Rapid self-healable poly(ethylene glycol) hydrogels formed by selective metal-phosphate interactions

Takeshi Sato,ab Mitsuhiro Ebara,a Shinji Tanaka,c Taka-Aki Asoh,a Akihiko Kikuchi,a* and Takao Aoyagiibd*

Supporting Information

1. Materials
2. Scheme S1: Synthesis of 4-arm PEG phos.
3. Figure S1: Stability text of 4-arm PEG phos solutions crosslinked by various metal ions.
4. Figure S2: Rheological properties of 4-arm PEG-phos with Ga³⁺.
5. Figure S3: Schematic illustration of coordination bond between Fe³⁺ and ascorbic acid.
6. Figure S4: Competitive assays.
7. Figure S5: Effect of H₃PO₄ concentration on gel formation.
8. Figure S6: Effect of pH on gel formation.
9. Figure S7: Color changes of metal chloride solutions before and after gelation.
10. Figure S8: UV-vis Spectra of FeCl₃aq mixed with HCl or H₃PO₄
11. Figure S9: UV-vis Spectra of TiCl₃aq mixed with HCl or H₃PO₄
12. Figure S10: UV-vis Spectra of VCl₃aq mixed with HCl or H₃PO₄
1. Materials

All ions used in this study, KCl (> 85.0%), YCl₃(99.9%), FeCl₂(99.0~102.0%), VCl₃ (99.%), GaCl₃(99.9%), TiCl₃ aqueous solution(20 w/w%), TiCl₄(99.0%), MnCl₂ (99.0%), PdCl₂(98.0%), GdCl₃(99.9%), PbCl₂(99.5%), NaCl(99.5%), CrCl₃(99.5%), BaCl₂(99.0%), AlCl₃(98.0%), NiCl₂(98.0%), FeCl₃(99.0%), CaCl₂(95.0%), and phosphoryl chloride(99.0%) were purchased from Wako pure chem. co. (Osaka, Japan) and used as received. Diisopropyl amine (98.0%) was also purchased from Wako pure chem. co. (Osaka, Japan) and dehydrated by KOH. Hydroxyl terminated two-arm poly(ethylene glycol) (2-arm PEG, Mn = 6,000) and hydroxyl terminated 4-arm poly(ethylene glycol) (4-arm PEG, Mn = 40,000) were kindly provided by NOF corporation (Tokyo, Japan). 2-arm PEG and 4-arm PEG were purified by precipitation before use. Briefly, the polymers were dissolved in chloroform (15.0 w/v. %) and dripped into n-hexane. After decantation, the precipitated polymer was filtered by vacuum filtration using a 5.0 μm pore membrane. The purified PEG was dried in a desiccator for 12 h.
2. Scheme S1: Synthesis of four-arm star PEG with phosphate end groups (4-arm PEG phos). 

\[
\begin{align*}
&\text{4-arm PEG-OH} \xrightarrow{\text{POCl}_3, 24\text{ h}} \text{4-arm PEG-Cl} \xrightarrow{\text{H}_2\text{O}, 3\text{ d}} \text{4-arm PEG-phos}
\end{align*}
\]
3. Figure S1: Stability test of 4-arm PEG phos solutions (5 w/v%) crosslinked by various metal ions (1 M).
4. Figure S2: Rheological properties of hydrogels. $G'$ (closed) and $G''$ (open) values of 4-arm PEG-phos with Ga$^{3+}$ in continuous step strain measurement at a constant frequency of 10 Hz at room temperature. Gel was swept from 1% to 50% strain, and then back to 1% strain.
5. Figure S3: Schematic illustration of coordination bond between Fe$^{3+}$ and ascorbic acid.
6. Figure S4: Competitive assays. 4-arm PEG-phos was gelated by Ti^{3+}, Al^{3+}, V^{3+}, Fe^{3+}, Ga^{3+}, and Fe^{3+}. Then, H_{3}PO_{4} (a) and ascorbic acid (b) aqueous solution (1M) was added to the gels.
7. Figure S5: Effect of H₃PO₄ concentrations on hydrogel formation. The concentration of metal chloride (MCl₃) was fixed at $1.8 \times 10^{-1}$ M.
8. Figure S6: Effect of HCl or ascorbic acid sodium salt concentration on hydrogel formation. The concentration of metal chloride (MCl₃) was fixed at 1.8 x 10⁻¹ M.

MCl₃ = 1.8 x 10⁻¹ M

<table>
<thead>
<tr>
<th>Ti³⁺</th>
<th>Al³⁺</th>
<th>V⁵⁺</th>
<th>Ga³⁺</th>
<th>Fe³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

MCl₃: HCl = 1:4

MCl₃: HCl = 1:3

MCl₃: HCl = 1:2

MCl₃: HCl = 1:1

MCl₃: HCl = 1:0.25

MCl₃: HCl = 1:0.1

MCl₃: HCl = 1:0.05

MCl₃: Ascorbic acid sodium salt = 1:1
Figure S7: Color changes of metal ion solutions before and after mixing with 4 arm PEG-phos. The concentrations of metal chloride solution and 4-arm PEG-phos were $6.0 \times 10^{-2}$ M and 10 wt%, respectively.
10. Figure S8: Optical observation of FeCl₃ solutions with HCl (a) and H₃PO₄ (b). The concentration of FeCl₃ was fixed at 8.3 x 10⁻³ M.
11. Figure S9: Optical observation of TiCl$_3$ solutions with HCl (a) and H$_3$PO$_4$ (b). The concentration of TiCl$_3$ was fixed at $8.3 \times 10^{-3}$ M.
12. Figure S10: Optical observation of VCl₃ solutions with HCl (a) and H₃PO₄ (b). The concentration of VCl₃ was fixed at 8.3 x 10⁻³ M.