Title	Effect of Relative Strength of Two Networks on the Internal Fracture Process of Double Network Hydrogels As Revealed by in Situ Small-Angle X-ray Scattering
Author(s)	Fukao, Kazuki; Nakajima, Tasuku; Nonoyama, Takayuki; Kurokawa, Takayuki; Kawai, Takahiko; Gong, Jian Ping
Citation	Macromolecules, 53(4), 1154-1163 https://doi.org/10.1021/acs.macromol.9b02562
Issue Date	2020
Doc URL	http://hdl.handle.net/2115/80360
Rights	This document is the Accepted Manuscript version of a Published Work that appeared in final form in Macromolecules, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://pubs.acs.org/doi/abs/10.1021/acs.macromol.9b02562.
Type	article (author version)
Additional Information	There are other files related to this item in HUSCAP. Check the above URL.
File Information	Supporting Information Macromolecules53-4_1154-1163.pdf

Supporting Information

Internal Fracturing in Double Network Hydrogels During Stretching as Revealed by in situ Small-Angle X-ray Scattering

Kazuki Fukao[1], Tasuku Nakajima[2,3,4], Takayuki Nonoyama[2,3], Takayuki Kurokawa[2,3],
Takahiko Kawai[5]* and Jian Ping Gong[2,3,4]*

[1] Graduate School of Life Science, Hokkaido University, Sapporo, 001-0021, Japan
[2] Faculty of Advanced Life Science, Hokkaido University, Sapporo, 001-0021, Japan
[3] Global Station for Soft Matter, Global Institution for Collaborative Research and Education (GI-CoRE), Hokkaido University, Sapporo, 001-0021, Japan
[4] Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, 001-0021, Japan
[5] Graduate School of Engineering, Gunma University, Ota, 373-0057, Japan

*Corresponding author
E-mail: kawaitakahiko@gunma-u.ac.jp (T. Kawai) and gong@sci.hokudai.ac.jp (J.P. Gong)

Small angle x-ray Scattering (SAXS) measurement

Calculation of the mesh size and the mesh deformation ratio of the first network. To calculate the mesh deformation ratio of the first network λ_{mesh} in two different directions, we fitted the SAXS profiles of DN gels at various deformation ratio λ (Figure S1) with Ornstein–Zernike (OZ) function using Origin Pro software, as follows.

$$I(q) = \frac{I_0}{1+\xi^2 q^2} \qquad \text{(S1)}$$

where I_0, ξ and q are the forward scattering intensity, the correlation length and scattering vector, respectively. The mesh deformation ratio λ_{mesh} was calculated based on the mesh size at global stretch ratio λ = 1 of the DN gels from following equation.

$$\lambda_{mesh} = \frac{\xi_{\lambda=x}}{\xi_{\lambda=1}} \qquad \text{(S2)}$$

Calculation of the void long-axis length and the void deformation ratio. To calculate the average void length $\langle L_{void} \rangle$ using Ruland streak method, the azimuth angle distribution at any scattering vector q was firstly obtained from 2D images by using Fit_2D (v12.077) software, and the data was fitted by Lorentzian function using Origin Pro software. Then the radian of full width at half maximum (FWHM) in azimuth direction of the streak at scattering vector q was obtained from the fitting curve. The void deformation ratio λ_{void} was calculated from following equation.

$$\lambda_{void} = \frac{\langle L_{void\,(\lambda=X)} \rangle}{\langle L_{void\,(\lambda=1)} \rangle} \qquad \text{(S3)}$$

where $\langle L_{\boldsymbol{void}\,(\boldsymbol{\lambda}=\mathbf{1})}\rangle$ is the void length at $\lambda_{\mathrm{DN}} = 1$. Since $\langle L_{\boldsymbol{void}\,(\boldsymbol{\lambda}=\mathbf{1})}\rangle$ cannot be obtained from the Ruland streak method, we estimated $\langle L_{\boldsymbol{void}\,(\boldsymbol{\lambda}=\mathbf{1})}\rangle$ of DN-4 by extrapolating the linear relation between the $\langle L_{void}\rangle$ and λ to λ=1. The $\langle L_{\boldsymbol{void}\,(\boldsymbol{\lambda}=\mathbf{1})}\rangle$ of DN-2 was calculated from $\langle L_{\boldsymbol{void}\,(\boldsymbol{\lambda}=\mathbf{1})}\rangle$ of DN-4 by considering the volume swelling ratio difference between the two DN gels.

Estimation of the first network mesh size from mechanical test

Indentation test. To calculate the mesh size of the first network, indentation test was also carried out for as-prepared first SN gels (PAMPS, thickness: 3 mm) with different cross-linked density. The indentation was performed at 0.25 mm/min using a universal mechanical testing device (AUTOGRAPH AG-X, Shimadzu Co., Japan). The Young's modulus E was calculated using the Hertz model for indentation between indenter and sample, as follows.

$$h = \left[\frac{3}{4}\left(\frac{1-{\nu_i}^2}{E_i} + \frac{1-{\nu_{ii}}^2}{E_{ii}}\right)\right]^{\frac{2}{3}} \cdot F^{\frac{2}{3}} \cdot R^{-\frac{1}{3}} \qquad \text{(S4)}$$

where h, F, R, ν_i, ν_{ii}, E_i and E_{ii} are displacement, force, radius of indenter, Poisson ratio of indenter, Poisson ratio of sample, Young’s modulus of indenter and Young’s modulus of sample, respectively. Since E_i is much higher than E_{ii}, the equation becomes following.

$$h = \left[\frac{3}{4}\left(\frac{1-{\nu_{ii}}^2}{E_{ii}}\right)\right]^{\frac{2}{3}} \cdot F^{\frac{2}{3}} \cdot R^{-\frac{1}{3}} \qquad \text{(S5)}$$

In this study, the radius of indenter R was 0.25 mm and ν_{ii} was assumed to be 0.5. E_{ii} can be determined from the slope a of the $F^{2/3}$–h plot at the range of h = 0.05 ~ 0.25 mm.

$$a = \left[\frac{3}{4}\left(\frac{1-\nu_{ii}{}^2}{E_{ii}}\right)\right]^{-\frac{2}{3}} \cdot R^{\frac{1}{3}} \qquad \text{(S6)}$$

$$E_{ii} = \frac{3}{4}(1-\nu_{ii}{}^2) \cdot R^{-1/2} \cdot a^{3/2} \qquad \text{(S7)}$$

The first network mesh size at the as-prepared state ξ_0 was estimated from the Young's modulus of sample, E_{ii}, as follows.

$$E_{ii} = \frac{3k_BT}{\xi_0^3} \qquad \text{(S8)}$$

where k_B and T are Boltzmann constant and measurement temperature. The mesh size of the first networks in DN gels ξ was estimated from the volume swelling ratio Q of the first network in swollen DN gels relative to its as-prepared state as follows.

$$\xi^3 = Q \times \xi_0^3 \qquad \text{(S9)}$$

Figure S1.

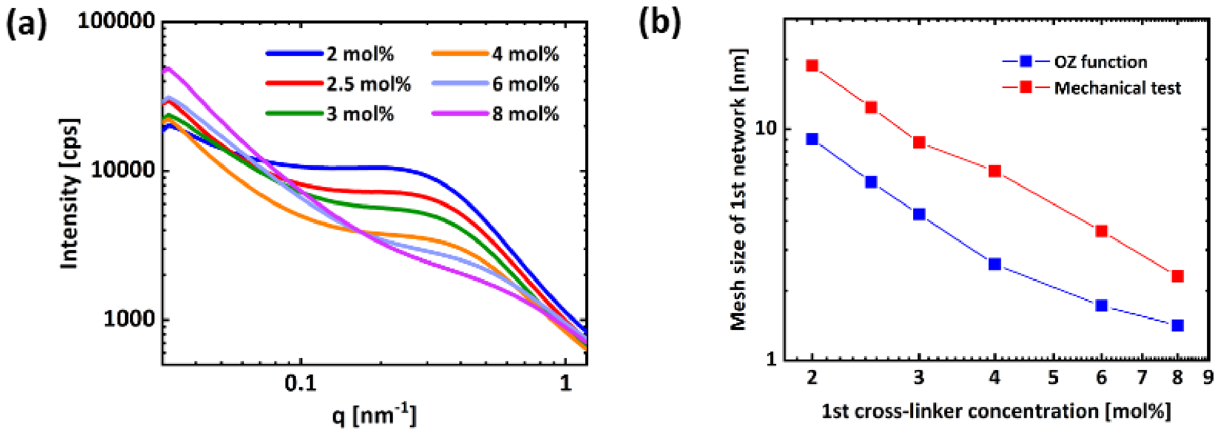


Figure S1. (a) SAXS 1D profiles of swollen DN gels with various concentration of the first network cross-linker. (b) Comparison of the mesh size of the first network obtained from OZ function fitting and indentation test.

Figure S2.

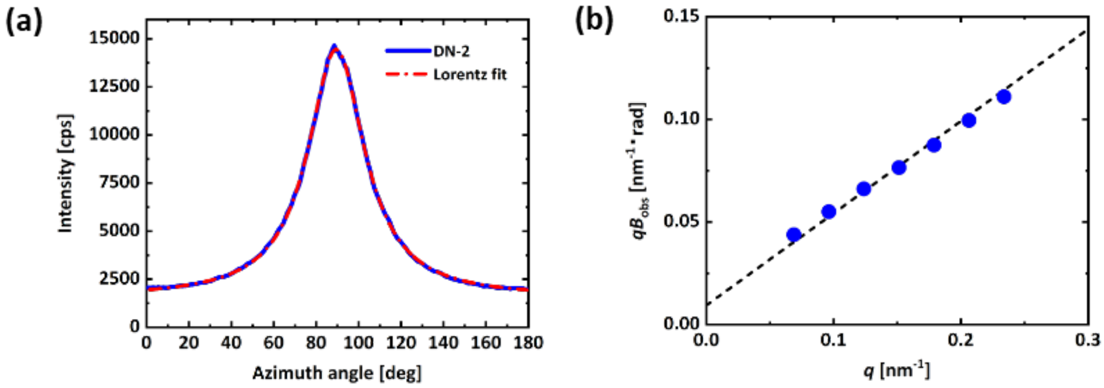
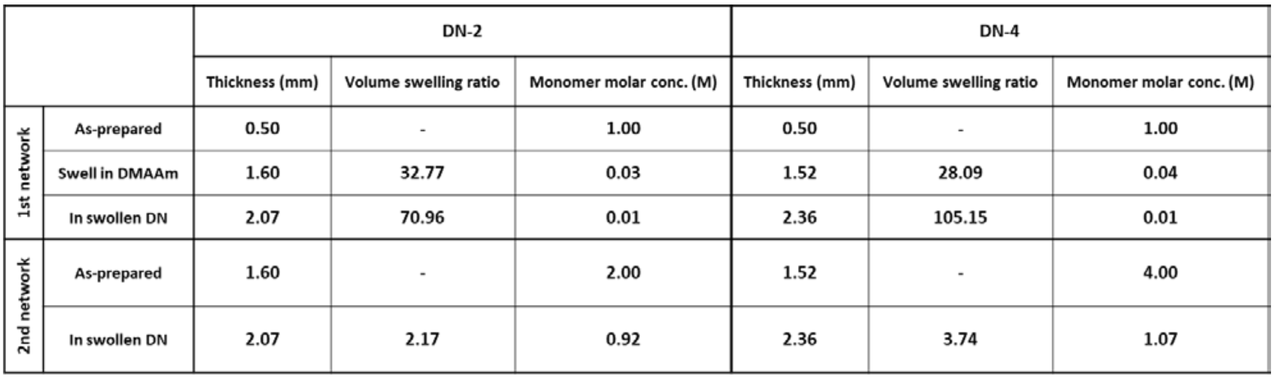


Figure S2. (a) Azimuth angle distribution of DN-2 and its Lorentz fitting curve. (b) The linear plot between the qB_{obs} and q.

Table S1.

Table S1. Summary of sample thickness, volume swelling ratio in relative to as-prepared state, and the monomer molar concentration of the two networks for DN-2 and DN-4 gels. The monomer molar concentrations at as-prepared state are the in-feed values.



		DN-2			DN-4		
		Thickness (mm)	Volume swelling ratio	Monomer molar conc. (M)	Thickness (mm)	Volume swelling ratio	Monomer molar conc. (M)
1st network	As-prepared	0.50	-	1.00	0.50	-	1.00
	Swell in DMAAm	1.60	32.77	0.03	1.52	28.09	0.04
	In swollen DN	2.07	70.96	0.01	2.36	105.15	0.01
2nd network	As-prepared	1.60	-	2.00	1.52	-	4.00
	In swollen DN	2.07	2.17	0.92	2.36	3.74	1.07