Thermoresponsive and Antifouling Hydrogels as Radiative Energy Driven Water Harvesting System

Diego Combita†, and Marya Ahmed‡*

†Department of Chemistry, University of Prince Edward Island, 550 University Ave. Charlottetown PE, C1A 4P3, Canada.

‡Department of Chemistry and Faculty of Sustainable Design Engineering, University of Prince Edward Island, 550 University Ave. Charlottetown PE, C1A 4P3, Canada. E-mail: marahmed@upei.ca

B5AMA synthesis

12 mmoles of 2-Aminoethyl methacrylamide (AEMA) were dispersed in anhydrous methanol (4 mL) and triethylamine (TEA) (10.6 mL) under inert atmosphere and the mixture was stirred for a minimum of 4 hours at room temperature. 10 mmoles of (R)-(-)-Pantolactone were then added and the reaction was allowed to proceed overnight under inert conditions at room temperature. Next day, triethylamine hydrochloride was precipitated by acetone addition and the white precipitates were filtered. The B5AMA monomer was purified from the filtrate by silica column chromatography, using 1% (v/v) TEA/acetone solution as an eluent. The fraction of the eluent containing the B5AMA monomer was concentrated by rotoevaporation and was precipitated in
ethyl ether to obtain the final product in the form of pure yellowish oil with 52% yield. The purified B5AMA was analyzed by 1H-NMR, using Bruker 300 MHz NMR (Figure S1).

![Figure S1. 1H-NMR spectra of B5AMA in D2O.](image)

**Co-monomer Screening**

The water release data obtained at 37 °C is normalized relative to the water release rate of pure poly(B5AMA) hydrogels. The reported ratio of comonomers to B5AMA monomer are the one optimized for the highest water release efficacies. NVC: N-vinylcaprolactam; DAA: Diacetone acrylamide; PEGM: Poly(ethylene glycol) methacrylate; HEMA: 2-hydroxyethyl methacrylate; MEO2MA: 2-(2-Methoxyethoxy)ethyl methacrylate.
<table>
<thead>
<tr>
<th>MONOMER</th>
<th>MONOMER /B5AMA ratio, mol/mol</th>
<th>RELATIVE WATER RELEASE</th>
</tr>
</thead>
<tbody>
<tr>
<td>B5AMA</td>
<td>---</td>
<td>1</td>
</tr>
<tr>
<td>NVC</td>
<td>0.36</td>
<td>1.2</td>
</tr>
<tr>
<td>DAA</td>
<td>0.51</td>
<td>1.3</td>
</tr>
<tr>
<td>PEGM (MW= 500)</td>
<td>0.52</td>
<td>1.3</td>
</tr>
<tr>
<td>HEMA</td>
<td>0.22</td>
<td>1.7</td>
</tr>
<tr>
<td>MEO₂MA</td>
<td>1.37</td>
<td>8.8</td>
</tr>
</tbody>
</table>

Table S1. Water release properties of poly(B5AMA) hydrogels copolymerized with monomers of different hydrophobicity.
Figure S2. DSC analysis of hydrated hydrogels of (A) poly(B5AMA-co-MEO₂MA), and (B) poly(B5AMA).

Figure S3. DSC analysis of (A) poly(MEO₂MA) hydrogel, (B) poly(B5AMA) hydrogel, and (C) poly(B5AMA-co-MEO₂MA) hydrogel.
Figure S4. VTT measurements indicating the decrease of the transparency of the hydrogels as a function of the temperature and were measured by the change in the optical absorbance of samples at 657 nm.

Figure S5. Linear regression of the swelling ratio of poly(B5AMA-co-MEO2MA) hydrogels, according to first-order kinetics.
Figure S6. Initial water release rate of hydrogels calculated at different temperatures.

Figure S7. Water release rate for poly(B5AMA-co-MEO2MA) hydrogels, plotted as a function of temperature.
Figure S8. Schematics depicting the mechanism of water absorption and release for poly(B5AMA-co-MEO2MA) hydrogels.

Figure S9. (A) poly(B5AMA-co-MEO2MA) hydrogels before (left) and after (right) water release at 60 °C. (B) SEM image of the hydrogel re-swelled after 5 cycles of water absorption and desorption.