Supplementary information

Fitting Procedure of extended Gent model

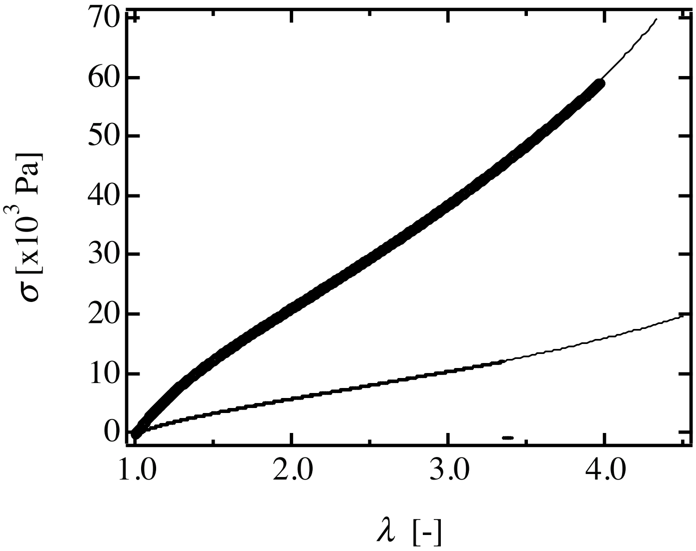
In order to estimate λ_{max} qualitatively, we utilized the extended Gent model, which was proposed in our previous study to predict the biaxial stress-elongation behavior of the 20k Tetra-PEG gel. The extended Gent model has no molecular origin and the phenomenological nature, and predicts the uniaxial stress (σ)-elongation (λ) relationship as

$$\sigma = \frac{C_1\left(\lambda - \lambda^{-2}\right)}{\left(1 - \frac{\lambda^2 + 2\lambda^{-1} - 3}{\lambda_{max}^2 + 2\lambda_{max}^{-1} - 3}\right)} + C_2\left(1 - \lambda^{-3}\right) \quad (1)$$

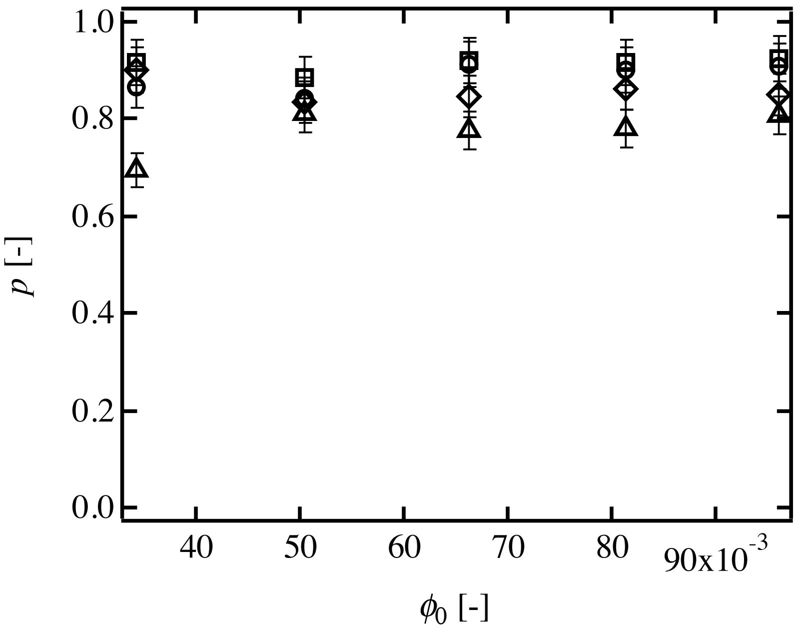
, where C_1, C_2, and λ_{max} are the fitting functions. The C_1 and C_2 have the relationship with elastic modulus (G) as $G = C_1 + C_2$. It was suggested that C_1 is almost the same value of G, C_2 is related to the stress coupling of different axes, and λ_{max} is related to the ultimate elongation ratio.

In this study, we assumed that W of the 5k, 10k, and *p*-tuned Tetra-PEG gels are also predicted by the extended Gent model, and estimated the fitting parameters from the uniaxial stretching measurement. Because the uniaxial stretching is only a deformation among physically accessible deformations, the estimation of W function from the uniaxial stretching has ambiguity. However, we believe that the estimation of λ_{max} is possible due to the following reason.

The extended Gent model predicts σ as the sum of two terms including σ_1 and σ_2, of which prefactors are C_1 and C_2, respectively. Supplementary Figure 6 shows the computation results of σ_1/σ_2 against the elongation ratio in the x direction (λ) with C_1/C_2 = 20 and 100. As clearly shown in Supplementary Figure 6, the contribution of σ_2 is extremely smaller than that of σ_1 in uniaxial stretching than that in other deformations. Thus, practically σ_2 has little effect on the estimation of λ_{max} from the uniaxial stretching. In addition, the fit results of the 20k Tetra-PEG gel from the uniaxial stretching were similar to that from the biaxial stretching. Therefore, we decided to utilize the extended Gent model to predict λ_{max} of the 5k, 10k and *p*-tuned Tetra-PEG gels. The fit of the extended Gent model worked well, and λ_{max} was successfully estimated from the fit. It should be noted that the precise estimation of C_2 is impossible from the uniaxial stretching, and we have to perform the biaxial stretching.

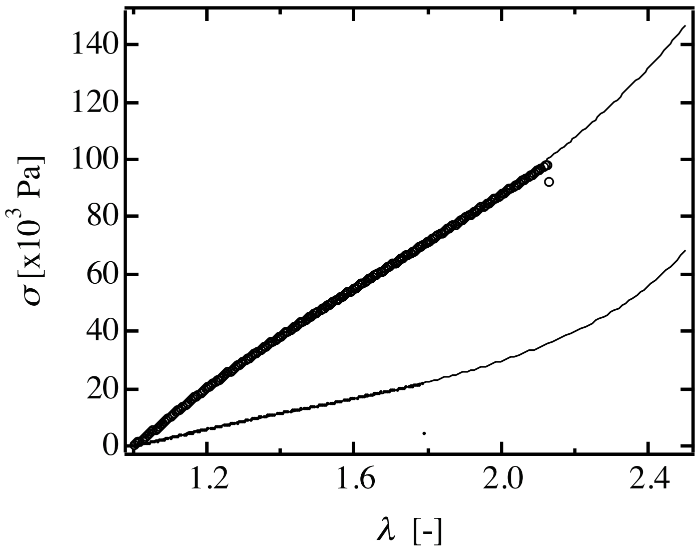


Supplementary Figure 1. Stress-elongation relationship of the p-tuned Tetra-PEG gels. Thick and thin symbols show the results of p = 0.89 and 0.61, respectively.

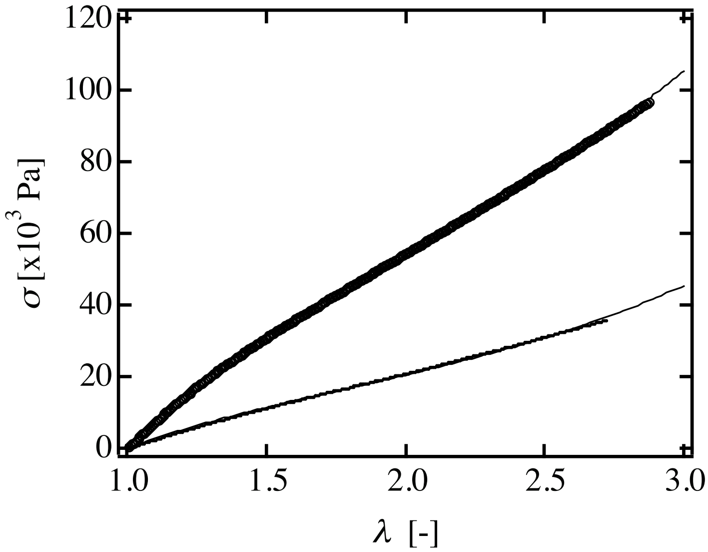


Supplementary Figure 2. The reaction efficiency (p) as a function of initial polymer volume fraction in the 5k, 10k, and 20k Tetra-PEG gels (5k, rhombus; 10k, circle; 20k, square).

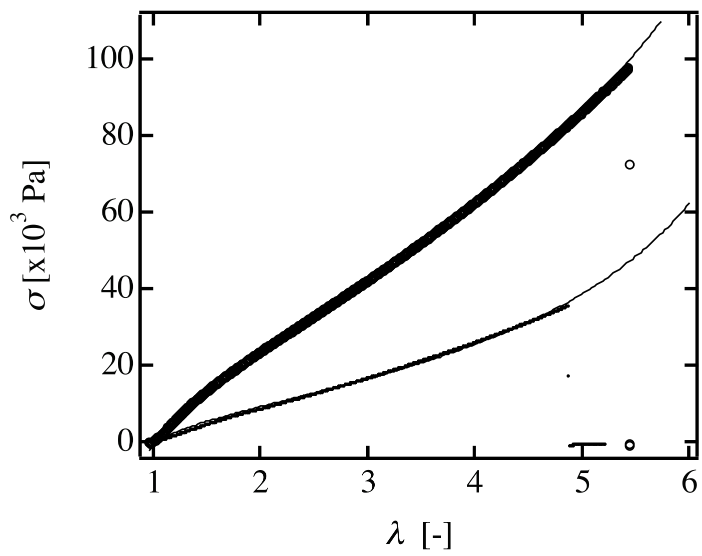
(a)


0
20
40
60
80
100
120
140
1.2
1.6
2.0
2.4
σ [x10³ Pa]
λ [-]

(b)

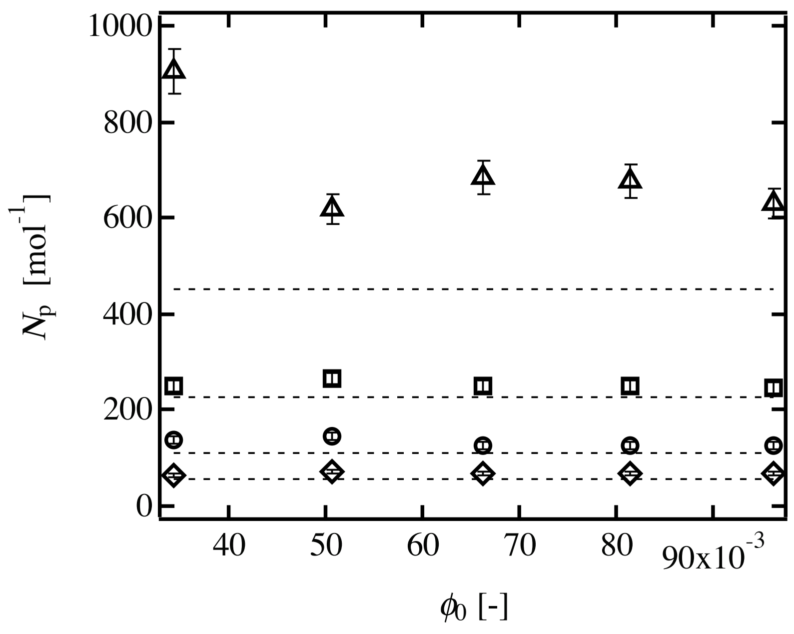

0
20
40
60
80
100
120
1.0
1.5
2.0
2.5
3.0
σ [x10³ Pa]
λ [-]

(c)

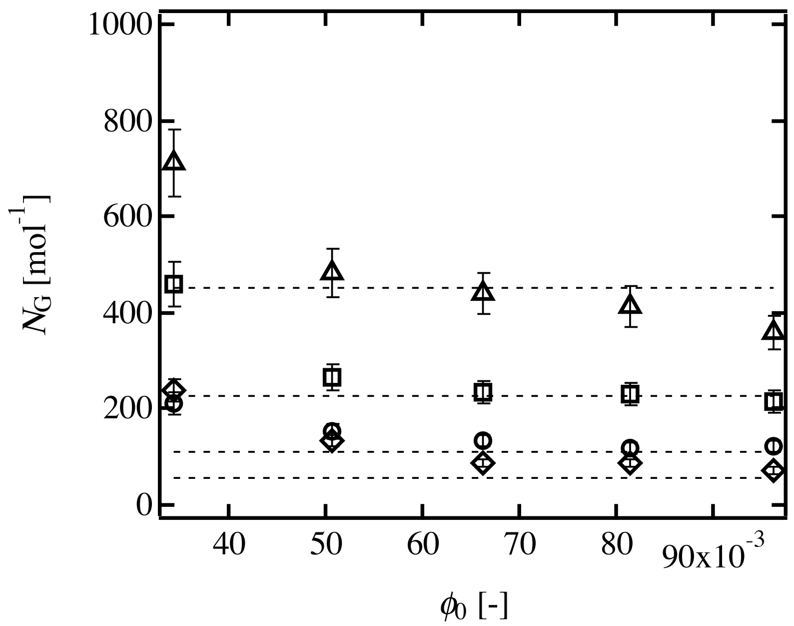


Supplementary Figure 3. Stress-elongation relationship of the 5k (a), 10k (b), and 20k (c) Tetra-PEG gels. Thin and thick symbols show the results of ϕ_0 = 0.051 and 0.096, respectively.

(a)

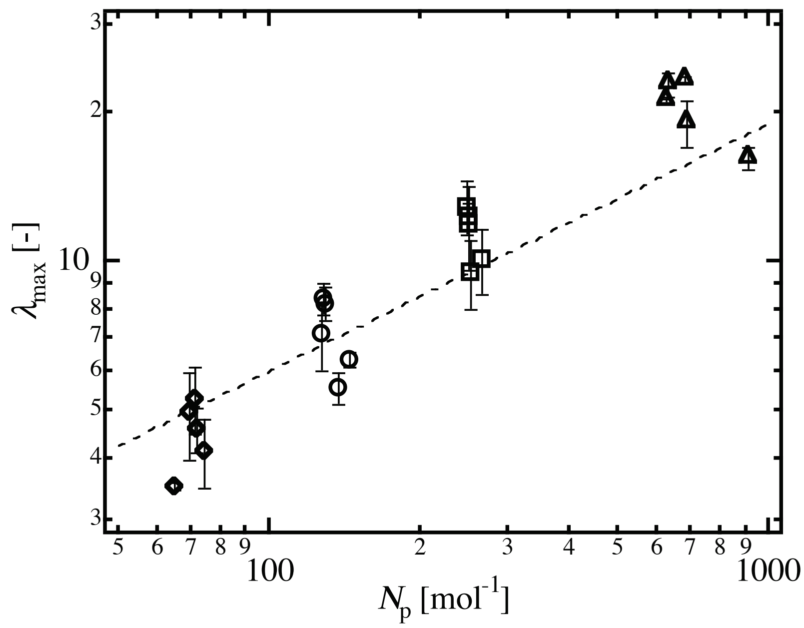


(b)

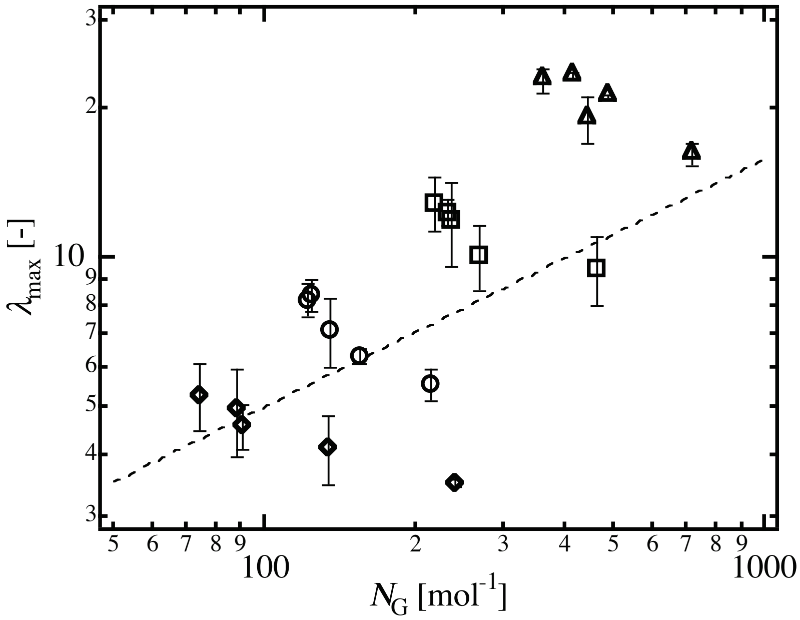


Supplementary Figure 4. (a) N_p **and (b)** N_G **of 5k, 10k and 20k Tetra-PEG gels (5k, rhombus; 10k, circle; 20k, square).**

(a)

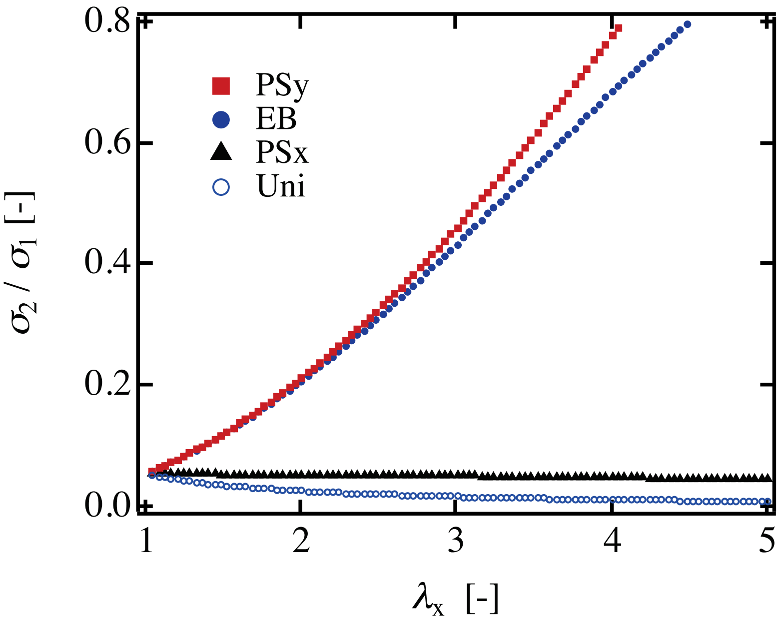


(b)

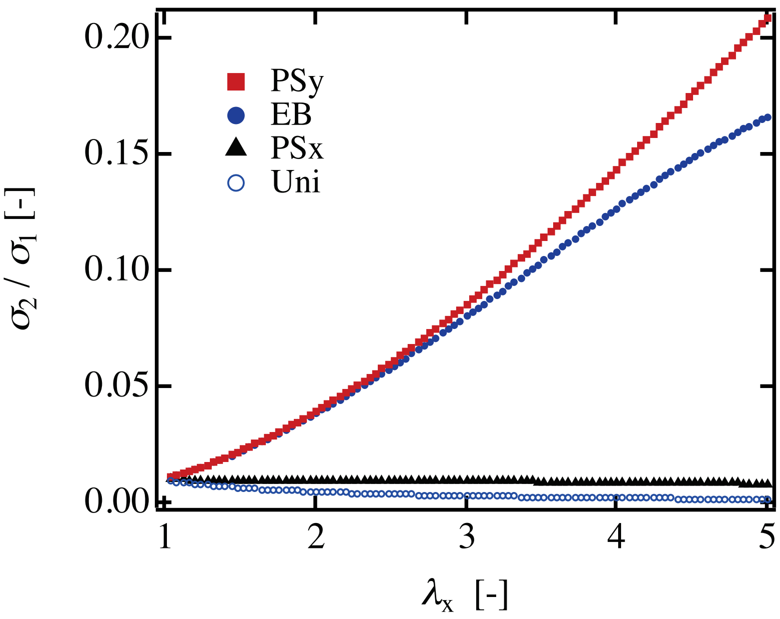


Supplementary Figure 5. λ_{max} **as a function of (a)** N_p **and (b)** N_G **in 5k, 10k and 20k Tetra-PEG gels (5k, rhombus; 10k, circle; 20k). The dotted line is the guide showing the relationship,** $\lambda_{max} \sim N^{1/2}$**.**

(a)



(b)



Supplementary Figure 6. **The stress ratio σ_2/σ_1 as a function of the elongation ratio in the x direction (λ_x) under the equi-biaxial stretching (EB), pure shear in the stretching direction (PSx), in the constrained direction (PSy), and uniaxial stretching deformation (Uni). (a) $C_1/C_2 = 20$, (b) $C_1/C_2 = 100$.**