

## Supporting information:

# Preparation of Heat-Induced Artificial Collagen Gels Based on Collagen-Mimetic Dendrimers

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## Experimental Procedure

### Synthesis of POG<sub>n</sub>-modified Dendrimers (POG<sub>n</sub>-den)

The detailed synthetic method was described in our previous report [1,2]. Acetylated POG5 and POG10 (Ac-POG5 and Ac-POG10) were synthesized by reacting POG5 or POG10 with acetic anhydride in an alkali aqueous solution at 4°C. After dialysis and subsequent lyophilization, a white solid was obtained. Ac-POG5: Yield, 96%. <sup>1</sup>H NMR: δ 1.96 (br, H<sub>β</sub> and H<sub>γ</sub> of Pro), 2.06 (br, H<sub>β</sub> of Hyp and H<sub>γ</sub> of Pro), 2.13 (s, Ac), 2.35 (br, H<sub>β</sub> of Pro and Hyp), 2.54 (br, H<sub>β</sub> of Hyp), 3.65 (m, H<sub>δ</sub> of Pro), 3.83 (m, H<sub>δ</sub> of Hyp), 3.96 (m, H<sub>δ</sub> of Hyp and H<sub>α</sub> of Gly), 4.26 (m, H<sub>α</sub> of Gly), 4.63 (br, H<sub>α</sub> of Pro and H<sub>α</sub> and H<sub>γ</sub> of Hyp); Ac-POG10: Yield, ~100%. <sup>1</sup>H NMR: δ 1.94 (br, Ac and H<sub>β</sub> and H<sub>γ</sub> of Pro and H<sub>β</sub> of Hyp), 2.09 (br, Ac), 2.18 (br, H<sub>β</sub> of Hyp), 2.32 (br, H<sub>β</sub> of Pro), 3.21 (br, H<sub>δ</sub> of Pro), 3.51 (br, H<sub>δ</sub> of Pro), 3.73 (br, H<sub>δ</sub> of Hyp and H<sub>α</sub> of Gly), 3.86 (br, H<sub>δ</sub> of Hyp and H<sub>α</sub> of Gly), 4.63 (m, H<sub>α</sub> of Pro and H<sub>α</sub> and H<sub>γ</sub> of Hyp), 7.90 (br, NH of Gly) [3].

PAMAM dendrimer (G4) was reacted with Ac-POG5 or Ac-POG10 using 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) in an alkali solution (pH 9-10) at room temperature. After stirring the reaction mixture for 3-4 days, the POG5-den reaction solution was dialyzed (pore size: 2 kDa). In the case of POG10-den, the crude compounds were purified by a Sephadex LH-20 column (GE Healthcare Technologies, Uppsala, Sweden) eluted with water and then dialyzed. After lyophilization, a white solid was obtained. Yield, 57% (POG5-G4); 93% (POG10-G4).

## Characterization

$^1\text{H}$  NMR analysis was performed using a JEOL JNM-LA400 instrument (JEOL, Japan). The fluorescamine analysis was performed according to our previous reports [1,2,4,5]. The HPLC system was equipped with a column, Cosmosil 5C18-MS-II (Nacalai Tesque, Inc., Japan) and a UV detector (210 nm; UV-2075Plus, Jasco Inc., Japan). 3  $\mu\text{l}$  samples (2 mg/ml) were injected and eluted with 2% phosphoric acid (A) and methanol (B) at 1.0 ml/min by PU-2089Plus (Jasco Inc.). The eluent was linearly increased from 5% (A) to 80% (A) after 30 min.

## (References)

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- [2] Suehiro T, Tada T, Waku T, Tanaka N, Hongo C, Yamamoto S, Nakahira A, Kojima C (2011) Temperature-dependent higher order structures of the (Pro-Pro-Gly)<sub>10</sub>-modified dendrimer. *Biopolymers* 95:270-277.
- [3] Melacini G, Feng Y, Goodman M (1996) Acetyl-terminated and template-assembled collagen-based polypeptides composed of Gly-Pro-Hyp sequences. 3. Conformation analysis by H-NMR and molecular modeling studies. *J Am Chem Soc* 118:10359-10364.
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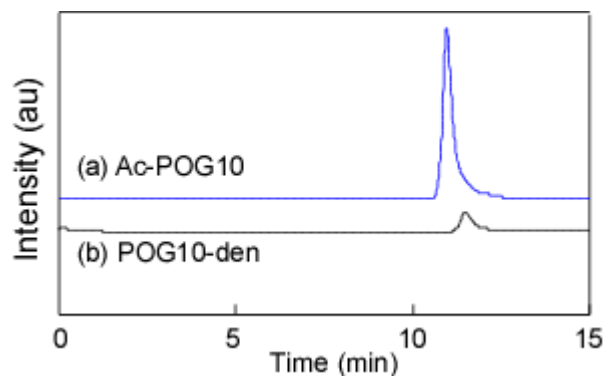


Figure S1. HPLC chromatograms of Ac-POG10 (a) and POG10-den (b).

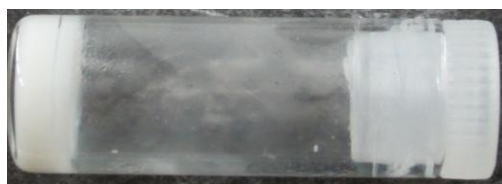


Figure S2. POG10-based hydrogel after the incubation at 80°C for 1 h.