Reversible photo-responsive hydrogels based on spiropyran

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Outline

Background

Self-protonating photo-responsive hydrogels

- Hydrogel fabrication
- Characterization
- Optimisation of hydrogel composition
- Photo-actuation properties
- Photo-induced shrinking and reswelling behaviour
- Porous hydrogels for improved reswelling kinetics

Conclusions
Background

• Spiropyran – Photochromic behaviour

Spiropyran  \( a = 1 \)
NIPAAm  \( b = 100 \)
MBAA  \( c = 2 \)

Background

- Size: 120-170 µm [1]
- Shrinking: to 68% of initial size after 120 s
- Maximum shrinking: to 52 % of initial size [1]
- Necessary time for reswelling: > one hour

Drawbacks

- Gels are soaked in 0.5 mM HCl overnight
- Operating only in acidic environment
- Suitable for single-use only

Spiropyran \( a = 1 \)
NIPAAm \( b = 100 \)
MBAA \( c = 2 \)

Self-protonating hydrogels

less hydrophilic

more hydrophilic

transition state
Hydrogel fabrication

- Photo-polymerised in circular PDMS moulds

\[ D^o = \left[ 1 - \frac{(d_{\text{max}} - d_x)}{(d_{\text{max}} - d_{\text{min}})} \right] \times 100\% \]
Optimization of hydrogel composition

- Photo-induced shrinking
# Shrinking/Reswelling Behaviour

<table>
<thead>
<tr>
<th>sample</th>
<th>20 [min] (Vis. light)</th>
<th>std dev</th>
<th>60 [min] (in darkness)</th>
<th>std dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(NIPAM) blank</td>
<td>87.85 %</td>
<td>1.18</td>
<td>97.44 %</td>
<td>1.60</td>
</tr>
<tr>
<td>1 % AA, 1 % BSP-A</td>
<td>67.33 %</td>
<td>1.85</td>
<td>100.45 %</td>
<td>0.64</td>
</tr>
<tr>
<td>2 % AA, 1 % BSP-A</td>
<td>59.37 %</td>
<td>4.26</td>
<td>96.48 %</td>
<td>1.34</td>
</tr>
<tr>
<td><strong>5 % AA, 1 % BSP-A</strong></td>
<td><strong>49.10 %</strong></td>
<td><strong>4.73</strong></td>
<td><strong>97.35 %</strong></td>
<td><strong>1.93</strong></td>
</tr>
<tr>
<td>2 % AA, 2 % BSP-A</td>
<td>61.31 %</td>
<td>5.20</td>
<td>83.69 %</td>
<td>1.27</td>
</tr>
<tr>
<td>5 % AA, 2 % BSP-A</td>
<td>45.50 %</td>
<td>5.33</td>
<td>82.69 %</td>
<td>3.33</td>
</tr>
<tr>
<td>5 % AA, 3 % BSP-A</td>
<td>77.22 %</td>
<td>1.12</td>
<td>76.44 %</td>
<td>1.46</td>
</tr>
</tbody>
</table>
Hydrogel 5-1

$x = 5$
$y = 1$
$z = 100$
Reproducible actuation

- DI water
- No external proton source
Reproducible actuation

- Comparison between with 5-1 and 0-1 hydrogels

![Comparison between 5-1 and 0-1 hydrogels](image)
Improved actuation kinetics

- 5-1 Hydrogel
- poly(ethylene glycol) $M_w = 2000\ \text{g/mol}$
  $M_w = 20000\ \text{g/mol}$

<table>
<thead>
<tr>
<th></th>
<th>Blank gel</th>
<th>2k gel</th>
<th>20k gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA [mol %]</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>BSP [mol %]</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>MBIS [mol %]</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>PBPO [mol %]</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>NIPAM [mg]</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>PEG 2k [mg]</td>
<td>-</td>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td>PEG 20k [mg]</td>
<td>-</td>
<td>-</td>
<td>200</td>
</tr>
<tr>
<td>Solvent [µL]</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
</tbody>
</table>
Porosity control

Blank hydrogel

2k hydrogel

20k hydrogel
Shrinking/Reswelling Behaviour
Swelling and protonation kinetics

\[ k_{\text{blank}} \approx 2.53 \times 10^{-3} \text{ [s}^{-1}] \]
\[ k_{2k} \approx 1.25 \times 10^{-3} \text{ [s}^{-1}] \]
\[ k_{20k} \approx 2.44 \times 10^{-3} \text{ [s}^{-1}] \]
Conclusions

✓ Self-protonating hydrogels

✓ Reproducible photo-actuation

✓ Capable of performing in DI water and neutral pH solutions

✓ Porous hydrogels for improved reswelling kinetics
Acknowledgments

- Jannick Theobald
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- Adaptive Sensors Group
- Insight SFI award
Thank you!