



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
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Citation	Macromolecules, 53(4), 1154-1163 https://doi.org/10.1021/acs.macromol.9b02562
Issue Date	2020
Doc URL	https://hdl.handle.net/2115/80360
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Type	journal article
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

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1 ***Small angle x-ray Scattering (SAXS) measurement***

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

6
$$I(q) = \frac{I_0}{1 + \xi^2 q^2} \quad (\text{S1})$$

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

10
$$\lambda_{\text{mesh}} = \frac{\xi_{\lambda=x}}{\xi_{\lambda=1}} \quad (\text{S2})$$

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

17
$$\lambda_{\text{void}} = \frac{\langle L_{\text{void}} (\lambda=x) \rangle}{\langle L_{\text{void}} (\lambda=1) \rangle} \quad (\text{S3})$$

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

5

6 ***Estimation of the first network mesh size from mechanical test***

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

$$12 \quad h = \left[\frac{3}{4} \left(\frac{1-\nu_i^2}{E_i} + \frac{1-\nu_{ii}^2}{E_{ii}} \right) \right]^{\frac{2}{3}} \cdot F^{\frac{2}{3}} \cdot R^{-\frac{1}{3}} \quad (S4)$$

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

$$16 \quad h = \left[\frac{3}{4} \left(\frac{1-\nu_{ii}^2}{E_{ii}} \right) \right]^{\frac{2}{3}} \cdot F^{\frac{2}{3}} \cdot R^{-\frac{1}{3}} \quad (S5)$$

17 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

1 from the slope a of the $F^{2/3}$ – h plot at the range of $h = 0.05 \sim 0.25$ mm.

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

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

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

6
$$E_{ii} = \frac{3k_B T}{\xi_0^3} \quad (\text{S8})$$

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

10
$$\xi^3 = Q \times \xi_0^3 \quad (\text{S9})$$

11

Figure S1.

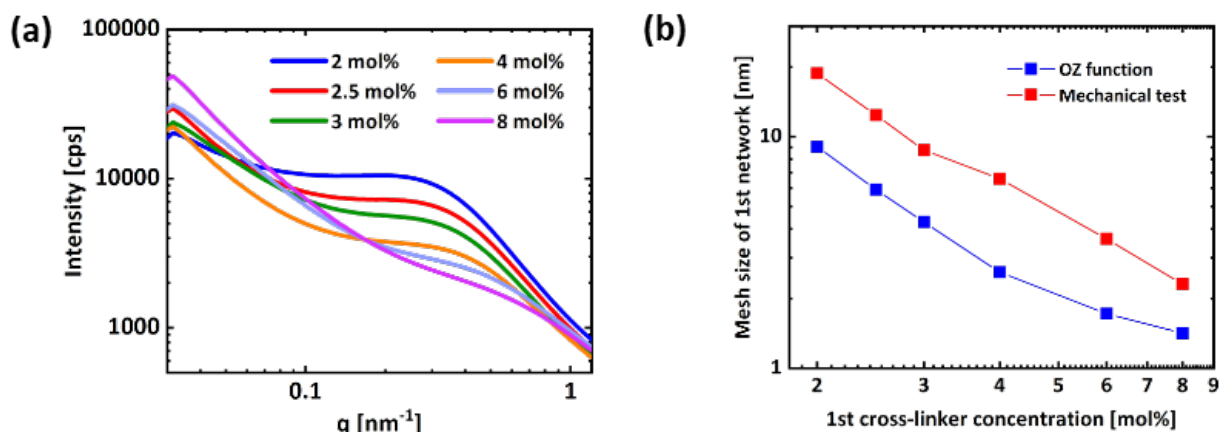


Figure S1. (a) SAXS 1D profiles of swollen DN gels with various concentration of the first network cross-linker. (b) Comparison of the mesh size of the first network obtained from OZ function fitting and indentation test.

Figure S2.

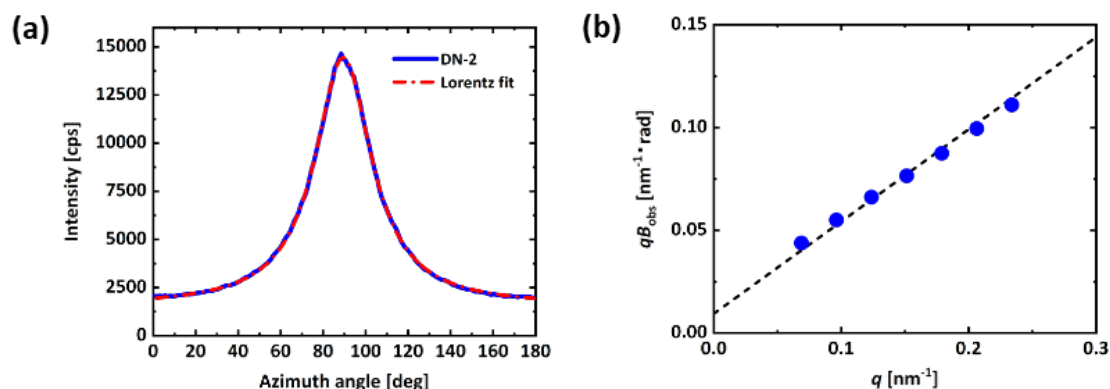


Figure S2. (a) Azimuth angle distribution of DN-2 and its Lorentz fitting curve. (b) The linear plot between the qB_{obs} and q .

1 **Table S1.**

2 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