## Supporting Information

### *Calculation of the swelling ratios of DN hydrogels*

To estimate $\chi$ parameter for PAAm – water system, eqs 1a and 1b were solved using the experimentally determined swelling ratios and cross-link densities of PAAm hydrogels, given in Figures 3B and 3C, respectively. For PEG-DM- and BAAm-cross-linked first network hydrogels, $\chi$ was calculated as 0.47 $\pm$ 0.02 and 0.49 $\pm$ 0.01, respectively. For the following calculations, $\chi$ was taken as 0.48 for all hydrogels. We also assume that all densities are equal to unity. From $\nu_e$ and $\phi_{2,1}^0$ of the first network (FN) hydrogel, the polymer concentration $\phi_{2,1}$ in the equilibrium swollen FN hydrogel and its swelling ratio $m_{rel,1}$ were calculated using eqs 1a and 1b. The polymer concentration $\phi_{2,2}^0$ in DN hydrogel after its preparation and $n_{21}$ ratio can then be calculated as:

$$\phi_{2,2}^o = (1-\phi_{2,1})C_2 + \phi_{2,1} \quad \text{(S1)}$$

$$n_{21} = \frac{(1-\phi_{2,1})C_2}{\phi_{2,1}} \quad \text{(S2)}$$

where $C_2$ is the monomer concentration (in $g.mL^{-1}$) of the second monomer solution. After substitution of $\phi_{2,2}^0$ and $\nu_e$ in eqs 1a and 1b, one may calculate swelling ratio $m_{rel,2}$ of DN hydrogels.

Figure S1 shows the variations of $\phi_{2,2}^0$ and $m_{rel,2}$ of DN hydrogels as functions of the $n_{21}$ ratio and the monomer concentration $C_2$ in the second monomer solution. Calculations are for a FN hydrogel formed at $\phi_{2,1}^0$ = 0.10 and $\nu_e$ = 50 $mol.m^{-3}$. For $n_{21}$ < 2.17, $\phi_{2,2}^0$ is less than $\phi_{2,1}^0$, that is the network chains are more diluted in DN hydrogels after their preparation as compared to FN hydrogel. As a consequence, the swelling ratio $m_{rel,2}$ of DN is below $m_{rel,1}$ of FN. The critical condition for obtaining an additional swelling in DN hydrogels is the equality of the dilution degrees $\phi_{2,2}^{0}$ and $\phi_{2,1}^{0}$ for FN and DN hydrogels at their preparation states. This requires a critical monomer concentration $C_{2,cr}$ in the second monomer solution, given by:

$$C_{2,cr} = \frac{m_{rel,1} - 1}{\left(m_{rel,1} / \phi_{2,1}^{o}\right) - 1} \tag{S3}$$

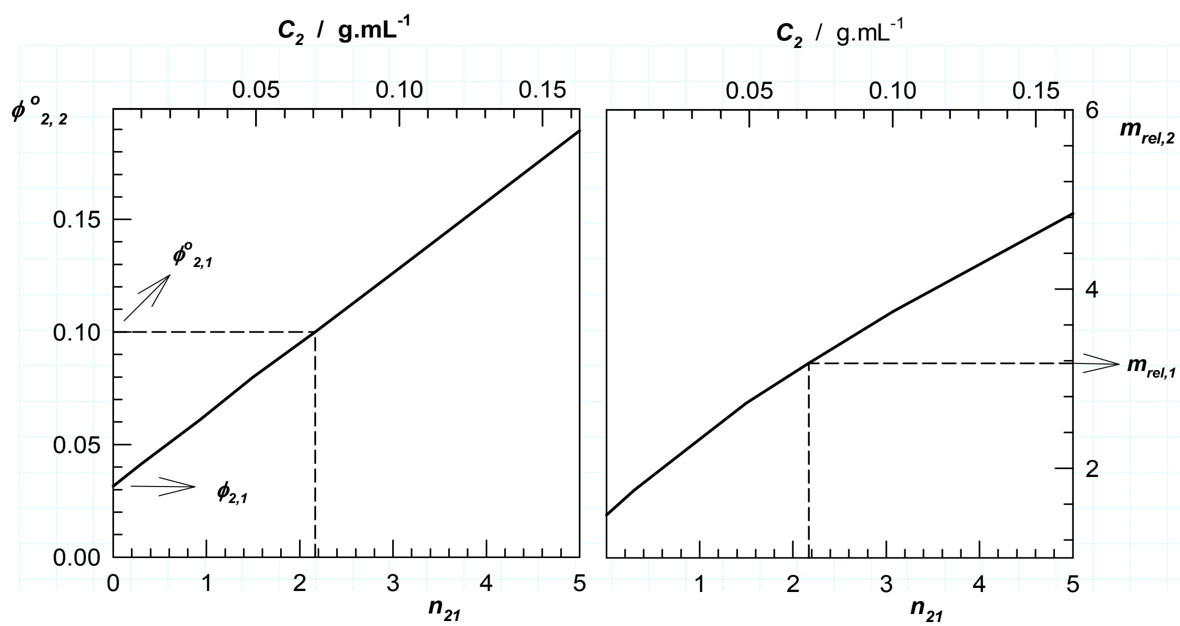


**Figure S1**. The variations of $\phi_{2,2}^{0}$ and $m_{rel,2}$ of DN hydrogels as functions of $n_{21}$ and the monomer concentration $C_2$ in the second monomer solution. Calculations are for $\phi_{2,1}^{0}$ = 0.10 and $\nu_e$ = 50 mol.m$^{-3}$.

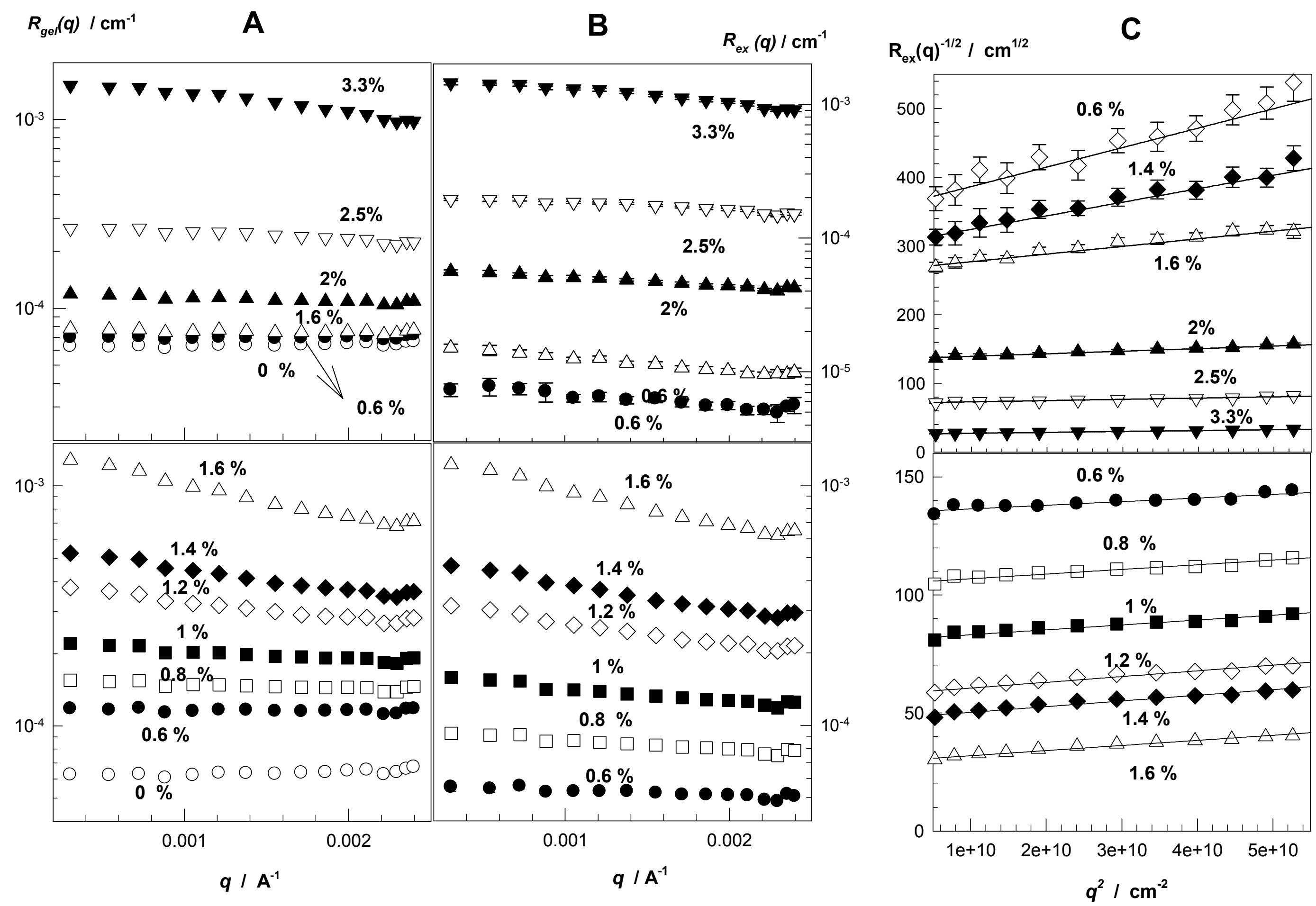


**Figure S2.** The scattering vector $q$ dependence of the scattering light intensities from the first network PAAm hydrogels after preparation $R_{gel}(q)$ (A), the excess scattering $R_{ex}(q)$ (B), and Debye-Bueche plots (C). Cross-linker = PEG-DM (upper panel), BAAm (bottom panel). The cross-linker contents (in mol %) are indicated. The data points indicated by 0 % in Figure A represent the scattering intensities $R_{sol}(q)$ from PAAm solutions at the same concentration as the gels.

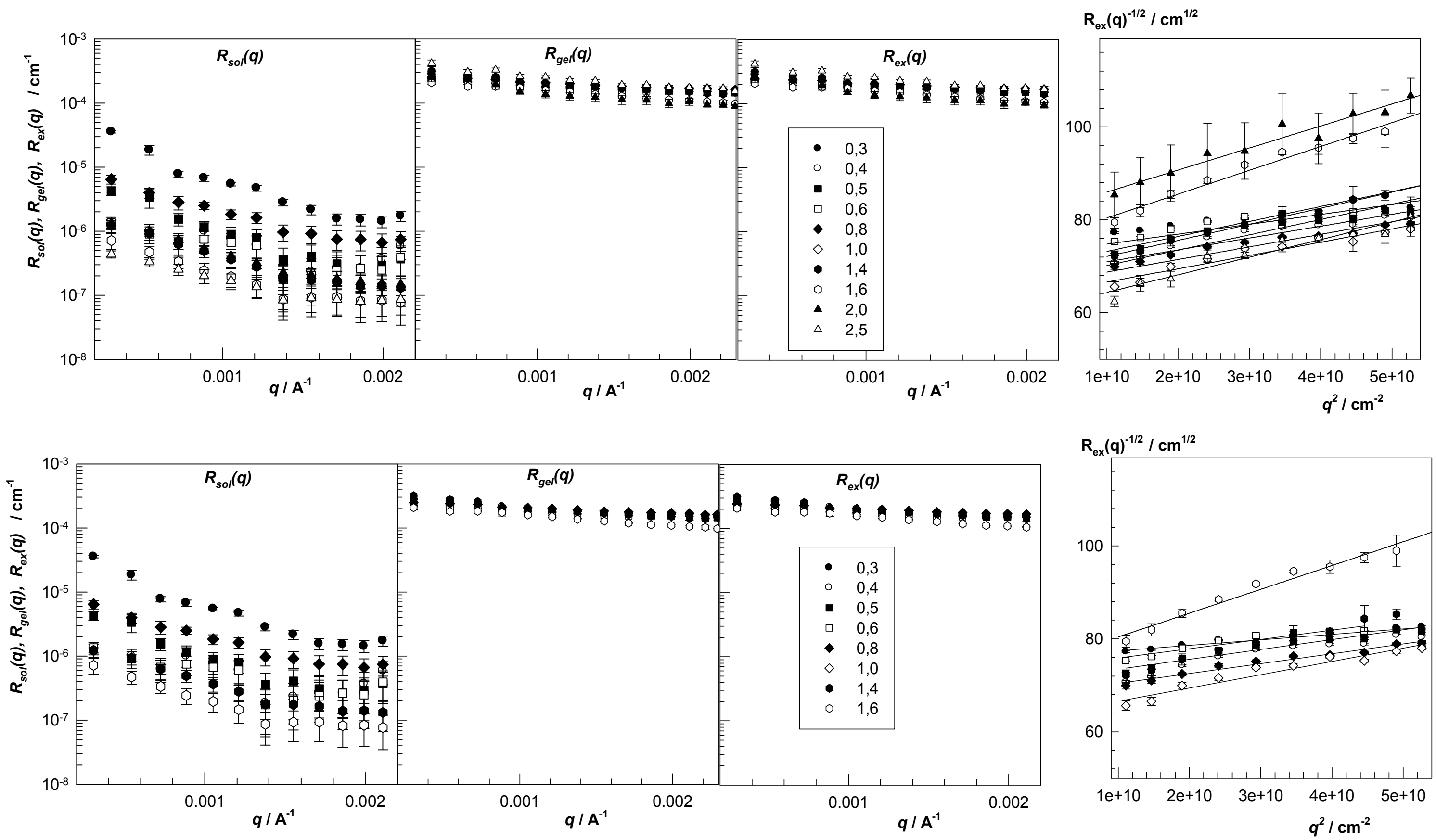


**Figure S3.** The scattering vector *q* dependence of scattered light intensities from PAAm solutions $R_{sol}(q)$, PAAm gels $R_{gel}(q)$, excess scattering $R_{ex}(q)$, and Debye-Bueche plots for the first network hydrogels formed using PEG-DM (upper panel) and BAAm (bottom panel). The gels are in equilibrium swollen state in water. The cross-linker contents (in mol %) are indicated.

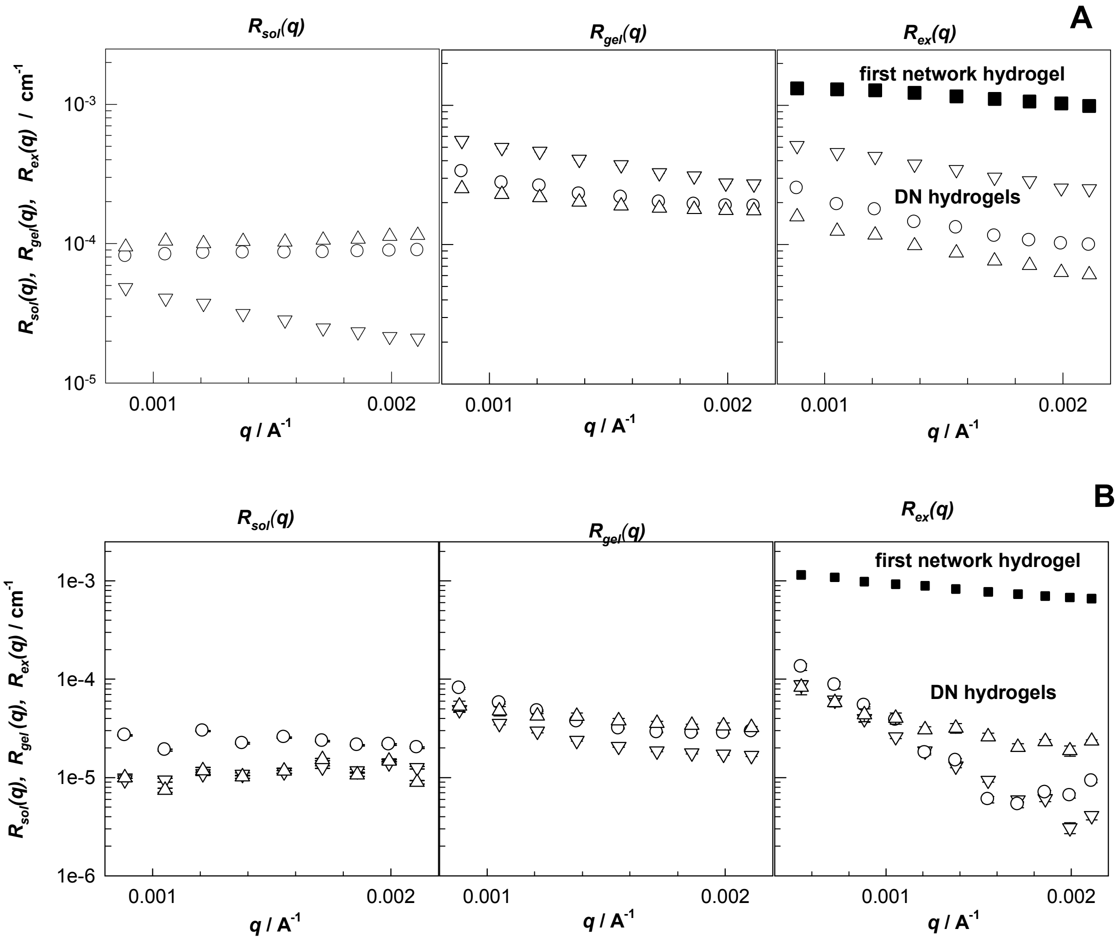


**Figure S4.** The scattering vector $q$ dependence of scattered light intensities from PAAm solutions $R_{sol}(q)$, DN hydrogels $R_{gel}(q)$, and excess scattering $R_{ex}(q)$ for DN hydrogels. First network cross-linker = 3.3 mol % PEG-DM (A), and 2 mol % BAAm (B). For comparison, excess scattering of the first networks are also shown by the filled symbols. A: $n_{21}$ = 0.75 (▽), 1.5 (O), and 3.0 (△). B: $n_{21}$ = 0.09 (▽), 0.18 (O), and 0.36 (△).

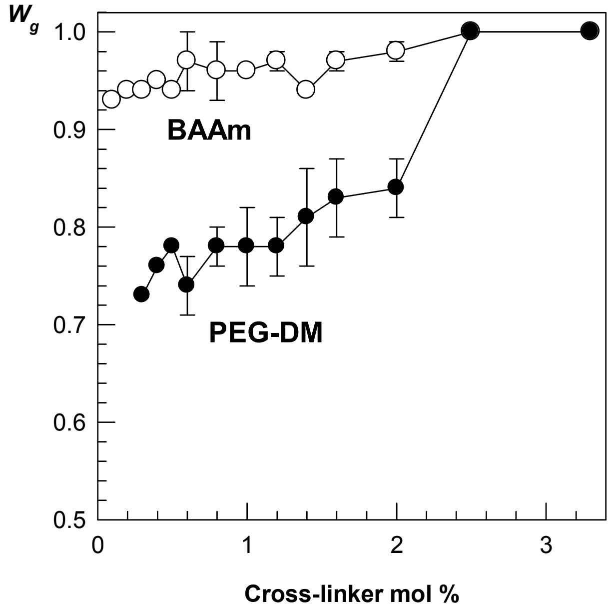


**Figure S5.** The gel fraction $W_g$ shown as a function of the concentration of BAAm and PEG-DM cross-linkers.

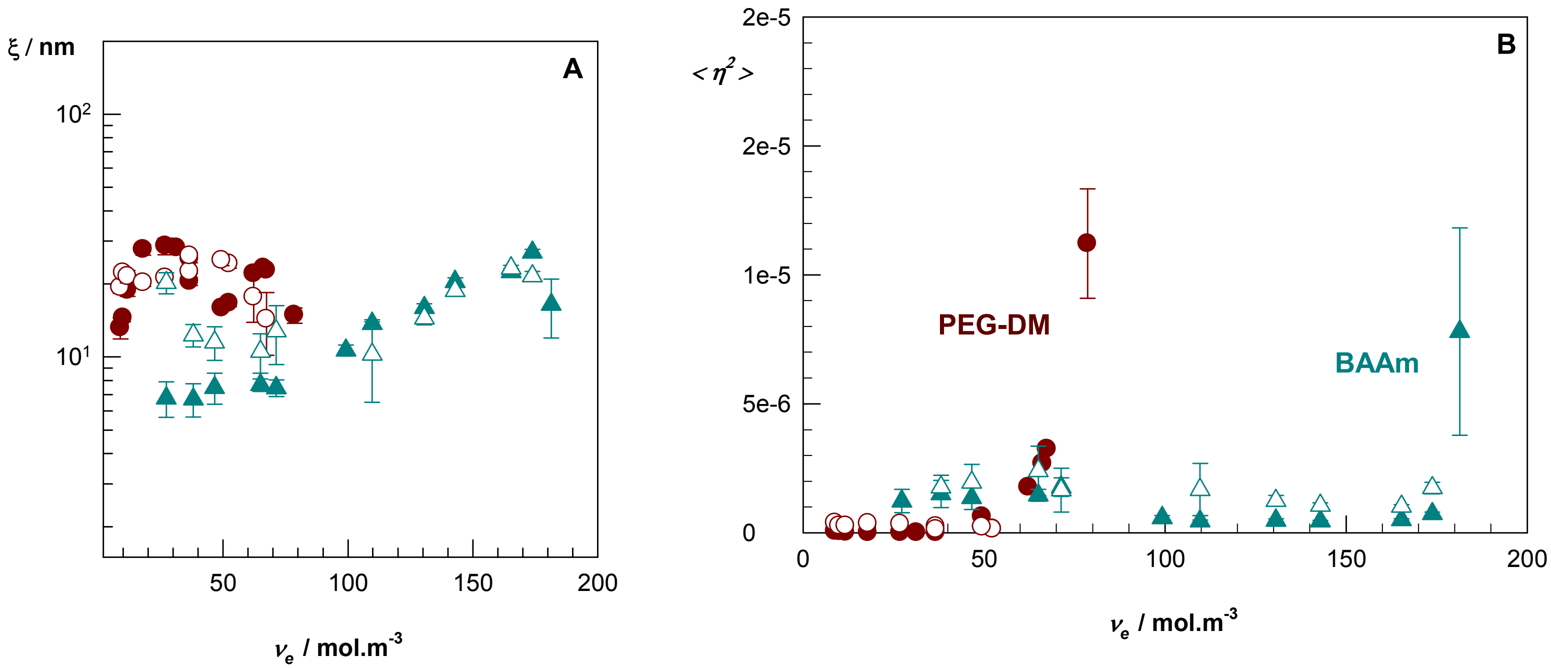


**Figure S6**. The correlation length of the scatterers $\xi$ (A), and the mean square fluctuation of the refractive index $\langle \eta^2 \rangle$ (B) in PAAm hydrogels formed using PEG-DM (circles) and BAAm cross-linker (triangles) shown as a function of the hydrogel cross-link density $\nu_e$. Filled and open symbols represent data obtained from hydrogels after preparation and after equilibrium swelling in water, respectively.

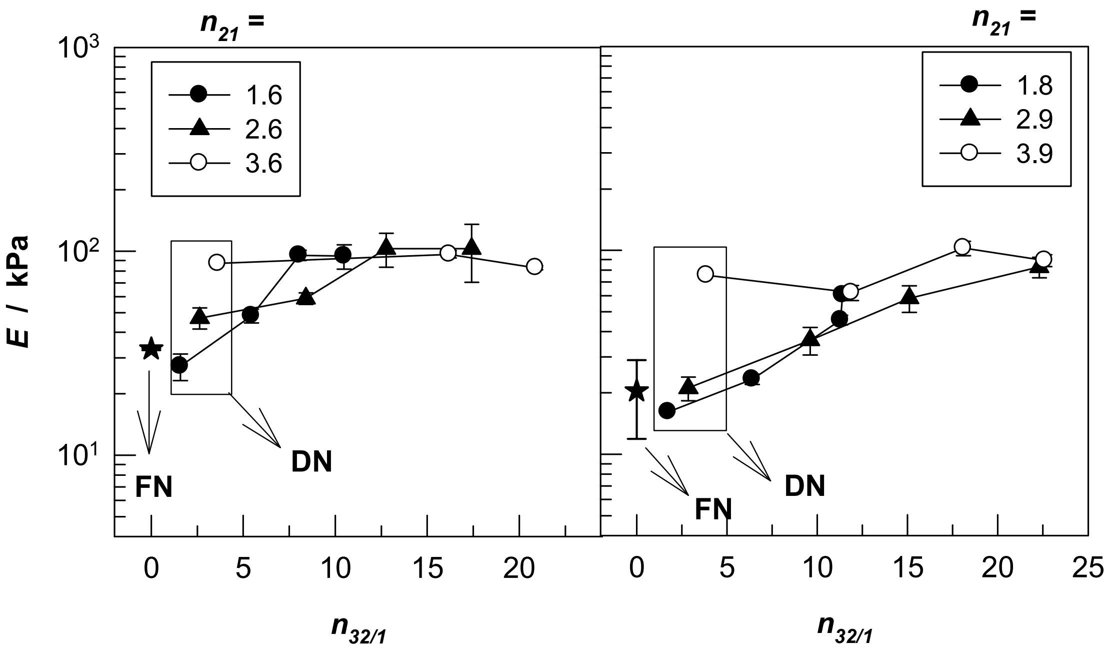


**Figure S7**. Young's modulus $E$ of TN hydrogels formed using 4.0 (left panel) and 3.3 mol % PEG-DM (right panel) as a first network cross-linker plotted against $n_{32/1}$. For comparison, $E$ of the first network (FN) and DN hydrogels (arranged in rectangle) are also shown. Standard deviations are less than 10 %.

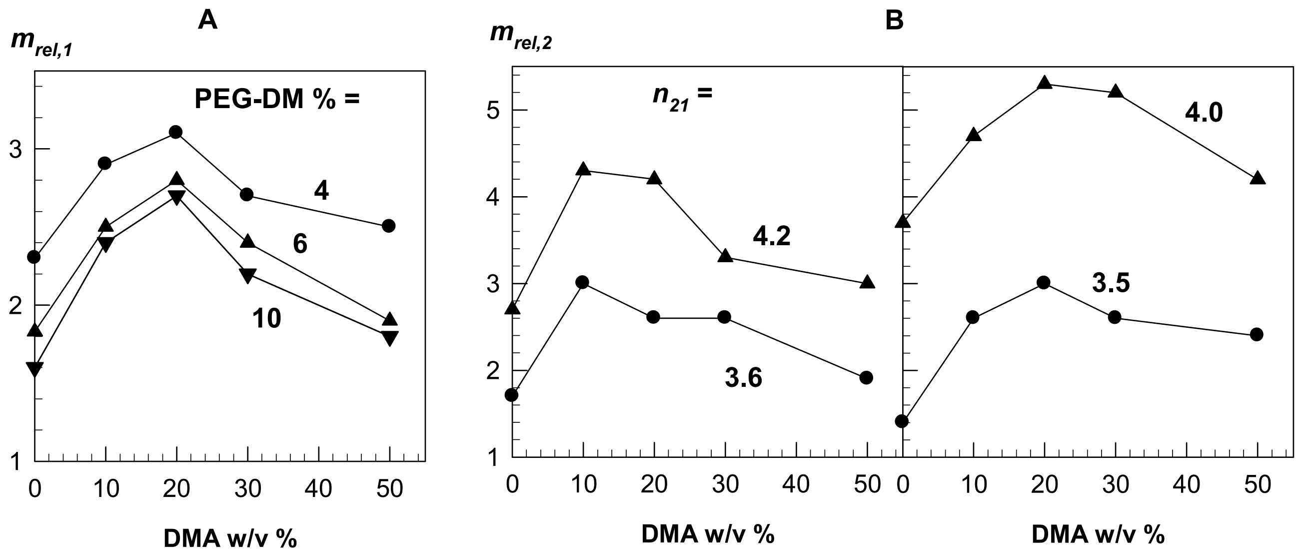


**Figure S8.** Swelling ratios of the first network ($m_{rel,1}$, A) and DN hydrogels ($m_{rel,2}$, B) based on PDMA shown as a function of DMA concentration in the external solution. (A): PEG-DM mol % of the hydrogels is indicated. (B): PEG-DM = 6 (left) and 10 mol % (right). $n_{21}$ ratio of DN hydrogels are indicated.

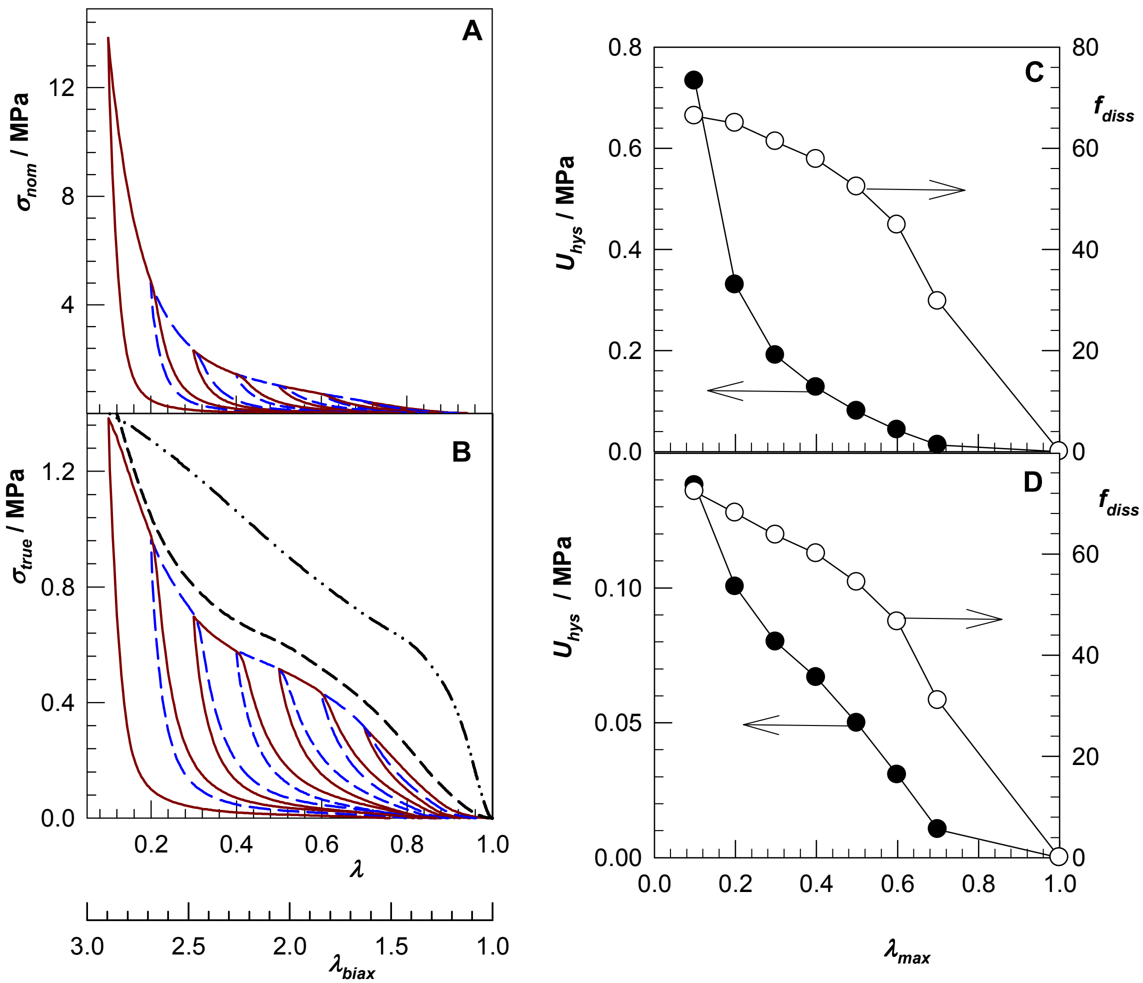


**Figure S9.** **(A, B):** Seven successive loading / unloading cycles with increasing maximum strain from 30 to 90 % ($\lambda_{max}$ = 0.7 to 0.1) as the dependences of nominal $\sigma_{nom}$ (A) and true stresses $\sigma_{true}$ (B) on the deformation ratio $\lambda$. The dashed and dash-dot-dot black curves in B represent $\sigma_{true}$ - $\lambda$ and $\sigma_{true}$ - $\lambda_{biax}$ plots of the virgin gel sample, respectively. **(C, D):** Hysteresis energy $U_{hys}$ (filled symbols), and the fraction of dissipated energy in each cycle $f_{diss}$ (open symbols) plotted against $\lambda_{max}$. $U_{hys}$ was calculated from the area between the loading and unloading curves. $f_{diss}$

was calculated from the ratio of $U_{hys}$ to the area under the loading curve. Calculations are from nominal (C) and true stresses (B). Synthesis parameters of TN hydrogel: $n_{21} = 4.0$, $n_{32/1} = 33$. PEG-DM = 10 mol %.

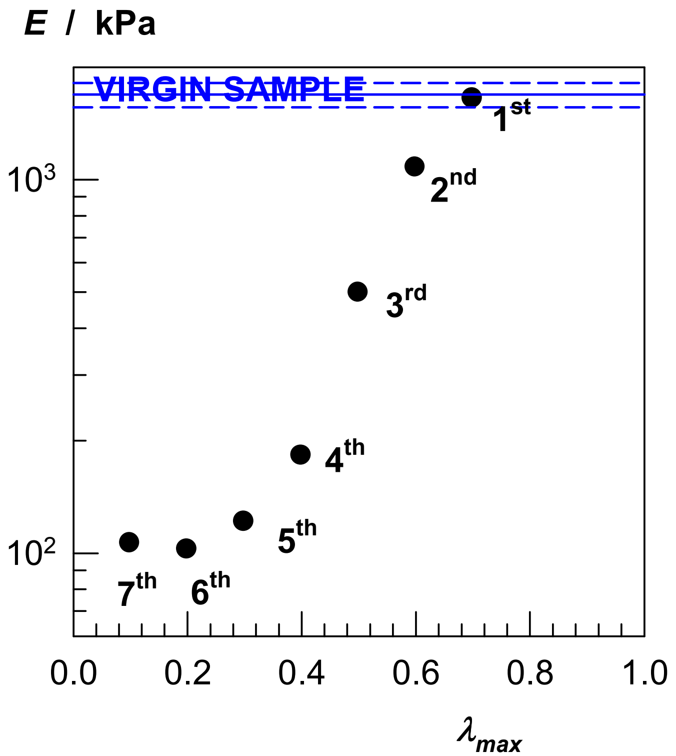


**Figure S10.** Young's modulus $E$ calculated from the slope of the successive loading curves in Figure 9A between $\lambda = 0.90$ and 0.85 plotted against $\lambda_{\max}$. The solid and dashed horizontal lines represent the modulus of the virgin gel sample and the standard deviations, respectively.