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Electronic Supplementary Information

Three Cooperative Diffusion Coefficients describing Dynamics of Polymer Gels

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Materials and Methods

Materials

Tetra-maleimide-terminated poly(ethylene glycol) (Tetra-PEG-MA) and Tetra-thiol-terminated poly(ethylene glycol) (Tetra-PEG-SH) were purchased from NOF Co. (Tokyo, Japan) and all the other reagents were purchased from WAKO. All materials were used without further purification.

Fabrication of Tetra-PEG gels

Details of Tetra-PEG precursors have been reported elsewhere.[8] Constant amounts of Tetra-PEG-MA and Tetra-PEG-SH were dissolved in phosphate-citric acid buffer. To control the reaction rate, the optimal ionic strength and pH of buffers were chosen. The Tetra-PEG gels formed from the prepolymers with different M_w (10 and 20 kg/mol) are called Tetra-PEG gel 10K and Tetra-PEG gel 20K, respectively. In the case of Tetra-PEG gel 20K, 68 mM of buffer solution (pH 3.8) was used. In the case of Tetra-PEG gel 10K, 68 mM of buffer solution (pH 3.8) was used for the lower polymer volume fraction (ϕ_0 : 0.034-0.081) and 64mM (pH 3.4) was used for the higher polymer volume fraction (ϕ_0 : 0.096, 0.110). The same amounts of two prepolymer solutions were mixed, and the resulting solution was poured into the mold. At least 12 h was allowed for the completion of the reaction before the following experiments, except for the dynamic viscoelasticity measurement were performed.

Dynamic Viscoelasticity Measurement

The resulting solutions of Tetra-PEG gels were poured into the gap within the double cylinder of a rheometer. The oscillatory shear rheological properties (the storage modulus G' and the loss modulus G'') were measured at 25 ℃ with the double-cylinder geometry (MCR302 ; Anton Paar). The applied strain and the frequency were 2.0% and 5.0 Hz, respectively.

Measurements of swelling pressure

Tetra-PEG gels were prepared as parallel plates (height : 1.0 mm, diameter : 25 mm). The initial weights of Tetra-PEG gels were measured. The prepared gel samples were immersed into aqueous solutions of polyvinylpyrrolidone (PVP) with different M_ws (29, 1300 kg/mol) that are called PVP29K and PVP1300K, respectively. The concentration of PVP (c_{pvp}) was tuned from 20 to 80 g/L. The weights of gels were measured at room temperature. On the basis of the difference in weight before and after the immersion, the concentrations of PVP that can suppress the swelling of gels (c_{pvp}') were measured. The swelling pressures of Tetra-PEG gels (π_{sw}) were calculated with the following equation.[12-14]

$$\pi_{sw} = 0.878c'_{pvp} + 17.25c'^{2}_{pvp} + 144.1c'^{3}_{pvp} \quad (6)$$

***Dynamic Light Scattering* (DLS)**

DLS measurements were performed on an ALV/CGS-3 compact goniometer system (ALV). A He-Ne laser with a power of 22 mW emitting polarized light at 632.8 nm was

used. Correlation functions at scattering angle 90˚ were taken at 25˚C. The measurement time was 30s with 40 measurements for each sample.

Swelling experiments

Tetra-PEG gels were prepared as spheres (about 8 μL) in paraffin oil. The gels were left in the paraffin oil for at least 12 hours before the swelling experiment to complete the reaction. The gels were taken out of the paraffin oil and washed by distilled water. After washing, the gels were immersed in distilled water as soon as possible. The change in diameter was recorded every 5 min by the optical microscope (MC120HD ; Leica). The experiments were conducted at 25˚C.

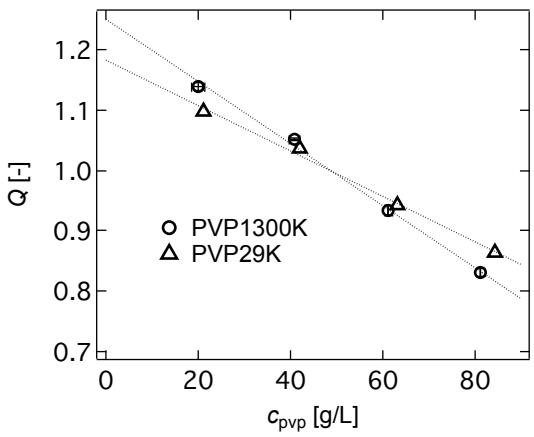

Fig. S1. The c_{pvp}-dependence of Q of Tetra-PEG gel (M_w : 10 kg/mol, ϕ : 0.050) with different M_w of PVP (M_w of PVP : 1300 kg/mol, circle; 29 kg/mol, triangle).

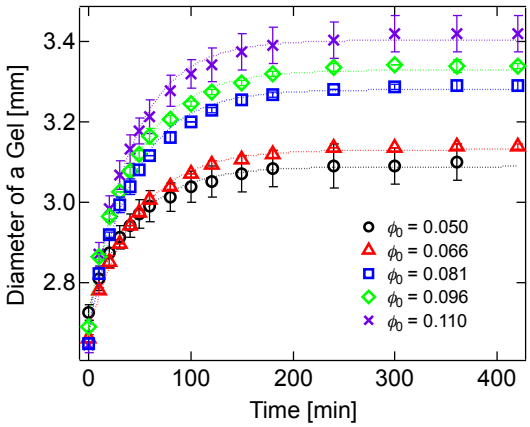

Fig. S2 The typical swelling curves of Tetra-PEG gel 20K (ϕ_0 : 0.050, circle; 0.066, triangle; 0.081, square; 0.096, diamond; 0.110, cross)

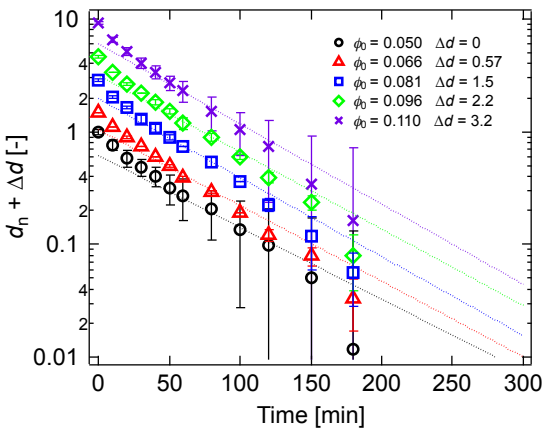

Fig. S3 The typical time courses of d_n during the swelling experiments for Tetra-PEG gel 20K (ϕ_0 : 0.050, circle; 0.066, triangle; 0.081, square; 0.096, diamond; 0.110, cross)