conducted with Bruker Platinum ATR. The aerogel samples were ground and pressed under the probe for testing. \(^{13}\text{C}\) CP MAS experiments were performed on BrukerAvance III 300 NMR spectrometer equipped with a 4 mm double resonance VT CPMAS probe. The \(^1\text{H}\) and \(^{13}\text{C}\) frequencies were 300.1 and 75.5 MHz, respectively. The magic angle spinning (MAS) was set to 12000 ± 5 Hz to eliminate chemical shift anisotropy. The \(^1\text{H}\) 90° pulse length was set to 3.75 µs. High-power two pulse phase modulation (TPPM) \(^2\) decoupling with a field strength of 65 kHz was applied to \(^1\text{H}\) channel during acquisition. The cross-polarization (CP) contact time and recycle delay were 1.5 ms and 2 s. Each spectrum was obtained by 4k scans at ambient temperature. The chemical shift was referenced to CH signal of adamantane (29.46 ppm) as an external reference.
Figure S1. Viscosity vs. time of BZ sols in DMSO and NMP at 90 °C and 130 °C.

Scheme S1. Possible cationic polymerization of PBZ catalyzed by TsOH$^3$. 

Scheme S2. Chemical structure of (a) BZ monomer and (b) PBZ.
Figure S2. PBZ aerogels

Table S1. Properties of PBZ aerogels.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shrinkage</th>
<th>Bulk Density (g/cm³)</th>
<th>Skeletal Density (g/cm³)</th>
<th>Porosity</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g) V₁.7-300nm</th>
<th>Total Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBZ-DMSO-90</td>
<td>26.1%</td>
<td>0.52</td>
<td>1.22±0.003</td>
<td>57.4%</td>
<td>129.6</td>
<td>0.54</td>
<td>1.10</td>
</tr>
<tr>
<td>PBZ-DMSO-130</td>
<td>26.8%</td>
<td>0.45</td>
<td>1.26±0.004</td>
<td>64.3%</td>
<td>92.2</td>
<td>0.63</td>
<td>1.43</td>
</tr>
<tr>
<td>PBZ-NMP-90</td>
<td>23.8%</td>
<td>0.46</td>
<td>1.19±0.002</td>
<td>61.1%</td>
<td>90.9</td>
<td>0.50</td>
<td>1.32</td>
</tr>
<tr>
<td>PBZ-NMP-130</td>
<td>20.3%</td>
<td>0.37</td>
<td>1.26±0.007</td>
<td>70.2%</td>
<td>81.8</td>
<td>0.26</td>
<td>1.88</td>
</tr>
</tbody>
</table>

* Total pore volume = 1/ρ_b - 1/ρ_s.

References