

## SUPPORTING INFORMATION for

### Preparation of inorganic/organic double-network ion gels using a cross-linkable polymer in an open system

Eiji Kamio,<sup>\*,1</sup> Masayuki Kinoshita,<sup>1</sup> Tomoki Yasui,<sup>1</sup> Timothy P. Lodge,<sup>2</sup> and Hideto Matsuyama<sup>\*,1</sup>

*1: Center for Membrane and Film Technology, Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe, Hyogo 657-8501, Japan.  
Tel.: +81-78-803-6180; Fax: +81-78-803-6180*

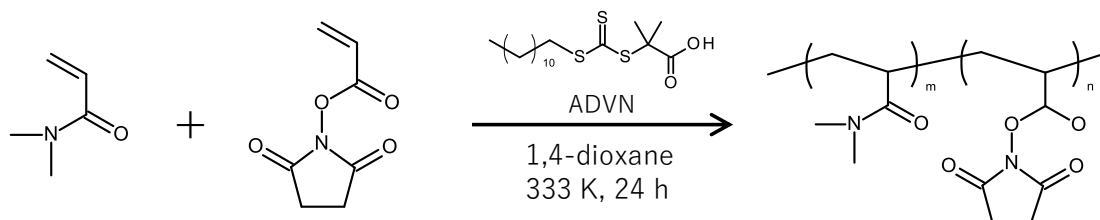
*E-mail: e-kamio@people.Kobe-u.ac.jp (EK), matuyama@kobe-u.ac.jp (HM)*

*2: Department of Chemistry and Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States*

#### Table of contents

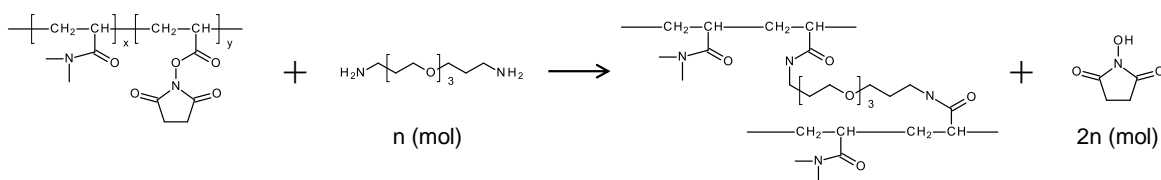
(1) Synthesis scheme for poly(DMAAm-co-NSA)	1
(2) Schematic diagram of the cross-linking reaction between poly(DMAAm-co-NSA) with DGBE	1
(3) <sup>1</sup> H-NMR spectrum of poly(DMAAm-co-NSA) solution after reaction with tertiary butylamine	2
(4) $\mu$ -DN ion gel prepared at 298 K	3
(5) Cyclic tensile stress loading-unloading curves of the $\mu$ -DN ion gels prepared using cross-linkable polymers with different NSA ratios	4-5
(6) Extent of NHS ester group reaction with DGBE	6
(7) Tearing energy of the $\mu$ -DN ion gels	7-8
(8) Cyclic tensile stress loading-unloading curves of the $\mu$ -DN ion gels prepared using precursor solutions with different diluent conditions of $r$	9
(9) Effect of diluent conditions on the thickness of the $\mu$ -DN ion gels	10

(1) Synthesis scheme for poly(DMAAm-co-NSA)



Scheme S1. Synthesis of poly(DMAAm-co-NSA).

(2) Schematic diagram of the cross-linking reaction between poly(DMAAm-co-NSA) with DGBE



Scheme S2. Cross-linking of poly(DMAAm-co-NSA) with DGBE.

(3)  $^1\text{H}$ -NMR spectrum of poly(DMAAm-co-NSA) solution after reaction with tertiary butylamine

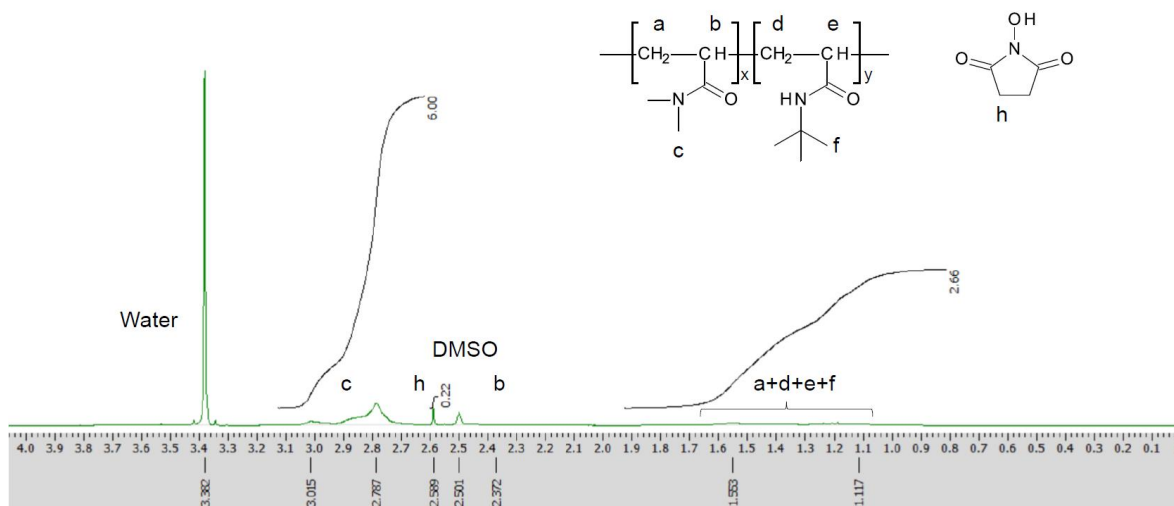


Figure S1.  $^1\text{H}$ -NMR spectrum of the poly(DMAAm-co-NSA) solution after the reaction with tertiary butylamine.

#### (4) $\mu$ -DN ion gel prepared at 298 K

In the preparation of the  $\mu$ -DN ion gel, the cross-linkable polymer with 5 mol% of NSA was used. The  $\mu$ -DN ion gel was prepared using a precursor solution with the ethanol/IL ratio of 2 ( $r = 2.0$  g/g) in a closed mold. The results of the uniaxial and cyclic tensile stress-stretching tests of the  $\mu$ -DN ion gel prepared at 298 K were shown in Figure S2. The  $\mu$ -DN ion gel prepared at 298 K was stronger than the single-network ion gel without silica nanoparticles (shown in Figure 2(a)), and clearly showed hysteresis in the cyclic stretching test (Figure S2(b)). Therefore, it was confirmed that the organic network formed at 298 K acted as a sacrificial bond to dissipate the load. On the other hand, the mechanical properties of the  $\mu$ -DN ion gel prepared at 298 K were different from those of the  $\mu$ -DN ion gels prepared at 333 K, i.e., the  $\mu$ -DN ion gel prepared at 298 K showed higher modulus and lower fracture strain than that prepared at 333 K. This is due to the different cross-linking degrees of the organic networks cross-linked at different temperatures.

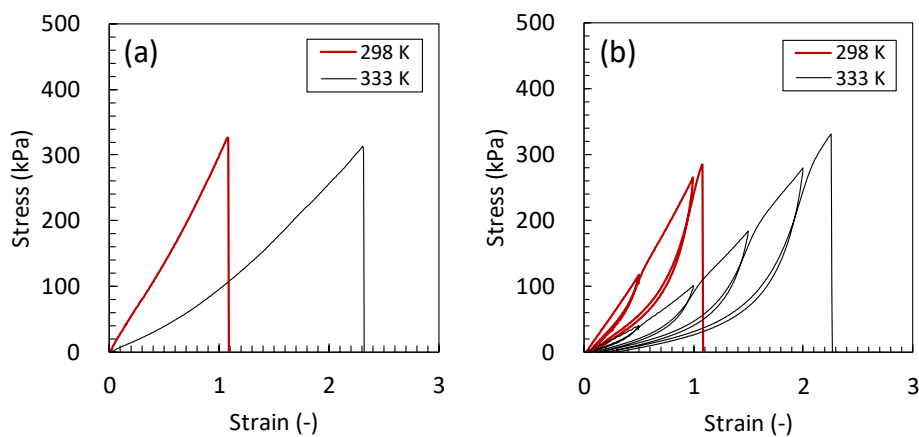


Figure S2. Tensile stress-strain curves of the  $\mu$ -DN ion gels at 298 K and 333 K. The  $\mu$ -DN ion gels were prepared in a closed mold using a precursor solution with the ethanol/IL ratio of 2 g/g containing a cross-linkable polymer with 5 mol% NSA. The IL content was 80 wt%. (a) Uniaxial stress-strain curves and (b) cyclic tensile stress loading-unloading curves.

(5) Cyclic tensile stress loading-unloading curves of the  $\mu$ -DN ion gels prepared using cross-linkable polymers with different NSA ratios

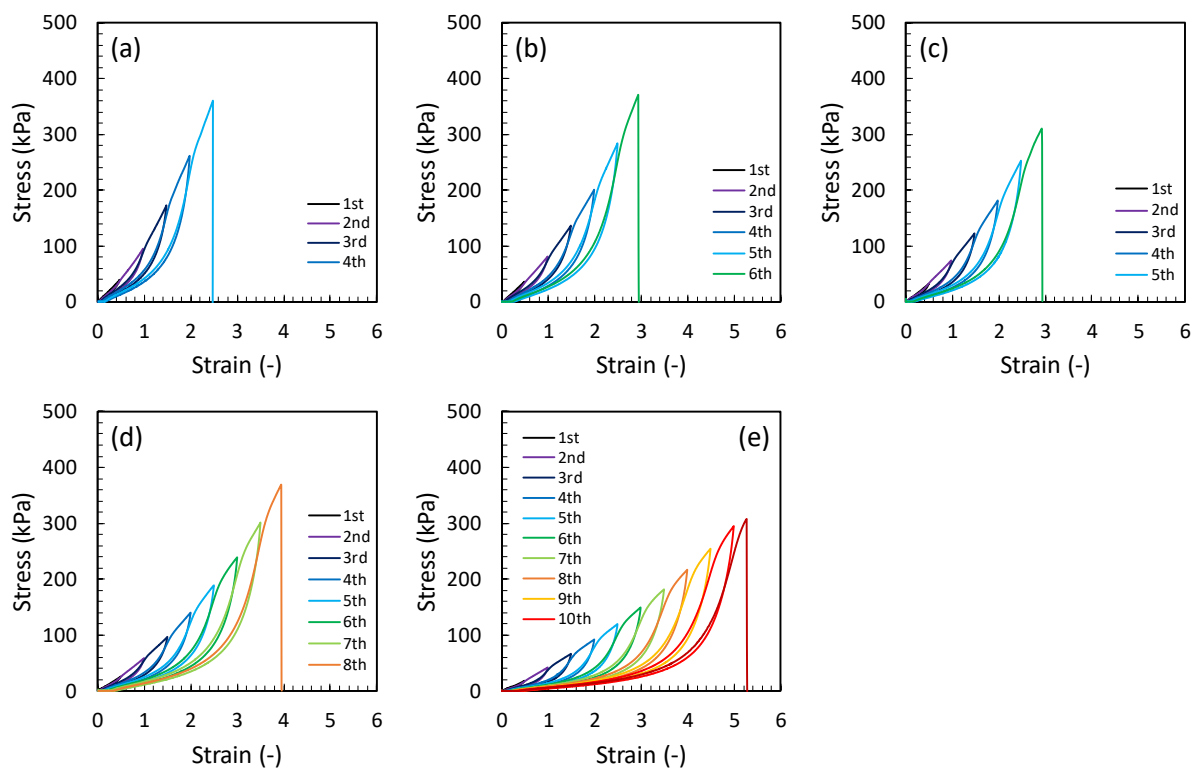
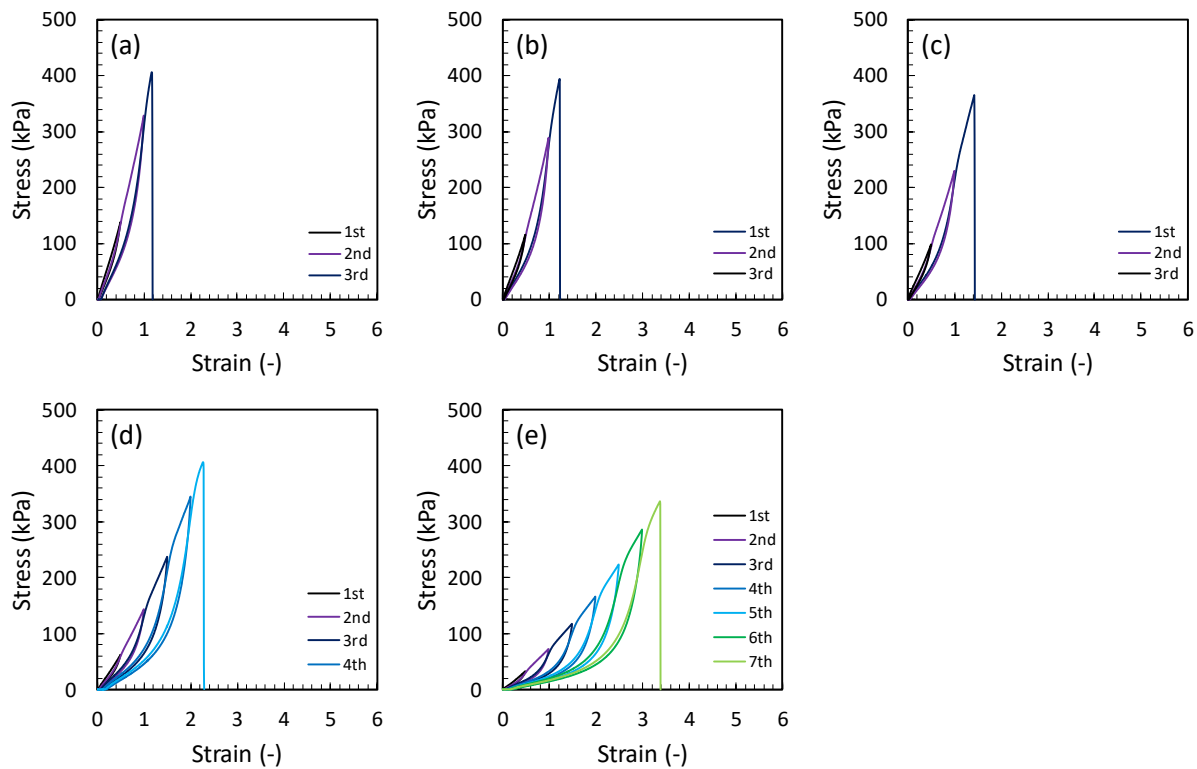


Figure S3. Energy dissipation of the  $\mu$ -DN ion gels prepared in closed molds using the cross-linkable polymer with different NSA ratios: (a) 5, (b) 4, (c) 3, (d) 2, and (e) 1 mol%. The  $\mu$ -DN ion gels were prepared using the precursor solutions with  $r = 2$  g/g.



## (6) Extent of NHS ester group reaction with DGBE

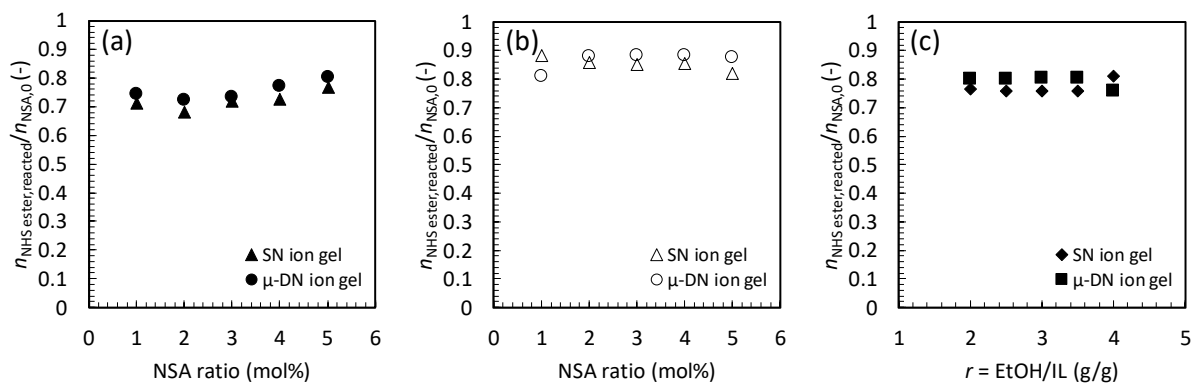


Figure S5 Extent of reaction of the NHS ester group in the polymer networks of the  $\mu$ -DN and SN ion gels (a) prepared in a closed mold using the precursor solutions of  $r = 2$  g/g with cross-linkable polymer with different NSA ratio, (b) prepared in an open mold using the precursor solutions of  $r = 2$  g/g with cross-linkable polymer with different NSA ratio, and (c) prepared in a closed mold the precursor solutions of different  $r$  with cross-linkable polymer having 5 mol% of the NSA ratio.

## (7) Tearing energy of the $\mu$ -DN ion gels

The fracture energies of the ion gels,  $G$  (J/m<sup>2</sup>), were measured by tearing tests. The samples were cut into trousers-shaped samples (75 mm in length with an initial notch of 20 mm, and 15 mm in width). The pulling velocity was 50 mm/min. The fracture energy, defined as the energy required for creating a unit area of fracture surface in a sample, was calculated by  $G = F_{ave}/d$ , where  $F_{ave}$  is the average force applied during the tear measurement and  $d$  is the thickness of the samples.

We prepared the  $\mu$ -DN ion gels using the cross-linkable polymers with the NSA ratio of 5 mol% and 1 mol%, and measured their tearing energies. We also prepared the SN ion gels using the cross-linkable polymers with the NSA ratio of 5 mol% and measured the tearing energy.

The results are shown in Table S1. In Table S1, the tearing energy of a classical inorganic/organic DN ion gel prepared using TEOS and DMAAm as the raw network materials was also shown.

Table S1. Tearing energies of the  $\mu$ -DN<sup>†</sup>, SN<sup>‡</sup>, and DN<sup>\*</sup> ion gels containing 80 wt% of [C<sub>4</sub>mim][Tf<sub>2</sub>N]

		$\mu$ -DN ion gels		SN ion gel	DN ion gel
Network raw materials	1st network	Silica nanoparticles	Silica nanoparticles	–	Tetraethyl orthosilicate
	2nd network	Cross-linkable polymer	Cross-linkable polymer	Cross-linkable polymer	DMAAm
	NSA ratio	1 mol%	5 mol%	5 mol%	–
Tearing energy (kJ/m <sup>2</sup> )		123.8	19.4	16.2	82.1

<sup>†</sup>, <sup>‡</sup>:  $\mu$ -DN and SN ion gels were prepared using a precursor solution of  $r = 2.0$  g/g in a closed mold.

\*: The data of the DN ion gel was cited from *Adv. Mater.*, 29 (47), 1704118, 2017.

Comparing the tearing energies of the  $\mu$ -DN and SN ion gels prepared using the cross-linkable polymer with 5 mol% NSA, the  $\mu$ -DN ion gel had larger tearing energy than the SN ion gel. In addition, comparing the tearing energies of the  $\mu$ -DN ion gels prepared using the cross-linkable polymers with 1 mol% and 5 mol% of the NSA ratios, the cross-linkable polymer with 5 mol% NSA gave much larger tearing energy than the cross-linkable polymer with 1 mol% NSA. This trend is consistent with that of fracture energy of the  $\mu$ -DN ion gels

shown in Figure 3(d). These results mean that the loosely cross-linked polymer network is effective to dissipate the loaded energy.

Comparing the tearing energy of the  $\mu$ -DN ion gel prepared using the cross-linkable polymer with 5 mol% NSA and that of a classical inorganic/organic DN ion gel, the  $\mu$ -DN ion gel had higher tearing energy. Therefore, it can be said that optimal design of the cross-linkable polymer enables us to create a  $\mu$ -DN ion gel tougher than the inorganic/organic DN ion gels.

(8) Cyclic tensile stress loading-unloading curves of the  $\mu$ -DN ion gels prepared using precursor solutions with different diluent conditions of  $r$

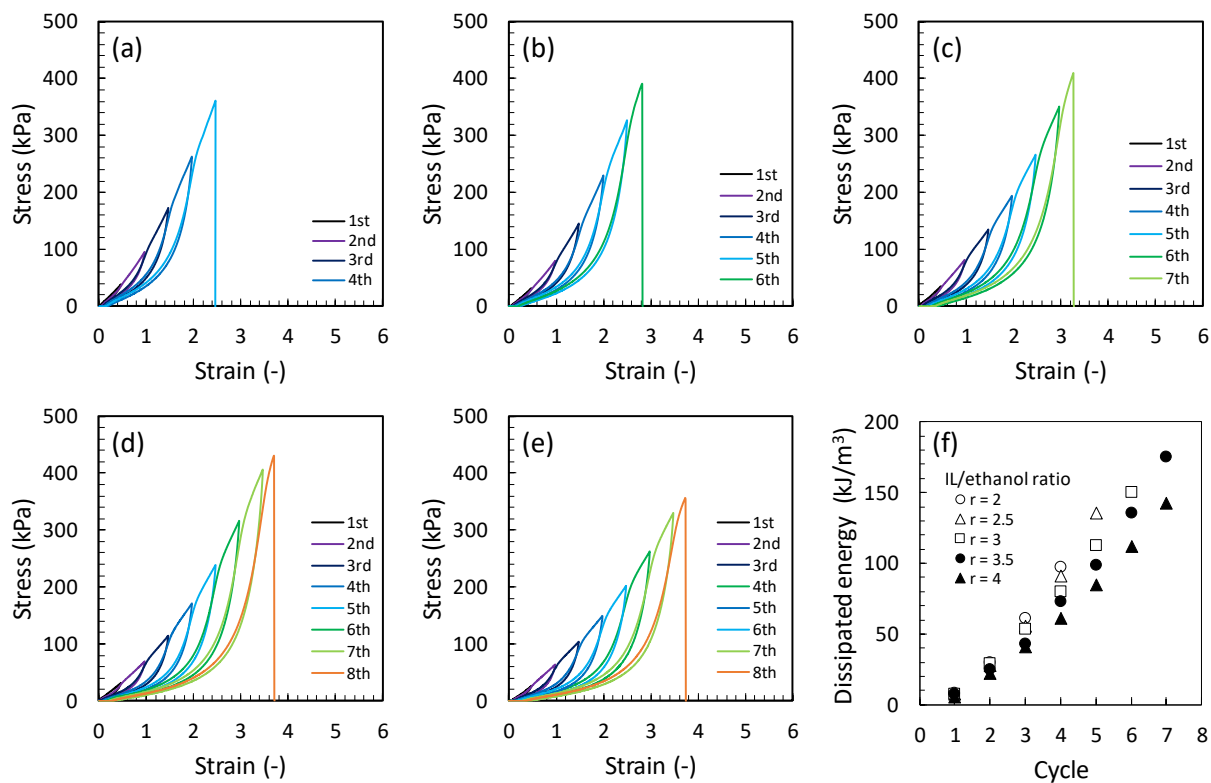


Figure S6. Energy dissipation of the  $\mu$ -DN ion gels prepared in closed molds using the cross-linkable polymer with an NSA ratio of 5 mol%. The  $\mu$ -DN ion gels were prepared under the diluent conditions of  $r =$  (a) 2.0, (b) 2.5, (c) 3.0, (d) 3.5, and (e) 4.0 g/g. (f) Relationship between the dissipated energy and cycle for the cyclic tensile loading test.

### (9) Effect of diluent conditions on the thickness of the $\mu$ -DN ion gels

The  $\mu$ -DN ion gels were prepared by gelling the precursor solutions in a mold. The depth of the precursor solution poured in the mold was adjusted about 2.5 mm. Then, the cross-linking reaction was conducted to make the  $\mu$ -DN ion gels containing ethanol. After the cross-linking reaction, the gel was heated to remove ethanol completely. Because the  $\mu$ -DN ion gels were very stick, it was tightly attached to the bottom of the mold. Therefore, the gels were shrunk only in the thickness direction. This means the thickness of the gel was decreased but the area was not changed. Figure S7 shows the relationship between the thicknesses of the  $\mu$ -DN ion gels prepared using the precursor solutions with different ethanol/IL ratio,  $r$ , and the estimated gel thicknesses from the ethanol/IL ratio of the precursor solutions. It was confirmed that the gel thickness can be controlled by adjusting the ethanol/IL ratio of the precursor solution.

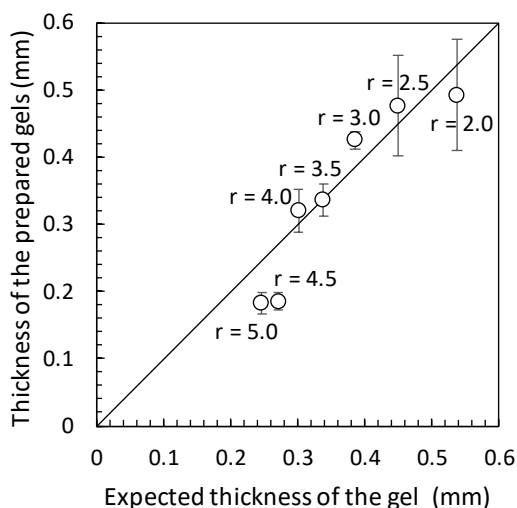


Figure S7. Relationship between the thicknesses of the  $\mu$ -DN ion gels prepared using the precursor solutions with different  $r$  and those estimated from  $r$ .